Influence of morphology on electrical and optical properties of graphene/Al-doped ZnO-nanorod composites

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Abstract

The development of future 3D-printed electronics relies on the access to highly conductive inexpensive materials that are printable at low temperatures (<100 °C). The implementation of available materials for these applications are, however, still limited by issues related to cost and printing quality. Here, we report on the simple hydrothermal growth of novel nanocomposites that are well suited for conductive printing applications. The nanocomposites comprise highly Al-doped ZnO nanorods grown on graphene nanoplatelets (GNPs). The ZnO nanorods play the two major roles of (i) preventing GNPs from agglomerating and (ii) promoting electrical conduction paths between the graphene platelets. The effect of two different ZnO-nanorod morphologies with varying Al-doping concentration on the nanocomposite conductivity and the graphene dispersity are investigated. Time-dependent absorption, photoluminescence and photoconductivity measurements show that growth in high pH solutions promotes a better graphene dispersity, higher doping levels and enhanced bonding between the graphene and the ZnO nanorods. Growth in low pH solutions yields samples characterized by a higher conductivity and a reduced number of surface defects. These samples also exhibit a large persistent photoconductivity attributed to an effective charge separation and transfer from the nanorods to the graphene platelets. Our findings can be used to tailor the conductivity of novel printable composites, or for fabrication of large volumes of inexpensive porous conjugated graphene-semiconductor composites.

Keywords: graphene, zinc oxide, nanorods, nanocomposites, persistent photoconductivity, printing

(Some figures may appear in colour only in the online journal)

1. Introduction

The development of 3D-printing technologies for realizing electronic components and materials is evolving very quickly. Presently, there is a strong interest in developing novel 3D-printable...
Demonstrated properties that make graphene promising for electronics include excellent (i) carrier mobility (up to $10^6 \, \text{cm}^2\, \text{V}^{-1}\, \text{s}^{-1}$) [7], (ii) electrical resistivity ($0.1–6 \, \text{k}\Omega/\square$ for a single layer with 97.7% optical transparency) [7], (iii) chemical stability and (iv) mechanical strength (double to that of CNTs) [7]. However, graphene is highly hydrophobic and hardly interacts with other materials. Moreover, the high-aspect-ratio of graphene nanoplatelets (GNPs), combined with large van der Waals forces typically lead to issues with undesired agglomeration into large particles. In order to use graphene in printing applications, it must therefore be properly dispersed in a suitable medium. High-quality dispersions are typically facilitated by introducing chemical surfactants [8] which unfortunately influence the electrical properties of graphene in an undesired way. A different approach to synthesize a conductive screen printing graphene ink with a resistance of $30 \, \Omega/\square$ at 25 μm thickness by gelation of a graphene dispersion was recently reported [9]. Despite all of these efforts it still remains a challenge to make a highly conductive graphene dispersion in a viscous medium, suitable for printing applications.

Here we propose a new approach to realize a graphene dispersion, effectively forming a conductive network, by growing zinc oxide nanorods (ZnO-NRs), degenerately doped with aluminum (Al), as highly conductive spacers on the surface of the GNPs. The potential advantages of these composites stem from the remarkable charge transport characteristics of graphene, combined with the excellent optical characteristics of ZnO. The expected enhancement of the optoelectronic properties of this composite might lead to important applications in optoelectronics, photovoltaics and photocatalysis [10].

Zinc oxide is a well-known unintentionally n-type semiconductor with a wide direct bandgap of 3.2–3.4 eV at room-temperature. It can be grown in different nanostructured shapes e.g. nanorods by inexpensive low-temperature ($<100 \, ^\circ\text{C}$) hydrothermal solution-based procedures [11, 12]. The morphology, length and diameter of the ZnO-NRs can be controlled by tuning the pH value, temperature of the growth solution, precursor concentration and growth duration [13].

ZnO-NRs can be grown on GNPs with excellent result despite of their hydrophobicity. It has been shown that the reduced lattice mismatch of less than 2% [14, 15] between ZnO-NRs and GNPs causes strong atomic level interactions which lead to strong bonding and high mechanical stability [16]. Moreover, the electrical interface between GNPs and ZnO-NRs shows excellent low-ohmic metallic behavior [17, 18] of great importance for conductive applications.

