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Synthesis and Study of Optical and Electrical Characteristics of Single-wall Carbon Nanotube/Gold Nanohybrid

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Abstract. Au nanoparticles of average size 3.0 nm have been deposited on SWCNT surfaces following a very lucid wet chemical process. The SWCNT/Au nanohybrid material has been characterized using field emission scanning electron microscopy (FESEM), energy dispersive x-ray analysis (EDAX), X-ray diffraction (XRD) study and Raman spectroscopy. Both optical and electrical characteristics of the hybrid sample have been studied. The PL emission intensity of the nanohybrid structure has been found to decrease on increasing the excitation wavelength in the plasmon absorption region. High temperature DC conductivity has increased appreciably when pristine SWCNT is treated with Au NPs. Such SWCNT- supported gold nanoparticles can serve as efficient catalysts in chemical industry. Also the tendency of gold-based nanoparticles to attach with biological molecules may make them useful in medical diagnostics. Increase in conductivity of SWCNT on decorating with Au NPs can find practical application as conducting filler in polymer composites.

Introduction

Carbon nanotubes (CNTs) embedded with noble metal nanoparticles (NPs) present a new class of nanohybrid materials into focus. CNTs when treated with acids, functional groups like carboxyl (–COOH), carbonyl (–C=O) or hydroxyl (–OH) etc. get attached to their surfaces [1, 2] and act as anchoring sites for metal NPs. Noble metal NPs exhibit distinct size dependent optical absorption associated with the excitation of surface plasmons involving the collective oscillation of the free electrons [3, 4]. Researchers made attempts to decorate CNT surfaces with noble metal NPs for application in sensor devices [5], catalysts for fuel cells [6, 7], solar cells [8, 9], hydrogen storage, fillers [10], etc.

Rahman *et al.* [11] synthesized dispersible samples of SWCNTs and MWCNTs by attaching gold NPs on the CNT surfaces by a lengthy chemical process. They observed that surface plasmon band of the hybrid sample was susceptible to variation in NP size, due to changes in electronic structure and strong electronic coupling in the nanohybrid. Biju *et al*. [12] synthesized hybrid samples by conjugating CdSe-ZnS QDs and gold NPs to side walls of functionalized SWCNT templates. They examined the photoluminescence properties of the prepared samples and noticed partial quenching of the PL intensity of the QDs caused by electronic interaction between SWCNTs and the NPs. But their prepared Au NPs had a broad size distribution. Cui *et al*. [13] reported fabrication of gold NP/NT hybrid to construct an electrochemical immune sensor, but could synthesize Au NPs only of size 20 and 40 nm in two different environments. Chu *et al.*[14] developed a method for site-specific deposition of gold NPs on SWCNTs using dip-pen nanolithography (DPN) or electrochemical dip-pen nanolithography (EDPN), thus involving costly equipment. They concluded

that such hybrid materials could find potential applications to fabricate site specific microelectrodes or single electron transistors (SET). Also Chu *et al.*[15] decorated gold NPs on surface-grown SWCNTs for the detection of nanotubes by surface enhanced Raman spectroscopy (SERS). They concluded that the strong SERS enhancement primarily resulted from the resonance between the optical field and electronic excitation in gold. Choi *et al.*[16] demonstrated a direct reduction route for depositing Au-NPs on SWCNTs, in which Au-NPs were spontaneously reduced on the surface of SWCNTs by immersing the CNTs into a solution containing Au^{3+} ions. But they obtained larger Au nanoparticles of average size 7 nm, and the Au-NPs produced using this technique had a broad size distribution. Shi *et al.* [17] adopted the citrate reduction technique to decorate SWCNTs with well dispersed Au NPs and observed significant catalytic activity of the samples in oxygen reduction reaction. However, the size of the Au-NPs deposited on the SWCNTs was relatively large (> 9 nm). Thus the synthesis, characterization and study of useful properties of SWCNTs decorated with exceedingly small (2-3 nm) monodispersed Au nanocrystals by cost-effective simple chemical route is a challenging task, and needs further investigation. Here we report a simple wet chemical technique to prepare SWCNT/Au nanohybrid material. Optical as well as electrical characteristics of the samples have been systematically studied. The proposed mechanism of synthesis of SWCNT/Au nanohybrid is:

$$CNT/[4HAuCl_4+6H_2O+4C_6H_5Na_3O_7] \rightarrow CNT/[4Au+12NaCl+4HCl+4C_6H_8O_7+3O_2]$$

where $HAuCl_4$: chloroauric acid, $C_6H_5Na_3O_7$: trisodium citrate.

