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State-space approach to vibration of gold nano-beam induced by ramp type heating

Hamdy M. Youssef\(^1\)\(^,*\) and Khaled A. Elsibai\(^2\)

In the nanoscale beam, two effects become domineering. One is the non-Fourier effect in heat conduction and the other is the coupling effect between temperature and strain rate. In the present study, a generalized solution for the generalized thermoelastic vibration of gold nano-beam resonator induced by ramp type heating is developed. The solution takes into account the above two effects. State-space and Laplace transform methods are used to determine the lateral vibration, the temperature, the displacement, the stress and the strain energy of the beam. The effects of the relaxation time and the ramping time parameters have been studied.

Keywords: Thermoelasticity; Euler-Bernoulli equation; Gold nano-beam; Ramp type heating.

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Many attempts have been made recently to investigate the elastic properties of nanostructured materials by atomistic simulations. Diao et al. [1] studied the effect of free surfaces on the structure and elastic properties of gold nanowires by atomistic simulations. Although the atomistic simulation is a good way to calculate the elastic constants of nanostructured materials, it is only applicable to homogeneous nanostructured materials (e.g., nanoplates, nanobeams, nanowires, etc.) with limited number of atoms. Moreover, it is difficult to obtain the elastic properties of the heterogeneous nanostructured materials using atomistic simulations. For these and other reasons, it is prudent to seek a more practical approach. One such approach would be to extend the classical theory of elasticity down to the nanoscale by including in it the hitherto neglected surface/interface effect. For this it is necessary first to cast the latter within the framework of continuum elasticity.

Nano-mechanical resonators have attracted considerable attention recently due to their many important technological applications. Accurate analysis of various effects on the characteristics of resonators, such as resonant frequencies and quality factors, is crucial for designing high-performance components. Many authors have studied the vibration and heat transfer process of beams. Kidawa [2] has studied the problem of transverse vibrations of a beam induced by a mobile heat source. The analytical solution to the problem was obtained using the Green’s functions method. However, Kidawa did not consider the thermoelastic coupling effect. Boley [3] analyzed the vibrations of a simply supported rectangular beam subjected to a suddenly applied heat input distributed along its span. Manolis and Beskos [4] examined the thermally induced vibration of structures consisting of beams, exposed to rapid surface heating. They have also studied the effects of damping and axial loads on the structural response. Al-Huniti et al. [5] investigated the thermally induced displacements and stresses of a rod using the Laplace transformation technique. Ai Kah Soh et al. studied the vibration of micro/nanoscale beam resonators induced by ultra-short-pulsed laser by considering the thermoelastic coupling term in [6] and [7]. The propagation characteristics of the longitudinal wave in nanoplates with small scale effects are studied by Wang et al. [8].

When very fast phenomena and small structure dimensions are involved, the classical law of Fourier becomes inaccurate.
The classical Fourier heat conduction equation is a parabolic equation, whereas, the non-Fourier heat conduction equation is a hyperbolic equation. A more sophisticated model is then needed to describe the thermal conduction mechanisms in a physically acceptable way. Modern technology has enabled the fabrication of materials and devices with characteristic dimensions of a few nanometers. Examples are superlattices, nanowires, and quantum dots. At these length scales, the familiar continuum Fourier law for heat conduction is expected to fail due to both classical and quantum size effects [9]. Among many applications, the studying of the thermoelastic damping in MEMS/NEMS has been improved in [10] and [11].

It is worthwhile to mention here that in most of the earlier studies, mechanical or thermal loading on the bounding surface is considered to be in the form of a shock. However, the sudden jump of the load is merely an idealized situation because it is impossible to realize a pulse described mathematically by a step function; even very rapid rise-time (of the order of $10^{-9}$ s) may be slow in terms of the continuum. This is particularly true in the case of second sound effects when the thermal relaxation times for typical metals are less than $10^{-9}$ s Misra et al. [13]. It is thus felt that a finite time of rise of external load (mechanical or thermal) applied on the surface should be considered while studying a practical problem of this nature. Most ultrafast heat sources (such as certain lasers) involve the emission of a pulse (for example) that heats a material over a finite time due to the finite rise time of the pulse.

Considering the aspect of rise of time, Misra et al. [14] and Youssef with many authors investigated many applications in which the ramp-type heating is used [15-21].

State-space methods are the cornerstone of modern control theory. The essential feature of state-space methods is the characterization of the processes of interest by differential equations instead of transfer functions. This may seem like a throwback to the earlier, primitive period where differential equations instead of transfer functions. But in the earlier period, these processes were simple enough to be characterized by a single differential equation of fairly low order. In the modern approach, the processes are characterized by system of coupled, first-order differential equations. In principle, there is no limit to the order (i.e., the number of independent first-order differential equations), and in practice the only limit to the order is the availability of computer software capable of performing the required calculations reliably [22]. In particular, the state-space approach is useful because: (1) linear systems with time-varying parameters can be analyzed in essentially the same manner as time-invariant linear systems, (2) problems formulated by state-space methods can easily be programmed on a computer, (3) high-order linear systems can be analyzed, (4) multiple input-multiple output systems can be treated almost as easily as single input-single output linear systems, and (5) state-space theory is the foundation for further studies in such areas as nonlinear systems, stochastic systems, and optimal control. For solving coupled thermoelastic problems using the state-space approach in which the problem is rewritten in terms of state-space variables, namely, the temperature, the displacement and their gradients, has been developed by Bahar and Hetnarski [23-25].

In this paper, the non-Fourier effect in heat conduction, and the coupling effect between temperature and strain rate in nanoscale beam will be studied. In the present work, a generalized solution for the generalized thermoelastic vibration of gold nano-beam resonator induced by ramp type of heating will be developed. The state-space and the Laplace transform methods will be used to determine the lateral vibration, the temperature, the displacement, the stress and the strain energy of the beam. The effects of the relaxation time and the ramping time parameters will be studied and represented graphically.

**Problem Formulation**

Since beams with rectangular cross-sections are easy to fabricate, such cross-sections are commonly adopted in the design of NEMS resonators. Consider small flexural deflections of a thin elastic beam of length $l$ ($0 \leq x \leq l$), width $b$ ($-\frac{b}{2} \leq y \leq \frac{b}{2}$) and thickness $h$ ($-\frac{h}{2} \leq z \leq \frac{h}{2}$), for which the x, y and z axes are defined along the longitudinal, width and thickness directions of the beam, respectively. In equilibrium, the beam is unstrained, unstressed, and at temperature $T_0$ everywhere [6].

In the present study, the usual Euler-Bernoulli assumption [6,7] is adopted, i.e., any plane cross-section, initially perpendicular to the axis of the beam, remains plane and
perpendicular to the neutral surface during bending. Thus, the
displacements are given by
\[ u = -z \frac{\partial w(x,t)}{\partial x}, \quad v = 0, \quad w(x,y,z,t) = w(x,t). \tag{1} \]

Hence, the differential equation of thermally induced
lateral vibration of the beam may be expressed in the form [6]:
\[ \frac{\partial^4 w}{\partial x^4} + \rho A \frac{\partial^2 w}{\partial t^2} + \alpha_T \frac{\partial^2 T_r}{\partial x^2} = 0, \tag{2} \]
where \( E \) is Young’s modulus, \( I = \frac{bh^3}{12} \) the inertial moment
about x-axis, \( \rho \) the density of the beam, \( \alpha_T \) the coefficient of
linear thermal expansion, \( w(x,t) \) the lateral deflection, \( x \) the
distance along the length of the beam, \( A = bh \) is the cross section area
and \( t \) the time and \( M_r \) is the thermal moment, which is
defined as:
\[ M_r = \frac{12}{h^3} \int_{-h/2}^{h/2} \theta z \, dz, \tag{3} \]
where \( \theta = T - T_0 \) is the dynamical temperature increment of the
resonator, in which \( T(x,z,t) \) is the temperature distribution and \( T_0 \)
the environmental temperature.

The non-Fourier heat conduction equation has the following form [17]:
\[ \frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial z^2} = \left( \frac{\partial}{\partial t} + \tau_0 \right) \frac{\partial^2 \theta}{\partial t^2} \left( \frac{\rho C_v}{k} \theta + \frac{\beta T_0}{k} e \right), \tag{4} \]
where \( e = \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \) is the volumetric strain, \( C_v \) is
the specific heat at constant volume, \( \tau_0 \) the thermal relaxation
time, \( k \) the thermal conductivity, \( \beta = \frac{E \alpha_e}{1 - 2\nu} \)
in which \( \nu \) is
Poisson’s ratio. Where there is no heat flow across the upper
and lower surfaces of the beam, so that \( \frac{\partial \theta}{\partial z} = 0 \) at \( z = \pm h/2 \)
For a very thin beam and assuming the temperature varies in
terms of a \( \sin(pz) \) function along the thickness direction,
where \( p = \pi / h \), gives:
\[ \theta(x,z,t) = \theta_1(x,t) \sin(pz). \]
Hence, equation (2) gives
\[ \frac{\partial^4 w}{\partial x^4} + \rho A \frac{\partial^2 w}{\partial t^2} + A \frac{\partial^2 \theta}{\partial x^2} + 12A \alpha_T \frac{\partial^2 \theta}{\partial x^2} \int_{-h/2}^{h/2} z \sin(pz) \, dz = 0 \tag{5} \]
and equation (4) gives
\[ \frac{\partial^2 \theta_1}{\partial x^2} \sin(pz) = \rho \frac{\partial \theta_1}{\partial t} \sin(pz) = \left( \frac{\partial}{\partial t} + \tau_0 \right) \frac{\rho C_v}{k} \theta_1 \sin(pz) = \frac{\beta T_0}{k} \frac{\partial^2 \theta_1}{\partial x^2} \sin(pz) \]
\[ \frac{\partial^2 \theta_1}{\partial x^2} \sin(pz) = \frac{\rho C_v}{k} \theta_1 \sin(pz) - \frac{\beta T_0}{k} \frac{\partial^2 \theta_1}{\partial x^2} \sin(pz) \]
\[ \frac{\partial^2 \theta_1}{\partial x^2} \sin(pz) = \frac{\beta T_0}{k} \frac{\partial^2 \theta_1}{\partial x^2} \sin(pz) \]
After doing the integrations, equation (5) takes the form
\[ \frac{\partial^4 w}{\partial x^4} + \rho A \frac{\partial^2 w}{\partial t^2} + \frac{24A \alpha_T}{h^2} \frac{\partial^2 \theta_1}{\partial x^2} = 0. \tag{6} \]
In equation (6), we multiply the both sides by \( z \) and
integrating with respect to \( z \) from \( -h/2 \) to \( h/2 \) then we obtain
\[ \left( \frac{\partial^2 \theta_1}{\partial x^2} - p^2 \right) \theta_1 = \left( \frac{\partial}{\partial t} + \tau_0 \right) \frac{\rho C_v}{k} \theta_1 = \frac{\beta T_0}{k} \frac{\partial^2 \theta_1}{\partial x^2} \sin(pz) = \frac{\beta T_0}{k} \frac{\partial^2 \theta_1}{\partial x^2} \sin(pz) \]
\[ \frac{\partial^2 \theta_1}{\partial x^2} - p^2 \theta_1 = \left( \frac{\partial}{\partial t} + \tau_0 \right) \frac{\rho C_v}{k} \theta_1 \]
\[ \theta_1 = \frac{\beta T_0}{k} \frac{\partial^2 \theta_1}{\partial x^2} \sin(pz) \]
Where, \( \eta = \frac{\rho C_v}{k} \).

Now, for simplicity we will use the following non-dimensional variables:
\[ (x', w', h') = \eta c_o (x, w, h), (t', \tau_o) = \eta c_o^2 (t, \tau_o), \]
\[ \sigma' = \frac{\sigma}{E}, \theta_1' = \theta_1, c_o = \frac{E}{\rho}. \tag{9} \]
Then, we have
\[ \frac{\partial^4 w}{\partial x^4} + A_1 \frac{\partial^2 w}{\partial t^2} + A_2 \frac{\partial^2 \theta_1}{\partial x^2} = 0, \tag{10} \]
and
\[ \frac{\partial^2 \theta_1}{\partial x^2} - A_3 \theta_1 = \left( \frac{\partial}{\partial t} + \tau_0 \right) \frac{\rho C_v}{k} \theta_1 = \frac{\beta T_0}{k} \frac{\partial^2 \theta_1}{\partial x^2} \sin(pz) \]
\[ \frac{\partial^2 \theta_1}{\partial x^2} - A_3 \theta_1 = \left( \frac{\partial}{\partial t} + \tau_0 \right) \frac{\rho C_v}{k} \theta_1 = \frac{\beta T_0}{k} \frac{\partial^2 \theta_1}{\partial x^2} \sin(pz) \]
\[ \theta_1 = \frac{\beta T_0}{k} \frac{\partial^2 \theta_1}{\partial x^2} \sin(pz) \]
Where
\[ A_1 = \frac{12}{h^2}, A_2 = \frac{24A \alpha_T}{\pi^2 h^2}, A_3 = p^2, A_4 = \frac{\pi^2 \beta h}{24k\eta}, \]
and we have canceled the prime for convenience.

**Formulations the Problem in the Laplace Transform Domain**

Applying the Laplace transform for equations (10) and (11)
defined by the formula
\[ \mathcal{L}\{f(t)\} = \int_0^\infty f(t) e^{-st} \, dt \]
Hence, we obtain the following system of differential equations

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The formal solution of equation (17) is given by
\[ V(\mathbf{x}, s) = \exp[A(s) \cdot \mathbf{x}] V(0, s), \] (20)

Where
\[
\begin{bmatrix}
\tilde{w}(0, s) \\
\tilde{\alpha}_1(0, s) \\
\tilde{\eta}(0, s)
\end{bmatrix}
\]

The characteristic equation of the matrix \(A(s)\) has the form
\[ k^6 - \ell k^4 + m k^2 - n = 0, \] (22)

Where
\[ \ell = \alpha_1 + \alpha_3, \quad m = \alpha_1\alpha_3 - \alpha_2\alpha_4 + \alpha_5, \quad n = \alpha_2\alpha_5. \]

The roots of the characteristic equation (22) \(k_1^2, k_2^2\) and \(k_3^2\) satisfy the following relations
\[ k_1^2 + k_2^2 + k_3^2 = \ell, \] (23a)
\[ k_1^2 k_2^2 + k_2^2 k_3^2 + k_1^2 k_3^2 = m, \] (23b)
\[ k_1^2 k_2^2 k_3^2 = n. \] (23c)

The Taylor series expansion for the matrix exponential is given by
\[ \exp\{A(s) \cdot \mathbf{x}\} = \sum_{i=0}^{\infty} \frac{[A(s) \cdot \mathbf{x}]^i}{i!}. \] (24)

Using the Cayley-Hamilton theorem [23-25], this infinite series can be truncated to
\[ \exp\{A(s) \cdot \mathbf{x}\} = L(\mathbf{x}, s) = a_0 I + a_1 A + a_2 A^2 + a_3 A^3 + a_4 A^4 + a_5 A^5, \] (25)

Where \(I\) is the unit matrix of order 6 and \(a_0 - a_5\) are some parameters depending on \(s\) and \(\mathbf{x}\) to be determined.

Using the Cayley-Hamilton theorem again [23,25], we obtain
\[ \exp\{k_1 \mathbf{x}\} = a_0 + a_1 k_1 + a_2 k_1^2 + a_3 k_1^3 + a_4 k_1^4 + a_5 k_1^5, \]
\[ \exp\{-k_1 \mathbf{x}\} = a_0 - a_1 k_1 + a_2 k_1^2 - a_3 k_1^3 + a_4 k_1^4 - a_5 k_1^5, \]
\[ \exp\{k_2 \mathbf{x}\} = a_0 + a_1 k_2 + a_2 k_2^2 + a_3 k_2^3 + a_4 k_2^4 + a_5 k_2^5, \]
\[ \exp\{-k_2 \mathbf{x}\} = a_0 - a_1 k_2 + a_2 k_2^2 - a_3 k_2^3 + a_4 k_2^4 - a_5 k_2^5, \]
\[ \exp\{k_3 \mathbf{x}\} = a_0 + a_1 k_3 + a_2 k_3^2 + a_3 k_3^3 + a_4 k_3^4 + a_5 k_3^5, \]
\[ \exp\{-k_3 \mathbf{x}\} = a_0 - a_1 k_3 + a_2 k_3^2 - a_3 k_3^3 + a_4 k_3^4 - a_5 k_3^5. \] (26)

The solution of this system of linear equations is given by
\[ a_0 = -F(k_2^3 k_3^2 c_1 + k_2^3 k_3^2 c_2 + k_2^3 k_3^2 c_3), \]
\[ a_1 = -F(k_2^3 k_3^2 s_1 + k_2^3 k_3^2 s_2 + k_2^3 k_3^2 s_3). \]
a_2 = F \{(k_x^2 + k_z^2) c_1 + (k_x^2 + k_{x'}^2) c_2 + (k_{x'}^2 + k_z^2) c_3 \},
\text{and} \\
a_3 = F \{(k_x^2 + k_z^2) s_1 + (k_x^2 + k_{x'}^2) s_2 + (k_{x'}^2 + k_z^2) s_3 \},
\text{for} \ a_4 = -F \{c_1 + c_2 + c_3 \},
\text{and} \\
a_5 = -F \{s_1 + s_2 + s_3 \}. 
\tag{27}

where
\begin{align*}
F &= \frac{1}{(k_x^2 - k_z^2) (k_{x'}^2 - k_z^2) (k_{x'}^2 - k_x^2)}, \\
c_1 &= (k_x^2 - k_z^2) \cosh (k_z x),
\end{align*}
\begin{align*}
c_2 &= (k_x^2 - k_z^2) \cosh (k_{x'} x),
\end{align*}
\begin{align*}
c_3 &= (k_{x'}^2 - k_z^2) \cosh (k_x x),
\end{align*}
\begin{align*}
s_i &= \frac{(k_x^2 - k_{x'}^2)}{k_i} \sinh (k_i x),
\end{align*}
\begin{align*}
s_i &= \frac{(k_x^2 - k_{x'}^2)}{k_i} \sinh (k_{x'} x),
\end{align*}
\begin{align*}
s_i &= \frac{(k_{x'}^2 - k_z^2)}{k_i} \sinh (k_z x),
\end{align*}
\begin{align*}
\eta &= \frac{\Delta \sinh (k_z (\ell - x))}{(k_x^2 - k_z^2) (k_z^2 - k_{x'}^2) \sinh (k_{x'} \ell)}
+ \frac{\Delta \sinh (k_{x'} (\ell - x))}{(k_{x'}^2 - k_z^2) (k_z^2 - k_x^2) \sinh (k_x \ell)}
+ \frac{\Delta \sinh (k_x (\ell - x))}{(k_x^2 - k_{x'}^2) (k_{x'}^2 - k_z^2) \sinh (k_{x'} \ell)}.
\tag{37}
\end{align*}

To get \( W(0,s), \bar{\eta}(0,s) \) and \( \bar{\eta}(0,s) \), we will consider the other end of the beam \( x = \ell \) is clamped and remains at zero increment of temperature as follows:
\begin{align*}
w(\ell,t) = \eta(\ell,t) = 0. 
\tag{34}
\end{align*}
After using Laplace transform, we have
\begin{align*}
\bar{\eta}(\ell,s) = \bar{\eta}(\ell,s) = \bar{\eta}(\ell,s) = 0. 
\tag{35}
\end{align*}
Hence, we obtain
\begin{align*}
\begin{bmatrix}
\bar{\eta}(\ell,s) \\
\bar{\eta}(\ell,s) \\
\bar{\eta}(\ell,s)
\end{bmatrix} = -G(s)
\begin{bmatrix}
\eta\big(0,s\big) \\
\eta\big(0,s\big) \\
\eta\big(0,s\big)
\end{bmatrix}.
\tag{36}
\end{align*}

After some complicated simplifications by using MAPLE software, we get the final solutions in the Laplace transform domain as follow:

The lateral deflection
\begin{align*}
\bar{w}(x,s) = \frac{\Delta \sinh (k_z (\ell - x))}{(k_x^2 - k_z^2) (k_z^2 - k_{x'}^2) \sinh (k_{x'} \ell)}
+ \frac{\Delta \sinh (k_{x'} (\ell - x))}{(k_{x'}^2 - k_z^2) (k_z^2 - k_x^2) \sinh (k_x \ell)}
+ \frac{\Delta \sinh (k_x (\ell - x))}{(k_x^2 - k_{x'}^2) (k_{x'}^2 - k_z^2) \sinh (k_{x'} \ell)}.
\tag{37}
\end{align*}

The temperature
\begin{align*}
\bar{\theta}(z,s) = -\frac{\alpha k_z^2 \Delta \sin (pz) \sinh (k_z (\ell - x))}{(k_z^2 - \alpha z) (k_z^2 - k_z^2) (k_z^2 - k_x^2) \sinh (k_z \ell)}
- \frac{\alpha k_x^2 \Delta \sin (pz) \sinh (k_x (\ell - x))}{(k_x^2 - \alpha z) (k_x^2 - k_z^2) (k_x^2 - k_{x'}^2) \sinh (k_x \ell)}
- \frac{\alpha k_{x'}^2 \Delta \sin (pz) \sinh (k_{x'} (\ell - x))}{(k_{x'}^2 - \alpha z) (k_{x'}^2 - k_z^2) (k_{x'}^2 - k_{x'}^2) \sinh (k_{x'} \ell)}.
\tag{38}
\end{align*}

The displacement
\begin{align*}
\bar{\eta}(0,s) = \frac{\eta_0}{t_0} \left(1 - \frac{e^{-t_0 s}}{s^2}\right) = G(s),
\tag{32}
\end{align*}
Applying the conditions (31) and (32) into equations (21), we obtain
\[ \vec{\alpha}(z, x, s) = -z \Delta k_1 \cosh(k_1(\ell - x)) \left( \frac{k_2^2 - k_1^2}{k_2^2 - k_1^2} \right) \sinh(k_1\ell) \]
\[ - z \Delta k_2 \cosh(k_2(\ell - x)) \left( \frac{k_2^2 - k_1^2}{k_2^2 - k_1^2} \right) \sinh(k_2\ell) \]
\[ - z \Delta k_3 \cosh(k_3(\ell - x)) \left( \frac{k_2^2 - k_1^2}{k_2^2 - k_1^2} \right) \sinh(k_3\ell) \]
\[ \left( k_2^2 - k_1^2 \right) \left( k_3^2 - k_1^2 \right) \sinh(k_1\ell) \]

(39)

The Strain
\[ \tau(z, x, s) = \frac{z \Delta k_1}{k_2^2 - k_1^2} \sinh(k_1(\ell - x)) \left( \frac{k_2^2 - k_1^2}{k_2^2 - k_1^2} \right) \sinh(k_1\ell) \]
\[ + \frac{z \Delta k_2}{k_2^2 - k_1^2} \sinh(k_2(\ell - x)) \left( \frac{k_2^2 - k_1^2}{k_2^2 - k_1^2} \right) \sinh(k_2\ell) \]
\[ + \frac{z \Delta k_3}{k_2^2 - k_1^2} \sinh(k_3(\ell - x)) \left( \frac{k_2^2 - k_1^2}{k_2^2 - k_1^2} \right) \sinh(k_3\ell) \]
\[ \left( k_2^2 - k_1^2 \right) \left( k_3^2 - k_1^2 \right) \sinh(k_1\ell) \]

(40)

Where
\[ \Delta = \frac{G}{\alpha_1 \alpha_2} \left( \alpha_1 - k_1^2 \right) \left( \alpha_1 - k_2^2 \right) \left( \alpha_1 - k_3^2 \right) \]

The Stress and the Strain-Energy

The stress on the x-axis, according to Hooke’s law is:
\[ \sigma_{xx}(x, z, t) = E(e - \alpha_T \theta). \]

(41)

By using the non-dimensional variables in (9), we obtain the stress in the form
\[ \sigma_{xx}(x, z, t) = e - \alpha_T T_0 \theta. \]

(42)

After using Laplace transform, the above equation takes the form:
\[ \tilde{\sigma}_{xx}(x, z, s) = \tilde{e} - \alpha_T T_0 \tilde{\theta}. \]

(43)

The strain energy which is generated on the beam is given by
\[ W(x, z, t) = \sum_{i, j=1}^{3} \frac{1}{2} \sigma_{ij} e_{ij} = \frac{1}{2} \sigma_{xx} e_{xx} = - \frac{1}{2} z \sigma_{xx} \eta. \]

(44)

or, we can write as follows:
\[ W(x, z, t) = -\frac{1}{2} z \left[ L^{-1}(\sigma_{xx}) \right] \left[ L^{-1}(\eta) \right]. \]

(45)

Where \[ L^{-1}(\tilde{f}(s)) = f(t) \] is the Laplace inverse.

Those complete the solution in the Laplace transform domain.

**Numerical Inversion of the Laplace Transform**

In order to determine the solutions in the time domain, the Riemann-sum approximation method is used to obtain the numerical results. In this method, any function in Laplace domain can be inverted to the time domain as
\[ f(t) = \frac{e^{\kappa t}}{t} \left[ \frac{1}{2} \mathcal{F}(\kappa) + \text{Re} \sum_{n=1}^{N} (-1)^{n} \mathcal{F} \left( \kappa - \frac{n\pi}{t} \right) \right] \]

(46)

Where Re is the real part and \( i \) is imaginary number unit. For faster convergence, numerous numerical experiments have shown that the value of \( \kappa \) satisfies the relation \( \kappa t \approx 4.7 \)
Tzou [26].

