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Research Article

Photoluminescence from SWCNT/Cu Hybrid Nanostructure Synthesized by a Soft Chemical Route

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We report a simple wet chemical technique to coat single wall carbon nanotubes (SWCNTs) with Cu nanoparticles. The SWCNT/Cu hybrid nanostructure has been characterized using field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray analysis (EDAX), X-ray diffraction (XRD) study, and Raman spectroscopy. Characteristic optical properties of the nanohybrid structure have been identified through UV-Vis and photoluminescence (PL) spectroscopy. When excited by a radiation of 400 nm wavelength, PL emission in the visible range of 480–620 nm was observed due to charge transfer. This property may be exploited in photovoltaic cells, solar energy conversion, and sensor devices.

1. Introduction

Carbon nanotubes (CNTs), with their exceptional electrical, mechanical, and optical properties [1–3], have drawn much attention of the researchers in the field of nanotechnology. On the other hand nanoparticles have attracted the researchers because of their unique chemical and physical properties [4, 5]. CNTs hybridized with metal nanoparticles bring forth a new class of nanostructured materials into focus [6–8] because of their unique resultant physical properties. Such CNT/metal nanohybrid materials find wide application in sensor devices [9], as catalysts for fuel cells [10, 11], in solar cells [12, 13], as fillers [14, 15], and so forth. Composites of metal nanoparticles and CNTs have been synthesized by various techniques, which include direct coating or deposition on CNTs of metal nanoparticles, such as Ag, Au, Cu, Pd, and Pt. Several methods such as solid-state reactions, capillary action, radiolysis, physical evaporation, electroless deposition, physisorption, self-assembly, and colloidal chemistry combined with electrostatic interactions or with sonication in aqueous solution [16] have been adopted. Zhang et al. [17] fabricated carbon nanotubes with totally filled Cu-nanowires by methane decomposition using Cu-microgrid as a catalyst. Reddy et al. [16] developed a new method for the synthesis of Cu_2O-coated multiwall carbon nanotubes (MWCNTs) on the basis of Fehling's reaction. Fabrication of MWCNT-reinforced Cu matrix composite for heat sink application was reported [18]. But only a few reports have been made on simple and efficient routes for strongly attaching noble metal nanoparticles or nanospheres to CNTs [19, 20]. Decoration of SWCNTs with extremely tiny (2-3 nm) monodispersed noble metal nanoparticles by cost-effective lucid chemical process is still a challenging task [21]. Here, we report a simple wet chemical process to decorate SWCNTs with Cu nanoparticles of average size 3 nm using hexadecyltrimethylammoniumbromide (HTAB) as reducing agent. A detailed study of the optical characteristics and photoluminescence properties of the synthesized samples has been undertaken for application in various devices.

2. Experimental Details

SWCNTs (1-2 nm outer diameter, length: 1–3 μm and purity >95%) were procured from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, and further purified following a chemical process [22, 23] for impurities like traces of catalyst materials and other carbon products. The purification process included heating in a muffle furnace at

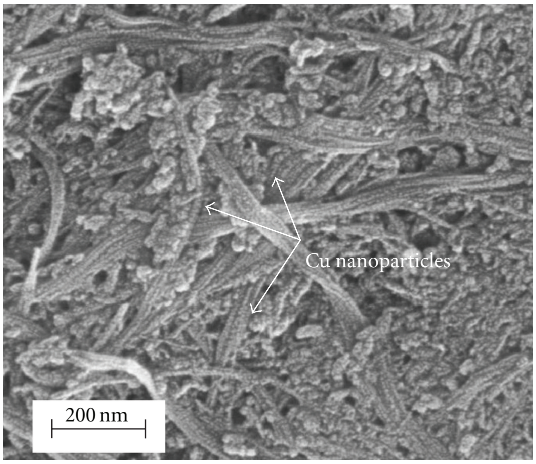

Figure 1: FESEM micrograph of SWCNT/Cu nanohybrid material.

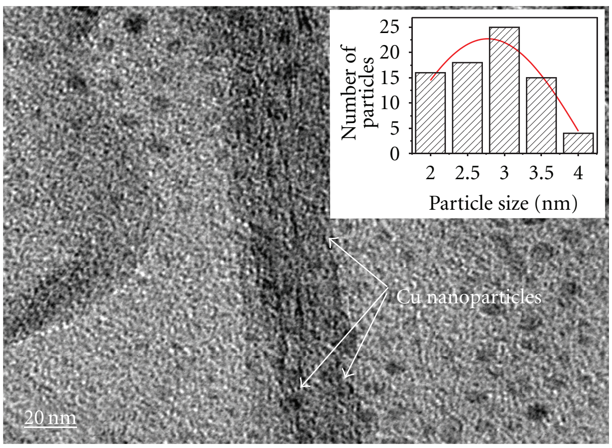

Figure 2: HRTEM micrograph of SWCNT/Cu nanohybrid material; inset shows the particle size distribution of Cu nanoparticles.