Experimental

350 mg of procured SWCNTs (1–2-nm outer diameter, length: 1–3 μm and purity > 95%) from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences were further purified following a chemical process. Purified SWCNTs were then treated with HNO_3/H_2SO_4 in the ratio 1:3 and stirred for 23 h. The acid-treated SWCNTs were then washed thoroughly with water followed by filtration using Millipore filtration apparatus.

33.6 mg of $HAuCl_4$ was added to 90 ml of de-ionized water and stirred at 100 ^oC for 30 min. SWCNTs were then added to 45 mL of $HAuCl_4$ solution and stirred at 80 ^oC for 30 min. Simultaneously, 1548 mg of trisodium citrate (reducing agent) was added to 60 mL of de-ionized water and stirred at 100^o C for 30 min. 30 mL of citrate solution was then added to the dispersion containing SWCNT and stirred at 80^o C for 30 min. The resultant dispersion was then filtered using Millipore filtration apparatus and the product powder was dried at room temperature. The hybrid structure was revealed in the FESEM (Carl Zeiss Ultra 55) micrograph. Compositional analysis of the samples was done by energy dispersive x-ray analysis (EDAX). XRD patterns were obtained using Philips PANalytical X-Pert Pro diffractometer. Raman spectroscopy was performed using LABRAM-HR800 Raman spectrometer with 514.5 nm Argon ion laser. To study the optical properties, the dried samples were dispersed separately in dimethyl sulfoxide (DMSO) and their optical absorbance spectra were observed using UV–visible (HITACHI U-3010) spectrophotometer. Photoluminescence spectra of the samples were studied using FL spectrofluorimeter (HITACHI F-2500) over a wide range of excitation wavelengths from 220 to 550 nm. For electrical conductivity measurements, circular pellets of uniform thickness were made out of the powder samples using a hydraulic press. Applying silver paste, two copper wires were attached to the either side of the pellet to measure its DC conductivity using 6514 Keithley Electrometer by two-probe method.

Results and discussion

Fig. 1 shows the FESEM micrograph of SWCNT/Au nanohybrid material. Here we can see the long strands of SWCNT bundles with uniformly coated Au NPs. Using FESEM micrograph and ‘Sigma Scan Pro 4.0’ software, the average particle size of the Au NPs has been calculated to be 3.0 nm.

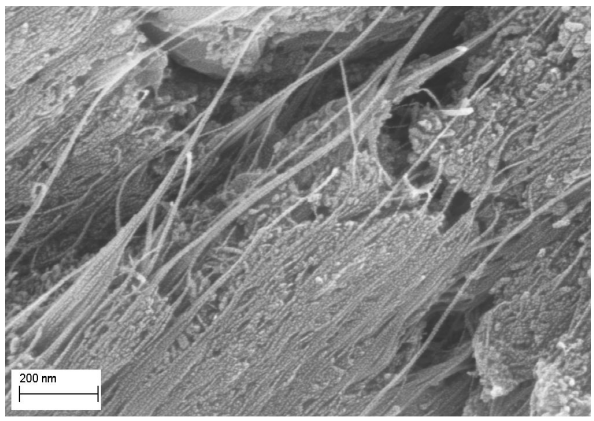

Fig. 1 FESEM micrograph of SWCNT/Au nanohybrid.

The EDAX spectrum of the hybrid sample is shown in Fig. 2. The presence of Au with SWCNTs (C) is clearly revealed in the figure. Si and O are due to the glass substrate on which the film of the hybrid material has been deposited. The inset shows the Gaussian fitted particle size distribution of Au NPs decorating the SWCNT bundles.

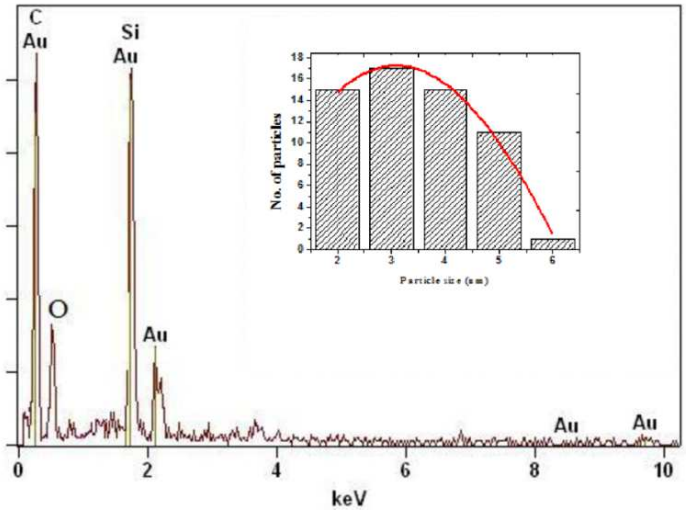

Fig. 2 EDAX spectrum of SWCNT/Au nanohybrid; inset shows the particle size distribution of the Au NPs.