**Numerical Results and Discussion**

Now, we will consider a numerical example for which computational results are given. For this purpose, gold (Au) is taken as the thermoelastic material for which we take the following values of the different physical constants:
\[ k = 318 \text{W/mK}, \quad \alpha_T = 14.2 \times 10^{-6} \text{K}^{-1}, \]
\[ \rho = 1930 \text{kg/m}^3, \quad T_0 = 293 \text{K}, \quad C_v = 130 \text{J/(kgK)}, \]
\[ E = 180 \text{GPa}, \quad \nu = 0.44. \]

The aspect ratios of the beam are fixed as \( \ell / h = 10 \) and \( b / h = 1/2 \). When \( h \) is varied, \( \ell \) and \( b \) changed accordingly with \( h \).

For the nanoscale beam, we will take the range of the beam length \( \ell (1-100) \times 10^{-12} \text{m} \). The original time \( t \) and the ramping time parameter \( t_0 \) will be considered in the picoseconds \((1-100) \times 10^{-12} \text{sec} \) and the relaxation time \( t_0 \) in the range \((1-100) \times 10^{-14} \text{sec} \).

The figures were prepared by using the non-dimensional variables which are defined in (9) for a wide range of beam length when \( \ell = 1.0, \quad \theta_0 = 1.0, \quad z = h/6 \) and \( t = 0.15 \).

Figures (1-5), represent the lateral vibration, the temperature, the displacement, the stress and the strain energy of the beam at different values of the relaxation time when \( t_0 = 0.0 \) (Biot) and \( t_0 = 0.02 \) (L-S) and we found that, the relaxation time has significant effects on all the studied fields. In the context of L-S, the values of the lateral vibration, the temperature, the displacement, the stress and the strain energy decreasing when the relaxation time value increases and it is very obvious in the peak points. In the context of L-S model, the speed of the wave propagation of all the studied fields vanish at points closed to the first edge of the beam more than
the points at the context of Biot model and the damping of the strain-energy appear in L-S model before Biot model.

FIG. 1. The lateral deflection $w$ for L-S and Biot theories

FIG. 2. The temperature for L-S and Biot theories

FIG. 3. The displacement for L-S and Biot theories

FIG. 4. The stress for L-S and Biot theories

FIG. 5. The strain-energy at L-S and Biot theories

FIG. 6. The lateral deflection $w$ at different time of ramping parameter

FIG. 7. The temperature at different time of ramping parameter

FIG. 8. The displacement at different time of ramping parameter
In figures (6-10), we represented the lateral vibration, the temperature, the displacement, the stress and the strain energy of the beam at different values of the ramping time parameter when \( t_d(0.10) \leq t \leq 0.15 \) and \( t_d(0.20) > t \leq 0.15 \) in the context of L-S model. We found that, the ramping time parameter has significant effects on all the studied fields. The increasing in the value of the ramping time parameter causes decreasing in the values of all the fields which is very obvious in the peak points of the curves. Also, the damping of the strain energy increases when the ramping time parameter increases.

**Conclusion**

This paper has investigated the vibration characteristics of the deflection, the temperature, the displacement, the stress and the strain energy of an Euler-Bernoulli gold nano-beam induced by a ramp type heating. An analytical direct method and numerical technique based on the Laplace transformation has been used to calculate the vibration of the deflection, the temperature, the displacement, the stress and the strain energy. The effects of the relaxation time and the ramping time parameter on all the studied fields have been shown and represented graphically. The non-Fourier law of heat conduction gives a finite speed of wave propagation and increases the damping of the strain energy.

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Appendix

\[ L_{11}(x,s) = a_0 - a_4 \alpha_5, \]
\[ L_{12}(x,s) = a_4 \alpha_4, \]
\[ L_{13}(x,s) = a_2 + a_5 \alpha_5, \]
\[ L_{14}(x,s) = a_1 - a_5 \alpha_5, \]
\[ L_{15}(x,s) = -a_5 \alpha_4, \]
\[ L_{16}(x,s) = a_5 + a_5 \alpha_5, \]
\[ L_{21}(x,s) = a_4 \alpha_2 \alpha_3, \]
\[ L_{22}(x,s) = a_0 + a_2 \alpha_4 + a_4 (\alpha_1^2 + a_2 \alpha_4), \]
\[ L_{23}(x,s) = -a_2 \alpha_2 - a_4 \alpha_2 (\alpha_1 + \alpha_5), \]
\[ L_{24}(x,s) = a_5 \alpha_2 \alpha_3, \]
\[ L_{25}(x,s) = a_1 + a_5 \alpha_4 + a_3 (\alpha_2 \alpha_4 + \alpha_1 + \alpha_5), \]
\[ L_{26}(x,s) = -a_2 \alpha_2 - a_5 \alpha_2 (\alpha_1 + \alpha_5), \]
\[ L_{31}(x,s) = -a_2 \alpha_3 - a_4 \alpha_5, \]
\[ L_{32}(x,s) = -a_2 \alpha_4 - a_4 \alpha_4 (\alpha_1 + \alpha_5), \]
\[ L_{33}(x,s) = a_0 + a_2 \alpha_3 + a_4 (\alpha_2 \alpha_4 - \alpha_3 + \alpha_5^2), \]
\[ L_{34}(x,s) = -a_5 \alpha_3 - a_5 \alpha_5, \]
\[ L_{35}(x,s) = -a_5 \alpha_4 - a_5 \alpha_4 (\alpha_1 + \alpha_5), \]
\[ L_{36}(x,s) = a_1 + a_5 \alpha_4 + a_5 (\alpha_2 \alpha_4 - \alpha_3 + \alpha_5^2), \]
\[ L_{41}(x,s) = -a_2 \alpha_3 - a_4 \alpha_5, \]
\[ L_{42}(x,s) = -a_2 \alpha_4 - a_4 \alpha_4 (\alpha_1 + \alpha_5), \]
\[ L_{43}(x,s) = a_1 + a_5 \alpha_3 + a_3 (\alpha_2 \alpha_4 - \alpha_3 + \alpha_5^2), \]
\[ L_{44}(x,s) = a_0 - a_4 \alpha_5, \]
\[ L_{45}(x,s) = -a_4 \alpha_4, \]
\[ L_{46}(x,s) = a_2 + a_4 \alpha_5, \]
\[ L_{51}(x,s) = a_2 \alpha_2 \alpha_3 + a_4 \alpha_2 \alpha_3 (\alpha_1 + \alpha_5), \]
\[ L_{52}(x,s) = a_1 \alpha_1 + a_5 (\alpha_2^2 + a_2 \alpha_4) + a_3 (\alpha_2 \alpha_4 + \alpha_4 \alpha_5), \]
\[ L_{53}(x,s) = -a_1 \alpha_2 - a_3 \alpha_2 (\alpha_1 + \alpha_5), \]
\[ L_{54}(x,s) = a_4 \alpha_2 \alpha_3, \]
\[ L_{55}(x,s) = a_2 \alpha_2 - a_4 \alpha_2 (\alpha_1 + \alpha_5), \]
\[ L_{61}(x,s) = a_1 \alpha_3 - a_3 \alpha_3 \alpha_5 - a_3 \alpha_3 (\alpha_2 \alpha_4 - \alpha_3 + \alpha_5^2), \]
\[ L_{62}(x,s) = -a_1 \alpha_4 - a_4 \alpha_4 (\alpha_1 + \alpha_5), \]
\[ L_{63}(x,s) = a_1 \alpha_5 + a_5 (\alpha_2 \alpha_4 - \alpha_3 + \alpha_5^2) + a_3 (\alpha_2 \alpha_4 \alpha_5), \]
\[ L_{64}(x,s) = a_2 \alpha_5 - a_4 \alpha_5, \]
\[ L_{65}(x,s) = a_2 \alpha_4 - a_4 \alpha_4 (\alpha_1 + \alpha_5), \]
\[ L_{66}(x,s) = a_0 + a_2 \alpha_5 + a_4 (\alpha_2 \alpha_4 - \alpha_3 + \alpha_5^2), \]
Optical absorption and photoelectron collection properties of silicon wafers with conical quantum nanocrystals structure

Yuriy Vashpanov* and Jae-II Jeong

A conical form of nano-sized quantum cluster was formed on the surface of p-type crystalline silicon [111] wafer by anode electrochemical etching in HF-based solution. The conical surface is highly effective in absorbing sunlight and transporting photoelectrons to semiconductor material. These are because each cone has a graded band gap with the energy level in the range from 1.1 to 3 eV which can be considered as consisting of quantum dots in different sizes. Since the boron concentration on the surface of each cone gradually decreases from top to bottom, a continuously varying electrical field is created along the cone height. This electric field is forcing photoelectrons generated in the cone to move rapidly to the direction perpendicular to wafer surface. Hence the drift time of photoelectrons can be less than their recombination time within the thin layer close to the bottom of the cone.

Keywords: Silicon; Nanocrystals; Electrochemical etching; Solar cells

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Searching new materials and methods which can increase the efficiency of the solar cell is important in both theoretical and practical application point of view [1]. Now, solar cells with the base of polycrystalline Cu(InGa)Se₂ (CIGS or CIS with no Ga) and of cadmium telluride thin films [2], with triple-junction on the base of GaInP-GaAs-Ge layers [3], with polymer mixtures combined with InP nanowires thin-film [4] are very promising. To further increase the efficiency, silicon solar cells with a tandem structure of silicon quantum dot/crystalline silicon is proposed [5]. However, the solar cells on the crystalline silicon base are currently reached to have efficiency of 24% [6], and are the most popular technique because there is well-developed production equipment, and the material is cheap and nontoxic.

A method of multilayered semiconductors, where the top layer absorbs short-wave light and the subsequent layers absorb long-wave sun light, is proposed [7]. Semiconductors with band gap energy matching to quantum energy of sun light can be used most effectively for solar cells. However, to cover all solar spectrums, the number of layers should be large. It has shown theoretically that in case of multilayer (n=20 to 25) thin film semiconductors with different band gaps in the range from $E_{g1}=1.1$ eV to $E_{g2}=3$ eV with a step $(E_{g2}-E_{g1})/n$. It is possible to achieve solar cells with efficiency near 60% [8]. It is known recently that a semiconductor band gap increases as crystal’s geometrical size decreases (quantum nano-size effect) [9]. For example, crystalline silicon quantum dots in different geometrical size from 2 nm to 6 nm have a magnitude of band gap energy from 3 to 1.3 eV [10]. Band-gap energy of crystalline silicon is around 1.1 eV [11]. Thus, this idea can be realized today with the help of nanotechnology when a serially connected quantum dots system with size in the range from 1 nm to 10 nm or nano-sized cone crystal on a crystalline silicon
surface is fabricated.

In this short communication, a new method of forming conical nanocrystals as anti-reflection layer, on the silicon surface and the preliminary analysis of its light collection efficiency are presented.

A nano-sized crystal having a cone shape has been produced on the surface of p-type crystalline silicon wafer in [111] direction by anode electrochemical etching in HF-based solution. The etching process lasts 5 minutes under the current density around 10 mA/cm². Before the etching process, boron is thermally diffused on to the silicon wafer. The boron concentration reaches to 10²² cm⁻³ on the surface of silicon wafer and decreases exponentially as it gets into the inside of the wafer according to Fick's law [12].

The atomic-force microscopy image of the thin layer of nano-sized conic clusters on crystalline silicon wafer, taken by Nanoscope IIIa Dimension 3000TM (Digital Instruments, USA) is shown in Fig. 1. Figure 1 shows that a large number of cones are almost uniformly disposed on the surface. The surface morphology of the silicon wafer is clearly different from that of the porous silicon which is fabricated through the similar electrochemical etching procedure [10]. Apparently, the difference is brought by the thermal diffusion of boron into silicon wafer. The silicon wafer absorbs practically all visible light spectral range, i.e., from violet to near infrared. The measurement shows that it reflects less than 2% of the sun light in the wavelength range from 300 nm to 1120 nm. This means that it works almost like a black body, i.e., the cone layer forms an anti-reflection layer on the p-type silicon layer. The small reflectivity values are probably induced by two physical reasons such as evanescing of wave along the surface of the cones and graded band gap semiconductor properties of the cones. It is possible to consider that the coned surface is working as a nanoscale grating (see Fig. 2). In this case, the lights will propagate along the coned surface. Hence they are mostly absorbed on the surface of each cone as the evanescent wave does [13]. The graded band gap can only be explained by quantum-size effect, i.e., the cone diameters in nano size increase as getting closer to its bottom. Hence it forms a quantum dot system. This system has a continuously varying band gaps within 1.1 to 3 eV. Hence each cone works like a serially connected quantum dot system with different band gap energies. The maximum energy appears at the top of the cones as shown in Fig. 3. The diameter of the top part is approximately 2 nm.

The number of photons from sun light in the waveband within λ₁ to λ₂ that get on square meter of semiconductor surface per second, can be calculated by Plank’s radiation law [14]:

\[ N = \int_{\lambda_1}^{\lambda_2} N(\lambda, T) d\lambda = \frac{\int_{\lambda_1}^{\lambda_2} Q(\lambda, T) \times \frac{\lambda}{hc} d\lambda}{\lambda_1^2 \left[\exp(\frac{c_2}{\lambda T}) - 1\right] \times hc} \]

Where, \( Q(\lambda, T) = \frac{c_1}{\lambda^2 \left[\exp(\frac{c_2}{\lambda T}) - 1\right]} \) is the blackbody spectrum (Plank’s radiation law),

\[ c_1 = 2\pi h c^2 = 3.741832 \times 10^{-16} \text{ W} \cdot \text{m}^2, \]

\[ c_2 = h c / k = 1.438786 \times 10^{-2} \text{ m} \cdot \text{K}, \]

\( \lambda \) wavelength of light, \( T (=5523.3) \) the black body’s temperature in Kelvin of the sun in sea level [15], \( h \) is Planck’s constant, \( c \) is speed of light, and \( k \) is Boltzmann’s constant [14].

Photons with higher energy are absorbed at the top part of cone. Light with quantum energy less than band gap energy of the cone cannot be absorbed. For example, the quantum of light...
with energy ~1.1 eV cannot be absorbed on the cone surface, because band gap energy of quantum dots are bigger than 1.1 eV. The photons with energy equal to the band gap can be maximally absorbed at the part of the cone, where its diameter corresponds to the band gap. The absorption spectral range of the silicon wafer, 300-1120 nm covers much of the solar energy from the sun as shown in the first curve of Fig. 4.

Compared with the silicon wafer with coned layer, silicon crystal absorbs only part of sun light within the waveband 300 nm to 1120 nm as shown in curve 2 of Fig. 4. From Eq. 1, the total number of photons absorbed in the silicon crystal for the given T, $N_{c-Si}$ can be calculated as

$$N_{c-Si} = \int_{300}^{1120} N(\lambda)F_{abs}(\lambda)d\lambda.$$  

Where, $F_{abs}(\lambda)$ is the absorption factor for each wavelength for crystalline silicon [16]. The ratio of $N$ to $N_{c-Si}$, $\gamma_{abs}$ ($\gamma_{abs} = N/N_{c-Si}$) represents the gain achieved by forming coned surface. $\gamma_{abs}$ is calculated as 2.784 for sample shown in Fig. 1. The efficiency of solar cell increased 2.784 times of that of crystalline silicon, when no other parameter is changed.

Since, the physical reason of efficiency decrease in solar cells is the recombination of photoelectrons in the p-type part and a p-n-junction area of semiconductor solar device [17]. One way of decreasing the recombination rate is to make the drifting time of non-equilibrium photoelectrons from p-type conical clusters shorter than that of the recombination. The graded band gap semiconductors under a special doping profile having a flat valence band as shown in Fig. 3 can create the condition. The electric field formed by the continuously different conductance band gap energies of nano-sized quantum cone crystal as shown in Fig. 3, forces the photoelectrons to move fast in the direction perpendicular to the silicon wafer surface. Thus, the conical clusters are making the photoelectrons to behave like ballistics electrons. These ballistics electrons have a short transit time in p-n-junction area that can lead to reduce recombination losses in the p-n-junction.

This exponentially varying doping profile of boron concentration is made before etching. Obviously, this exponential profile is kept even after etching treatment. Thus, the configuration of graded band gap structure as shown in Fig. 3 is achieved. Precise estimation of Fermi level position and band gaps of conic quantum dot systems depend on the boron concentration. The estimation cannot be done easily but it is very important in optimizing technological process of solar cells.

Photoelectrons, which are generated by the trapped photons p-type conical nano-sized clusters, recombine with holes during their transit time period $\tau_{rec}$ when no electric field exists. This recombination will lead to efficiency loss for solar cells. However, with electrical field in conical clusters, the photoelectrons transit the p-type layer shorter than $\tau_{rec}$. If $\tau_{drift}$ the transit time under the electric field is considerably less than $\tau_{rec}$, the current losses in anti-reflection layer will be reduced. Determining the transit time in nanostructures is a really complex problem. However, the drift time from the semiconductors physics, which is based on quantum mechanics laws is used, the effective electric field is calculated as

$$\mathbf{E} = \frac{\Delta E_C}{e \cdot l}$$

for the profile of conductance band as shown in Fig. 3, where $\Delta E_C$ is gradient of conducting band gap energy, $e$ is electron charge and $l$ is the height of conical clusters. In this

FIG. 3. The configuration of graded band gap structure of conic nanocrystal.

FIG. 4. A photons density per second of solar radiation spectrum (a curve 1) and a absorbing in crystalline silicon photons spectrum (calculated from data of absorption spectrum [16]) (a curve 2).
case, \( \tau_{drift} \) is calculated as \( \tau_{drift} = \frac{l}{\mu_n E} = \frac{l^2}{\mu_n \Delta E_c} \). The condition \( \tau_{drift} \leq \tau_{rec} \) will be achieved when \( l \leq \sqrt{\mu_n \Delta E_c \tau_{rec}} \).

For silicon, since \( \mu_n \approx 1400 \, \text{cm}^2/\text{Vsec} \), \( \tau_{rec} = 10^{12} \, \text{sec} \) [11] and \( \Delta E_c = 0.1 \pm 2.9 \, \text{eV} \), the maximum \( l \) value satisfying the relationship is around 118 nm. Thus, photoelectrons can go through the p-type anti-reflected layer without significant recombination when the cone height is less than 100 nm. In practice, this condition can be easily obtained under the current technology of manufacturing solar cells. Since it is desired to decrease the height of each cone for the minimization of internal resistance of the conical cluster, photoelectrons will leave more rapidly the p-type layer without recombining with holes. The minimum speed of the photoelectrons can be around \( 10^5 \, \text{m/s} \). This speed is more than 4 times that of thermal electrons at room temperature in the silicon crystal. The speed of thermal electrons is around \( 2.3 \times 10^5 \, \text{m/s} \) [11]. For this reason, the efficiency of solar cell will be increased compared with that of the solar cells based on crystalline silicon by reducing the recombination rate 4 times.

It is considered that the current losses in the solar cells based on crystalline silicon are attributed to different physical effects: The thermalization of photoelectrons causes 29.2\% loss, the incomplete collection of photoelectrons 4.5\%, added shunting resistor 4.7\%, and the recombination in junction area 19.2\% [17]. With the anti-reflection layer, the losses due to the photoelectron thermalization and the incomplete collecting of photoelectrons will be eliminated by the graded band gap presence. Ballistics electrons have a higher probability of passing the cones. Therefore the efficiency of solar cell with conical nano-sized cluster layer can be characterized with the photocurrent \( I_{ph} \), the recombination current \( I_{rec} \), and current through added shunting resistor, \( I_f \). The efficiency increment \( \gamma \) can be calculated as

\[
\gamma = \frac{\gamma_{abs} I_{ph} - \gamma_{b} \xi_{rec} I_{f}}{I_{ph} - \xi_{rec} I_{f}} = \frac{\gamma_{abs} I_{ph} - \gamma_{b} \xi_{rec} I_{ph} - \xi_f I_{ph}}{I_{ph} - \xi_{rec} I_{ph} - \xi_f I_{ph}}
\]

\[
= \frac{\gamma_{abs} - \gamma_{b} \xi_{rec} - \xi_f}{1 - \xi_{rec} - \xi_f} = 3.539
\]

Where \( \gamma_b \), \( \xi_{rec} \) and \( \xi_f \) represent transit time ratio of ballistic electrons to thermal electrons, and losses by recombination and shunting resistor, respectively. The efficiency of commercial silicon solar cell is about 15 to 20\% [18]. With the assumption of preserving other parameters of solar cells, the efficiency should increase to \( \gamma \) times, i.e., the efficiency will be calculated as \( 3.539 \times (15-20\%) = 53-70\% \).

As the conclusion, generating ballistic electrons with the conical form quantum clusters layer will lead to a significant improvement in the solar cell efficiency based on crystalline silicon. The anti-reflecting and photoelectrons collecting thin layer can easily be formed by the etching method described before. Silicon solar technologies will have good perspectives in competing with other materials of high efficiency. The conical form quantum clusters layer will not essentially increase the manufacturing cost of solar cells. For more impactful and functional than silicon, it may be necessary to use a germanium (or another narrow-band-gap semiconductor), which has the band gap energy of 0.7 eV. In this case, more infrared spectral range of the sun light will be absorbed. This means that the efficiency will be increased more.

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Effect of nitrogen on deposition and field emission properties of boron-doped micro- and nano-crystalline diamond films

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In this paper, we report the effect of nitrogen on the deposition and properties of boron doped diamond films synthesized by hot filament chemical vapor deposition. The diamond films consisting of micro-grains (nano-grains) were realized with low (high) boron source flow rate during the growth processes. The transition of micro-grains to nano-grains is speculated to be strongly (weekly) related with the boron (nitrogen) flow rate. The grain size and Raman spectral feature vary insignificantly as a function of the nitrogen introduction at a certain boron flow rate. The variation of electron field emission characteristics dependent on nitrogen is different between microcrystalline and nanocrystalline boron doped diamond samples, which are related to the combined phase composition, boron doping level and texture structure. There is an optimum nitrogen proportion to improve the field emission properties of the boron-doped films.

Keywords: Chemical vapor deposited diamond film; Nitrogen effect; Boron doping; Microcrystalline; Nanocrystalline; Electron field emission

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Chemical vapor deposited (CVD) diamond films have attracted intensive interests owing to its outstanding properties, such as wide band gap, super-hardness, high thermal conductivity, high carrier mobility and high chemical inertness. However, it is somehow limited for electronic application of diamond due to its insulating property, unless the dopants are incorporated into diamond [1]. Various elements (e.g. nitrogen N, boron B, sulfur S, and phosphorus P) have been introduced into diamond to adjust their electronic properties. The nucleation process [2], growth mechanism [3], impurity distribution [4] and properties [5-7] affected by doping have been extensively investigated. However, in previous work, the understanding on how the dopants (mainly refer to N and B) modify the growth and properties of diamond films was mostly emphasized on the sole doping by boron or nitrogen. Recently, there are a few reports on the diamond deposition with co-dopants [8,9]. Hartmann et al. [8] reported that in highly boron-doped micro-diamond, large (small) additions of nitrogen would stabilize the diamond structure (induce more graphite formation). The electronic structure of boron-doped nano-diamond films can be markedly modified by nitrogen and there was an optimized gas proportion to achieve improved field emission [9]. However, the corresponding underlying mechanism is still not very clear. Furthermore, growth features related to the co-doping of boron and nitrogen are desirable to be investigated in detail.

In this letter, by hot filament CVD (HFCVD), the microcrystalline diamond (MCD) and nanocrystalline diamond (NCD) films with co-introducing boron and nitrogen were synthesized by adjusting the gas proportion of nitrogen and boron in the reaction ambient. The effect of nitrogen on the
deposition, structural characteristics and electron field emission (EFE) properties of boron-doped diamond films has been systematically investigated.

The polycrystalline diamond films were synthesized by a HFCVD system [5]. The p-type Si (111) substrates were abraded by diamond paste and cleaned ultrasonically in ethanol solution for nucleation enhancement. A spiral tantalum wire was used as the filament, and its heating temperature was about 2200°C. The total pressure was 4 kPa with 2% CH₄ in the precursor gases of methane (CH₄, flow rate: 4 sccm) and hydrogen (H₂, flow rate: 200 sccm). The substrate temperature was approximately 800°C monitored by an optical pyrometer. The boron source was introduced by bubbling the H₂ gas (flow rates: 2, 10 sccm) through the liquid trimethylborate (B(OCH₃)₃) (ambient temperature kept at 25°C), and the nitrogen gas flow rates were 1, 4, and 8 sccm at different boron flow rates. For simplification, in this letter, the boron flow rate (determining the boron doping level) is expressed by the corresponding bubbling H₂ flow rate. Six films were grown for 4 hours with the flow-rate ratios of N:B = 1:2, 4:2, 8:2, 1:10, 4:10 and 8:10 in sccm, respectively, and the obtained films were labeled as sample (a)~(f) in turn.

The morphologies, microstructure and phase composition of the as-grown diamond films were characterized by means of scanning electron microscope (SEM, JXA-8200), X-ray diffraction (XRD, Rigaku D/MAX-RA with Cu Kα radiation), and Raman spectroscopy (Renishaw inVia Raman microscope with 514.5 nm line of Ar⁺ laser). The electron field emission (EFE) measurements were performed in the chamber at a high vacuum of 10⁻⁷ Pa.

Figure 1 shows the SEM images of the six diamond films (a)~(f). The morphologies of samples (a), (b) and (c) deposited with 2 sccm boron flow rate are similar, and the evident twin features are represented in the well (111) faceted grains. The average grain size is about 2 µm for the samples, and the samples are named as MCD films. As the boron flow rate increases to 10 sccm, all samples (samples d, e, and f, named NCD films) show round shaped grains consisting of nano-sized crystals, and the morphologies are weekly dependent on the nitrogen flow rate. It worth pointing out that, there are many (100) faced grains with the size of about 500 nm appearing in the NCD films (Figs. 1(d)~(f)). The high magnification image (the inset of Fig. 1(d)) shows that many nuclei appear on the profile faces of the grains. Previous literature reported that the homoepitaxial (111) diamond growth can be easily interrupted by re-nucleation under
a suitable condition, while the (001) textured layer is more stabilized especially when the [001] axes perpendicular to the substrate [10]. In our case, the abundant re-nucleations cover the non-[001] grains in NCD films. Therefore, the [100] grains are grown with non-[001] grains, which results in the formation of round shaped features.