2. Experimental details

All the chemicals required for the hydrothermal growth presented in this work, including the multilayer GNP powder, were purchased from Sigma-Aldrich. The first step was to seed the GNPs with a layer of ZnO nanoparticles (ZnO-NPs) [19]. GNPs with a concentration of 0.5 g l$^{-1}$ were initially dispersed in DI-water using an ultrasonic bath for 10 min. Subsequently this solution was mixed with a 100 ml solution of 0.005M of zinc acetate (Zn(CH$_3$COO)$_2$·2H$_2$O) and 0.025M of KOH in water at 60 °C in an ultrasonic bath for 10 min. The seeded GNPs were subsequently washed in water and centrifuged (3000 rpm, 10 min) three times, followed by annealing in nitrogen at 300 °C for 30 min to enhance the attachment of the ZnO-NPs to the GNPs. For the growth of ZnO-NRs, we prepared two solutions of 0.025M of Zn(NO$_3$)$_2$·6H$_2$O and 0.025M of C$_6$H$_{12}$N$_4$ (HMT) in DI-water with pH 6.6 and pH 11 (by adding ammonia), respectively. These two different pH growth solutions resulted in significantly different ZnO-NRs morphologies. A 0.002M aqueous solution of Al(NO$_3$)$_3$·9H$_2$O was stirred overnight and added to the growth solution to supply the Al for doping of the NRs. Finally the seeded GNPs were added to the growth solution under stirring for 2 h at 75 °C.

3. Results and discussion

Figure 1(a) shows a schematic of the grown nanostructures. The ZnO:Al-NRs play two major roles for the final composites. First, they make a physical spacer between the GNPs proportional to their length. These physical spacers prevent GNPs from agglomerating and make the structure more porous. The porosities can, depending on the application, be filled by a proper matrix material. Second, degenerately doped ZnO-NRs grown on one GNP will form low-ohmic electrical connections to a neighboring GNP. Previous studies have shown that the formation of low-resistance direct contacts between the particles is the most crucial factor for realization of highly conductive polymer composites [20]. The sharp NRs can also more easily penetrate through any polymer matrix filling up the porosities between the GNPs and increase the probability of direct contact formation between GNPs. The overall electrical transport properties depend on the resulting complex conductive network between the GNPs in the matrix.

To make sure that the ZnO-NPs in the seed layer are also doped with Al, a piece of pure Al was inserted into the solution during the seeding of the GNPs. The high pH value of 13 of the seed solution will lead to a partially dissolving of Al in the solution and to doping of the ZnO-NPs [21]. Figure 1(b) shows GNPs decorated with ZnO:Al-NPs. The photoluminescence (PL) measurements discussed below clearly show the effects of the high Al-doping on the optical properties of the ZnO-NPs.

The two different morphologies of ZnO-NRs grown at different pH (6.6 and 11) were investigated for better performance
regarding both conductivity and dispersity. ZnO-NRs grown at pH 6.6 (figure 1(c)) are hexagonal, thicker (mean diameter 313 nm), longer (1–2 μm) and more sparse compared to ZnO-NRs grown at pH 11. The NRs grown at high pH are more needle-like with a mean diameter and length of 196 nm and 0.5–1.5 μm respectively (figure 1(d)). The density of ZnO-NRs on the GNP surface was estimated, 1.4 μm⁻² for the samples grown at pH 6.6 and 2.4 μm⁻² for the samples grown at pH 11 by counting in the SEM image.

Figure 1. (a) Schematics of ZnO-NRs grown on both sides of GNPs by the hydrothermal solution-based procedure. (b) Scanning electron microscopy (SEM) image of GNPs decorated with Al-doped ZnO nanoparticles. (c) Thick hexagonal low-density ZnO-NRs grown at pH 6.6. (d) Thin needle-like, high-density ZnO-NRs grown at pH 11. The insets show the size distribution of the nanorods diameter.

Figure 2(a) shows the abundance of different elements in the samples extracted from energy dispersive x-ray spectroscopy (EDS). Carbon (C) is the most abundant element observed in all composites with an atomic ratio of 6.5 compared to Zn. The presence of 0.5–1.5 at% Al is also detected in the doped composites, which basically represents the lower boundary for a typical EDS system. The doping concentration in the samples is estimated in the range of 0.7–1.2 at% based on the dopant concentration in the growth solution [22, 23]. The presence of
oxygen (O) is almost 60 at% higher than Zn in the samples. This excess of O could be related to the hydroxyl groups OH− and/or carboxyl groups −COOH, or to adsorbed water on the GNP or ZnO surfaces during the synthesis [24].

