Preparation and characterization of copper oxide nanoparticles decorated carbon nanoparticles using laser ablation in liquid

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Abstract. Carbon nanoparticles CNPs decorated by copper oxide nano-sized particles would be successfully equipped using technique named pulsed laser ablation in liquid. The XRD pattern proved the presence of phases assigned to carbon and different phases of copper oxide. The chemical structure of the as-prepared nanoparticles samples was decided by Energy Dispersive Spectrum (EDS) measurement. EDS analysis results show the contents of Carbon, Oxygen and Copper in the final product. These nanoparticles were spherical shaped with a size distribution 10 to 80 nm or carbon nanoparticles and 5 to 50 nm for carbon decorated copper oxide nanoparticles, according to Transmission Electron Microscopy (TEM) images and particle-size distribution histogram. It was found that after doping with copper oxide, nanoparticles become smaller and more regular in shape. Optical absorption spectra of prepared nanoparticles were measured using UV–VIS spectroscopy. The absorption spectrum of carbon nanoparticles without doping indicates absorption peak at about 228 nm. After doping with copper oxide, absorption shows appearance of new absorption peak at about (254-264) nm, which is referred to the movement of the charge between 2p and 4s band of Cu⁺ ions.

Keywords. Nanoparticles (NPs), pulsed laser ablation in liquid medium (PLAL), Transmission Electron Microscopy (TEM), Copper Oxide.

1. Introduction
Carbon is a standout amongst the most various components in nature. Carbon-based nanomaterial has pulled in more interest for late years. There are extensive variety of carbon nanostructures have been synthesized, for example, carbon nanotubes, fullerenes, Nano fibers, Nano diamond, carbon nanoparticles, and different carbonaceous nanomaterial [1]. Carbon nanoparticles (CNPs), which assign to the type of round carbon-related nanomaterial, display numerous superior optical characteristics, such as stabilized photoluminescence property (PL), wide excitation wavelengths (λex) and tunable radiation. Among luminescent semiconductor substrate such as quantum dots, CNPs
exhibit further advantages of biological compatibility, minimum cell toxicity, effortless functionalization, perfect solubility in water circumference. Therefore, CNPs have encountered developing respect in many promising fields, for example, imaging in biomedicine, delivery of drugs in body, optoelectronic [2].

Furthermore, it could be the host to therapeutic agents, attributable to their great surface functional groups such as amine, amide, carbonyl, alcoholic hydroxyl [3]. Nanoparticles of metal oxides are already greatly synthesized because of their unique applications. Nano-copper oxide (CuO) is p-type narrow band gap semiconductor (1.2 eV at room temperature) is basically utilized in a part of numerous applications, for example, catalysis, photo-catalysis, gas sensors, solar energy transformation, and electronics [4].

Other carbon compounds broadly examined are the carbon-containing nanoparticles, usually called carbon nanocomposites. These matters have gotten fabulous notice because of exceptional properties. Like high surface area and regular pore dimension, thermal and mechanical steadiness [1]. Nanoparticles of metal or metal oxide, which were propped on small dimensional of carbon Nano-scale materials have created noteworthy enthusiasm for different applications. These nanoparticles are extremely stable since they are embedded in the carbon matrix [1].

The incorporation of different metal oxide nanostructures on surface of carbon Nano-dimensions substrate let them to be helpful for many applications not just due to particular physical and chemical properties of upheld particles, but furthermore to their big area of the surface, sprightly weight, high mechanical quality, and great electrical and thermal transfer features [5].