In the XRD spectra (see Fig. 2) for all the samples, two peaks are generally observed at 43.9° and 75.2°, which are assigned to the characteristic diamond diffraction patterns of (111) and (220) respectively. Note that the (400) diffraction peak is negligible at high 2θ angle (not shown), implying that the (100) orientation growth is not evident. In addition, the Si (222) peak appears in the XRD spectra of samples (a) and (d), because the diamond films are thin and the signals from the beneath substrate Si are evident. It is thus speculated that the diamond films deposited at low nitrogen-flow rates (samples (a) and (d)) generally have low growth rates [4], with respect to the other samples (b), (c), (e) and (f) deposited at high nitrogen-flow rates. The serials MCD films (see Fig. 2A) are mainly [111] texture by comparing the relative intensity ratio of (111) to (220) peak, while the NCD samples (see Fig. 2B) are mainly mixed [110] and [111] texture. For the series of both MCD and NCD films, the intensity ratios of (111) to (220) peak increase with increasing the flow rate of nitrogen, which means that the [111] texture tends to be presented with higher nitrogen concentration introduced. The average grain sizes are 13.2, 12.8 and 15.5 nm for samples (d)-(f), respectively, estimated from (111) peak by the well-known Scherrer formula<sup>[11]</sup>: \( d = \frac{0.9 \lambda}{D \cos \theta} \), where \( \lambda \) is 1.54016 Å, \( D \) is the full width at half maximum (FWHM). Obviously, the grain size varies insignificantly with the additions of nitrogen for NCD films, which is consist with the observations in the SEM images.

Figure 3 shows Raman spectra obtained from the as-grown samples. It is found that for the MCD samples (see Fig. 3A), the zone-centre phonon band of diamond became asymmetry and downshift to about 1300 cm<sup>-1</sup> due to the Fano interference [12]. In addition, two broad bands around 500 and 1200 cm<sup>-1</sup> appear in the low frequency part, which are in agreement with the two maxima of phonon density of states of diamond [13,14]. The peak at around 500 cm<sup>-1</sup> shows a blue-shift with the increase of the introducing nitrogen, implying that the boron content is reduced [5].

However, the Raman spectra of the NCD films (Fig. 3B) are completely different from that of the MCD films. The spectra show the typical features of the NCD films and mainly consist of five featured peaks at around 500, 1140, 1350, 1480, and 1540 cm<sup>-1</sup>, while the diamond peak at ~1332 cm<sup>-1</sup> is nearly absence. The strong peaks at ~1350 cm<sup>-1</sup> and ~1540 cm<sup>-1</sup> correspond to the D (disordered carbon) band and G (graphitic carbon) band, respectively. The shoulder peak at ~1140 cm<sup>-1</sup> is usually referred to the signature of nanodiamond [15] and/or is accompanied by another peak at ~1480 cm<sup>-1</sup> related to the presence of transpolyacetylene (TPA) states in the grain boundaries of NCD films [16]. When the nitrogen concentration increased, the peak around 500 cm<sup>-1</sup> decreased continually (inset of Fig. 3B) and the 1140 cm<sup>-1</sup> peak became more visible, indicating the incorporation of boron has been prevented and the addition of nitrogen improves the diamond structure, which are consistent with the results reported in refs 17 and 18.

As previous reported that high concentration of nitrogen and methane was desirable to grow NCD film [19], however, in our experiments the nitrogen and methane were kept constant.

![FIG. 2. XRD spectra of the serial MCD films (A) and NCD films (B) deposited with various N: B (flow rate in sccm) ratios of 1:2, 4:2, 8:2, 1:10, 4:10, and 8:10, labeled as samples (a)–(f) in turn.](http://www.nmletters.org)

![FIG. 3. Raman spectra of the serial MCD films (A) and NCD films (B) deposited with various N: B (flow rate in sccm) ratios of 1:2, 4:2, 8:2, 1:10, 4:10, and 8:10, labeled as samples (a)–(f) in turn.](http://www.nmletters.org)
with low concentrations. We further fabricated a series of samples fabricated with a boron flow rate of 5 sccm by adjusting the nitrogen flow rate. The SEM images as shown in Fig. 4 indicted that the features of the deposited films are similar with samples (d) ~ (f) but content more diamond grains. Therefore, the transformation from MCD to NCD is gradually occurred with increasing the boron flow rate, which is related to the existence of more activated boron atoms and CHx ions decomposed from B(OCH3)3 in the reactive gases. The increase of boron atoms could significantly change the growth ambience to decrease the grain size, and the CHx ions will reduce the relative concentration of H atoms, resulting in the increase of non-diamond phase content and hindrance to the diamond phase growth [20].

The EFE characteristics illustrated as the current density-electric field ($J$-$E$) and Fowler-Nordheim ($F$-$N$) curves are plotted in Fig. 5 for all the samples. The important parameters for EFE, i.e., turn-on field ($E_0$, defined as the applied field corresponding to the current density of 0.5 $\mu$A/cm$^2$) and FE current density ($J_e$), are summarily listed in Table 1. For both MCD and NCD samples, the EFE properties are enhanced (with low $E_0$ and high $J_e$) at an optimum nitrogen flow rate (i.e., samples (b) and (f)). The F-N plot shows two straight lines in the region of the low and high voltage regions for all the curves, suggesting that electron emission in those samples are due to Fowler-Nordheim tunneling through the surface potential barrier, which is varied at different applied field regions [21]. Note that at nearly the same turn-on field, the current densities in our experiments are smaller than the previous data in the order of mA/cm$^2$ [9]. The origination is not clear in the current work, and further study is being carried out.

It is known that in N- and/or B-doped polycrystalline diamond films, a number of sp$^2$-bonded carbon generally appear and trend to accumulate on the grain surface and boundaries [22]. The sp$^2$-bonded phase overcoated between grains can lower down the energy barrier and even additively plays a conductive channel for EFE [23]. Note that too much non-diamond phase would relatively degrade the EFE properties due to the larger work function as compared to diamond [24]. In our experiments, for MCD films, small amount of incorporated nitrogen would

| Sample | $E_0$ (V/$\mu$m) | $J_e$ ($\mu$A/cm$^2$) at $E$= 23 V/$\mu$m |
|--------|-----------------|-----------------------------------------|
| a      | 14.0            | 33.0                                    |
| b      | 10.0            | 89.4                                    |
| c      | 13.3            | 52.9                                    |
| d      | 12.7            | 34.2                                    |
| e      | 16.0            | 26.7                                    |
| f      | 11.3            | 74.2                                    |

Fig. 5. Current density-electric field curve (A) and Fowler-Nordheim curve (B) of diamond films deposited with N: B (flow rate in sccm) ratios of 1:2, 4:2, 8:2, 1:10, 4:10, and 8:10, labeled as samples (a)~(f) in turn.

Table 1. The electron field emission properties of the diamond films deposited with various N: B ratios of 1:2, 4:2, 8:2, 1:10, 4:10 and 8:10 in sccm, labeled as samples (a)~(f) in turn.
introduce sp²-bonded phase, which can enhance the EFE property by reducing the energy barrier (see Fig. 5(A)) [25]. However, the excessive nitrogen reduces the conductivity by preventing the incorporation of boron, leading to the degradation of EFE properties. For the case of NCD films with superabundant non-diamond phase, the increasing incorporation of nitrogen can enhance diamond component and depress the formation of non-diamond phase (as shown in Raman spectra), which would consequently enhance the EFE property (see Fig. 5(B)).

Furthermore, it should be pointing out that the EFE properties of best MCD film (sample (b)) is superior to all the NCD films. For understanding this issue, on the one hand, the incorporation of excess boron species substantially reduces the concentration of dangling bonds that markedly decrease the amount of impurity bands in NCD films [26], which would strongly influence the EFE properties of the products. On the other hand, the [111] texture of MCD films possess much rougher surface than the NCD films, which provides a higher field enhancement factor than the mixed [110] and [111] geometry [27].

In summary, we fabricated boron-doped microcrystalline diamond (MCD) and nanocrystalline diamond (NCD) films by adjusting the gas proportion of nitrogen and boron in the reaction ambient. The XRD results show that the MCD films are of predominated [111] texture, while the NCD films are mixed [110] and [111] texture. The Raman spectra demonstrate that the nitrogen has different effect on the content of non-diamond phase and conductivity for NCD films as compared with MCD films. The discrepancy of EFE characteristics between MCD and NCD are ascribed to the differences in the content of sp²-bonded carbon, texture feature, and boron concentration in the films. The optimized nitrogen introductions have been realized to improve EFE properties of N- and B-doped CVD diamond films.

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Synthesis of silver nanoparticles by *Lactobaciluus acidophilus* 01 strain and evaluation of its *in vitro* genomic DNA toxicity

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Silver nanoparticles synthesized by dried biomass of *Lactobacillus acidophilus* 01 strain was evaluated against toxicity of genomic DNA isolated from bacteria (*E. coli*) fungi (*Beauveria bassiana*) algae (*Seenedesmus acutus*) and human blood adopting standard condition was discussed in the present study. Synthesized silver nanoparticles were characterized by UV-Vis spectroscopy and SEM. The UV-Vis spectroscopy revealed the formation of silver nanoparticles by yielding the typical silver plasmon absorption maxima at 430 nm and SEM micrograph indicates the uniform spherical particles within the size range of 45–60 nm. The energy dispersive X-ray spectroscopy (EDX) of the nanoparticle confirmed the presence of elemental silver signal as strong peak. The above synthesized silver nanoparticles didn’t cause any toxic effect on all the tested genomic DNA at all tested concentrations which reveals nil genomic nanoparticles induced toxicity.

**Keywords:** Lactobacillus acidophilus; Silver nanoparticles; Antibacterial activity; Biosynthesis

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Nanotechnology is significant on account of its pre-eminence upon the comprehension, use, and control of matter at magnitudes of a minute scale, akin to approaching atomic levels, with which to manufacture new substances, instruments, and frameworks [1]. Nanoparticles possess exceptional physical and chemical properties which lead to rapid commercialisation. Nanotechnology is currently employed as a tool to explore the darkest avenues of medical sciences in several ways like imaging [2], sensing [3], targeted drug delivery [4], gene delivery systems [5] and artificial implants [6]. Hence, nanosized organic and inorganic particles are catching increasing attention in medical applications due to their amenability to biological functionalization [7]. Based on enhanced effectiveness, the new age drugs re-nanoparticles of polymers, metals or ceramics can combat conditions like cancer [8] and fight human pathogens like bacteria [9]. Silver nanoparticles (Ag-np) are among the most commercialised nanoparticles due to their antimicrobial potential. Ag-np based cosmetics, therapeutic agents and household products are in wide use, which raised a public concern regarding their safety associated with human and environmental use. No safety regulations are in practice for the use of these nanomaterials [10]. Production of silver nanoparticles can be achieved through different methods. Chemical approaches are the most popular methods for the production. However, some chemical methods cannot avoid the use of toxic chemicals in the synthesis protocol. Since noble metal nanoparticles such as silver, gold nanoparticles are widely applied to human contacting areas. There is a growing need to develop environmentally friendly processes of nanoparticles synthesis that do not use toxic chemicals [11].

Biological systems have a unique ability to control the structure phase and nano structural topography of the inorganic...
crystals [12]. Biological methods based on microbes such as bacteria are able to absorb and accumulate metals and can be used in the reduction of metal ions and thus known to synthesis of nanoparticles [13]. Now, there are lots of issues are raised on release of nanoparticles and their impact on non target organisms. Environmental Protection Agency, announced its intent to request information regarding analytical test methods, fate and transport in the environment, and other relevant information from manufacturers of nanomaterials [14]. There is now a wider debate about the risks and benefits of the many manufactured nanomaterials [15].

*Lactobacillus acidophilus* 01 strain used in the study was isolated by serial dilution technique using Modified Lactobacillus Agar (HI-media, India). The bacterium was identified based on cultural and biochemical characteristics. For inoculum preparation, a loopful of bacterial culture was inoculated in a 250 ml of conical flask containing 100 ml sterile MRS broth. The flask was incubated at 30°C for 32 h on a rotary shaker at 200 rpm, and the cells were harvested by centrifugation at 3000 rpm for 15 minutes and the collected cell pellets was dried in hot air oven at 60°C for 24 h.

In a typical procedure of nanoparticle synthesis, the dried cell pellets were washed thrice with Milli-Q-deinosed water and the washed cell pellets were transferred to 500 ml of conical flask containing 200 ml of milli-Q-deinosed water and kept on a rotary shaker at 200 rpm for 72 h. After the incubation, the cell suspension was filtered through Whatmann filter paper (no. 1). Silver nitrate (AgNO₃, 1mM) was mixed with 50 ml of cell filtrate in a 250 ml of Erlenmeyer flask and agitated at 30°C under dark conditions, the flask was observed for color change from pale yellow to brown. Control was run along with experimental flask.

The reaction mixture was analyzed periodically using UV-Vis spectrophotometer. The absorbance was measured in the range 400–800 nm, which includes the plasmon absorbance peak of the silver nanoparticles centered at 430 nm. Further the samples were characterized by SEM and EDX. The genomic toxicity of silver nanoparticles was evaluated by obtaining the genomic DNA from bacteria (*E. coli*) fungi (*Beauveria bassiana*) algae (*S. acutus*) human blood. Genomic DNA isolation from respective sources was performed by standard methods [15] and the extracted pure DNA was stored at 20 µg/ml in Tris buffer under pH 7.8 at -20°C. The aliquots of silver nanoparticles were added separately into the respective purified DNA sample, incubated at 37°C for about 24 h. The electrophoresis was done using Tris acetate buffer containing 15 µg/ml ethidium bromide in mini submarine apparatus at 100 amps for 30 minutes. After electrophoresis the gel was visualized under UV transilluminator.

In the present study, biological synthesis of silver nanoparticles by *Lactobacillus acidophilus* 01 strain is primarily confirmed by color change of the reaction mixture from pale yellow to brown clearly indicating the formation of silver nanoparticles (see Fig. 1). The characteristic brown color due to the excitation of Plasmon vibrations in the nanoparticles provides a convenient signature of their formation [16]. Synthesized silver nanoparticles are characterized by UV-Vis spectroscopic, a strong broad surface Plasmon peak located at 430 nm on 14th and 21st day (see Fig. 2). The surface plasmon band remains in the range of 420–440 nm throughout the reaction period suggesting that the particles are dispersed in the aqueous solution with no evidence for aggregation after the complete of reaction. It has been observed that the nanoparticle solution is extremely stable for more than six months with no signs of aggregation even at the end of this period. It is known that silver cations are highly reactive and tend binding strongly with electron donar groups containing sulphur, oxygen or nitrogen [17]. But Mineian *et al.* [18] did not observe any extra cellular bio synthesis activity from *Lactobacillus acidophilus*. When we challenged the cell biomass of *Lactobacillus acidophilus*, it was observed that the silver was reduced...
intracellularly by *Lactobacillus acidophilus*. The primordial assay of silver nanoparticles is performed by EDX. Figure 3 shows the EDX spectrum of the silver nanoparticles. Strong signals from the silver particles were observed (42.44% in mass), while weaker signals from C, O, Al and S atoms are also recorded. The SEM micrograph at 30000 times magnification was shown in Fig. 4. The SEM micrograph showed spherical nanoparticles with the size range of 45–60 nm. Mineian *et al.* [18] got nanoparticles with the size range of 20–25 nm.

The genomic toxicity with all the tested concentrations of silver nanoparticles didn’t show any distinct effect in case that all tested genomic DNA no fragmentation or degradation was observed all in the tested genomic DNA samples. A clear sharp distinct DNA band observed in the entire tested DNA samples as in control (see Fig. 5) clearly reveals the non-toxicity of silver nanoparticles on genomic DNA and its best compatibility with genetic material of the organisms.

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Label-free colorimetric estimation of proteins using nanoparticles of silver

Siddhartha Shrivastava and Debabrata Dash*

Metallic nanoparticles have received considerable attention in bioassays and diagnostics due to their unique surface plasmon resonance (SPR) properties. Gold nanoparticles have been employed for the development of SPR-based colorimetric bioassays. In the present report we have described a sensitive colorimetric approach for estimation of proteins, within a detection limit of 10−80 µg/mL, using unmodified silver nanoparticles. Besides the common advantages of colorimetric assay such as simplicity, high sensitivity, and low cost, our method has a label-free design and provides an important and attractive alternative to classical sensing probes and systems. The present work will contribute to the development of nanotechnology-based diagnostic tools.

Keywords: Silver nanoparticles; Agglutination; Surface plasmon resonance; Colorimetric estimation; Bovine serum albumin; Immunoglobulin

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Colorimetric bioassay based on nanomaterials has received considerable attention in last few years. Gold nanoparticles have been explored mostly among metallic nanomaterials, and variety of colorimetric sensors have been developed against analytes, such as DNA, metal ions, carbohydrate and proteins [1-10] employing unique optical properties of nanogold. These assays have employed either modified (type I) or unmodified nanoparticles (type II) [8]. Use of DNA-modified gold nanoparticle conjugate as indicator pioneered development of type I sensors [1], while Rothberg et al. [2,3] developed type II sensors employing unmodified nanogold. Gold-based sensors have provided comparable or even better sensitivity and selectivity than their conventional fluorescent counterparts [8].

Owing to inherent photostability, ease of synthesis, biocompatibility, ability to conjugate to biological molecules and innate anti-bacterial as well as anti-platelet properties, nanosilver has established its biomedical potential [11-13]. However, though silver nanoparticles possess unique optical properties similar to nanogold, little attention has been paid on nanosilver-based colorimetric assays. Only a few reports are available in literature describing the use of functionalized nanosilver coupled with appropriate ligands in colorimetric detection of DNA, metal ions and proteins [11,14-17]. Functionalization of nanosilver can cause its chemical degradation rendering it to be easily oxidized [8]. On the contrary silver nanoparticles have the advantage of higher extinction coefficient as compared to gold particles of comparable sizes.

In our earlier reports we have described synthesis of highly stable, biocompatible nanoparticles of silver and have analyzed their anti-bacterial, anti-platelet and protein stabilizing properties in absence of any modification. Unmodified silver nanoparticles have been shown to be ideal sensors for enzymatic reactions involving dephosphorylation of adenosine triphosphate (ATP) by calf intestine alkaline phosphatase and peptide phosphorylation by protein kinase A [8]. In the present study we describe a sensitive colorimetric assay for quantification of proteins employing unmodified nanoparticles of silver. Our method is based on unique surface plasmon resonance (SPR) of these particles in dispersed and aggregated states and provides a
sensitive approach of estimation of proteins in range of about 10–80 µg/ml, thus potentially broadening the applicability of nanosilver-based sensors.

Material and Experiments

Chemicals and Reagents

Silver nitrate, Sodium hydroxide, sodium chloride, hydrazine, liquid ammonia (30%), and D-glucose were procured from Merck India. Bovine serum albumin (BSA) (fraction V) and immunoglobulin G (IgG) were purchased from Sigma Aldrich. Filters (pore size 0.2 µm) were purchased from Sartorius. All other chemicals were of analytical grade. Mill-Q grade deionized water (Millipore) was used for preparation of the solutions.

Synthesis of silver nanoparticles

Preparation and characterization of highly stable biocompatible nanoparticles of silver have been described in our earlier reports [11-13]. Briefly, silver nitrate (17 mg) was dissolved in 100 ml deionized water, to which ammonia was added at final concentration of 0.01 M. The pH of the solution was adjusted to 7.4 using citric acid. A blend of reducing agents like D-glucose (0.01 M) and hydrazine (0.01 M) was added drop wise to the solution of silver salt under constant stirring to ensure complete reduction of silver ions to nanoparticles. The final solution of nanosilver at concentration of 540 µg/ml (pH 7.4) was stored in air tight bottles till further experiments. Size, morphology and distribution of silver nanoparticles were characterized using transmission electron microscope (Technai-12) and UV-Vis spectrophotometer (Pharmacia Biotech). Nanoparticles were found to be spherical in shape with average size of 10–15 nm. The solution of nanoparticles was sonicated (Labsonic 2000 U, B. Braun) for 2 min and passed through filters of 0.2 µm pore size (Sartorius) before each experiment.

Colorimetric estimation of proteins using unmodified silver nanoparticles

Incubation mixtures (final volume 500 µl), containing globular proteins (BSA or IgG) over concentration range 0–250 µg/ml, silver nanoparticles (50 µg) and NaCl (10 g/100 ml), were incubated in siliconized glass tubes for 10 min at RT to produce color change. Aliquots were diluted 1:4 and absorbance was recorded at 407 nm, the characteristic absorption maximum for disperse nanosilver of size 10–15 nm. A concentration-dependent curve was obtained using these values.

For detection of unknown protein, 400 µl of test sample was treated identically (final volume becomes 500 µl) and absorption at 407 nm was recorded. Absorption values for test sample were extrapolated on standard concentration curves for BSA or IgG in order to obtain concentration of the unknown proteins.

Transmission electron microscopy

Size and morphology of silver nanoparticles and nanosilver-BSA complex were analyzed under Technai-12 transmission electron microscope equipped with SIS Mega View III CCD camera. Samples were prepared by placing a drop of specimen solution onto carbon-coated copper grids followed by air drying. Grids were monitored under the microscope operated at an accelerated voltage of 100 kV. Measurements were carried out using AnalySIS software (SIS, Germany).

Absorption spectrophotometry

Absorption spectra of silver nanoparticles, BSA, IgG and conjugates were recorded at wavelengths ranging from 220 to 500 nm in a Beckman spectrophotometer (model DU-640B) equipped with constant temperature cell holder.

Results and Discussion

Nanosilver has propensity to interact with proteins [8,11]. To test that unmodified nanoparticles of silver could act as sensing probes for protein estimation, agglutination of nanosilver was investigated in presence of increasing concentrations of protein (see Fig. 1). BSA was elected as the representative protein for the study due to its well characterized structure and properties as well as its immense physiological significance [18-20]. Colloidal solution of 50 µg nanosilver was incubated with increasing concentrations of BSA (0–250 µg / ml) and nanoparticle agglutination was induced by NaCl (10 g/m of NaCl. Tube 11, control solution of nanosilver in absence of NaCl.

FIG. 1. Agglutination of silver nanoparticles. Tubes 1–10, nanosilver incubated with 0, 1, 10, 30, 50, 70, 90,110, 150 and 250 µg/mL BSA, respectively, and treated with 10 gm % of NaCl. Tube 11, control solution of nanosilver in absence of NaCl.
gm % final concentration). Pure solution of nanosilver changed color from dark orange to grey upon addition of NaCl, indicative of altered SPR following aggregation of nanoparticles. Incubation with ascending concentrations of BSA demonstrated progressive resistance to color change ensued upon NaCl treatment. Nanosilver solution supplemented with 150 or 250 μg/ml of BSA retained the pristine dark orange color after addition of NaCl attesting the dispersed distribution of particles in solution. Above observations suggested that BSA interacts with silver nanoparticles and prevents agglutination of particles in a concentration-dependent manner. The extent of nanosilver aggregation determines the SPR, which is reflected from specific color of nanoparticle solution. Protein content of a solution can be estimated conveniently based on such color change. Similar colorimetric approach using unmodified gold nanoparticles has been attempted, where nanoparticles were shown to exhibit resistance to salt-induced aggregation in presence of ATP [21]. However, there has been no report describing protein estimation employing unmodified nanoparticles.

In order to estimate protein concentration a standard curve of absorbance (at 407 nm) of BSA-nanosilver complex in presence of NaCl versus BSA concentration was generated. Absorbance was found to increase linearly with BSA concentration in the range from 10–80 μg/ml, beyond which it turned into a plateau (see Fig. 2). We were able to determine accurate concentrations of unknown solutions of BSA using this curve. We also obtained a similar curve using another globular protein, IgG, where absorbance (at 407 nm), too, increased linearly over protein concentration 10–80 μg/ml (see Fig. 3).

FIG 2. Concentration of BSA versus absorbance at 407 nm.

FIG 3. Concentration of IgG versus absorbance at 407 nm.

FIG 4. Electron microscopic analysis of nanosilver agglutination. a) Spherical, uniformly sized and dispersed nanoparticles of silver in absence of salt. b-f) nanoparticles of silver in presence of NaCl and 0, 1, 10, 50 110 μg/ml BSA, respectively. Scale bar; 50 nm. Inset in each figure shows corresponding color of nanosilver solution.
Subsequently, electron microscopy was performed to examine details of interaction between silver nanoparticles and BSA (see Fig. 4). Spherical, uniformly sized nanoparticles of silver remained well dispersed in solution in the absence of NaCl (see Fig. 4a). Upon exposure to salt aggregates of nanoparticles were evident and free nanoparticles were not visible (see Fig. 4b). Addition of 1 µg/ml BSA did not bring about any change in agglutination of nanoparticles (see Fig. 4c). However, nanosilver solution supplemented further with increments of BSA (10, 50 and 110 µg/ml) exhibited progressive resistance to nanoparticle agglutination (see Fig. 4d-f). Thus, BSA at 10 µg/ml completely prevented aggregation of nanoparticles in response to NaCl treatment and retained uniform distribution of particles identical to nanosilver distribution in absence of salt having enhanced absorbance at 407 nm (see Fig. 4f). Electron microscopic analysis suggests that interaction between proteins and nanosilver prohibits agglutination of latter in response to salt treatment. As inhibition of agglutination is dependent on amount of protein, the characteristic SPR at 407 nm can be used as indicator of protein concentration in the solution.