The resistivity of the composite layer samples, comprising the investigated microparticles, is measured by a standard four-point method. To do that, the layered materials must first be smoothly deposited. To deposit the randomized GNP/ZnO:Al-NRs microparticles, we used a vacuum filtration method [8]. A water dispersion containing the microparticles was filtered by an Anodisc membrane filter from Whatman (25 mm diameter, 0.2 μm pore size) and dried at 70 °C in an oven. The layer thickness, varying from 20 to 50 μm, was measured by a contact profilometer. As shown in figure 2(b), the resistivity of pure GNP is the lowest and it increases after decoration with ZnO:Al-NPs. This increase can be explained by the synthesis procedure and/or the spacing induced by the doped ZnO nanoparticles. Growth of undoped ZnO-NRs on the decorated GNP results in a further increase of the resistivity for both investigated morphologies, effectively converting the layers to insulators. This high resistivity shows that the GNP are physically separated from each other by the non-intentionally doped ZnO-NRs. For the doped samples, the resistivity strongly decreased and the nanocomposites again became conductive due to the enhanced conductivity of the degenerately doped ZnO:Al-NRs. This shows that the electrical current is passing through the ZnO-NRs. The ZnO-NRs (nanoneedles) grown at pH 11 show a comparably higher resistivity compared to those grown at pH 6.6. This suggests that nanoneedle-shaped GNP are better dispersed. This hypothesis is supported by the optical UV–vis data discussed below.

To compare the dispersity of the two morphologies, and the attachment of ZnO-NRs to the GNP, time-dependent UV–vis spectroscopy was employed. Figures 3(a)–(c) show the absorption spectra of the GNP with different morphologies of grown ZnO:Al-NRs, dispersed in isopropanol, after every 5 min and after 24 h. The absorption spectra of pure GNP exhibit a rather flat absorption characteristics dominated by spectral features beyond 1500 nm related to hydroxyl and/or carboxyl groups on the GNP surfaces (figure 3(a)). Figures 3(b) and (c) display a strong absorption peak at about 380 nm for dispersions of GNP/ZnO:Al-NRs due to the ZnO bandgap. The broad absorption shoulder, and spectrally unresolved absorption edge, reflect various scattering mechanisms [25] in the samples, which lead to strong spectral convolution effects. The dispersions of GNP and GNP/ZnO:Al-NRs grown at pH 11 show a uniform decrease in absorption with excitation time due to particles settling. Figure 3(b) shows that the absorption in GNP/ZnO:Al-NRs grown at a pH 6.6 changes non-uniformly with wavelength. The long wavelength absorption response in our dispersions is dominated by the GNP, while it relates to ZnO at short wavelength. The non-uniform decrease in absorption observed in 3(b) indicates the presence of two phases (separated GNP and ZnO:Al-NRs) in the dispersion. The ZnO:Al-NRs settle faster than the GNP. In contrast, GNP/ZnO:Al-NRs grown at a pH 11 forms a single phase in the dispersion, as evident from the uniform settling rate in figure 3(c). This implies that ZnO:Al-NRs are better attached to GNP in high pH growth solutions.

To study the quality of bonding between the GNP and the ZnO-NRs, and also to see the effects of Al-doping level in

![Figure 3. Time-dependent UV–vis spectroscopy. Temporal evolution of the absorption spectra after 0, 5, 10, 15, 20 min and 24 h, respectively, for the dispersion of (a) GNP, (b) GNP/ZnO:Al-NRs grown at pH 6.6 and (c) GNP/ZnO:Al-NRs grown at pH 11 in isopropanol. (Figure (a) has a different vertical scale.)](image)
the ZnO-NRs, room-temperature micro-PL (μ-PL) measurements were pursued on nanostructure deposits on gold coated silicon wafers using a 80 μW, 266 nm laser excitation. The main peak in figure 4 shows the ZnO near-bandedge emission (NBE) at 3.25–3.38 eV in agreement with the absorption measurements. The broad peak at 2.4 eV indicates the visible light emission via deep levels in ZnO caused by zinc and oxygen vacancies [19]. The origin of the oscillations at 1.7–2 eV are not well understood but they are a common feature for all the samples. For easier comparison, all the PL data were normalized to the peak at 1.9 eV. Three sets of ZnO-nanorod morphologies (ZnO-NPs and ZnO-NRs grown at pH 6.6 and 11) in four different composites (undoped ZnO, ZnO:Al, GNP/ZnO, GNP/ZnO:Al) were investigated under the same conditions (figures 4(a)–(c)).