Different techniques have been utilized for the preparation of carbon nanomaterial decorated by semiconductor nano-scale particles [6, 7, 8, and 3]. Pulsed laser ablation in liquid environment (PLAL) is a one of these methods. It is well-known system to produce NPs, where solid positioned in a colloidal medium [9]. Thus, Laser Ablation in solution is a strategy to manufacture a wide range of nanostructure materials. In its procedure, laser beam, which is an intensive one, is illuminate surface of metal target resulting in the generation of plasma plume within the fluid–target binding forming micro-bubbles. These bubbles grow to achieve a specific basic mix of pressure and temperature and after that collapse [10]. The result is generation and expulsion of Nano-dimension clusters from the objective substrate into the restricting environment, ensuing the fashioning of solutions of nanoparticles. Morphology, size and chemistry of Nano-scale particles surface could be administered through varying parameters of used laser, type of the desired material and liquid circumference [11]. PLAL can use to prepare an extensive variety of novel substances and the final products are typically inside the shape of nanoparticles that stay suspended within the liquid medium, and can be separated by filtration and evaporation of the liquid [12]. In addition, this method is simple and does not require a vacuum system [13]. In this work, carbon nanoparticles decorated with different copper oxide nanoparticles ratio were prepared using PLAL and characterization of these nanoparticles were studied by several techniques.

2. The Used Matters and Techniques

2.1 NPs Solution Production
Carbon doped by copper oxide nanoparticles would be synthesized by irradiation of a pure graphite pellet (99.9% purity, diameter of 0.5 cm and thickness of 2 mm) with laser, which is positioned at a vessel base and immersed by 3 ml of de-ionized water. Q-switched Nd:YAG laser of following features was employed to produce the nanoparticles: wavelength of 1064 nm, frequency of 1 Hz, pulse width of 9 ns, and laser fluence of 10.6 J/cm² for 75 pulses. After production of carbon nanoparticles, copper target (96.53% purity, diameter of 1.5 cm and thickness of 3mm) was put in these carbon nanoparticles colloidal and was ablated by same laser at different doping ratio.

2.2 Characterization
Prepared carbon nanoparticles doped with copper oxide Nano-colloids were distinguished by both optical and structural methods. A double-beam UV–Vis spectrophotometer (Schimatzu) was utilized to register optical absorption of NPs colloids in the range 200-800 nm. Photoluminescence (PL) was measured to determine energy structure of nanoparticles by (Elico, SI74, spectrofluorometric
detector, Shimadzu RF-551). The measurement was carried out in Science collage /University of Baghdad. X-ray diffraction (XRD) measurements of NPs colloidal, which dropped and dried on glass slides, were achieved using Shimadzu XRD 6000 with Cu-Kα radiation source at 20 angle = (10 – 80°). Transmission electron microscope (TEM type Philips) was used to discuss the morphological properties of the NPs. Samples were prepared for TEM analysis by dropping Nano-colloids onto a model copper grid coated with gold (contains about 200 meshes). EDS measurements were done by (Inspect S 50 /FEI Company/ Netherlands) at Al-Khofa University. Samples were prepared for EDS by dropping few drops of solutions on slides of glassy substrate and let it dry for ten minutes.

3. Result and discussion

‘Figure 1’ shows the optical absorption spectra of colloidal NPs. UV-visible spectrum of synthesized carbon nanoparticles without doping indicates absorption peak at about 228 nm. This may be contributed the π→π* transition typically found in the carbon which is in a range of 180 - 280 nm [14]. It is of the aromatic sp² domains, and leads to very low fluorescence intensity [2]. While after doping with copper oxide, the optical absorption shows appearance of new absorption peak at about (254-264) nm, which indicates the charge transformation among what named 2p oxygen orbital’s and 4s of Cu²⁺ ions [15]. Change in the UV-visible spectrum could be due to complex formation between copper and CNPs.

![Figure 1. Absorbance spectra of carbon nanoparticles prepared at 10.6 J/cm² in de-ionized water (0%) and then doped with different ratio (26, 29, 39 and 43) % of CuO NPs.](image)

The photo luminescent spectra of the synthesized carbon decorated copper oxide nanoparticles were studied using the same excitation wavelengths of 350 nm as shown in ‘figure 2’. PL spectra for all suspensions are ranging from 390 to 550 nm. The maximum intensity of fluorescent emission was obtained between (452-460) nm, which is correlated with blue wavelength [14].

The photoluminescence intensity yield of the C-CuO NPs was observed to be highest for carbon NPs alone than that of the other samples. This could be due to the quenching of the luminescence of carbon NPs in the presence of CuO [16].