Conclusions

In the presented report, we have described a sensitive colorimetric approach for estimation of proteins, within a detection limit of 10–80 µg/ml, using unmodified nanoparticles of silver. Besides the common advantages of colorimetric assay such as simplicity, high sensitivity, and low cost, our method has a label-free design and provides an important and attractive alternative to classical sensing probes and systems. The present work may contribute to future application of nanoparticle-based technologies to the development of diagnostic tools.

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Green synthesis and characterization of palladium nanoparticles and its conjugates from solanum trilobatum leaf extract

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An important area of research in nanotechnology deals with the synthesis of nanoparticles of different chemical compositions, sizes and controlled monodispersity. Currently, there is a growing need to develop environmentally benign nanoparticle synthesis in which no toxic chemicals are used in the synthesis protocol. Palladium nanoparticles (PdNp) are of interest because of their catalytic properties and affinity for hydrogen. Our protocol for the phyto-synthesis of PdNp under moderate pH and room temperature offers a new means to develop environmentally benign nanoparticles. Solanum trilobatum is enlightened in our present study as it is enriched with phytochemicals to reduce palladium chloride ions. Poly MVA a dietary supplement based on the nontoxic chemotherapeutic lipoic acid-palladium complex (LA-Pd) is been hypothesized as the new paradigm of cancer therapy. Hence forth we successfully conjugated lipoic acid (S-PdNp-LA) and vitamins (S-PdNp-Vitamin-LA) to palladium nanoparticles synthesised from Solanum trilobatum leaf extract. These nanoparticles (S-PdNp, S-PdNp-LA, S-PdNp-Vitamin-LA) were characterized with UV-Vis Spectroscopy, SEM and FTIR analysis, which revealed that S-PdNp are polydisperse and of different morphologies ranging from 60~70 nm (S-PdNp), 65~80 nm (S-PdNp-LA) and 75~100 nm (S-PdNp-Vitamin-LA) in size.

Keywords: Nanoparticles; Palladium; Lipoic acid; Palladium lipoic acid complex; Poly-MVA; Green synthesis; Solanum trilobatum

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In modern nanoscience and nanotechnology the production of nanomaterials with the preferred quality is one of the most stimulating aspects. In addition, nanoparticles refer to nanoscale materials that have an aerodynamic equivalent diameter of 100 nm or less [1] yet, it has been shown that there is a strong tendency with several nanoscale materials sold commercially of agglomerating and therefore existing as much larger micrometer scale particles further complicating studies regarding exposure and effect. An important area of research in nanotechnology deals with the synthesis of metallic nanoparticles of different chemical compositions, sizes and controlled monodispersity [2]. To date, metallic nanoparticles are mostly prepared from noble metals (ie. Ag, Pt, Au and Pd) [3]. Recently, the advances in fabrication of palladium nanoparticles (PdNPs) have gained great importance owing to their application both in heterogeneous and homogeneous catalysis, their high surface-to-volume ratio and their high surface energy [4].

Biosynthetic methods employing either biological microorganisms or plant extracts have been suggested as possible ecofriendly alternatives to chemical and physi

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methods [5-19]. The rate of reduction of metal ions in the method of using plants has been found to be much faster than the method of using micro-organisms and stable. The synthesis of nanoparticles can be carried out by both intracellular and extracellular methods such as leaf broth, sundried leaves, fruits, growing plants on metal-rich soil, gold-rich agar media, etc. and the results obtained were positive in all cases. Extracellular nanoparticle synthesis using plant leaf extracts rather than whole plants would be more economical owing to easier downstream processing.

Biological processes using microorganisms, plants, and plant extracts have been used to synthesize nanoparticles of gold and silver with wide applications in the field of medicine, cancer treatment, drug delivery, commercial appliances, sensors, etc. There is relatively little knowledge in literatures concerning the biological synthesis of palladium nanoparticles. The only success was the recent findings on the production of PdNPs using coffee and tea extract [20]. It has also been found that the antioxidants such as geniposide, chlorogenic acid, crocins and crocetin were the reducing and stabilizing agents for synthesizing palladium nanoparticles (3 to 5 nm) in water crude extract of Gardenia jasminoides Ellis’ [21]. This study appeared to be a new promising biosynthetic nanocatalyst for the development of an industrial process. An extremely simple green approach that generated by Mallikarjuna et al., 2008 [22] in bulk quantities of nanocrystals (20~60 nm) of noble metals such as silver (Ag) and palladium (Pd) using coffee and tea extract at room temperature is noteworthy. Currently, however, the exact mechanism for the synthesis of palladium nanoparticles is unclear. Our protocol for the phyto-synthesis of palladium nanoparticles under moderate pH and room temperature offers a new means to develop environmentally benign nanoparticles.

Palladium Lipoic Acid (LAPd) is a formulation used in a prescription version called DNA Reductase and a dietary supplement called Poly MVA. The active ingredient is the palladium-lipoic acid polymer, which exists as a trimer of palladium-lipoic acid joined to thiamine. This arrangement is unique in that it allows the molecule to be both water and lipid soluble, as well as exist as a liquid crystal. This liquid crystalline structure allows it to store a great deal of energy and thus serve as a semiconductor [23-25]. “Palladium Lipoic Compounds” a specific class of compounds has become the centre piece of nontoxic cancer therapy in recent research.

It acts by modulating cellular energy helping the human body to build up the immune system and have an energetic life. Hence Poly-MVA that is a variant of Palladium Lipoic Acid (LAPd) acts as an anti-oxidant supplement and helps us lead a life free from many diseases [26]. Poly-MVA is one of the first available formulations of Palladium Lipoic acid in the market which helps in fighting many diseases such as diabetic neuropathy, retinopathy which causes blindness, controls blood sugar levels in the body; prevent cardiomyophath and helps in slowing the aging process by normalizing the free radicals in the body [27]. The palladium lipoic complexes in Poly-MVA work in novel ways that do not harm the body as a whole only the cancer cells specifically, partially by converting free radicals into a usable form of energy [28-29].

To the best of our knowledge, there are no reports on the reduction of aqueous palladium chloride ions from the leaves of Solanum trilobatum. Hence in this study, we synthesized palladium nanoparticles using screened leaf extract of the Solanum trilobatum plant. Fourier-transform infrared spectroscopy (FTIR) analysis was used to identify the biomolecules responsible for reducing palladium ions and stabilizing the palladium nanoparticles formed. In addition this study is also focussed on the conjugation of palladium nanoparticles (S-PdNp) with Lipoic acid (LA-S-PdNp) and Vitamins (Vitamin-LA-S-PdNp).

Experimental Section

Synthesis of palladium nanoparticles from Solanum trilobatum leaf extract

The broth used for reduction of PdCl₂ ions to palladium was prepared by taking 20 g of thoroughly washed and finely cut Solanum trilobatum leaves in a 500 ml Erlenmeyer flask with 100 ml sterile distilled water and then boiling the mixture for 1 min. The process of boiling the leaves leads to rupture of the walls of leaf cells and, thus, release of intra-cellular material into solution. After boiling, the solution was decanted, filtered and 5 ml of this broth was added to 100 ml of 0.226 M PdCl₂ aqueous solution.

Palladium Nanoparticles from Solanum trilobatum leaf extract conjugated with Lipoic acid

15 mL of the leaf extract was taken and added 0.226 M PdCl₂ aqueous solution with 1 ml of lipoic acid (15mg lipoic acid was dissolved in 0.5ml of ethanol and 0.5 ml of water) and kept for incubation at room temperature for 24 hrs. The mixture was centrifuged at 4,500 rpm to separate the capped PdNPs. The pellet obtained was resuspended in 1 ml of phosphate buffer (pH 7).
Palladium Lipoic Acid Complex Conjugated With Vitamins (Poly MVA)

The vitamin (Vitamins B1, B2, and B12) was added to the leaf extract containing palladium lipoic acid complex and kept for incubation at room temperature for 24 hours. Then after the incubation period the colour of the leaf extract was changed from yellow to brown colour. The mixture was centrifuged at 4,500 rpm to separate the capped PdNPs. The resulting palladium nanoparticle solution was purified by repeated centrifugation at 15,000 rpm for 20 min, with the pellet produced by this process redispersed in deionized water.

UV-Vis spectroscopic Studies

The bioreduction of Pd ions in aqueous solution was monitored by periodic sampling of aliquots (0.2 ml) of the suspension, then diluting the samples with 2 ml deionized water and subsequently measuring UV-vis spectra of the resulting diluents. UV-vis spectra of these aliquots were monitored as a function of time of reaction on a Hewlett-Packard diode array spectrophotometer (model HP-8452) operated at a resolution of 2 nm.

FTIR Observations

Samples of the aqueous solution of the palladium nanoparticles were prepared by using centrifugation and suspended with phosphate buffer and analyses done by FTIR. Samples were measured by Bruker Tensor 27 FTIR spectrometer in attenuated total reflection mode (Pike Technologies, Gladi ATR for FTIR with diamond crystal) and using spectral range of 4000–400 cm\(^{-1}\) with resolution of 4 cm\(^{-1}\). The FTIR spectra of leaf extracts taken before and after synthesis of PdNPs were analyzed which was discussed for the possible function groups for the formation of S-PdNps, S-PdNp-LA, S-PdNp-LA-Vit

SEM observations

Samples of the aqueous suspension of palladium nanoparticles were prepared by placing a drop of the centrifuged suspension on carbon-coated copper grids and allowing water to evaporate. SEM observations were performed on a Zeiss EVO 40 Electron Microscope.

Results and Discussion

The biosynthetic method employing plant extracts have drawn attention as a simple and viable alternative to chemical procedures and physical methods. Such reliable and eco-friendly methods help in endorsing extra interest in the synthesis and application of nanoparticles which are good for mankind. Metal nanoparticles can be synthesized by reducing metal ion using some chemical molecules. In green synthesis, it is believed that natural material extract act as reducing agent for the generation of metal nanoparticles. In this work we have shown the ability of the solanum phytochemicals to interact with palladium chloride ions and reduce them to form palladium nanoparticles.

The reaction media offered a change in color from yellow (before the addition of palladium chloride, see Fig. 1a) to brown (after complete reduction of PdCl\(_2\) ions in the solanum leaf broth-Fig. 1b). The colour turned dark brown when the S-PdNps was conjugated with lipoic acid (see Fig. 1c) and still darker with addition of vitamins to it (see Fig. 1d). The stability of palladium nanoparticles can be attributed to the formation of stable bonding between metallic palladium and reducing sugars, the phytochemicals such as saponins, tannins, terepenoids, flavonoids, anthocyanins, betacyanins, proteins and steroids and phenolic acids present in the leaf broth of Solanum trilobatum [30]. Sathish kumar et al., 2009 [31] hypothesized terpenoids to be the surface-active molecules that stabilized the palladium nanoparticles, and that the reduction of metal ions is possibly facilitated by these and/or sugars. Therefore, many plant extracts can be used to synthesize metal nanoparticles owing to the existence of phytochemicals and reducing sugars in them.
We also made an attempt of conjugating palladium to lipoic acid, a thiol rich molecule which exhibited a dark brown colour than that of unconjugated palladium (see Fig. 1c). Chen et al., 1984 [32] in his study used a shorter chain thiol (C₆H₁₃SH) to protect the surface of palladium. As thiol cap (lipoic acid) enables weaker Pd-S bonding interactions it can easily break from the surface of the Pd nanoparticles during a longer reaction time. Studies have evidently illustrated that glutathiones (a thiol rich molecule) used for capping gold quantum clusters (AU-n-SG-m) (-SG, glutathione thiolate) has been well known for the stability of the AUNPs synthesized chemically. In addition the electrons present in the conduction band of nanoparticulate gold makes them potential candidates to bind with thiols and amines [33]. We have deduced from these observations that the aggregation of palladium nanoparticles and thiol-capped palladium nanoparticles in our present work could be due to the high Pd=C₃H₁₇:SH molar ratios resembling the formation of thiol-protected gold nanoparticles [34]. As a result, palladium nanoparticles may be easily tagged with various proteins and bio-molecules rich in amino acids leading to important biomedical applications. Formation of palladium nanoparticles and its complexes were centrifuged at 8000 rpm for 10 min separately to isolate the palladium nanoparticles free from proteins or other compounds present in the solution. The pellets obtained after centrifugation were redispersed in water prior to further analysis.

Reduction of the aqueous palladium chloride ions was tracked by monitoring changes in color with UV-Vis spectroscopy. The relationship between the UV-visible radiation absorbance characteristics and the absorbent’s size and shape is well established. Fig. 2a, 2b, and 2c shows the UV-vis spectra recorded from the aqueous palladium chloride-Solanum leaf broth reaction medium as a function of time of reaction. After completion of the reaction, the wavelength of the surface plasmon band stabilizes at 270 nm, 240 nm and 200nm for S-PdNP, S-PdNP-lipoic acid and S-PdNP-lipoic acid-vitamin respectively. The nanoparticle absorption band is slightly asymmetrical with indications of an additional weaker component at 370 nm. The presence of this shoulder indicates either formation of stable aggregates of the palladium nanoparticles in solution or shape anisotropy in the particles.

The intensity of the color arises from the surface plasmons, which are dipole oscillation arising when an electromagnetic field in the visible range is coupled to the collective oscillations of conduction electrons [35]. The broad surface plasmon peak is well known for the metal nanoparticles in size ranging from 2 to 100 nm and the absorption peak at 320 nm correspond to the wavelength at which the real and imaginary parts of the dielectric function of metals almost vanish [36]. With the increase in the particle size, the optical absorption spectra of metal nanoparticles that are dominated by surface plasmon resonances may shift towards longer wavelengths. Therefore the position of absorption band also strongly depends upon dielectric constant
of the medium and surface-adsorbed species [37]. Based on Mie's theory, spherical nanoparticles give rise to a single surface plasmon resonance band in the absorption spectra, whereas anisotropic particles confer two or more surface plasmon resonance bands depending on the shape of the particles [38]. In present investigation, all reaction mixtures show a single surface plasmon resonance band revealing spherical shape of silver nanoparticles, which is addressed through SEM images.

The $\lambda_{\text{max}}$ shift in the absorbance spectra observed in Fig. 2b (240nm) and 2c (200nm) may possibly be due to the surface modification of the S-PdNPs. The surface plasmon resonance being the major cause for the absorption is affected by surface modification with covalent coupling. The covalent coupling can be extended either via the carboxylic or the amino groups of lipoic acid/vitamins. In the case of lipoic acid capped nanoparticles, the disulfides are reduced by the palladium chloride ions to two thiol groups (\(-S-S-\rightarrow-SH+SH\)), which may be involved in the binding of lipoic acid to S-PdNPs. This type of capping can be of pH dependent and may lead to the precipitation of nanoparticles [33]. Thus the phenolics and other phytochemicals within Solanum trilobatum not only result in effective reduction of palladium ions to nanoparticles but their chemical framework is also effective at wrapping around the S-PdNPs to provide excellent robustness against agglomeration. Therefore, by changing the size and shape of S-PdNPs, the SPB and scattering may be tuned for application in cellular imaging, drug delivery and therapy. Figures 3a, 3b, and 3c indicate the size and morphology of S-PdNP, S-PdNP LA, and S-PdNP-LA-Vit respectively. SEM measurements on these particles expelled a spherical shape within the size range of 60-70 nm (see Fig. 4a).

65-80 nm (see Fig. 4b) and 75-100 nm (see Fig. 4c) which can be assigned to bioorganic compounds present in the leaf broth [32]. Such size distribution analysis of capped (PdNPs capped with lipoic acid and vitamins) and non-capped PdNPs confirms that the particles are well dispersed.

The analysis of IR spectra gives an idea about biomolecules bearing different functionalities which are present in underlying system. The FTIR spectra of samples containing PdNPs and its conjugates are illustrated in Fig. 4a-4c. Comparison between spectra of samples (S-PdNP, S-Pd NP-lipoic acid and S-Pd NP-lipoic acid-vitamin) reveals only minor changes in the positions as well as on the magnitude of the absorption bands. The FTIR spectrum of the S-PdNP showed bands at 661, 1584, 1637, 2377, 2675 and 3473 cm\(^{-1}\) along with other small bands (see Fig. 4a). The intense band absorbance at 3473 cm\(^{-1}\) is the characteristic of the hydroxyl functional group in alcohols and phenolic compounds and the band at 1637 cm\(^{-1}\) can be assigned to the amide I band of the proteins released by the Solanum leaves or to C=C groups/aromatic rings. In addition some weaker bands centered at 1584 and 2377 cm\(^{-1}\) characteristic to the amide III and amide I band in proteins also indicates a small concentration of protein in the PdNP solution synthesized using solanum leaf extract [39]. Effectively the C-N stretching vibration of aliphatic amines or to alcohols/phenols coincides with the band at 661 cm\(^{-1}\). Thus it is obvious that bands at 1637 and 2675 cm\(^{-1}\) assigning to the carbonyl groups and secondary amines, respectively signifies that PdNP synthesized using the Solanum leaf extract are surrounded by some proteins and metabolites having functional groups of amines, alcohols, ketones, aldehydes, and carboxylic acids.

**FIG. 3.** SEM images of Palladium nanoparticles synthesised from Solanum trilobatum leaf extract at 10X magnification (a) Solanum trilobatum leaf extract-Palladium Chloride (60-70 nm); (b) Solanum trilobatum leaf extract-Palladium nanoparticles-Lipoic acid (65-80); (c) Solanum trilobatum leaf extract-Palladium nanoparticles-Lipoic acid-Vitamin (75-100 nm).
On the other hand the spectrum of S-PdNP-lipoic acid explains the presence of six bands (see Fig. 4c) which clearly demonstrates the absence of the –N-H stretch assigned to amide group (band at 3400.86 cm\(^{-1}\)) and S=O stretch of Sulfoxides (band at 1045.37 cm\(^{-1}\)), but the presence of CH\(_2\) bend corresponding to Alkanes (band at 1383.95 cm\(^{-1}\)) and the C-O stretch assigning to alcohols (band at 1120.43 cm\(^{-1}\)) on comparing with the peaks of S-PdNP (see Fig. 3a). Deficient of S=O stretch assigned to sulfoxides (band at 1045.78 cm\(^{-1}\)) but the occurrence of C-O stretch contributing to alcohols (band at 1107.73 cm\(^{-1}\)) when compared with the peaks of S-PdNP (see Fig. 3a) were observed in the spectral bands of S-PdNP-Lipoic acid-vitamin (see Fig. 3c). The band around 1120.43 cm\(^{-1}\) and 1107.73 cm\(^{-1}\) in Fig. 3b and Fig. 3c respectively can be assigned to C=O stretching vibrations of the carbonyl functional group in ketones, aldehydes, and carboxylic acids [40, 41, 43]. The band around 1120.43 cm\(^{-1}\) and 1107.73 cm\(^{-1}\) matches to the ether and aromatic groups [42-43], whereas, the band around 1383.95 cm\(^{-1}\) and 1390 cm\(^{-1}\) corresponds to geminal methyls [42].

To a large extent, the band at 1069 cm\(^{-1}\) might be contributed by the –C-O- groups of the polyols such as flavones, terpenoids and the polysaccharides present in the biomass [43]. The absorbance band centered at 1636 cm\(^{-1}\), 1639 cm\(^{-1}\) and 1638 cm\(^{-1}\) (3a, 3c and 3e) is associated with the stretching vibration of –C=C- or aromatic groups [42-43]. These bands are due to amide I bond of proteins, indicating predominant surface capping species having –C=O functionality which are mainly responsible for stabilization. A broad intense band around 3473.55 cm\(^{-1}\), 3430.51 cm\(^{-1}\), 3400.86 cm\(^{-1}\) and 3431.74 cm\(^{-1}\) in 3a, 3b and 3c respectively can be assigned to the N–H stretching frequency arising from the peptide linkages present in the proteins of the extract [44]. The shoulders around the band can be identified as the overtone of the amide-II band and the stretching frequency of the O-H band, possibly arising from the carbohydrates and/or proteins present in the sample. However, although there is adequate evidence for the presence of surface bound proteins, the conclusion regarding the presence of the specific compound cannot be made unless the individual component is isolated and identified.

The spectra exhibiting broad asymmetric band around 2100 cm\(^{-1}\) can be assigned to the N-H stretching band in the free amino groups of PdNPs [44]. Since these band disappeared in the IR spectra of the final product it can be concluded that the reducing agents are largely derived from these water soluble heterocyclic compounds. Therefore, it reflects that water soluble heterocyclic compounds such as flavones are the reducing and capping ligands of the nanoparticles. Flavones could be adsorbed on the surface of the metal nanoparticles, possibly by interaction through π-electrons of carbonyl groups in the absence of other strong ligating agents in sufficient concentrations. Likewise, the oxygen atoms herein might facilitate the adsorption of the heterocyclic components on to the particle surface in stabilizing the nanoparticles [42]. Therefore it appears more likely that the reduction of palladium ions and stabilization of synthesized palladium nanoparticles is the responsibility of many functional groups, including amines, alcohols, ketones, aldehydes, alkenes and carboxylic acids, that are present in various plant metabolites and reducing sugars.

**Conclusion**

The rapid biological synthesis of palladium nanoparticles using leaf broth of *Solanum trilobatum* provides an economic and efficient route for the synthesis of nanoparticles with tunable optical properties. The approach of phytosynthesis appears to be cost efficient eco-friendly and easy alternative to conventional methods of palladium nanoparticles synthesis. The capping of bioorganic compound present in the leaf broth around each nanoparticle furnish uniform chemical environment for its stability. The palladium nanoparticles obtained were further characterized by conjugating with lipoic acid and vitamins. The nanoparticles thus synthesized from the herbal extracts can be used as an alternative to the chemically formulated palladium alpha-lipoic acid complex. However the beneficial effects of the
herbally synthesized formulation against many age-related disorders (cardiovascular and neurodegenerative diseases) can be further explored using invitro and invivo studies.

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Click chemistry approach to functionalize two-dimensional macromolecules of graphene oxide nanosheets

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A facile “click chemistry” approach to functionalize 2D macromolecules of graphene oxide nanosheets with poly (ethylene glycol) of different molecular weights, polystyrene, palmitic acid and various amino acids was presented. FTIR, TGA, Raman spectroscopy, XPS, XRD, TEM, AFM and SEM were utilized to characterize the products. High degree of functionalization was achieved on the flat surfaces of graphene oxide, affording polymer-grafted 2D brushes and amino acids-immobilized nanosheets, which show improved solubility in organic solvents. The click chemistry strategy reported herein provides a facile and general method for functionalization of graphene oxide with macromolecules and desired biomolecules.

Keywords: Graphene; Click chemistry; Chemical modification; PEG; Amino acids

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Graphene, a novel kind of two-dimensional (2D) macromolecule, has drawn tremendous attentions in the domain of scientific research. Due to its special properties of Young’s modulus, thermal conductivity, mobility of charge carriers and specific surface area, it shows wide applications in energy-storage materials, “paper-like” materials, polymer composites and so on [1-3]. Graphene oxide (GO), derived from the oxidation of graphite, possesses abundant oxygen-containing functional groups, which not only render GO moderate water-dispersibility but also offer reactive sites for the further modification. Therefore, various reactions utilizing these oxygen-containing groups have been developed [4-8]. Haddon et al. have modified GO with long-chain alkylamine, making GO dispersed well in organic solvent [9]. Stankovich and coworkers functionalized GO with isocyanate derivatives and the resulting products show good solubility in polar aprotic organic solvents [10]. Chen et al. demonstrated that porphyrin and fullerene modified-graphene afforded the useful nonlinear optical properties [11]. In addition to small molecules, polymers were also employed to functionalize GO in order to improve the performance of GO in distinct domains. Yang et al. synthesized poly(2-(dimethylamino) ethyl methacrylate) (PDMAEMA) grafted GO by ATRP [12], while Salavagione et al. functionalized GO with poly(vinyl alcohol) by esterification of carboxylic groups [13]. However, to functionalize GO with a facile and general strategy is still a challenge.

In addition, click chemistry, characterized by its modular nature, high selectivity and yields, has attained great development in recent years. Among various types of click reactions, the Cu-catalyzed Huisgen 1, 3-dipolar cycloaddition of azides and alkynes plays a particularly important role in organic synthesis for its excellent performance such as stability against dimerization or hydrolysis [14]. Since the azide-alkyne click chemistry has been demonstrated as a useful tool to modify carbon nanotubes (CNTs) [15-21], it would be quite efficient for the functionalization of GO, the analogue of CNTs. Most recently, the click chemistry has been tried to functionalize GO [22,23]. However, the reaction conditions and related influential
factors have not been investigated. Since GO is a new type of atypical two dimensional (2D) macromolecules, it is vitally significant to evaluate the optimized "click" condition to modify its surface, in order to enlarge its application, especially in the areas of composites, multifunctional materials and devices. Herein, we employ azide-alkyne click chemistry to functionalize GO with linear polymers, various amino acids, aliphatic chains, and investigated the effect factors of reaction conditions.

**Experimental Part**

**Materials**

Graphite powder (40 μm) was obtained from Qingdao Henglide Graphite Co., Ltd. DMF, K₂S₂O₇, P₂O₅, KMnO₄, 30% H₂O₂ and concentrated H₂SO₄ were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. NH₂(CH₂)₃N₃ and azide-terminated PEG, PS, C₁6, Gly and Phe were synthesized in our lab [18, 20, 24]. CuBr (Aldrich, 98%) was obtained from Aldrich and purified according to the published procedures [25]. N,N,N′,N″,N‴-pentamethyldiethylenetriamine (PMDETA, 99%), N-hydroxysuccinimide (NHS, 98%), N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC-HCl, 99%) were purchased from Alfa Aesar and used as received.