Two distinct changes are readily observed in the μ-PL spectra after doping the ZnO-NRs with Al; first, the deep level emission (DLE) is suppressed due to filling of the defects levels by electrons (Al is a donor in ZnO). This observation has previously been reported for Ga-doped ZnO-NRs [26]. Furthermore, the NBE is also suppressed by Al-doping more significantly. The ratio of NBE-to-DLE integrated intensities ($I_{\text{NBE}}/I_{\text{DLE}}$) for different samples are summarized in table 1. In all the samples the $I_{\text{NBE}}/I_{\text{DLE}}$ ratio is decreased by adding Al to the composite. This decrease in the UV-to-visible emission ratio can be explained by introducing impurity levels in the bandgap with the doped metal ions and reducing the crystalline quality of ZnO [27–29]. Although it has been reported that post thermal treatment can improve the ZnO:Al crystallinity [28], our samples were measured without thermal treatment. Second, a blue-shift in the band-edge emission is observed which we attribute to the Burstein–Moss effect [23, 27, 30].

Another interesting general observation in the μ-PL spectra is that ZnO-NRs grown on GNPs exhibit a significantly stronger

![Figure 4. μ-PL room-temperature measurement for different ZnO-NRs composites grown at (a) pH 6.6, (b) pH 11, and (c) different GNP/ZnO-NPs composites. (d) Comparing PL spectra for GNP/ZnO:Al composites for three different ZnO morphologies.](image-url)
band-edge PL emission intensity compared to isolated ZnO-NRs. Previous reports in the literature attribute this to a reduction in the concentration of oxygen vacancy surface defects in the ZnO by oxygen groups adsorbed on the GNP's [31, 32] or more probably to resonant excitation of graphene plasmons [33–35].

Comparing the μ-PL for the two ZnO-NRs morphologies in figure 4(d) shows that thicker ZnO-NRs grown at pH 6.6 display a stronger band-edge PL emission than the thinner needle-like ZnO-NRs grown at pH 11 due to a lower surface-to-volume ratio. A high surface defect concentration on the thinner Zn-NRs not only causes a lower band-edge emission in the optical characteristics, but also leads to a higher electrical contact resistance (figure 2(b)).

To further support our conclusions, we measured the spectrally resolved photoconductivity of our samples. A significant persistent photoconductivity (PPC) in ZnO has been demonstrated in many articles [36–39]. The PPC observed in ZnO is attributed to a spatial charge separation mechanism induced by the built-in electric field caused by a surface space-charge layer [40]. Oxygen vacancies in the ZnO structure can chemically absorb oxygen from the air and become a hole trap. During illumination with photons with larger energy than the bandgap of ZnO, photogenerated holes will migrate to these surface traps and photodesorb the oxygen. At this point the separated mobile photoelectrons remain in the ZnO conduction band and result in a PPC.

Figure 5 below shows the results of pulsed optical excitation of an undoped GNP/ZnO-NR sample at 300 K. The measured current is recorded at a bias of 1 V under optical excitation with different wavelengths from 320 to 400 nm. There was no detected photoresponse for wavelengths longer than the corresponding bandgap energy. A large PPC effect was observed that increased at shorter wavelengths. In contrast, no PPC was observed in any of the highly Al-doped samples, not even under 254 nm illumination. This absence of PPC in highly doped samples can be explained by electrostatic screening of the surface oxygen ions that prevents holes from migrating towards the surface [40].

Time-resolved PPC was measured in detail to compare the effect of nanocomposite morphology on the lifetime of the photogenerated electrons. Figure 6 shows the time-dependence PPC of undoped GNP/ZnO-NR samples with different morphology after 350 nm excitation. After switching on the light, the surface chemisorbed oxygen traps the migrating photogenerated holes leaving behind an increasing density of mobile electrons in the conduction band, which results in an increasing PPC. Eventually, the complex processes involving charge carrier dynamics and surface oxygen chemisorption/desorption are in balance and the PPC saturates. By switching off the incident light, the PPC slowly decays due to recombination of photogenerated electrons and surface oxygen chemisorption. A detailed analysis of the continuity equation for the investigated complex composite materials is beyond the scope of this paper. Instead we focus on a more qualitative analysis of the decay process.