350°C and soaking in 6 M HCl overnight, followed by sonication, filtration, and washing thoroughly in deionized water until pH became neutral. Purified SWCNTs were treated with HNO_3/H_2SO_4 in the ratio 1 : 3 and stirred for 36 h. The acid-treated SWCNTs were washed thoroughly with water followed by filtration using Millipore filtration apparatus. Due to acid treatment, carboxylic acid groups were attached to the defect sites of the SWCNTs. To prepare the SWCNT/Cu nanohybrid material, we added 164 mg of Cu (II) nitrate in 40 mL of 2-propanol and sonicated for 2 min using 250 W piezo-U-sonic ultrasonic cleaner. 478 mg of acid-treated SWCNTs was poured to 20 mL of the previous solution and stirred for 30 min using a magnetic stirrer (REMI 2MLH). Simultaneously, to 60 mL 2-propanol, 1000 mg of HTAB was added and stirred for 30 min. 30 mL of the freshly prepared solution was added to the solution containing SWCNTs and stirred for 30 min. The resultant solution was then filtered using Millipore filtration apparatus, washed thoroughly with deionized water, and left for drying at room temperature.

For its nanostructural property study, characterization of the as-prepared sample was done by FESEM (Carl Zeiss Ultra 55) and XRD (Philips PANalytical X-Pert Pro diffractometer with CuKα radiation $\lambda = 0.154056$ nm). The nanostructure of the surfaces of SWCNTs decorated with Cu nanoparticles was confirmed by FESEM micrographs. Composition analysis of the sample was done using EDAX (JEOL JEM 2100). Raman spectra of pristine SWCNT and SWCNT/Cu hybrid structure were recorded to study the effect of the attachment of Cu nanoparticles on SWCNT surfaces. Raman spectroscopy was performed using LABRAM-HR800 Raman spectrometer using 514.5 nm Argon ion laser. To study the optical property of SWCNT/Cu hybrid, the dried sample was dispersed in dimethyl sulfoxide (DMSO) and its optical absorbance characteristics were studied using UV-Vis (Hitachi U-3010) spectrophotometer. Photoluminescence spectra were studied using a Fluorescence spectrophotometer (Perkin Elmer, LS55).

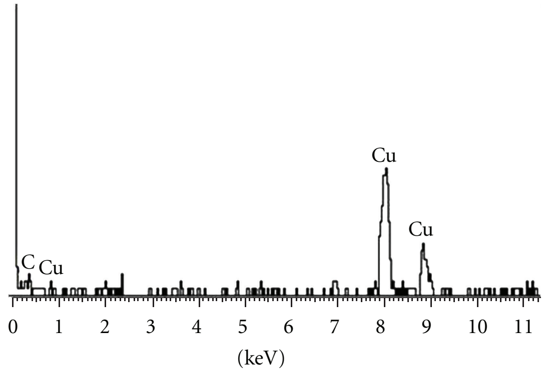

Figure 3: EDAX spectrum of SWCNT/Cu hybrid.

3. Results and Discussions

Figure 1 shows the FESEM micrograph of SWCNT/Cu nanohybrid sample. It is observed that Cu nanoparticles have been attached and uniformly decorated on the surfaces of SWCNT bundles.

The HRTEM micrograph of the hybrid sample is shown in Figure 2. From the micrograph, the average size of the Cu nanoparticles decorating the SWCNT surfaces has been calculated to be 3 nm, using “Sigma Scan Pro 4.0” software. The Gaussian-fitted particle size distribution of Cu nanoparticles is shown in the inset of Figure 2.

The EDAX spectrum of SWCNT/Cu hybrid is shown in Figure 3. The EDAX spectrum clearly indicates the presence of Cu nanoparticles with SWCNTs (C). The absence of oxygen (O) at around 0.5 keV indicates that oxide formation of the metal nanoparticles has not taken place.

Figure 4(a) shows the XRD pattern of pristine SWCNT (i.e., the purified SWCNT) and SWCNT/Cu hybrid structure. The peaks centred at 26°, 42°, and 44° correspond to (0 0 2), (1 0 0), and (1 0 1) reflections, respectively, of the graphitic planes of the SWCNT (JCPDS card no. 75-1621). The XRD pattern of SWCNT/Cu nanohybrid gives the peaks assigned to (1 1 1) and (2 0 0) planes of cubic phase of Cu (JCPDS card no. 04-0836) along with (0 0 2) and (1 0 1) reflections of