**Preparation of GO, GO-N₃, GO-PEG.**

GO was synthesized from natural graphite powder and the specific process is presented in our published paper [26, 27]. The water solution of GO (100 ml, 7.5 mg/ml) reacted with 3-azidopropan-1-amine (NH₂(CH₂)₃N₃) (7.5 g, 75 mmol) for 24 h at room temperature under the catalytic action of EDC (4.79 g, 25 mmol) and NHS (2.475 g, 22 mmol). The reaction product, GO-N₃, was centrifuged for 5 min at 1000 rpm and washed five times with ultrapure water and then kept in water. Alkyne-terminated PEG (400 mg) was added into a round flask (250 ml) containing GO-N₃ (16 ml, 2.5 mg/ml), and then DMF (144 ml), CuBr (200 mg, 1.3 mmol), PMDETA (294 μl) were added to the flask under the atmosphere of N₂. The coupling reaction between azide and alkyne proceeded for 150 min at 60°C in an oil bath. Then, the reaction product was centrifuged for 10 min at 5000 rpm and washed five times with DMF. All products were dried in a vacuum oven at 60°C overnight, and then graded them into powder for the use of analytical measurement.

**Measurements**

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 6 TGA instrument under nitrogen with a heating rate of 20°C/min. Infrared spectra (IR) were recorded on BRUKER VECTOR 22 spectrometer. Scanning electron microscope (SEM) images were measured by Hitachi S4800 field-emission SEM system. Raman measurements were carried out using a LabRam-1B Raman spectroscopy equipped with a 632.8 nm laser source. X-ray Diffraction (XRD) was carried out in X’Pert PRO diffractometer equipped with Cu Kα radiation (40 kV, 40 mA). Atomic force microscopy (AFM) was done using a Digital Instrument Nanoscope IIIa scanning probe microscope, operating at the tapping mode, with samples prepared by spin-coating sample solutions onto freshly cleaved mica substrates at 2500 rpm. X-ray photoelectron spectroscopy (XPS) were performed with a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with Mg Kα radiation (hv = 1253.6 eV) at a power of 250 W. Transmission electron microscope (TEM) was performed in FEI-PHILLIPS CM 200 electron microscope.

![Scheme 1. Functionalization of 2D macromolecules of GO nanosheets by azide-alkyne click chemistry.](http://www.nmletters.org)
Results and Discussion

Our functionalization protocol is shown in Scheme 1. Carboxylic groups of GO react with 3-azidopropan-1-amine (NH$_2$(CH$_2$)$_3$N$_3$) to form GO-N$_3$ by EDC condensation. Subsequently, alkyn-terminated poly(ethylene glycol) (PEG) with different molecular weight, polystyrene (PS), propargyl alcohol-esterified palmitic acid (C16), glycine (Gly) and phenylalanine (Phe), react with azide groups via click chemistry, affording GO-PEG, GO-PS, GO-C16, GO-Gly and GO-Phe, respectively.

Typically, the case of PEG was selected to show the results of click chemistry in details and the molecular weight of PEG is 750 unless specially labelled. Figure 1A shows the FTIR spectra of GO, GO-N$_3$ and GO-PEG. The peaks at 1720 and 1626 cm$^{-1}$ can be assigned to the stretching of carboxyl groups and the aromatic C=C stretching, respectively. After the EDC condensation, azide groups were attached to the surfaces of GO, which could be confirmed from the appearance of the characteristic IR absorption peak of azide groups at 2098 cm$^{-1}$.

For GO-PEG, the disappearance of the peak at 2098 cm$^{-1}$ and the presence of the peak at 1100 cm$^{-1}$ related to the stretching of C-O groups of PEG indicated the successful azide-alkyne coupling reaction on the nanosheets.

To explore the effect of reaction conditions on the nanoscale click coupling, we traced the reaction process by FTIR measurements at 25, 40 and 60°C, by taking out part of the reaction solution at a given time on the basis of extremely sensitive azido absorption in FTIR spectrum (see Fig. 1B). With the peak at 1626 cm$^{-1}$ as an internal standard, the integration ratio of the peaks at 2098 and 1626 cm$^{-1}$ ($I_{N3}/I_{G}$) represents the degree of the click conversion. Generally, the value of $I_{N3}/I_{G}$ decreases drastically at first and then quite slowly until almost zero (see Fig. 1C), indicating that the reaction rate is very fast in the beginning but quite slow in the end. Moreover, the temperature has significant influence on the click reaction. A ca. 93.0% conversion was achieved within 30, 60, and 900 min at 60, 40, and 25°C, respectively. In other words, 68.6, 93.3 and 98.8% conversions were found at the same reaction time of 60 min for cases of 25, 40 and 60°C, respectively. In our previous study, the click coupling reached equilibrium on CNTs at around 8 h [20]. Herein, the elevated click rate on GO is likely attributed to the fact that both faces of GO can be readily attacked while CNTs can be only accessed on their outer surfaces.

Accordingly, 60°C was chosen as the temperature to complete other click reactions (see Scheme 1). Interestingly, the azido peak at 2098 cm$^{-1}$ cannot be detected in the corresponding FTIR spectrum after 150 min in all cases except GO-PS in which

![FTIR Spectra and Conversion](http://www.nmletters.org)
the azido peak can be still slightly observed (see Fig. 2). It is shown that the “graft-to” click efficiency is affected by two main factors under the same reaction conditions: the molecular weight and flexibility (or chemical structure) of reactants [28]. In our system, all of alkyne-terminated PEG with different molecular weights (including 350, 750 and 1900 g/mol) reacted with azide groups of GO-N$_3$ efficiently for the disappearing of azido peak within 150 min. This suggests that molecular weight of this kind of flexible and “thinner” polymer has little effect on the click coupling on the flat nanosurface of GO sheets. Compared with alkyne-terminated PEG (1900), alkyne- terminated PS with a comparable molecular weight (Mn=2500 g/mol) is much more rigid and “thicker”, resulting in stronger steric hindrance effect and much lower contacting (or click) probability between rigid nanosheets and PS chains. This result is similar to our previous investigation that two hard nanoparticles are difficult to be clicked together except a soft interlayer exists [19]. Nevertheless, small rigid molecules such as phenylalanine can be easily immobilized to GO-N$_3$ nanosheets for its high contacting chance associated with high mobility, casting affirmative light on the click fabrication of multifunctional biomolecules-conjugated graphene.

TGA was further employed to confirm the successful click reactions on the surfaces of GO. It should be noted that the larger weight than 100% of samples is the result of N$_2$ absorption during the measurement. As shown in Fig. 3, the whole weight loss of GO is ca. 51.0% and nearly all weight loss occurs at ca. 210 °C, which is presumably due to pyrolysis of the labile oxygen-containing functional groups. It was thought that the weight loss should increase after EDC condensation because of the attachment of azide moieties, but in fact the weight loss is decreased to 39.1% due to the partial reduction of GO during the reaction, which can be proved from our XRD datum (see Fig. 3D). In addition, the changed color of reaction solution from brown to dark also indicates the process of reduction. The weight loss of 15.8% at ca. 210°C can be ascribed to the pyrolysis of the residual labile oxygen-containing functional groups while the weight loss of 23.3% between 210 and 500°C is due to the pyrolysis of azide moieties. For GO-PEG, on account of the polymer decomposition, the increased weight loss of 52.4% was observed. Calculated from corresponding TGA weight loss data, the content of PEG molecules on the surfaces of GO is ca. 0.17 mmol per gram of GO-PEG, corresponding to one PEG chain per 250 carbon atoms. We also traced the click reaction by TGA and found that the weight loss of GO-PEG at 3 min at 60°C was almost equal to that at one hour at 25°C (Figure S2 in Supporting Information), further confirming the much faster click reaction at elevated temperature. In addition, the TGA of GO-Phe is also performed and presented in Fig. S6, showing the similar result to the PEG case.

Raman spectroscopy is a powerful approach to investigate the structural and electronic properties of graphene. As shown in Fig. 3B, the pristine graphite is characterized by a strong band at ~1575 cm$^{-1}$ (G band) which corresponds to an E$_{2g}$ mode of graphite and a weak band at ~1330 cm$^{-1}$ (D band) related to the vibration of carbon atoms with dangling bonds in plane terminations of disordered graphite. After the process of oxidation, GO shows a broadened G band shifted to 1595 cm$^{-1}$ and a broadened D band with high intensity at 1330 cm$^{-1}$. The intensity ratio of the D and G bands (I_D/I_G) is commonly used to evaluate the quality of carbon materials. The ratio of $I_D/I_G$ increases gradually from natural graphite (0.403) to GO (1.234), to GO-N$_3$ (1.397) and then to GO-PEG (1.399), revealing the increased degree of functionalization that is quite similar to the case of CNTs [29]. Meanwhile, we also obtained Raman spectra
of GO-C16, GO-Gly and GO-Phe, and the value of $I_D/I_G$ is 1.404, 1.455 and 1.486, respectively (see Fig. S5).

XPS was used to study surface elemental composition of different specimens. Figure 3C shows the XPS spectra of GO, GO-N$_3$ and GO-PEG. The nitrogen content increased from 1.2% for GO (nitrogen absorption from atmosphere) to 4.9% for GO-N$_3$ and then decreased to 3.8% for GO-PEG, confirming the successful attachment of azide groups and PEG. In addition, the carbon content of GO-C16 is as high as 80.9% compared with the content of 65.8% for GO-N$_3$, which also proves the accomplishment of the click coupling reaction (Table S1 in Supporting Information).

XRD measurement is also performed to further study the changes in structure. As shown in Fig. 3D, the initial graphite powder shows the typical sharp diffraction peak at $2\theta = 26.5^\circ$, with the corresponding d-spacing of 0.336 nm. For GO, no diffraction peaks from the parent graphite material is observed, but a new broad peak at $2\theta = 10.0^\circ$ appears, with a d-spacing of 0.885 nm. The increase of the d-spacing is due to the decoration with epoxide and hydroxyl groups intercalated between the GO layers during the oxidation process and a conversion of hybridization of the oxidized carbon atoms from sp$_2$ to sp$_3$ [30]. Due to the introduction of 3-azidopropan-1-amine, GO-N$_3$ shows a diffraction peak at $2\theta = 8.8^\circ$, corresponding to a d-spacing of 1.005 nm. In addition, GO-N$_3$ exhibits a new diffraction peak at $2\theta = 18.8^\circ$, demonstrating the partial reduction of GO-N$_3$ during the reaction process. For GO-PEG, the left shift diffraction peak at $2\theta = 6.6^\circ$, corresponding to a d-spacing of 1.339 nm, can be ascribed to the attachment of PEG chains. What is more, GO-PEG suffer a further reduction for the diffraction peak at $2\theta = 22.4^\circ$.

TEM analyses of GO and GO-PEG were performed by
FIG. 5. Photographs of GO and GO-PEG placed in solvents (from left to right: GO in dichloromethane, GO in chloroform, GO-PEG in dichloromethane and GO-PEG in chloroform).

placing a single drop of the DMF solution onto a holey carbon-coated copper grid. As shown in Fig. 4A, 4B, GO displays a morphology like a large crumpled paper while the edge of GO-PEG scrolls just as a tube, similar with the previous study which reported that the polymer-coated graphene scrolls and folds above the polymer’s glass transition temperature [31]. AFM is a direct and reliable method to examine the degree of exfoliation of GO to graphene single sheets. The as-prepared GO and GO-PEG sheets were characterized by tapping mode AFM and the results are shown in Fig. 4C, 4D. The average thickness of GO nanosheets is ca. 1 nm, which indicates a completed exfoliation to be single-layer nanosheets, and lateral dimensions of ca. 1 μm are observed. For GO-PEG, the surface topography become more complicated and the thickness increased to ca. 8 nm, which demonstrates the successful attachment of PEG. Moreover, the saddleback-like height profile of GO-PEG illustrates that more carboxylic groups locate on the edge of GO nanosheets.

In addition, the final products including GO-PEG show improved solubility in a variety of solvents such as chloroform, dichloromethane and so on (see Fig. 5), which will make considerable contribution to the application of graphene in the area of composites and other aspects.

Conclusions

In summary, an efficient click chemistry approach to functionalize 2D macromolecules of graphene oxide nanosheets has been presented and demonstrated with linear polymers and various amino acids. High degree of functionalization was achieved on the flat surfaces of GO, affording polymer-grafted 2D brushes and amino acids-immobilized nanosheets. The click chemistry strategy opens the door for facile functionalization of GO with macromolecules and desired biomolecules. The relevant work is in progress and will be reported later.

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Electronic Supplementary Information (ESI) available: [SEM of GO and GO-PEG; TGA of GO-PEG at different reaction time, IR, XRD, XPS, Raman of GO-Gly, GO-Phe, and GO-C16, TGA of GO-Phe].

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Current sustainability and electromigration of Pd, Sc and Y thin-films as potential interconnects

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The progress on novel interconnects for carbon nanotube (CNT)-based electronic circuit is by far behind the remarkable development of CNT-field effect transistors. The Cu interconnect material used in current integrated circuits seems not applicable for the novel interconnects, as it requires electrochemical deposition followed by chemical-mechanical polishing. We report our experimental results on the failure current density, resistivity, electromigration effect and failure mechanism of patterned stripes of Pd, Sc and Y thin-films, regarding them as the potential novel interconnects. The Pd stripes have a failure current density of (8–10)×10^6 A/cm^2 (MA/cm^2), and they are stable when working current density is as much as 90% of the failure current density. However, they show a resistivity around 210 μΩ·cm, which is 20 times of the bulk value and leaving room for improvement. Compared to Pd, the Sc stripes have a similar resistivity but smaller failure current density of 4–5 MA/cm^2. Y stripes seem not suitable for interconnects by showing even lower failure current density than that of Sc and evidence of oxidation. For comparison, Au stripes of the same dimensions show a failure current density of 30 MA/cm^2 and a resistivity around 4 μΩ·cm, making them also a good material as novel interconnects.

Keywords: Carbon nanotube-based field effect transistors; Carbon nanotube-based circuit; Interconnects; Current density; Electromigration; Resistivity

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Since the state-of-the-art $p$-type CNT-FETs require palladium (Pd) electrodes [1], and $n$-type CNT-FETs require scandium (Sc) or yttrium (Y) electrodes [2,4], it is a natural choice to use the same electrode materials as the interconnects for the novel CNT-FET-based circuits, if any of them fulfills the requirements of such interconnects. This allows the fabrication of electrodes (either for $p$-type or $n$-type FETs) and interconnects in one deposition step thus simplifying the processing, and also maximally reduces the risk of contamination and interface effect that a metal other than the electrode materials (i.e., Pd, Sc or Y) brings to the circuit, which may degrade the performance of CNT-FETs.

For an interconnect material, sustainability of current density, resistivity, chemical and thermal stability, as well as technical compatibility and cost are some of the key parameters to be considered. Electromigration, which may lead to opens or shorts in interconnects of an integrated circuit after hours of use, is another important factor [12-19]. Indeed, the change of interconnects from Al to Cu in the development of integrated circuit industry is partly because of the electromigration [20-22]. Here we report our experimental results on the current sustainability, resistivity and electromigration effects of patterned stripes of Pd, Sc and Y thin-films, as well as Au stripes for a comparison, regarding them as potential interconnects.

Thin-film stripes with thickness of 40–80 nm, width of 1–4 μm and length of 100, 300, 500, 700 and 1000 μm are made into a 4-lead structure (as shown in Fig. 1a) on SiO$_2$(500nm)/Si substrates by using standard photolithography techniques. The Pd, Sc and Y thin films are fabricated with an electron-beam deposition system (Kurt J. Lesker, AXXIS), which has a base vacuum of $5 \times 10^{-9}$ torr. The Au films are made with a sputtering system (Kurt J. Lesker, KJLC PVD 75), which has a base vacuum of $8 \times 10^{-8}$ torr. Film thickness is measured by using an Ambios XP-1 Stylus Profiler. The crystalline structure of the films is measured with an X-ray diffraction system (SHIMADZU, XRD-6000). The resistance of the samples is measured with a home-made automation system consists of source meters Keithley 2400 and Keithley 2410, which has a measurement error around 0.05% for 4-lead resistivity measurements. The failure current density values of Pd, Sc, Y and Au stripes are measured first from 2–3 samples of each materials, then a working current with current density set at approximately 60%, 70%, 80%, 90% and 100% of the measured failure current density is applied to a fresh sample, respectively, each for 40 hours (unless the sample breaks shortly).

The interconnection for novel CNT-based integrated circuit may be required to have a limited line-width and thickness (thus a small cross-sectional area), but to support a working current up to mA. As a result, they should sustain a current density up to MA/cm$^2$. From the Pd stripe samples (see Fig.1a) with varied

![FIG. 1. (a) SEM image of a 100 μm long stripe sample. The arrow shows the motion direction of electrons under test; (b) Plot of the failure current densities of Pd stripes; (c) Failure current densities of Sc stripes; (d) Failure current densities of Y stripes.](http://www.nmletters.org)
width from 2.2 to 3.5 μm, failure current densities (at which the stripe breaks) of 7.6–10.4 MA/cm² are measured, as shown in Fig. 1b. Thus for a Pd stripe of 1 μm wide and 50 nm thick, for instance, it can sustain a maximum current of 4–5 mA. The failure current densities in Sc stripes and Y stripes are mostly 4–5 MA/cm² and 1.5–3.5 MA/cm², respectively (see Fig. 1c and Fig. 1d). Though the values are sample dependent, clearly Pd stripes can sustain much higher working current density than Sc and Y stripes do.

The 4-lead structure of the stripe (see Fig. 1a) enables us to obtain the resistivity values of these samples directly. The average resistivity values of Pd, Sc and Y stripes are measured to be around 216, 213, and 265 μΩ·cm, respectively. Surprisingly, the measured resistivity of our Pd thin films is about 20 times of the Pd bulk resistivity [23]. In sharp contrast, the resistivity values for Sc and Y stripes are only 3.5 and 4.5 times of the bulk values of their counterparts, respectively. This implies a big room for improving the quality of Pd film, though the present Pd film has already shown a high current sustainability.

We have studied the electromigration effects of the samples by monitoring the change of resistance when a large working current is running in a stripe for a long period of time up to 200 hours. For Pd stripes, as typically shown in Fig. 2a, an obvious increase of resistance with time can be observed under a working current of 5.12 MA/cm², which is 75% of the failure current density ~ 6.83 MA/cm². Next, by increasing the current density to 5.97 MA/cm², and about 87% of the failure current density, the sample keeps in a steady regime by showing a slowly increasing resistance. Under a working current of 6.83 MA/cm², it causes a quick increase of resistance until the stripe breaks. For Sc stripes, typically the sample resistance shows a decrease under a working current of 50–60% of the failure current density, then a quick increase when the working current keeps on increasing (see Fig. 2b), until the stripe breaks. Y stripes, however, show a random trend. Figure 2c plots the measured data of one of the Y samples. The phenomenon of linear increasing resistance with time, similar to what is measured in our Pd stripes, has been observed previously in Cu and Al (4% Cu) [17,24]. Theoretically this is attributed to the dynamics of vacancy and defects in the electromigration process [15,25-27]. On the other hand, the annihilation of vacancy and imperfection can lead to decrease of the resistance at the beginning of the electromigration in low current [15], as what is observed in our Sc stripes.

When running a current close to the maximum sustainable value (i.e., the failure current) in a stripe for a long time, or when the current density exceeds the maximum sustainable value, it results in break of the stripe thus failure of the circuit. Three underlying mechanisms that may result in break (failure) of a thin-film stripe are electromigration-induced stress, thermomechanical stress, and heat-induced melting effect.

FIG. 2. (a)-(d) Resistivity versus time under increasing working current in Pd, Sc, Y and Au stripes, respectively. The environment temperature is kept at 300 K.
[28-31]. It is predicted that when the current is not high enough to induce significant Joule heating, the stress is tensile at the cathode end and compressive at the anode end [28]. Because materials fracture more easily under tensile stress than under compressive stress, a thin film is expected to fail at the cathode under low current. As the current level increases and Joule heating becomes more dominant, the whole stress (electromigration and thermomechanical) turns to being compressive, so the film will fail at the anode end. In the third situation, the current is large enough so that the electromigration stress is smaller than the thermomechanical stress, then the film is expected to fail catastrophically toward the center.

Figure 3 shows scanning electron microscope images of a Pd stripe before and after it breaks. The break region is melting-like, as shown in Fig. 3c and Fig. 3d, which might be caused by the combination of electromigration force and Joule heating effect. Figure 4 shows that, for the same Pd stripe, after the stripe is broken by running a high working current for a long time, the change of surface morphology is obvious at the anode region (see Fig. 4c and Fig. 4d), but not at the cathode region (see Fig. 4a and Fig. 4b). This is consistent with the theoretical predictions [28].

Y films can wet well to CNTs and make Ohmic contact [32]. However, it can also be easily oxidized, and indeed this nature has been applied to obtain high-performance gate dielectrics for graphene-based devices [33]. Weak peaks of Y$_2$SiO$_3$ (or a mixture of Y$_2$O$_3$ and SiO$_2$) are found in the X-ray diffraction patterns of the Y films. Formation of oxides is surely not favorable for the materials to be used as interconnects. At the break points of Y stripes, often plenty of voids are observed (see Supplementary).

For a comparison, we have also measured the similar properties of Au stripes. An average failure current density of 30 MA/cm$^2$ is measured, which is slightly higher than 29 MA/cm$^2$ as reported by Hadeed and Durkan [28]. The resistivity of Au stripes is measured to be 4.0-4.3 \( \mu \Omega \cdot \text{cm} \), 1.8 times of the bulk resistivity of Au, 2.35 \( \mu \Omega \cdot \text{cm} \). As typically shown in Fig. 2d, the resistance of an Au stripe keeps on decreasing in a low working current. When the working current is approaching the maximum sustainable value, the resistance starts to increase quickly till break of the stripe. This behavior is different from those observed in Pd and Sc stripes. After the Au stripes are broken, big particles and voids are observed in the samples (see Supplementary).

In conclusion, Pd is a potential candidate as the interconnect material for novel CNT-FET-based circuits. A failure current density of 8-10 MA/cm$^2$ is measured in the Pd micro-stripes, and they are remarkably stable when the working current density is as much as 80-90% of the maximum sustainable density. However, our Pd samples show a resistivity around 210 \( \mu \Omega \cdot \text{cm} \), which is 20 times of the bulk value, leaving plenty of room for further improvement. The Sc stripes show similar resistivity but half of the failure current density compared to those of Pd samples. Y films seem not suitable for interconnects when they show much lower failure current density than Pd and Sc, and evidence of oxidation. For comparison, Au films could also be considered as a good interconnect material, which has a failure current density of 30 MA/cm$^2$ and a resistivity around 4 \( \mu \Omega \cdot \text{cm} \), providing that the diffusion of Au atoms dose not degrade the performance of novel CNT-FETs.

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![Fig. 3](http://www.nmletters.org)

FIG. 3. (a)-(d) SEM images of the same Pd stripe (2.42 \( \mu \text{m} \) wide, 300 \( \mu \text{m} \) long) before and after it has been running a working current for long time. (a) original morphology; (b) after running a current of 11 mA (corresponding to a current density of 5.93 MA/cm$^2$) for 4 hours; (c) after subsequently running a working current of 15 mA (corresponding to a current density of 8.09 MA/cm$^2$) for 1 more hour, causing break at the center of the stripe; (d) A close look at the broken region as highlighted in (c), showing melting-like morphology.
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Passivated ZnSe nanocrystals prepared by hydrothermal methods and their optical properties

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Homogeneous ZnSe nanocrystals were prepared via surfactant-assisted hydrothermal method. Surfactants agent CTAB was used to control the particle morphology and the growth rate. The structure, morphology and optical properties of ZnSe nanocrystals have been investigated by XRD, TEM and luminescence spectroscopy. The results indicated that the size of ZnSe nanocrystals ranged from 3.0 nm to 5.0 nm with cubic zinc blende structure. ZnSe nanocrystals coated by CTAB were revealed high dispersibility and distribution under TEM. Compared to the bulk ZnSe, the absorption edges and photoluminescence peaks of ZnSe nanocrystals were blue shifted to higher energies due to the quantum confinement effect. The emission intensity was strengthened after coated CTAB compared to bare sample. This was mainly due to the surface passivation. Meanwhile, we simply explored the formation mechanism of ZnSe nanocrystal in hydrothermal system.

Keywords: Zinc selenide; Nanocrystals; Surface passivation; Photoluminescence

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Semiconductor nanocrystals (NCs), or quantum dots (QDs), have been extensively studied due to their quantum confinement effects which exhibit unique size dependent electronic and optical properties [1,2]. Narrow and intensive emission spectra, continuous absorption bands, high chemical and photobleaching stability, and surface functionality are among the most attractive properties of these materials, which are not available from either bulk materials or isolated atoms. At present, synthetic procedures have been developed for a few group II-VI and III-V. As one of the Zn-based II-VI compounds, ZnSe is a direct band-gap semiconductor, with one room-temperature band-gap energy and an emission at 2.7 eV making it a potentially good material for blue-diode lasers and other photoelectronic devices [3-5]. It is known that ZnSe nanocrystal is interesting luminescent material in the blue to the ultra violet range due to quantum confinement effect and have been widely studied for its fundamental properties and potential use in technological applications. It is used as widely tunable for light emitting diodes (LED) [6-8] especially a very well succeedaneum for biomedical labeling to replace some high toxicity nanomaterials such as CdS, CdSe and CdTe quantum dots. For higher quality and lower fabrication costs, a variety of physical and chemical techniques have been tested to produce materials in nanoscale with properties required by industries. Molecular beam epitaxy (MBE) [9] is one of the most normal methods. Other methods such as metal organic chemical vapor deposition (MOCVD) [10,11] and vapor phase epitaxy (VPE) [12,13] were also reported. However, all of these methods required special device and usually included toxic metal organic reagents as raw material [14]. It is believed that the most straightforward way to synthesize ZnSe is direct combination of element zinc and selenium at high temperature. Li et al has reported a successful fabrication of ZnSe by hydrothermal method in specific solvents such as pyridine which is virulent, so it must be synthesized at glove-box [15]. Hua Gong et al once reported analogy method at low-temperature and the products presented hollow microsphere and powder [16]. In hydrothermal syntheses, reaction time, temperature, and mole ratios of the precursors and solvent were very important to the
formation of nanocrystals. Low temperature, high concentration, and short reaction time minimized the crystal size. In this paper, monodisperse spherical ZnSe nanocrystals were synthesized, which showed low surface defect concentrations and good luminescence properties.