During the decay, the PPC is proportional to the density of electrons in the conduction band which in general decays stretched exponentially with time [41]. Evidently (figure 6), the photoconductivity (after subtracting the dark conductivity) \( \sigma_{ph} \) decays exponentially according to:

\[
\frac{d\sigma_{ph}}{dt} = -\frac{\sigma_{ph}}{\tau_d},
\]

\[
\ln\sigma_{ph} = -\frac{t}{\tau_d} + \ln\sigma_0.
\]

### Table 1. The NBE-to-DLE integrated intensity ratio \( I_{NBE}/I_{DLE} \) for different ZnO-NRs composites.

| Material            | Grown at pH 6.6 | Grown at pH 11 |
|---------------------|-----------------|----------------|
| ZnO-NRs             | 2.46            | 0.15           |
| ZnO:Al-NRs          | 1.78            | 0.11           |
| GNP/ZnO-NRs         | 4.25            | 0.46           |
| GNP/ZnO:Al-NRs      | 1.85            | 0.21           |

Figure 5. The cycled PPC response for a GNP/ZnO-NRs sample at 300 K and 1 V applied bias.

Figure 6. Time-dependence of the PPC \( \sigma_{ph} \) after switching off the light for three different GNP/ZnO-NRs morphologies under 350 nm illumination at 300 K and 1 V applied bias.
**Table 2.** Dark conductivity ($\sigma_d$), PPC directly after switching off the light ($\sigma_0$) and excess electron lifetime ($\tau_d$) of three different undoped samples at 300 K.

| Sample                             | $\sigma_d$ (S cm$^{-1}$) | $\sigma_0$ (S cm$^{-1}$) | $\tau_d$ (s) |
|------------------------------------|---------------------------|---------------------------|--------------|
| ZnO-NRs                            | $1.7 \times 10^{-9}$      | $1.1 \times 10^{-10}$     | 56           |
| GNP/ZnO-NRs, pH 11                 | $7.3 \times 10^{-10}$     | $3.9 \times 10^{-10}$     | 107          |
| GNP/ZnO-NRs, pH 6.6                | $2.1 \times 10^{-6}$      | $3 \times 10^{-7}$        | 877          |

Here, $\tau_d$ is the decay time constant (excess electron lifetime) and $\sigma_0$ is the observed PPC directly after switching off the light. The extracted electron lifetime for samples with different morphology are calculated by a linear fitting to equation (2) and reported in table 2.

While the ZnO-NRs sample exhibits a long electron lifetime of about 56 s, the composite samples of graphene and ZnO-NRs have much longer electron lifetimes (107 and 877 s). The prolonged electron lifetime in these composites can be explained by an efficient transfer of photogenerated electrons to the graphene. This electron injection into the graphene causes a strongly reduced recombination rate and thus an enhanced PPC. The sample grown at pH 6.6 shows a significantly longer electron lifetime compared to the sample grown at pH 11. We conclude that the charge transfer between the ZnO-NRs and the graphene is more effective in the samples with thicker NRs grown at lower pH compared to the thinner needle-like NRs grown at higher pH.

The two morphologies of GNP/ZnO-NRs have different advantages and drawbacks. Thinner ZnO-NRs grown in a high pH solution exhibit a better dispersity and an improved attachment between the GNP and ZnO-NRs, but also show a higher resistivity due to more surface defects and lower charge transfer between ZnO-NRs and GNP. In contrast, the thicker ZnO-NRs grown at a lower pH display a lower resistivity and better charge transfer between ZnO-NRs and GNP, but also a weaker GNP/ZnO-NRs bonding and a poorer dispersity. For conductive printing applications, lower resistance samples with thick ZnO-NRs are preferred. However, if the surface of the nanorod defects could be passivated by a proper post-growth treatment, the thinner GNP/ZnO-NRs morphology could be advantageous.

Growth and in situ doping of conjugated GNP/ZnO-NRs nanocomposites by a simple solution-based method as demonstrated in this work is economically desirable for mass production. For conductive purposes, the nanocomposite materials can be mixed by different polymers and tested for printing performance. Although we have primarily focused on conductive applications, our reported nanocomposites can be used in any optoelectronic, photochemical or photovoltaic application that requires high-porosity conjugated organic/semiconductor hybrids with a tunable conductance level.

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