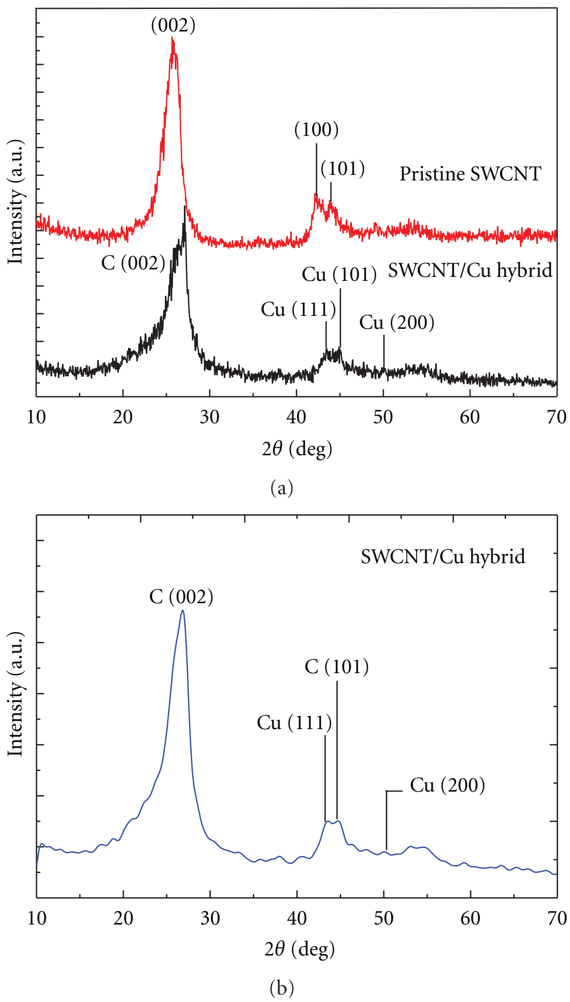

Figure 4: (a) XRD pattern of pristine SWCNT and SWCNT/Cu hybrid. (b) Smoothened XRD pattern of SWCNT/Cu hybrid.

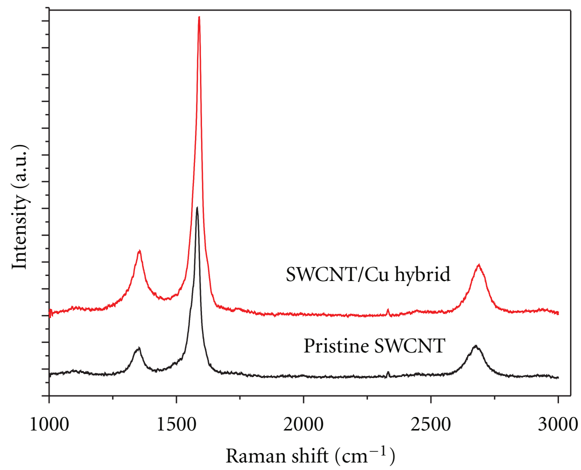

Figure 5: Raman spectra of pristine SWCNT and SWCNT/Cu hybrid.

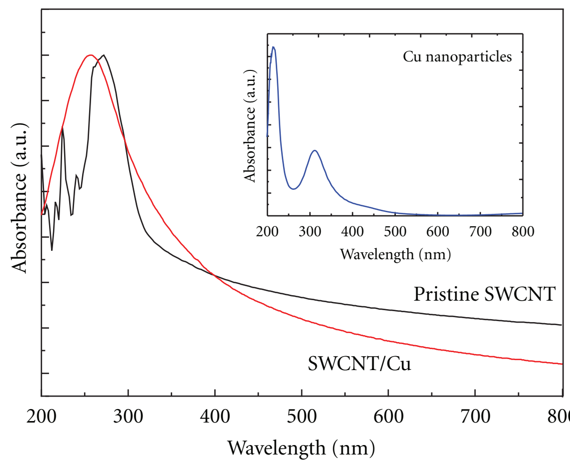

Figure 6: Absorption spectrum of pristine SWCNT and SWCNT/Cu hybrid; inset shows the absorption spectrum of Cu nanoparticles.

the graphitic planes of SWCNTs, excluding the minor peak at 54° which is a noise due to the sample holder. Figure 4(b) shows the smoothened XRD pattern of SWCNT/Cu hybrid. The reflection planes are clearly revealed in this figure. The results thus demonstrate that Cu nanocrystals of cubic face centred (fcc) lattice structure have been attached onto the surfaces of SWCNT bundles.

In Figure 5, the Raman spectra of pristine SWCNT and SWCNT/Cu hybrid have been shown. I_D/I_G factor increased on coating SWCNT bundles with Cu nanoparticles.