**Experimental procedure**

The starting materials were Se (99.95% A.R.), Zn (90% A.R.), NaOH (96% A.R.), and cetyl trimethyl ammonium bromide (CTAB). 12 mol/L NaOH aqueous solutions was poured into a bunsen beaker, and then CTAB was added and magnetically stirred until the CTAB thoroughly dissolved. The solution was placed into a 30 ml Teflon-lined autoclave. Zn and Se metal powders were directly added into the autoclave, adjusting CTAB content to 0%, 5%, 10% (mol), and the ratio of Zn:Se = 1.5. The obtained suspension solution was kept at fixed concentration and filled about 60% of autoclave. The autoclave was then sealed and heated in an oven at a rate of 3°C/min. After heat treatment at 150°C for 2 h, the autoclave was cooled to room temperature naturally. The products were viscous fluid, added some water and collected by centrifugal sedimentation, then washed with ionized water then absolute alcohol repeated. Finally, the solid power samples were dried under vacuum at 40°C in a drying chamber in the same prepared condition. The as-prepared solid powders were stored away from light because they were unstable and easily oxidized in air.

The crystal structure of the samples was examined by X-ray diffractometer (XRD) with Ni-filtered CuKα radiation at room temperature. The scanning speed and step for measurements were 3°/min, and 0.02° in the range of (2θ=10-80°). The size and shape of the samples were characterized by transmission electron microscopy (TEM). The optical properties sample was measured by LAMBDA 950 Uv-vis spectrometer (Perkin Elmer. PE) and the photoluminescence spectra under ultraviolet (UV) region were measured by a Xe lamp (FLS-920T) at room temperature.

**Results and discussion**

Figure 1 shows the XRD patterns for ZnSe NCs with different nominal content of CTAB at 0, 5%, 10% and marked as A, B, C respectively. The result indicated that all products were single phase and no peaks characteristic of impurity phases were observed, which indexed to the phase of ZnSe with a cubic blende ZnSe (JCPDS card, No.05-0522, a=5.667 Å), The typical broadening of the three diffraction peaks were observed, which indicated that the size of the ZnSe was very small and three peaks at 27.33°, 45.65° and 53.94° corresponded to the (111), (220) and (311) planes of cubic ZnSe, respectively. The average diameter of the ZnSe particles can be calculated using Scherer’s formula:

\[ d = \frac{k \cdot \lambda}{\beta \cdot \cos \theta} \]

Where λ is the wavelength of the X-rays and equals 1.54056 Å, k = 0.89, β is the half-peak width of the diffraction peak, and θ is the Bragg angle. The average diameter of the three samples was obtained according to above equation: A = 4.50 nm, B = 4.15 nm and C = 3.84 nm.

Figure 2 gives the TEM image and electron diffraction pattern of ZnSe NCs (The scale is 10 nm). The results showed that the nano size ZnSe particles produced by this method were spherical. Figure 2a was the sample without CTAB and we can observe that a majority of products were aggregated (sample A). Figure 2b displayed the image that CTAB concentration at 5% (sample B), compared to sample A, the particles were separated by adsorbed CTAB layer and the dispersibility of the particle was improved. The reason can be explained that CTAB is adsorbed on particle’s surface in the solution. When the content of CTAB increased to 10% (Sample C), all particles were monodisperse and micelles were formed with the cation head pointing outwards in NaOH solution, so Zn²⁺ and Se²⁻ should react at the outer-layers of the micelles to form ZnSe; that is why under TEM, hollow particles were observed. Moreover, the surface defects diminished and the surface of particles grew much more intact (see Fig. 2c). The images demonstrated that ZnSe nanocrystals with uniform and narrow-dispersed size distribution without aggregation were synthesized successfully. Electron diffraction technique confirmed the zinc-blende crystalline structure of the ZnSe nanocrystals with the (111),

**FIG. 1. XRD patterns of ZnSe nanocrystals:** (A) without CTAB, (B) 5 mol% CTAB, (C) 10 mol% CTAB.
(220) and (311) diffraction rings in the electron diffraction pattern. According to Fig. 2, we conclude that the optimum content of CTAB was about 10%. It is reported that oleic acid played multiple roles in the formation of ZnSe NCs by acting not only as the reaction and shape controller but also as the stabilizing agent [17]. We can deduce that CTAB played similar roles by acting as the shape controller and growth speed indicator [18]. Surfactant CTAB can shielding the hydrophobic parts within the micellar interior, with the increases of surfactant concentration, the self-organization of micelles will produced [19]. It is indicated that another role of CTAB was to decrease the whole surface tension, making surface energy of the whole system reduce and improve the dispersibility of ZnSe nanocrystals. Figure 3 presents the histogram based on the TEM image (sample C), which revealed that the particle diameter ranged from 3.0–5.0 nm and the results was consistent with the calculated result measured by XRD.

Controlling the diameter is an important research objective for the NCs materials because diameter has a great effect on the luminescence properties. In the process of preparing ZnSe through hydrothermal synthesis employed Zn and Se as source materials and NaOH as hydrothermal medium, we concluded the forming mechanism as follows, when reactant concentration obviously increased, the solution was over-saturated, accelerating the velocity of nucleation and sharply increasing the quantity of the critical core. Meanwhile, reactant consumption also multiplied as there was no redundant reactant to consume; hence, the critical core growth was inhibited, as a result the grain size of product was smaller. At the same time, during the course of allegro formation of crystals, surface defects may increase by

![TEM image and selected area electron diffraction pattern of ZnSe nanocrystals.](image1)

![Histogram based on the TEM (sample C) image.](image2)
the reason that there wasn’t enough time for the surface atoms arrayed neatly. The result reflected that the surfactant CTAB sharply decreased surface defect, making surface smooth. Meanwhile, a growth mechanism of the ZnSe nanocrystals was proposed, the reactions in the hydrothermal solution can be formulated as the following:

\[
\begin{align*}
\text{Zn} + 2\text{H}_2\text{O} + 2\text{OH}^- & \rightarrow [\text{Zn(OH)}_2]^2^- + \text{H}_2 \\
\text{Se} + 2\text{OH}^- + \text{H}_2 & \rightarrow \text{Se}^{2-} + 2\text{H}_2\text{O} \\
[\text{Zn(OH)}_2]^2^- + \text{Se}^{2-} + \text{H}_2 & \rightarrow \text{ZnSe} + 4\text{H}_2\text{O}
\end{align*}
\]

Zn and Se react with NaOH respectively and are dissolved in the hydrothermal solution. Then Se is reduced to Se\(^{2-}\) by H\(_2\) generated in reaction (1). In order to completely reduce Se to Se\(^{2-}\), the excessive Zn powders are used to generate enough H\(_2\) and maintain sufficient reducing ambient in the hydrothermal system. That is the reason in the experiment of prepared ZnSe nanocrystals the ratio of Zn:Se is 1.5.

Figure 4 gives the excitation spectrum of uncoated solid power sample (sample A) and Fig. 5 presents the emission spectra of ZnSe NCs, respectively. Monitored by 390 nm emission, a main broad band in the 200–280 nm range peaking at around 245 nm in the excitation spectrum which assigned to the higher excited state transitions of ZnSe NCs were observed [20] (In the measurement, we collected the spectrum range from 200 to 400 nm. But after 300 nm, there were no other absorption peak in spectra so the spectra were ending at 310 nm in picture). As shown in Fig. 5, when excited by 245 nm, four emission bands from 300 to 650 nm with maxima at about 390 nm, 467 nm, 560 nm and 590 nm were observed. The first maximum at 390 nm is the exciton emission. The exciton emission can be attributed to the direct recombination of the electron-hole pair, an electron-hole pair will be generated when an intrinsic NC is excited by photons with energy higher than its band gap. The direct recombination of the electron-hole pair, typically being quantum confined in the case of nanocrystals [21], gives the well-known band edge emission at 390 nm which related to the higher excitonic states. The results were in accordance with the other results [22,23]. As a shoulder on a broad peak at 390 nm, the second band centered at 467 nm is attributed to band edge emission of few bigger particles. Two much broader peaks in the region of 550–650 nm were usually assigned to self-activated luminescence, probably as a result of some donor-acceptor pairs related to Zn-vacancy and interstitial states [24,25].

In ZnSe NCs surface, there were large quantity of dangling bonds which can induce defects and adatoms, in such circumstances, surface levels were formed because over half of atoms migrated to surface and became surface atoms which caused NCs have large specific surface area. Energy that excited to surface level was lower than that of to conduction band, so electrons were easily excited to surface level, and then came back to valence band to recombination with hole, causing surface state emission [26]. “Self-purification” mechanisms are often claimed to reasonably this effect, as the distance a defect must move to reach the surface of a nanocrystal is very small. Self-purification can be explained through energetic arguments and is an intrinsic property of defects in semiconductor nanocrystals. The formation energy of defects in nanocrystals increases as the size of the nanocrystals decreases [27]. The surface dangling bond states that lie within the band-gap typically quench the PL intensity. Surface passivation usually reduces the number of the surface dangling bonds [28]. It is observed that with the CTAB concentration increasing, the band edge emission intensity increased slightly because hackly surface was modified to some extent after being caped by CTAB.
Accordingly, a decrease in PL intensity was observed for nanocrystals with no CTAB owing to more defects in those nanocrystals (sample A). In this study, the CTAB capping layer was used not only as a passivation medium, but also to promote dispersivity of nanocrystals, which make the surface perfect and smooth, so band edge emission improved by reason that more electrons were excited to conduction band. The smooth surface and improved dispersivity could be reflected in TEM. The luminescence peaks, covering a wavelength region of approximately 350~450 nm, are extremely narrow, the FWHM (full width at half maximum) of the all emission spectrum was under 40 nm. These values demonstrate clearly that a large size distribution is obtained [29].

Figure 6 displays the absorption spectra of ZnSe NCs (inset gives the optical absorbance with wavelength), the optical absorption increased sharply at wavelength 380 nm due to the direct transitions of the band gap of ZnSe and a slight wavelength shift from 380 nm to 375 nm was observed with the CTAB increased, this might be related to the decrease of grains, which also reflected that CTAB can control the particle growth rate. Meanwhile, there was a weak band appears at about 430~440 nm, we can interpreted it as non-uniformity of particles. From TEM image, we can see that not all particles were arranged form 3~5 nm, and the absorption band of which particles was in 380 nm. Beside, there were few bigger particles, whose absorption band would red-shifted, so we observed weak absorption, this results was in accordance with the emission spectrum. The quantum confinement effect can be qualitatively explained using the effective mass approximation (EMA), when the NCs size was smaller than exciton Bohr radius, the electrons and holes were independently confined, and Coulomb interaction was then a perturbation, so the electron–hole transition energy to the $i$ th excited state of the NCs was determined by formula

$$E = E_g + E_s = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) \frac{1.8e^2}{\varepsilon R}$$

Where $\hbar$ is Planck’s constant; $E_g$ is the band gap energy of ZnSe NCs, $R$ is the radius of ZnSe NCs, $m_e$ is the effective masses of electrons, $m_h$ is the effective mass of holes, and $\varepsilon$ is the dielectric constant or relative permittivity of ZnSe. The second term on the right hand side shows that the effective band gap is inversely proportional to $R^2$ and increases as size decreases. On the other hand, the last term in $E_g$ indicates the Coulomb interaction energy, which decreases the energy of electron-hole pair state [30]. Consequently, we could calculate the size of ZnSe NCs that was base on an infinite confinement spherical well potential model. The parameters used for the calculation were: $E_g = 2.7$ eV, $m_e = 0.16 m_o$, and $m_h = 0.75 m_o$ ($m_o$ is the mass of electron). Accordingly, considering the Coulomb interaction, the particle size was calculated ranges from 2.8 to 5.3 nm, in reasonable agreement with the XRD and TEM results. Figure 6 inset shows the $(ahv)^2$ versus $hv$ graph. The direct absorption band gap of the ZnSe nanoparticles can be determined by fitting the absorption data to the equation (as shown in the inset of Fig. 6)

$$\alpha = B(hv - E_g)^{1/2} / hv$$

In which $hv$ is the photon energy, $\alpha$ is the absorption coefficient $E_g$ is the absorption band gap and $B$ is a constant relative to the material. The absorption coefficient can be obtained from the equation $\alpha = \frac{2.303 A}{d}$ where $A$ is the absorbance and $d$ is the thickness of the sample. Extrapolation of these curves on energy axis for zero absorption coefficients, gives the value of optical band gap energy. The band gap was found to be 3.2 eV for sample which showed blue shift of 0.5 eV from the standard band gap for bulk ZnSe (2.7 eV) [31].

**Conclusions**

In summary, spherical, low surface defect, homogeneous distribution and luminescence ZnSe nanocrystals were successfully prepared by environment friendly method. The
ZnSe nanocrystals were stable with diameters ranging from 2.5 to 5.0 nm derived in this work. The emission peaks were at 390 nm, which was strengthened after being encapsulated by CTAB. The optical absorption studies showed that the ZnSe NCs has optical band gap of 3.2 eV. Finally, we believe this work will be guidance on the foundation study of nanocrystals luminescence.

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Reducing SU-8 hygroscopic swelling by ultrasonic treatment

Du Liqun1,2*, Zhang Benzhuang2 and Liu Yaping2

The volume expansion of SU-8 resist brings serious dimensional errors to electroformed structures. Two approaches have been proposed to reduce resist distortions during electroforming: electroforming at room temperature and adding auxiliary features for mask patterns. However, the former method induces higher internal stresses in the electroformed metal layers. And the latter method makes it difficult to predict the expansion behaviors of the resists. In the paper, the thermal expansion of the SU-8 mould is calculated by ANSYS firstly, and the lower thermal expansion value indicates that hygroscopic swelling plays a leading role in SU-8 mould distortions. An original technique is presented to reduce SU-8 hygroscopic swelling by ultrasonic treatment. The dimensional errors of the electroformed structure fabricated on the ultrasonic treatment mould are 50% lower than the one without ultrasonic treatment. Simulation of hygroscopic swelling is conducted by finite element analysis, and the results indicate that the hygroscopic strain ε of SU-8 after electroforming is declined from 6.8% to 3.1% because of ultrasonic. The measurements show that ultrasonic treatment increased the water contact angle of cured SU-8 from 70.8° to 74.9°. Based on these results, the mechanism of ultrasonic effect on hygroscopic swelling is proposed from the view of ultrasonic vibration decreasing the number of hydroxyl groups in SU-8. The research presents a novel method to improve the precisions of electroformed structures. It has no influence on the internal stresses of final structures and does not increase the complexities of mask layouts.

Keywords: SU-8; Hygroscopic swelling; Electroform; Ultrasonic; Hydrophilicity

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SU-8 resist has become a prevalent mould material to electroform MEMS devices because of its mechanical and chemical stability and its ability to produce high-aspect-ratio moulds by UV-LIGA technology [1,2]. However, electroforming processes based on SU-8 mould still face serious challenges. It is well known that the dimensions of electroformed structures are usually shrunk compared with the masks. This is mainly due to SU-8 mould distortions caused by thermal expansion and hygroscopic swelling during electroforming [3]. The relative dimensional errors of electroformed structures may reach 23% [4], which are unacceptable in practical applications, and the tapered structures cannot be corrected using a scaled or biased mask pattern. Furthermore, resist displacements will limit the maximum producible aspect ratio of a metal structure when the cavity of the mould will close at the top under the worst conditions [5].

Some works have been published to analyze PMMA swelling during electroforming. Two approaches have been proposed to reduce PMMA swelling. (i) Electroform at room temperature since the lower temperature may decelerate the solvent molecules diffusing rate throughout the resist thickness [6]. However, lower electroforming temperature induces higher internal stress in electroformed metal layer [7]. (ii) Improve the layout design of masks: auxiliary structures are introduced to
form trenches around the part in PMMA \[8,9\]. Then, the mass of the resist that swells is reduced. While auxiliary features can dramatically decrease tapers for linear structures, they increase skew for curved structures in some cases \[5\]. Additionally, complicated geometries pose a challenge for designing auxiliary features because the features must follow the perimeter of the part uniformly. Complex non uniform geometries of the auxiliary structures make it difficult to predict the expansion behaviors of the resists \[10\].

The above two methods are applicable to the processing based on SU-8, but apparently the same problems exist. Compared with PMMA, the number of publications on SU-8 swelling is very limited. Experimental and simulative studies have been taken on the thermal swelling of SU-8 \[3\]. And the influences of different post-exposure bake (PEB) temperatures on the thermal swelling of SU-8 were investigated \[4\]. However, as far as we know, no effective method which is independent of processing parameter and mask pattern has been proposed to reduce SU-8 hygroscopic swelling during electroforming.

In this paper, a novel research for the effect of ultrasonic treatment on SU-8 swelling is presented. The ultrasonic treatment was introduced to the electroformed Ni-structure fabricating process. And the dimensional errors of electroformed structures fabricated with and without ultrasonic treatment were measured respectively. The experimental results are presented and the mechanism of ultrasonic effect on SU-8 swelling is discussed.

**SU-8 mould distortions**

**SU-8 mould distortions during electroforming**

Electroformed structures based on resist moulds exhibit large dimensional errors. These errors result from thermal expansion and hygroscopic swelling of the resist since electroforming is performed in aqueous electrolyte at an elevated temperature \[5,6\].

Figure 1 shows the distortions of SU-8 mould during electroforming, with \(r\) and \(w\) respectively the initial thickness and width of SU-8 film, \(l\) the initial width of cavity in SU-8 mould, \(h\) and \(d\) respectively the height and top width of electroformed layer. Because SU-8 is confined by a rigid substrate, the distortions at the substrate interface are nearly zero. Under this condition, the top of the SU-8 structures becomes wider than the bottom, which produces a tapered metal structure with narrower top widths.

**Thermal expansion**

It is useful to find out which factor, thermal expansion or hygroscopic swelling, is the most important reason for SU-8 mould distortions. Thus, finite element analysis was taken by ANSYS to calculate the sole effect of thermal expansion in the total dimensional errors. For the long linear three-dimensional structure as shown in Fig. 2a, plane model (cross section with width \(w = 400 \mu m\), thickness \(t = 56.2 \mu m\), as shown in Fig. 2b) can be employed as an approximation to calculate the sidewall distortion. In view that the resist is confined by a substrate, zero displacement is applied on the bottom surface, and all other boundaries are free surfaces. The thermal expansion coefficient (CET) of SU-8 is 52 ppm/℃; Young’s modulus is 4.02 GPa; Poission’s ratio is 0.22. The temperature load is 26℃ (from room temperature 24℃ to electroforming temperature 50℃).

![SU-8 structure](image)

**FIG. 1.** Schematic of SU-8 mould distortions due to volume expansion of SU-8.

![Finite element analysis model](image)

**FIG. 2.** Simulating of SU-8 thermal expansion.

The simulated result is shown in Fig. 2c. It is known that the top width of SU-8 only increases by 0.27 \(\mu m\) due to thermal expansion. In fact, moisture and thermal diffusion are two interactive processes. When the polymer absorbs external molecules its CET always changes. For SU-8, the value of CET will reduce after absorbing water molecules \[11\]. Thereby, the
practical thermal expansion value will be smaller than 0.27 μm. On the other hand, the experimental total width increases more than 9 μm (will be shown in Fig. 6, measuring point 1). The analysis results indicate that the dimensional error produced by thermal expansion is less than 3% in the total error.

Hygroscopic swelling

From above analysis, it is known that swelling is the predominant reason for SU-8 mould distortions. The mechanism of moisture diffusion in epoxy has been widely studied. And it has been proved that the hydroxyl groups of epoxy resins play the leading role in moisture uptake process, where water molecules can form strong hydrogen bounds [12,13]. In general, each SU-8 monomer contains eight reactive epoxy groups, and therefore high degree of cross linking can be obtained and form three-dimensional network after photo-thermal activation. During cross linking reaction, hydroxyl groups generated. Hydroxyl groups have significant affinity to polar molecules such as water. Consequently, SU-8 could absorb a lot of water when exposed to aqueous surroundings, which causes swelling.

The water absorption process of epoxy can generally be expressed by Fick’s law [14],

\[
\frac{\partial C}{\partial \tau} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right)
\]  

Where \( C \) is the concentration of water; \( \tau \) is time; \( D \) is water diffusion coefficient; and \( x, y \) and \( z \) are axes along the concentration gradient.

\( D \) varies with temperature, and can be described by the classic Arrhenius function [15],

\[
D = D_0 \exp \left( \frac{-E_D}{RT} \right)
\]  

Where \( D_0 \) is a constant; \( E_D \) is the activation energy for diffusion; \( R \) and \( T \) represent the ideal gas constant and absolute temperature respectively.

The volume expansion with respect to the moisture content has been found to be linear to a good approximation for SU-8 [16]. Therefore, the hygroscopic strain \( \varepsilon \) induced by swelling can be related to the concentration of water according to

\[
\varepsilon = \beta C
\]  

Where \( \beta \) stands for the coefficient of hygroscopic swelling (CHS). \( \varepsilon \) is a function of time. At a constant temperature, \( \varepsilon \) will increase up to a maximum value with stroatched time.

Experiments

Processes to fabricate metal microstructures

SU-8 2015 (MicroChem Crop.) and mirror-polished Ni substrates were used in this study.

The detailed UV-LIGA processes to fabricate metal microstructures are as follows:

1) Ultrasonic wash Ni substrate for 20 min in acetone and ethanol in sequence, and then dry it after flushing with deionized water.
2) Spin coat SU-8 2015 for 18 s at 800 rpm to produce a film of approximately 60 μm thick, and then self-planarize on a level surface for 30 min.
3) Soft bake for 40 min at 65°C followed by 40 min at 85°C, and then slow cool to room temperature.
4) Expose for 5 min, hard contact. The exposure dose is 400 mJ/cm².
5) Post-exposure bake for 1.5 min at 85°C, and then slowly cool to room temperature.
6) Develop for 5.5 min in SU-8 developer (MicroChem Crop.).
7) Electroform for 6.5 h at 50°C. The detailed parameters are presented in Table 1.

| Table 1. Compositions of electroforming solution and process conditions |
|---------------------------------------------------------------|
| Composition          | Operational condition |
| Ni(NH₄)₂SO₄ · 4H₂O | pH                 | 3.8~4.5 |
| NiCl₂ · 6H₂O         | Temperature        | 50°C    |
| H₃BO₃              | Current density    | 0.5~2 A/dm² |
| Wetting agent       | Cathode agitation speed | 75 mm/s |

Ultrasonic treatment

Ultrasonic treatment was performed by a self-designed ultrasonic device as shown in Fig. 3. Its vibrating frequency is 20 kHz. When the uncrosslinked regions of the resists disappear after development, SU-8 moulds become easily damaged. Therefore the ultrasonic processing was carried out before rather than after development. After PEB, the SU-8 coated Ni-substrates were bolt fixed on the worktable, and then the ultrasonic energy was imposed to the SU-8 resist for 10min at the constant input power (125 W).

Dimension measurements of SU-8 moulds and electroformed Ni-structures

In order to distinguish the different effects of ultrasonic treatment on the mould distortions before electroforming and the swelling during electroforming, the top dimensions of SU-8

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moulds were measured by stereomicroscope after development. After electroforming, the electroformed samples were manual polished until preconcerted heights (measured by inductance micrometer) were achieved. And then the lateral dimensions of Ni-structures corresponding to these heights were measured by stereomicroscope.

Results and discussion

Ultrasonic effect on development process

Figure 4 shows the photo mask used in the study. Three kinds of characteristic positions, according to different resist geometry around them, are chosen to be measuring points, and 1, 2, 3 are the serial numbers of them. The widths of all measuring points in mask are 400 μm.

Table 2 summarizes the results of dimension measurements for SU-8 moulds before electroforming, where l means the width of cavity in SU-8 mould (shown in Fig.1), and the subscripts, “unultrasonic” and “ultrasonic”, stand for the samples fabricated by the conventional method described in section 3.1 without ultrasonic treatment and the experimental samples which were subjected to ultrasonic treatment, respectively.

Compared with the mask, the dimensions of the resist moulds are slightly shrunk. This is expected to be a combined effect of diffraction during exposure [17] and swelling due to absorbing developer during development [18]. For the same measuring points of the non ultrasonic and the ultrasonic samples in Table 2, the widths of the cavities in SU-8 moulds are almost identical. This phenomenon reveals that ultrasonic treatment has little influence on the subsequent development process.

![FIG. 3. Ultrasonic device](image1)

![FIG. 4. The mask and measuring points](image2)

![FIG. 5. Local photos of an electroformed Ni-structure.](image3)

![FIG. 6. Dimensional errors of electroformed Ni-structures compared with SU-8 moulds.](image4)

| Measuring point | 1    | 2    | 3    |
|-----------------|------|------|------|
| l<sub>unultrasonic</sub> (μm) | 398.5 | 398.1 | 397.5 |
| l<sub>ultrasonic</sub> (μm)    | 398.6 | 398.1 | 397.7 |

Ultrasound effect on electroforming process

Figure 5 shows local photos of an electroformed Ni-structure and the measuring points correspond to Fig. 4 are marked. The bright area in Fig. 5 is electroformed Ni-layer while the dark area is SU-8.