XRD measurements were studied through interval scan from 10° to 80°. In XRD spectrum of CNPs made by laser at fluence of 10.6 J/cm² for 75 pulses in ‘figure 3’, there are significant diffraction pattern that could be viewed at 20 of 26.58° and 43.78°, which returning to the (002), and (101) reflection phases of carbon respectively (JCPDS No.41-1478 and 06-0675) [17]. While in XRD pattern of carbon NPs decorated with copper oxide NPs of different concentration (26%, 29%, 39%, 43%), new peaks of copper oxide will be appeared at 20 (38.5° and 48.64° corresponded to (111), (202) crystal planes of CuO with monoclinic phase, respectively. The peaks have well consent with the standard pattern of monoclinic CuO (JCPDS Card No. 05-0661) [18].
Figure 2. Photoluminescence spectra of carbon nanoparticles doped with different ratios (26, 29, 39 and 43) % of copper oxide nanoparticles.

Figure 3. XRD pattern of carbon nanoparticles doped with different ratios (26, 29, 39 and 43) % of copper oxide nanoparticles.

In addition, typical diffraction peak of Cu$_2$O (110) and Cu (111) is observable in the XRD pattern for carbon doped by copper oxide nanoparticles at 2θ= 43.2° and 29.56° respectively. It can be seen that intensity pattern of carbon nanoparticles still observable in the XRD pattern for carbon doped copper oxide nanoparticles. It can be ascribed to the fact that CNPs cannot be reduced under the Nano composite preparation conditions [19].

The morphology and particle size of prepared nanoparticles was determined by TEM images and the particle size distribution histogram. It was found to be in a range of 10–80 nm for carbon Nanodimensional particles synthesized with laser ablation in de-ionized water at 10.6 J/cm$^2$ as shown in ‘figure 4’.
Figure 4. (a) TEM image of carbon nanoparticles prepared by laser ablation of carbon target in de-ionized water at 10.6 J/cm² laser fluence (0% CuO), (b) Size distribution of prepared carbon nanoparticles, and (c) EDS spectrum of nanoparticles.

TEM image shows little aggregation of nanoparticles due to a small electrostatic repulsive force between them produced by the electric double layer on the nanoparticles’ surfaces [20]. The chemical composition of the as-synthesized carbon nanoparticles samples was determined by Energy Dispersive Spectrum (EDS) measurement. EDX spectra in ‘figure 4c’ indicated the presence of only C, and O in the colloidal (O was from the TEM grid) [12].

While ‘figure 5’ show morphology, size distribution, and chemical composition for carbon nanoparticles decorated by copper oxide nanoparticles with ratio 43% CuO. It can be seen that the nanoparticles are mostly of spherical shape with a size distribution between 5 to 50 nm, as depicted in the size histogram in the figure inset. It was found that after doping with copper oxide, nanoparticles become smaller and more regular in shape and turn over shape that is more spherical. Carbon-metal oxide NPs are formed by binding metal to the peripheral carboxylic bonds of carbon by ion exchange. The result is carbon nanoparticles surrounded by metal oxide nanoparticles, so peripheral charges of carbon can help in stabilizing the metal particles in solution.
Figure 5. (a) TEM image of carbon nanoparticles doped with 43% of copper oxide nanoparticles prepared by laser ablation, (b) Size distribution of prepared nanoparticles, and (c) EDS spectrum of nanoparticles.

EDS analysis results show the contents of Carbon, Oxygen and Copper in the final product. The ratio of weight (%) of C, O, and Cu matters in the as-prepared final nanoparticles sample are 9.82, 12.25, and 4.11, respectively.

4. Conclusions
In conclusion, Carbon nanoparticles decorated by copper oxide Nano-colloidal had been effectively manufactured by ablation with pulsed laser technique in a liquid medium. It is found that doping of carbon nanoparticles with copper oxide nanoparticles will result in formation of decorated nanoparticles that are more uniform in shape and smaller. In addition, that doping will cause quenching of photoluminescence spectra of carbon nanoparticles.

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