I_D/I_G for pristine SWCNT is 0.256, while for SWCNT/Cu hybrid it has been found to be 0.279. This increase in I_D/I_G factor indicates that Cu nanocrystals have adhered to the SWCNT surfaces via chemical bonding [15]. The position of G mode of pristine SWCNT blue shifted from 1,580 to 1,591 cm^{-1} on decorating SWCNT walls with Cu nanoparticles. This blue shift indicates charge transfer between Cu nanoparticles and SWCNT bundles [24–26].

The UV-Vis absorption spectrum of pristine SWCNT and SWCNT/Cu hybrid is shown in Figure 6. The absorption peak position is blue-shifted by 17 nm on decorating Cu nanoparticles onto SWCNT walls. This blueshift may be due to the size effect of Cu nanoparticles. No plasmon absorption band has been recorded for the hybrid sample as reported earlier by several researchers [27].

The inset of Figure 6 shows the absorption spectrum of Cu nanoparticles synthesized separately using similar technique. A prominent plasmon absorption band is observed for Cu nanoparticles in the range of 280–350 nm with peak absorption around 320 nm, which is greatly quenched in the case of SWCNT/Cu nanohybrid material, although appreciable absorption (with peak absorbance around 260 nm) still remains up to little beyond 400 nm. Figure 7 shows the PL emission from the SWCNT/Cu nanohybrid material at varying excitation wavelength from 260 to 300 nm.

The SWCNT/Cu hybrid sample has shown broad PL emission in the range 325–500 nm, when excited by UV radiation of wavelength varying from 260 to 300 nm which falls in the absorption range of the SWCNT/Cu nanohybrid. The emission from the hybrid sample is attributed to

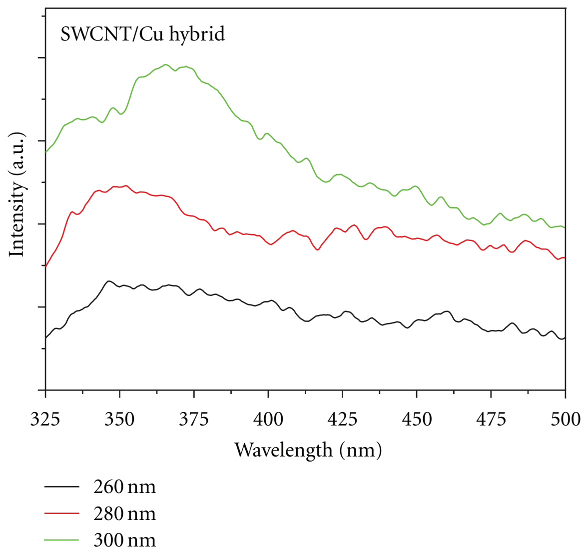

Figure 7: PL emission spectra of SWCNT/Cu hybrid at varying excitation wavelengths.

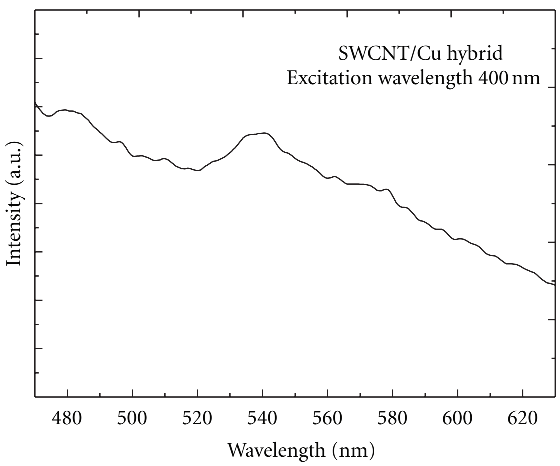

Figure 8: PL emission spectra of SWCNT/Cu hybrid at 400 nm excitation wavelength.

the charge transfer from Cu nanoparticles to SWCNTs. The emission intensity increased with the increase in excitation wavelength. This increase in PL intensity may be because of the fact that the rate of charge transfer from Cu nanoparticles to SWCNT bundles increased with the increase in excitation wavelength. On increasing the excitation wavelength to 400 nm, a broad PL emission spectrum is obtained in the visible range of 480–620 nm, as shown in Figure 8. No noticeable change in emission pattern is observed although the emission intensity is appreciably enhanced. No such emission has been observed with the pristine SWCNT sample.

4. Conclusions

We reported a very simple chemical technique to coat SWCNT surfaces with Cu nanoparticles of average size 3 nm. The samples were characterized for their structural and compositional morphology using microscopy and spectroscopy analyses. The PL emission intensity of the nanohybrid structure increased on increasing the excitation wavelength from 260 to 300 nm and covered a region from 325 to 500 nm in the UV-visible part of the electromagnetic spectrum. When excited by a radiation of 400 nm wavelength, an emission spectrum in the range of 480 to 620 nm was observed with a peak emission around 540 nm. Such CNT/Cu nanohybrid material can find application in photovoltaic and solar energy conversion as well as in sensor devices.

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