The dimensional errors for both non ultrasonic and ultrasonic Ni-structures are shown in Fig. 6, where the numbers in the data labels correspond to the different measuring points (shown in Fig. 4 or Fig. 5). In ordinate, dimensional error δ = l - d, where d is the width of electroformed metal structure (shown in Fig. 1).

Figure 6 clearly demonstrates that the swelling values greatly diminish when SU-8 is subjected to ultrasonic. In addition, it is visible that the larger the SU-8 mass around...
measuring points is, the greater the dimensional errors will be. In order to deeply illustrate the considerable effect of ultrasonic treatment on SU-8 swelling, the electroformed structure dimensional errors at 50μm height in the fitting curves (shown in Fig. 6) are listed in Table 3, where δ\text{unultrasonic} and δ\text{ultrasonic} are the dimensional errors of unultrasonic and ultrasonic samples respectively, and error decreasing: α=(δ\text{unultrasonic}−δ\text{ultrasonic})/δ\text{unultrasonic}.

Table 3. The dimensional errors of electroformed Ni-structures

| Measuring point | 1    | 2    | 3    |
|-----------------|------|------|------|
| δ\text{unultrasonic (μm)} | -8.3 | -9.7 | -11.4 |
| δ\text{ultrasonic (μm)}    | -3.4 | -4.4 | -5.6  |
| α (%)               | 59.0 | 54.6 | 50.9  |

Take measuring point 1 for example, ultrasonic treatment decreases the dimensional error of Ni-structure by 59.0%. This is a significant improvement to a MEMS device which always requires higher dimensional accuracy.

Simulation

If SU-8 is a simply freestanding film, and if the hygroscopic strain ε in SU-8 is uniform and isotropic, then all of the dimensions would simply grow by the magnitude of ε when SU-8 expands. However, the situations become complicated since the resist is bonded to a rigid substrate. Therefore, ANSYS was adopted to calculate the hygroscopic strain ω, along the direction perpendicular to the substrate surface under a certain hygroscopic strain ε, as shown in Fig. 7, where h0 is the initial thickness of SU-8 film; Δt is increased value of thickness due to swelling; ω,=Δth0. The physical properties of SU-8 used in this model are introduced in section 2.2.

Finite element analysis reveals the relationship between ω, and hygroscopic strain ε of SU-8. The results are exhibited in Fig. 8.

For the large plane sheet sample which is confined by a substrate, the hygroscopic strain along the direction perpendicular to the substrate is

\[ \omega, = 1.2247\varepsilon \]  

(4)

for both \( t_0=56.2 \text{ μm} \) (for non-ultrasonic sample) and \( t_0=52.7 \text{ μm} \) (for ultrasonic sample). When the resist is freestanding, \( \omega, =\varepsilon \), as shown in Fig. 8.

During experiment, the thicknesses of SU-8 resist have been measured as soon as electroforming finished, Δt =4.7 μm for non ultrasonic sample and Δt =2.0 μm for ultrasonic sample. According to equation (4), Table 4 is obtained.

As can be seen from Table 4, the hygroscopic strain ε of SU-8, after immersed in electroforming solution for 6.5 h, declined from 6.8% to 3.1% because of ultrasonic.

Table 4 \( \omega, \) and ε for non-ultrasonic and ultrasonic samples

|                  | Unultrasonic | Ultrasonic |
|------------------|--------------|------------|
| Δt (μm)          | 4.7          | 2.0        |
| \( \omega, \) (%) | 8.4          | 3.8        |
| ε (%)            | 6.8          | 3.1        |

Furthermore, the hygroscopic strain ε calculated in this way can be used to predict swelling of SU-8 mould by ANSYS. The simulated results for measuring point 1 are presented in Fig. 9, where “1-s-ultrasonic” and “1-s-unultrasonic” represent measuring point 1 for ultrasonic sample and non-ultrasonic sample, respectively.

![FIG. 7. Schematic of plane sheet model swelling.](image)

![FIG. 8. Relationship between ω, and ε.](image)

![FIG. 9. Results of simulated dimensional errors and experimental dimensional errors.](image)
simulated results. Although not agreeing with the experiment quite well, this simulation method is useful. In a way, it can be used to improve mask design and predict electroformed structure dimensional errors. Moreover, when the processing parameters and the electroforming time are settled, the hygroscopic strain $\varepsilon$ is certain and unrelated to the geometries of moulds. So the dimensional error simulations based on $\varepsilon$ are applicable to arbitrary shape moulds used in electroforming.

**Mechanism of ultrasonic effect on SU-8 swelling**

It is known that the value of absorbed moisture in crosslinked epoxy resins is deeply depended on the quantity of hydroxyl groups, in other words, depended on the level of the hydrophilicity [12,13,19]. To deeply understand the ultrasonic effect on the hydrophilicity of SU-8, it is necessary to consider the change of contact angle after ultrasonic processing.

Therefore, the water contact angles of SU-8 were measured by Drop Shape Analysis System (DSA100, KRÜSS GmbH) at 50°C. The results show that the water contact angle of SU-8 increases from 70.8° (before ultrasonic processing) to 74.9° (after ultrasonic processing), which indicates that the hydrophilicity of SU-8 decreases while exposed to ultrasonic.

In view of water contact angle change, the mechanism of ultrasonic effect on SU-8 swelling can be explained as follows. It has been found out that ultrasonic can induce chemical bonds in polymers breaking [20]. For this study, when the samples are exposed to ultrasonic a part of hydroxyl groups may break away from the SU-8 backbones, as shown in Fig. 10. Thereby, the hydrophilicity of SU-8 reduces, which makes the amount of moisture absorbed in the same time decreases. As a result, the swelling potential of SU-8 mould declines and the dimensional errors of electroformed structures diminish. However, SU-8 still keeps three-dimensional networks and cannot be dissolved by SU-8 developer or electroforming solution.

**Summary and prospect**

1) The finite element analysis results indicate that the dimensional error produced by thermal expansion is less than 3% in the total error, so hygroscopic swelling is the predominant reason for SU-8 mould distortions.

2) The ultrasonic treatment was introduced to the electroformed Ni-structure fabricating process after PEB. For a 400 $\mu$m mask, ultrasonic treatment decreases the dimensional error of Ni-structure by more than 50% at 50 $\mu$m height.

3) Simulation of hygroscopic swelling is conducted by ANSYS, and the results indicate that the hygroscopic strain $\varepsilon$ of SU-8 declined from 6.8% to 3.1% because of ultrasonic.

4) The increased water contact angles of cured SU-8 before (70.8°) and after (74.9°) ultrasonic processing indicates that the hydrophilicity of SU-8 decreases since exposed to ultrasonic.

5) The mechanism of the ultrasonic effect on SU-8 swelling is discussed. When the samples are exposed to ultrasonic a part of hydroxyl groups may break away from the SU-8 backbones, which decreases the hydrophilicity of SU-8 and in turn reduces the mould swelling.

Although this work reveals that ultrasonic treatment can reduce SU-8 hygroscopic swelling, further studies optimizing the ultrasonic process parameters such as ultrasonic frequency, acoustic power and exposure time are ongoing.

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Towards the low temperature growth of uniform diameter multi walled carbon nanotubes by catalytic chemical vapour deposition technique

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Mesoporous MCM-41 molecular sieves containing f-block transition elements (gadolinium) with various Si/Gd ratios (50, 75 and 100) were synthesised by a hydrothermal method. Their mesoporous structure was confirmed by X-ray diffraction, nitrogen sorption studies, thermogravimetric analysis, scanning and transmission electron microscopy. The local environment of Gd in the material was studied by electron paramagnetic resonance. The compatibility of the catalyst for the synthesis of uniform diameter CNTs by varying the temperature from 400 to 650°C with fixed flow rates of N2 and C2H2 (140 ml/min and 40 ml/min, respectively). The product is mostly metal containing thin MWCNTs with diameter of 10–20 nm. Characterisation shows that a combination of Gd-MCM-41 (100) catalyst gives a high yield of high quality MWCNTs under optimum growth conditions.

Keywords: MWCNTs; Gd carbon nanotubes; Contrasting agents; Magnetic resonance imaging

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Carbon nanotubes (CNTs) are attractive materials for applications in future LSI interconnects because of their excellent electrical, thermal and mechanical properties. Recently, the electrical properties of multiwalled CNT bundles grown by chemical vapor deposition (CVD) have been intensively investigated for interconnect applications [1-4]. Low-temperature growth of CNTs is one of the most fundamental issues to be resolved for development of CNT based on interconnects technology compatible with LSI manufacturing processes.

Generally, carbon nanotubes have been synthesized by three different techniques: arc discharge between two graphite electrodes [5], laser evaporation of carbon target [6] and chemical vapour deposition (CVD) [7]. The major drawback of arc discharge and laser evaporation methods is that they are extremely uncontrolled in terms of process parameters, resulting in CNTs that contains significant fractions of unwanted material and that are difficult to manipulate and assemble in specific designs. CVD method is based on the thermal decomposition of hydrocarbon compounds over transition metal catalyst particles. It appears to be a simple and economic technique to synthesize this kind of material at a low temperature, ambient pressure and it represents the best hope for large scale production.

To date, all the metal-catalyzed CNT growth studies have mainly focused on transition metals. Curiously, f-block transition elements also referred to as inner transition elements have still not been well explored. One reason could be that inner transition elements are not known to be highly catalytic as the transition elements. It has also been suggested that lanthanoids such as gadolinium and europium exhibit insufficient carbon solubility, slow carbon diffusion, and limited carbide formation to catalyze CNT growth [8]. Recently, gadolinium and europium were used...
as catalyzed to synthesize single walled carbon nanotubes [9]. Gd (III) ion exchanged NaY zeolite has been reported as a gastrointestinal contrast agent [10]. However, Y zeolite has a pore size of around 1.3 nm and the small pores hinder the water movements. Also, the extra-framework metal ion is held inside the channel mainly by Coulomb interaction, hence it is prone to leaching and the toxic gadolinium hydroxide would form and precipitate out under physiological conditions. In general, MCM-41 of the M41S family are materials of interest because of their remarkable properties such as high surface, large pore volume and narrow pore size distribution and the ease with which their surface can be functionalized [11]. Mesoporous silica would be an excellent carrier for the metal and as it is porous: water can freely move in and out of the frame, yet the rigidity of the frame would impede the rotational movement of the metal and improve the relaxation of water. Nanosized silica with size of less than 100 nm is small enough to pass through the body, and also is able to enter cells. Nanosized porous silica, as a container, can deliver drugs with gate control to cells [12] with MRI capability one can thus have a very powerful imaging and drug delivery system.

Hence, in this present work, for the first time we used gadolinium metal support with MCM-41 as a sacrificing template for the synthesis of high quality and uniform diameter of multiwalled carbon nanotubes by low temperature CVD process. The formation of highly graphitized MWCNTs with metal particles was confirmed by XRD, TGA, SEM, TEM, HRTEM and Raman spectroscopy.

**Experimental Methods**

**Synthesis of Gd-MCM-41 molecular Sieves**

Gd-MCM-41 with various ratios (Si/Gd = 50, 75, and 100) were synthesized hydrothermally according to our previous report [13,14] using a gel composition of 1:X:0.2:0.89:120 SiO$_2$:Gd(NO$_3$)$_3$:CTAB:H$_2$SO$_4$:H$_2$O. Sodiummetasilicate and gadolinium nitrate are used as the source for silicon and gadolinium respectively, whereas cetyltrimethyl ammonium bromide (CTAB) and sulphuric acid were used as structure directing template and pH adjuster respectively.

**Synthesis of carbon nanotubes**

Experiments to produce CNTs were carried out in a horizontal furnace at atmospheric pressure. About 100 mg of the catalyst was spread on a long quartz boat, which was placed inside a quartz tube. The reaction mixture containing acetylene and nitrogen gas was passed over the catalyst bed for a predetermined time. The experiments were carried out at different reaction temperatures: 450, 500, 550 and 600°C. The catalyst was then activated by passing nitrogen gas (99.9% purity) for 30 min at a flow rate of 140 ml/min. Acetylene gas (99.99% purity) was then passed at a rate of 40 ml/min for 10 min through the reaction chamber, while the nitrogen gas flow rate was maintained at 140 ml/min. Prior to collecting samples from the tubes, the furnace was cooled down to room temperature by maintaining a nitrogen flow. The sample was collected as black powder from the quartz boat.

**Characterization of Catalysts and Carbon nanotubes**

The powder XRD diffraction patterns for the calcined mesoporous Gd-MCM-41 molecular sieves with various ratios were obtained with a stereoscan diffractometer using nickel-filtered Cu Kα radiation (λ = 0.15418 nm) and a liquid nitrogen cooled germanium solid-state detector. Surface area, pore volume and pore size distribution were measured by nitrogen adsorption at −196°C with an ASAP-2010 porosimeter from micromeritics corporation (Norcross, GA). The samples were degassed at 350°C at 10⁻³ mbar overnight prior to the adsorption experiments. The mesopore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99 by assuming that all the mesopores were filled with condensed nitrogen in the normal liquid state. Pore size distribution was estimated using the Barrett, Joyner and Halenda (BJH) algorithm (ASAP-2010 built-in software from micromeritics). The thermal properties of the mesoporous sample Gd-MCM-41 and the purity of CNTs were investigated by thermogravimetric analysis (TGA). The coordination environment of gadolinium were analysed by electron paramagnetic resonance (EPR) spectroscopic technique (Varian E112 Spectrometer operating in the X-band 9.2 GHz frequency) at liquid nitrogen temperature. Scanning electron microscope (JEOL JSM 840) was performed to analyse the morphology and microstructure of catalysts and CNTs, respectively. The growth morphology and crystallinity of the tubular structures were confirmed by transmission electron microscopy (Phillips CM 200, TEM). In addition, FT-Raman spectroscopy (FRA 106 BRUKER) using an excitation wavelength of 1064 nm of Nd:YAG Laser was also employed to characterized the carbon nanotubes.

**Results and discussion**
Physico-chemical characteristics of Gd incorporated MCM-41 materials

The physico-chemical characteristics of the Gd incorporated MCM-41 materials that were used for the synthesis of carbon nanotubes were investigated by means of XRD, N₂ sorption studies, TGA, SEM, TEM and EPR analysis.

XRD of the catalysts

In order to aware about the periodic and porous nature of the materials, the XRD analysis was performed. The XRD patterns of Gd-MCM-41 (Si/Gd = 50, 75 and 100) are shown in Fig. 1 in which the intense peak between 2.1 to 2.4 (2θ) due to (100) plane and weak planes between 4 and 5.5 are due to (110) and (200) planes confirmed the hexagonal mesophase of the material which are similar to that of pristine MCM-41 [11]. The XRD patterns of Gd (III) incorporated samples show the hexagonal porous structure and the gradual broadening of peaks decreases and also it reveals that the structure ordering increases as the loading of Gd (III) increases respectively, due to this the pore structure would be well ordered hexagonal pores. This result also provides indirect evidence that Gd (III) is indeed incorporated into the mesoporous silica framework.

$\text{FIG. 1.} \quad \text{X-ray diffraction patterns of Gd-MCM-41 catalysts.}$

N₂ sorption studies

The N₂ sorption analysis was employed for Gd-MCM-41 materials and their data are presented in Table 1. The N₂ sorption studies were typical for type IV, with a hysteresis loop characteristic of mesoporous materials (see Fig. 2). The isotherms exhibited three stages. The first stage is due to monolayer adsorption of nitrogen to the walls of the mesopores at a low relative pressure ($P/P_0 < 0.25$). The second stage is characterized by a steep increase in adsorption ($P/P_0 > 0.25$). As the relative pressure increases, the isotherm exhibits a sharp inflection characteristic of capillary condensation within the uniform mesopores. The $P/P_0$ at the inflection is related to the diameter of the mesopore [15] and the steepness of this step indicates the uniformity of pore size distribution. The third stage in the adsorption isotherm is the gradual increase in volume with $P/P_0$ due to multilayer adsorption on the outer surface of the particles. The isotherms of mesoporous materials with high metal content generally show a strong increase at high pressure, attributed to the condensation of nitrogen within voids formed by crystal aggregates. The samples exhibit isotherms with a well-developed step in the relative pressure ($P/P_0$) range corresponding from 0.25 to 0.45. A characteristic hysteresis loop observed for sample in the region of $P/P_0$ above 0.3 is assigned to capillary condensation in the mesopores [16]. It should be noted that, as the metal contents in MCM-41 increase, a sharp inflection step i.e. characteristic of capillary condensation, has been shifting to the higher $P/P_0$ values lead to increase in pore size. This observation can also be supported by XRD patterns of Gd-MCM-41, where the $d$-spacing values and pore volume are also increased with increase in metal content.

$\text{FIG. 2.} \quad \text{N}_2 \text{ sorption isotherms of Gd-MCM-41 catalysts.}$

$\text{Table 1. Textural properties of the catalysts.}$

| Catalysts       | $d_{100}$ (nm) | Unit cell $a_0$ (nm) | Surface area (m²g⁻¹) | Pore size BJH (nm) | Total Pore Volume BJH (cm³g⁻¹) |
|-----------------|----------------|----------------------|-----------------------|-------------------|-------------------------------|
| Gd-MCM-41 (50)  | 3.49           | 4.03                 | 662                   | 3.39              | 0.498                         |
| Gd-MCM-41 (75)  | 3.51           | 4.12                 | 695                   | 3.42              | 0.551                         |
| Gd-MCM-41 (100) | 3.51           | 4.12                 | 810                   | 3.43              | 0.587                         |
Thermogravimetric analysis

The thermal properties of the mesoporous sample Gd-MCM-41 were investigated by TGA. The thermograms of the as-synthesized Gd-MCM-41 (50), Gd-MCM-41 (75) and Gd-MCM-41 (100) catalysts are presented in Fig. 3. The initial weight loss up to 120°C is due to desorption of physically adsorbed water and the weight loss from 120°C to 350°C are attributed to the organic template. The oxidative desorption of the organic template takes place at 180°C and the minute quantity of weight loss above 350°C to 550°C is related to water loss from the condensation of adjacent Si-OH groups to form siloxane bond [11,17].

SEM and TEM analysis for the catalyst

The particle size and morphology of Gd-MCM-41 (100) sample was determined by SEM analysis and shown in Fig. 4. The formation of various periodic mesoporous materials starts with nucleation, which involves the surfactant-silicate interactions, and these interactions facilitate the assembly of the surfactant-silicate species in the desired morphology. However, the presence of foreign ions in the synthesis gel alters the structure directing action of the template and the attenuations further depend on the nature of metal source used. In accordance with this, the micrographs show marked differences in the structure of the MCM-41 surface after the metal incorporation [18]. The size and morphology of Gd-MCM-41 (100) catalysts were investigated with TEM are presented in Fig. 5. The TEM picture of MCM-41 exhibits an image with strong contrast dark lines indicative of the regular crystal lattice of MCM-41in the hexagonal array an ordered mesopore structure.

EPR analysis

Gadolinium (III) ions are often used in paramagnetic complexes due to their good paramagnetism. The EPR spectrum with three and more absorption signals is usually assigned to isolated Gd³⁺ ions, while a single broad absorption signal encompassing g = 2 is assigned to the group of Gd³⁺ ions [19]. After crystallization the EPR spectra mainly consist of relative large line with g = 2.0 suggesting that the surrounding of Gd³⁺ ions are experiencing weak crystal fields resulting from structural relaxation [20] which is shown in Fig. 6.

The role of reactor temperature during growth

An important parameter, which greatly affects the microstructure and the yield of CNTs, for the activity of catalytic metals and the decomposition of carbon source are both, correlated with the growth temperature. In this section, we have preferred low metal content catalyst Gd-MCM-41 (100) to study the influence of reaction temperatures ranging from 400 to 650°C. Figure 7 depicts the percentage yield of CNTs as a

![FIG. 3. TGA of the Gd-MCM-41 catalysts.](image)

![FIG. 4. SEM image of Gd-MCM-41 (100) catalyst.](image)

![FIG. 5. TEM image of Gd-MCM-41 (100) catalyst.](image)

![FIG. 6. EPR spectrum of Gd-MCM-41 (100) catalyst.](image)
function of growth temperature. A poor yield (65.06 %) was obtained for temperature at 400°C, possibly due to slow catalytic decomposition of C₂H₂, while CNTs growth became significant at 450°C. The low yield of CNTs (72.15 %) at 450°C may be related to non uniformity from the catalyst or defect formation in the graphite sheets at lower temperature. The incomplete crystallization of the graphite sheet results in a rough surface and curved shape of the nanotubes. It can be seen in Fig. 7, at the temperature of 550°C, the yield of CNTs on Gd-MCM-41 (100) catalyst is 89.25 %. It is generally accepted that CNTs are formed by carbon atom dissolution, diffusion and precipitation through the catalyst in the CVD process [21]. The dissolution, diffusion and precipitation of the carbon atoms are affected by temperature as well as by the carbon concentration.

When the deposition temperature is higher than 550°C, the yield of CNTs is decreased up to 68.45 %. At higher temperature, the decomposition of C₂H₂ promotes and consequently increases the concentration of carbon atoms, which can result in a dissolution rate that is higher than the rates for diffusion and precipitation. In that case carbon atoms will accumulate on the surface of the catalyst to form a carbon shell [22]. The catalyst particles then lose their activity and it retards the growth of CNTs. Moreover, when the temperature is too high, a chemical reaction may take place between the carbon and the metal, leading to the formation of metal carbide, which is passivity the catalyst and then started dropping at approximately 600°C. At too high temperatures, the catalyst become highly mobile and quickly agglomerates into metal particles that are too large particles to initiate CNTs nucleation. These sintered large particles are rapidly encapsulated by carbon deposits and become inactive. Hence 550°C was found to be optimum low growth temperature to achieve the very high yield and hollow structure of good crystalline MWCNTs which showing the graphitic layers of the tubes.

The role of Gd-MCM-41 catalysts for the growth of MWCNTs

![Graph showing the percentage of CNTs yield with various temperatures.](http://www.nmletters.org)

The growth of CNTs was done using Gd-MCM-41 with different Si/Gd ratios (50, 75 and 100) with N₂ and C₂H₂ flow rate of 140 ml/min and 40 ml/min, respectively were purged inside the tubular furnace for 10 min at optimized temperature of 550°C. The results are given in Table 2. The activity of the catalysts followed the order Gd-MCM-41 (100) > Gd-MCM-41 (75) > Gd-MCM-41 (50). High carbon yield was observed over Gd-MCM-41 (100) of about 78.70 % than other Si/Gd ratios, where the yield of Si/Gd = 50 and 75 were 62.78 and 68.09 %, respectively which may be ascribed to its greater ability to decompose unsaturated hydrocarbons. If the metal catalyst is exposed to acetylene, metal particles can easily diffuse on the surface to form larger particles, leading to MWCNT growth. The percentage of carbon yield for above mention catalysts are presented in Table 2, it can be clearly understood that support plays a prominent role in determining the dispersion and hence the catalytic activity of the metals in the production of CNTs.

![Table 2. Influence of the catalysts](http://www.nmletters.org)

| Catalysts    | Reaction temperature (°C) | Flow rate          | CNTs yield (%) |
|--------------|----------------------------|--------------------|----------------|
|              |                            | Nitrogen (ml/min)  | Acetylene (ml/min) |                |
| Gd-MCM-41 (50) |                            |                    |                | 62.78          |
| Gd-MCM-41 (75) | 550                        | 140                | 40             | 68.09          |
| Gd-MCM-41 (100) |                            |                    |                | 78.70          |

Though Gd³⁺ ion is toxic and when it is sequestered by chelation or encapsulation with another material, it reduced the toxicity therefore we utilized nanosized mesoporous siliceous material as a chelating agent in order to reduce the toxicity of gadolinium ion. Since, in our present study, we have used porous silica material to reduce the toxicity of metal and it would be an excellent carrier for the metal because of its porous nature. Furthermore, carbon nanotubes with gadolinium have access to water molecules because of active centers (for Gd³⁺–OH₂...
bonding), since carbon nanotubes are known to be good transporters of water [23] and protons [24], whereas the active centers in gadofullerenes do not have this access. From a practical point of view, the rate of proton exchange is especially important since it contributes to the proton relativity [25]. These gadolinium carbon nanotubes are the contrast agent materials where superparamagnetic metal centers have access to many coordinated or exchanging water molecules per Gd\(^{3+}\) ion. These Gd\(^{3+}\) nanotubes species are linear superparamagnetic molecular magnets with MRI efficacies are more than any Gd\(^{3+}\) based contrast agent in future clinical use.

**Characterization of carbon nanotubes**

**XRD**

Figure 8 shows the XRD pattern of Gd containing MWCNTs synthesized at temperature of 550°C. The highest sharp peak at 2θ = 25.8° can be assigned to graphite (002), indicating that graphite layers are regularly stacked. While the other peaks at 44.3° (101) correspond to the remaining graphitic particles, a similar trend was observed by previous reporters [26].

**TGA**

Figure 9 shows the synthesized MWCNTs characterized by TGA in air. The weight loss is due to the combustion of carbon with oxygen and therefore, corresponds to the carbon content in the sample. The major mass loss observed in the temperature range of 375~585°C due to the oxidation of carbon nanotubes, which is consistent with previous report [27].

**SEM and TEM analysis**

SEM image of CNTs prepared by Gd-MCM-41 (100) catalyst with an optimized condition of flow rate of acetylene and temperature were 40 ml/min and 550°C respectively, is shown in Fig. 10. The image clearly shows thinner nanotubes with metal particles at the tip of the tubes, and it also in agreement with TEM observations.

![SEM image of CNTs using Gd-MCM-41 (100) catalyst.](image)

**FIG. 10.** SEM image of CNTs using Gd-MCM-41 (100) catalyst.

![TEM image of bamboo shaped Gd containing MWNTs at 550°C.](image)

**FIG. 11.** TEM image of bamboo shaped Gd containing MWNTs at 550°C.

The TEM image (see Fig. 11a) indicates that CNTs grown are multiwalled and bamboo shaped. The structure shows that the CNTs grow with layers of graphite deposited on the surface of Gd catalyst were separated from the catalyst surface resulting in the growth of CNT with closed end (see Fig. 11b). However, if the deposition on Gd catalyst is too fast due to higher...
decomposition rate of $\text{C}_2\text{H}_2$, the catalyst surface would be encapsulated by the deposits, which prevent the evolution of CNTs. In this condition, the passivation of the catalyst can occur in a catastrophic manner. Therefore, one of the requirements for the CNTs growth is that the decomposition kinetics of $\text{C}_2\text{H}_2$ should be controlled to supply carbon for nanotube growth without passivation of the catalyst surface. The present work shows that the flow rate of the reaction gas and the reaction temperature are the effective process parameters to control the decomposition kinetics. A reaction temperature of 550°C with 10 min duration and a precursor flow rate of 40 ml/min appear to constitute the optimal conditions for CNTs growth in Gd-MCM-41 catalysts, since they produce a high yield with uniform size of MWCNTs.

To the best of our knowledge, growth mechanism of bamboo like MWCNTs is not entirely clear so far. Many authors proposed the possible mechanism on the basis of their experimental results. Smith et al [28] put forward that bamboo morphology in CNTs may be the result of subtle changes in the growth conditions near the seed metal. Wu et al [29] pointed out that formed nanoparticles lead to growth of bamboo like CNTs; Zhao et al [30] suggested that the difference between the carbon surface and bulk diffusion in the catalyst causes the periodic compartment structures in the bamboo shaped CNTs. In this study, it can be seen that catalyst particles were encapsulated on closed end bamboo like MWCNTs in Fig. 11b. These observations suggest that the growth mode of bamboo like MWCNTs over Gd-MCM-41 (100) catalyst may be consistent with the tip growth mode [31]. Moreover, Gd catalyst nanoparticles tend to form large metallic clusters to form MWCNTs. Also, nonuniformity of diffusion and deposition of carbon on Gd catalyst particles possibility exists according to the tip growth mechanism. These factors may be the causes of bamboo like MWCNTs. Figure 12 presents the HRTEM image of as grown MWCNTs. From this Figure, it is revealed that the diameter of the central hollow portion of MWCNTs is about 10–20 nm. The graphite layer lattice fringes are parallel to the tube axis and also the multiple graphitic walls of the CNTs are clearly visible in this image (see Fig. 12). It should be beneficial for further investigating of the unique structures, properties and applications of gadolinium produce MWNTs.

**Raman spectroscopy**

Raman Spectroscopy is an important tool for investigating CNTs, which provides information about the crystalline nature of the sample. Figure 13 shows the Raman spectrum of the sample obtained by Gd-MCM-41 (100) at the optimized temperature and flow rate of acetylene are 550°C and 40 mL/min respectively. The Raman band emerging in low wavenumbers region of 100–400 cm$^{-1}$ are characteristic of low frequency region of SWCNTs, which can distinguish between SWCNTs and MWCNTs [32]. Additionally, no Raman band appearing in the low wavenumber region below 400 cm$^{-1}$ is observed. Only two Raman bands emerging in the high wavenumber region are in accordance with the characteristic band of the Raman spectra of MWCNTs, further, certifying that the CNTs synthesized in this contribution are multi-wall carbon nanotubes. In the first order Raman scattering region (0–2000 cm$^{-1}$), two intense peaks are observed at 1347 and 1595 cm$^{-1}$, which are referred to as D- and G-bands, respectively. The G-band corresponds to the tangential stretching high frequency $E_{2g}$ mode of highly oriented pyrolytic graphite (HOPG) and indicates the presence of crystalline graphitic carbon in the CNTs, while the D-band originates from disorder in the sp$^2$ hybridized carbon atoms, characteristics for lattice distortions in the curved graphene sheets or tube ends. Furthermore, pyrolytic carbon particles deposited on nanotubes also contributed to the D-band intensity [33,34]. In the present system, G band is at higher intensity, indicating that the CNTs are graphitized, which is in agreement with the result of TEM observation.

![HRTEM image of MWNTs grown over Gd-MCM-41 (100) catalyst.](http://www.nmletters.org)

**FIG. 12.** HRTEM image of MWNTs grown over Gd-MCM-41 (100) catalyst.

![Raman spectrum of CNTs.](http://www.nmletters.org)

**FIG. 13.** Raman spectrum of CNTs.
Conclusions

CNTs possess many desirable qualities that play a central role in the field of nanotechnology. Of the three main techniques for CNT synthesis, CVD based methods are suitable because of their scalability and product purity. The growth of MWCNTs over Gd-MCM-41 catalyst by CVD under atmospheric pressure using acetylene as carbon source at low temperature (550°C) has been demonstrated. The obtained MWCNTs showed dominant bamboo like morphology. The morphologies, graphitization degree and microstructures of the products were systematically studied. The results show that the combination of Gd-MCM-41 (100) catalyst exhibits highly selective and high yield of uniform diameter of MWCNTs under optimized conditions that too at low reaction time (10min). The TEM image which clearly illustrates that CNTs formed are free from amorphous carbon and also confirms the Gd particles present at the tip of the tube. The graphite layer lattice fringes are parallel to the tube axis and also the multiple graphic walls of the CNTs are clearly visible in HRTEM. The gadolinium incorporated with mesoporous silica was found to be stable under reaction conditions, allowing slow reduction and nucleation of metallic clusters for highly selective MWCNTs. This study suggested that the mesoporous molecular sieves could be a promising catalytic template for high yield synthesis of CNTs. As a result, in the near future, the researchers hope to use existing methods of attaching disease-specific antibodies and peptides to gadolinium nanotubes so they can be targeted to cancerous tumors and other diseased cells.

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Review

Functionalization of carbon nanotubes and other nanocarbons by azide chemistry

Jin Han and Chao Gao*

Following the conventional carbon allotropes of diamond and graphite, fullerene, carbon nanotubes (CNTs) and graphene as 0D, 1D and 2D graphitic macromolecules have been discovered recently in succession, declaring the unlimited potential of carbon-based nanomaterials and nanotechnology. Although CNTs exhibit significant potential applications in advanced materials and other fields due to their extraordinary mechanical strength and electrical/thermal conductivity properties, their low solubility, poor wettability and bad dispersibility in common solvents and solid matrices have limited their processing and applications. Thus, the attempt to achieve wettable/processable CNTs by functionalization has attracted increasing attention in both scientific and industrial communities. In recent years, azide chemistry has been demonstrated as a powerful means to covalently modify CNTs. It consists of two major approaches: click chemistry and nitrene chemistry, which both involve the usage of various azide compounds. The former one is based on highly reactive and stereospecific Cu(I) catalyzed azide-alkyne cycloaddition reaction; the latter one is based on the electrophilic attack to unsaturated bonds of CNTs with nitrenes as reactive intermediates formed from thermolysis or photolysis of azides. In this mini-review paper, the azide chemistry to functionalize CNTs is highlighted and the corresponding functionalization routes to build CNT-based complex structures are also discussed. Besides, covalent functionalizations of other graphitic nanomaterials such as fullerene and graphene, via azide chemistry, are commented briefly.

Keywords: Carbon nanotubes; Functionalization; Click chemistry; Nitrene chemistry; Nanocomposites; Fullerene; Graphene

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covering from nanocomposites to nanodevices and nanobiotechnology [4-9].

Despite such fascinating properties and significant potential applications, CNTs showed low solubility, poor wettability and bad dispersibility in common solvents and solid matrices, which pose a big challenge for their processing and applications. To meet such a challenge, chemistry approach was employed to modify the outer surface bonds of CNTs. Triggered by the pioneering work of Smalley [10] and Haddon [11], thousands of relevant papers and hundreds of patents have been published, which developed into the new research rush of chemistry of CNTs, as demonstrated by the further increasing publications (see Fig. 2). Except the dispersing and wetting of CNTs, chemical functionalization may result in other effects: (1) introduction of reactive functional groups on CNT surfaces, (2) grafting of polymer chains on CNTs, (3) fabrication of hybrid structures with integrated and tailor-made properties, (4) tuning the intrinsic properties of CNTs such as hydrophobicity, conductivity, optical property, biocompatibility, toxicity, etc., and (5) expanding the applications of CNTs.

Various chemical reactions such as hydrogenation [12], halogenation [13], esterification [14], amidation [15], cycloaddition [16], radical addition [17], nucleophilic addition [18], electrophilic addition [19], inorganic complex addition [20], ozonolysis [21], surface-initiated polymerization [22-24], and physical methods such as plasma treatment [25], π-π stacking [26] and solid-phase mechanical milling [27] have been tried to functionalize CNTs, offering alternative approaches to solubilization of CNTs with desired functionality and surface characters. These have been summarized and commented in recently published reviews. Considering the versatility and efficiency of CNT functionalization, the attention of this mini-review will be paid to azide chemistry that mainly includes azide-alkyne click chemistry and nitrene chemistry.

**Functionalization of CNTs via click chemistry**

**The concept of azide-alkyne click chemistry**

The concept of click chemistry was presented by Sharpless in 2001 [28]. The synthetic appeal of click reactions relies upon their tolerance of water and oxygen, simple reaction conditions,
and high yield. In this field, the copper(I)-mediated Huisgen 1, 3-dipolar cycloaddition of organic azides and alkyne leading to 1, 2, 3-triazoles is the cream of the crops without any doubt (see Scheme 1) [29]. It has exhibited great synthetic advance in chemistry, biology, and materials science [30]. Its application in functionalization of CNTs has been proved to be very successful and is presented in the following context.

**Scheme 1.** Copper(I)-mediated Huisgen 1, 3-dipolar cycloaddition of azides and alkynes.

### Click coupling functionalization

This type of functionalization of CNTs is typically a covalent-bond functionalization, and generally involves three main steps: (1) modification of CNTs with reactive azide or alkyne groups, (2) modification of the decorations (i.e., clickable reagents) with corresponding groups (alkyne or azide), (3) click coupling between CNTs and decorations. As far as we know, the decorations can be polymers, nanocrystals and functional organic compounds (see Table 1).

In 2005, for the first time, Adronov et al. reported the application of azide-alkyne click chemistry to functionalize CNTs with polymers [31]. The CNTs were first decorated with alkynes via Pschorr-type arylation with p-aminophenyl propargylether and then modified with well-defined azide-terminated polystyrene (PS) (see Scheme 2) by click coupling using several types of Cu (I) catalysts. The combination of Raman, FTIR, UV-vis, TGA, TEM and AFM measurements confirmed the click coupling. The Cu (I)/1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU) catalyst system was found to be most effective for the coupling. The PS-coated CNTs had relatively high graft density of 1 polymer chain for every 200-700 carbons, and consisted of about 45% PS and exhibited good organosolubility (the highest is 233 mg/L in THF) in THF, CHCl₃ and CH₂Cl₂. Sulfonation of the PS-coated CNTs by acetyl sulfate made the materials water-soluble and the solubility could be adjusted by varying the degree of sulfonation [32]. Moreover, the materials possessed pH responsibility which meant the materials are soluble in water at pH between 3 and 13, otherwise, formed precipitates.

The click coupling reaction between the alkyne-containing CNTs and azide-terminated poly (N, N-dimethylacrylamide) -block-poly (N-isopropylacrylamide) (PDMA-b-PNIPAM) diblock polymer micelles was also investigated [33]. The well-defined diblock polymer was synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization with an azide-containing chain transfer reagent. It is worthy to point out that when the micelle formed above the critical micellization temperature, the azide groups would locate at the periphery of micelles and the click coupling would be facilitated, resulting in an enhancement of grafting density.

Preparation of CNTs coated with amphiphilic polymer brushes was first reported by our group by combining conventional “grafting to” and “grafting from” strategies and using a clickable macroinitiator (see Scheme 3) [34]. The clickable macroinitiator, poly (3-azido-2-(bromo-2-methylpropanoyloxy) propylmethacrylate) with alkyl bromo groups for initiating atom transfer radical polymerization (ATRP) and azido groups for the click reaction was first synthesized by postmodification of poly(glycidyl methacrylate) (PGMA) with sodium azide, followed by 2-bromoisobutyl bromide. Clicking the clickable macroinitiator onto azide-functionalized CNTs afforded a CNT-based clickable macroinitiator. Poly (n-buty1 methacrylate) (PbMA), PS, and poly (ethylene glycol) (PEG) were subsequently grafted on CNTs via ATRP grafting from and click grafting to approaches, resulting in CNT-supported amphiphilic polymer brushes. The brushes could undergo self-assembly at the chloroform/water interface to form a special film, indicating that the brushes could form Janus structure. Such a “Gemini grafting” strategy paves the way for construction of complex structures on CNTs.

Covalent layer-by-layer (LbL) click chemistry was also introduced to functionalize CNTs (see Scheme 4) [35]. The clickable polymers of poly (2-azidoethyl methacrylate) (polyAzEMA) and poly (propargyl methacrylate) (polyPgMA) were alternately coated on alkyne-modified CNTs, forming a core-shell structure. The TEM pictures (see Fig. 3) show that the thickness of the clicked polymer shell on CNTs increases considerably with increasing layers of polymer clicked on...
MWCNTs and the polymer shell is uniform and even. Alkyne-modified rhodamine B was also installed on the CNTs with azide polymer layer. The confocal fluorescence image (see Fig. 4) presented a uniform red remarkable fluorescence, suggesting that there are a large number of residual azido groups on the surfaces.

Table 1. Overview of click reactions on CNTs.

| Clickable substrate | Clickable reagents | Catalyst/Conditions | Ref. |
|---------------------|--------------------|---------------------|------|
| ![Clickable substrate](image1) | ![Clickable reagents](image2) | CuI or (PPh₃)₃CuBr/DMF/60 °C/24 h | [31] |
| ![Clickable substrate](image3) | ![Clickable reagents](image4) | CuSO₄·5H₂O, sodium ascorbate/H₂O/55 °C/24 h | [33] |
| ![Clickable substrate](image5) | ![Clickable reagents](image6) | CuBr, PMDETA/DMF/r.t./24 h | [34] |
| ![Clickable substrate](image7) | ![Clickable reagents](image8) | CuBr, PMDETA/DMF/r.t./24 h | [35] |
| ![Clickable substrate](image9) | ![Clickable reagents](image10) | CuSO₄·5H₂O, sodium ascorbate/H₂O, acetonitrile/r.t. | [36] |
| ![Clickable substrate](image11) | ![Clickable reagents](image12) | CuBr, PMDETA/DMF/r.t./24 h | [37] |
| ![Clickable substrate](image13) | ![Clickable reagents](image14) | CuI, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)/DMF/70 °C/48 h | [38] |
| ![Clickable substrate](image15) | ![Clickable reagents](image16) | CuSO₄·5H₂O, sodium ascorbate/NMP/70 °C/48 h | [39] |
The preparation of CNT-Au nanocrystal composites was reported by Rao et al. [36]. The CNTs were first treated with concentrated HNO$_3$ to generate carboxyl groups on the surface, then with thionyl chloride to convert the carboxyl groups into acyl chloride, followed by reaction with 4-azidobutylamine to obtain azide-functionalized CNTs, and finally, reacted with hexynethiol-capped Au nanocrystals to afford the composites.

Gao and co-workers reported the preparation of superparamagnetic CNT-Fe$_3$O$_4$ nanohybrids (see Scheme 5) via click chemistry [37]. The direct coupling between
alkyne-decorated CNTs and azide-decorated Fe₃O₄ particles failed, while the coupling reaction took place efficiently by using the CNTs coated with polymer layers. TEM images in Fig. 5 clearly showed the presence of Fe₃O₄ particles on the surfaces of

Scheme 4. Functionalization of MWCNTs gets through covalent LbL-click approach and further modification of the functionalized MWCNTs with fluorescent dye and polystyrene by click chemistry (Reprinted with permission from ref. 35. Copyright 2009, American Chemical Society).

Scheme 5. Preparations of CNT-Fe₃O₄ nano-hybrids via click chemistry (Reprinted with permission from ref. 37. Copyright 2009, Royal Society of Chemistry).
Functionalization of CNTs by click chemistry, showing the versatility of click chemistry in the functionalization of CNTs.

Functionalization of CNTs via nitrene chemistry

The concept of nitrene chemistry

A nitrene (R⁻N=) is regarded as the nitrogen analogue of a carbene [41]. They are formed as intermediates during thermolysis or photolysis of azides with expulsion of nitrogen gas, but cannot be isolated from the reaction system due to their extremely high reactivity (see Scheme 6). The nitrogen atom has only six electrons available and is therefore considered as an electrophile. One of the well-known reactions of nitrene is cycloaddition to unsaturated bonds, affording aziridine compounds. Hence, chemists come up with the idea of functionalization of CNTs via electrophilic attack of nitrene based on the unsaturated bonds of CNT and the electrophilic nature of nitrene. The used azides and reaction conditions are summarized in Table 2.

Scheme 6. Formation of nitrene intermediates from azides.

Nitrene cycloaddition functionalization of CNTs

The pioneering work for the functionalization of CNTs via nitrene chemistry was done by Holzinger et al. in 2001 [42]. Around 200-fold excess of nitrene precursor, ethyl or tert-butyl azidoformate, was added to the heated suspension of CNTs in 1,1,2,2-tetrachloroethane. The reaction took place with N₂ release and after a short time the product precipitated. The precipitates were collected and washed with diethyl ether. The nitrene-functionalized CNTs could be dissolved in DMSO. In a detailed study of nitrene functionalization, a variety of nitrene precursors were employed, containing various groups, such as alkyl chains, aromatic groups, dendrimers, crown ethers, and oligoethylene glycol units [43]. When bifunctional nitrene precursors were used, cross-linked CNTs were formed which could benefit for the development of CNT-based high performance materials such as foils and fibers [44]. Ford et al. employed azido-terminated PS to directly react with CNTs at 130 °C in 1,2-dichlorobenzene, resulting in the nanocomposites with functionalization density of 1 PS chain per 48 carbon atoms of CNTs [45].

An improved green, low cost, general and efficient one-step technology to synthesize highly dispersible functional CNTs...
Scalable synthesis of functional azides up to hundreds of grams with various reactive groups (i.e., -OH, -NH₂, -COOH and -Br) was achieved at first. The azides were anchored onto the convex surfaces of CNTs via nitrene addition under a relatively mild condition in one-step without significant damage to CNTs. The typical TEM images in Fig. 6 show that MWCNTs modified with hydroxyl groups (MWCNT-OH) exhibit much better dispersibility than pristine MWCNTs, and the networks of CNTs were exfoliated as many individual nanotubes and some nanotubes were cut to shorter ones through ultrasonication and functionalization. All of the samples show no obvious surface damage or corrosion after the one-step functionalization and the smooth curve surfaces remain intact. Such a fine effect is essentially different from that of aforementioned nitric acid oxidation method which may lead to serious surface eroding or even degraded completely. The degree of functionalization could be easily controlled by varying the feed ratio of the azide compounds to CNTs. A series of reactions, such as surface polymerizations, amidation and reduction of metal ions were performed on the functional CNTs, affording CNT-polymer and CNT-Pt nanohybrids (see Scheme 7). These reactions also
confirmed the reactivity of immobilized functional groups, laying the foundation for further material-design. Besides, biocompatible hyperbranched polyglycerol (HPG) was grafted from the surfaces of hydroxyl group-decorated CNTs by in situ anionic ring-opening polymerization of glycidol [47]. Fluorescent molecules of rhodamine 6B were attached to the HPG-coated CNTs by esterification to generate fluorescent CNTs. Alternatively, biomolecules such as peptides could be attached to CNTs for the purpose of targeted drug-delivery [48].

Zhu et al. prepared water-soluble carborane cage-functionalized CNTs [49]. The azide-modified $C_2B_{10}$ cage were anchored on the CNTs via nitrene cycloaddition. By refluxing the ethanolic solution of $C_2B_{10}$ cage-functionalized CNTs with sodium hydroxide, both the $C_2B_{10}$ cages and the aziridine rings

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**Scheme 7.** Further chemical reactions on nitrene-functionalized CNTs (Reprinted with permission from ref. 46. Copyright 2009, American Chemical Society).
were transformed, affording water-soluble CNTs with nido-C3B6 cages and ethoxide groups on the side walls. The composites were investigated with tissue distribution experiments and found to preferentially distribute in tumor cells than in blood and other organs, suggesting that they are potential candidates as effective boron delivery nanovehicles for boron neutron capture therapy in cancer treatment. Frechet et al. prepared CNT-based forests from silicon substrates and functionalized them with perfluoroarylazides via nitrene cycloaddition by UV exposure through a photomask to create functional patterns (see Table 2) [50]. Immobilization of ATRP initiators on the forest and the following surface polymerization of N-isopropylacrylamide afforded the forest surface with PNIPAM polymer patterns. An interesting synthetic mimic to the back of the Stenocara beetle of the Namib desert, a stable micropatterned superhydrophilic-superhydrophobic surface, was also prepared in two steps: (1). blanket modification with molecule 1 to generate superhydrophilic surfaces; (2). reaction with molecule 2 by UV exposure through a photomask to reverse the superhydrophilic nature of the exposed region to the superhydrophobic nature and keep the unexposed region without change.

Therefore, linear and dendritic polymers, inorganic molecules, and organic functional molecules can be bonded to CNTs via nitrene chemistry, displaying the high efficiency of nitrene chemistry in the preparation of functional CNTs. The greatest advantage of nitrene chemistry over click chemistry lies in that pristine CNTs can be directly used as materials for nitrene coupling whereas pre-modification of CNTs is generally needed for click chemistry functionalization.

**Functionalization of fullerene and graphene via azide chemistry**

Except CNTs, functionalizations of fullerene and graphene have also attracted increasing attention for both scientists and engineers. Functionalization of the two allotropes of CNTs via azide chemistry has been demonstrated as a powerful way to form new functional materials and similarly, it falls into two sections: click chemistry and nitrene chemistry.

**Functionalization of fullerene via click chemistry**

Functionalization of fullerene via click chemistry was carried out in recent years. Generally, azide or alkyn-containing compounds (see Scheme 8) [51]. Giordani et al. anchored 4-(trimethylsilylethynyl)aniline onto multilayer fullerenes via Pschorr-type arylation and coupled them with the azide-decorated zinc porphyrin after eliminating the trimethylsilyl group using tetra-n-butylammonium fluoride (see Scheme 9) [52].

**Functionalization of fullerene via nitrene chemistry**

The research on modification of fullerene via nitrene chemistry was initiated in 1993. Prato et al. refluxed an equimolar solution of C-60 and (trimethylsilyl)-ethoxymethyl azide in chlorobenzene to prepare functional C-60 (see Scheme 10(a)) [53]. This type of modification via nitrene cycloaddition has a great advantage that mainly monoaddition occurs and thus there is relatively little crosslinking which is often brought by the multifunctional nature of C-60 [54]. In the following years, various functional molecules were incorporated onto C-60 in this way, such as oligosaccharides and metal-oligopyridine complexes, and photo-induced cycloaddition method was also developed. In 1994, Hawker reported the synthesis of C-60 pendent PS via nitrene addition, which initiated the research on preparation of C-60-polymer nanocomposites via nitrene chemistry (see Scheme 10(b)) [55]. C-60 was then combined with many kinds of polymers, such as polyether [56], poly (acrylic acid) [57], poly (p-phenylene vinylene) [58], polyferrocenylsilane [59] and so on. Preparations of the polymer composites with various structures, like star [56], palmtree [60], miktoarm [61], and end-cap [56,57], were reported.

Recently, our group developed a facile technology to synthesize functional multilayer fullerenes (alternative name, carbon nano-onions, CNOs) in large-scale (see Scheme 11) [62]. In situ ring-opening polymerization (ROP) of e-caprolactone and ATRP of styrene were successfully carried out with CNO-OH and CNO-Br as initiators, respectively.

**Preliminary functionalization of graphene via azide chemistry**

Graphene, as an emerging 2D nanomaterial, is very attractive due to its unique attributes [63,64]. Researches on its functionalization via azide chemistry have been explored recently. For example, Choi et al. modified graphene with azidotrimethylsilane via nitrene addition [65]. Our group developed a general approach to functionalize graphene nanosheets by nitrene chemistry from oxidized graphene (see Fig. 7). Desired functional groups (e.g., -OH, -NH2, -COOH, -Br, etc.), alkyl chains, and polymers could be covalently and stably linked on graphene sheets. Significantly, the nitrene
-functionalized graphene sheets are still individually dispersed and highly conductive, opening the door for fabrication of multifunctional high-performance composites [66]. Our group also explored the functionalization of oxidized graphene nanosheets (OGNs) by click chemistry, allowing that various amino acids and polymers, such as PEG and PS, can be attached to OGNs [67]. Now the chemistry of graphene and OGNs is calling chemists for more devotion to exploit this new mine.

**Conclusions and outlook**

Azide chemistry, including click chemistry and nitrene chemistry, has been demonstrated as a highly efficient, modular...
approach to functionalize carbon nanomaterials. The one-step nitrene chemistry methodology has pushed the experimental functionalization towards large-scale production. The strategies, such as “grafting to”, “grafting from”, their combination and layer-by-layer coating, are all available for preparing complex structures. Azide chemistry provides unlimited resources for the advance of these carbon-based nanomaterials, which probably initiates the revolution of new materials, energy and techniques.

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