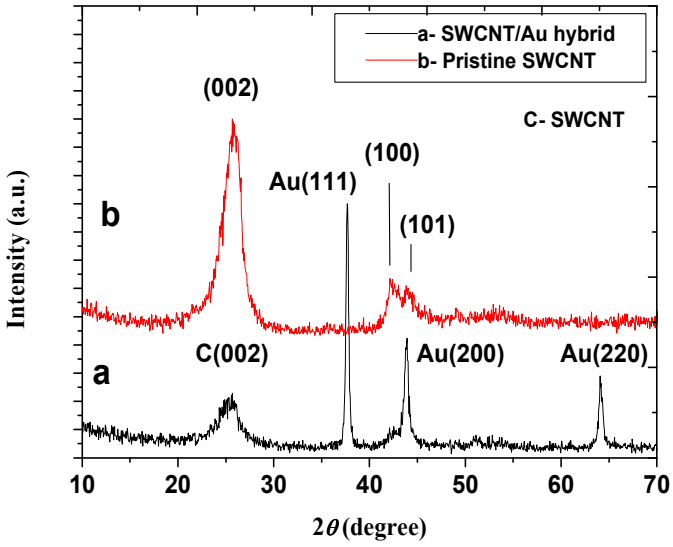

Fig. 3 XRD pattern of pristine SWCNT and SWCNT/Au nanohybrid.

Fig. 3 shows the XRD pattern of pristine SWCNT and SWCNT/Au nanohybrid. The peaks centered at 26°, 42° and 44° correspond to (0 0 2), (1 0 0) and (1 0 1) reflections, respectively, of graphitic planes of the CNTs (JCPDS card no.75-1621). The peaks centered at 38°, 44° and 64° correspond to (1 1 1), (2 0 0) and (2 2 0) reflections, respectively, of planes of the cubic phase of Au (JCPDS card no. 00-004-0784). The Raman spectrum of pristine SWCNT and SWCNT/Au nanohybrid is shown in Fig. 4. The I_D/I_G value of the hybrid sample has been calculated to be 0.388 whereas the value is 0.246 for the pristine SWCNT. This increase in I_D/I_G value (ratio of the intensities of the D-band peak to G-band peak) indicates the attachment of the Au nanocrystals on the SWCNT surfaces via chemical bonding. The position of G mode of pristine SWCNT blue shifted from 1580 to 1594 cm^{-1} on decorating SWCNT walls with Au NPs. This blue shift indicates charge transfer and electronic interaction between Au NPs and SWCNT bundles [3, 18-20].

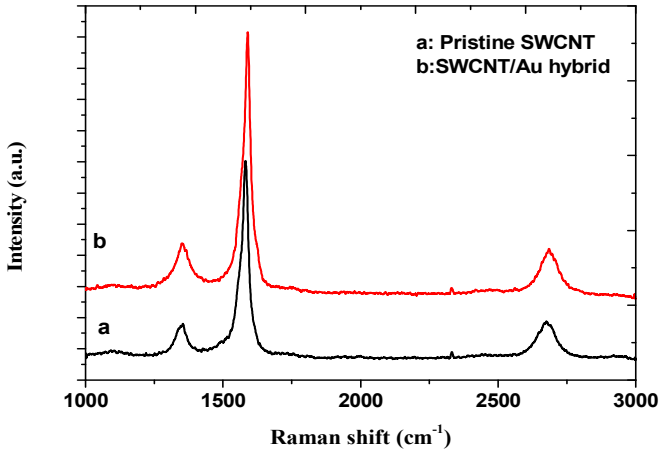

Fig. 4 Raman spectrum of pristine SWCNT and SWCNT/Au nanohybrid.

Fig. 5 shows the absorption spectrum of pristine SWCNT and SWCNT/Au nanohybrid. For both the pristine and hybrid samples, the absorption peaks are obtained around 279 nm. The inset shows absorption spectrum of as prepared Au colloidal solution which has been synthesized separately using similar technique. The peak around 520 nm is observed due to SPR absorption of Au NPs.

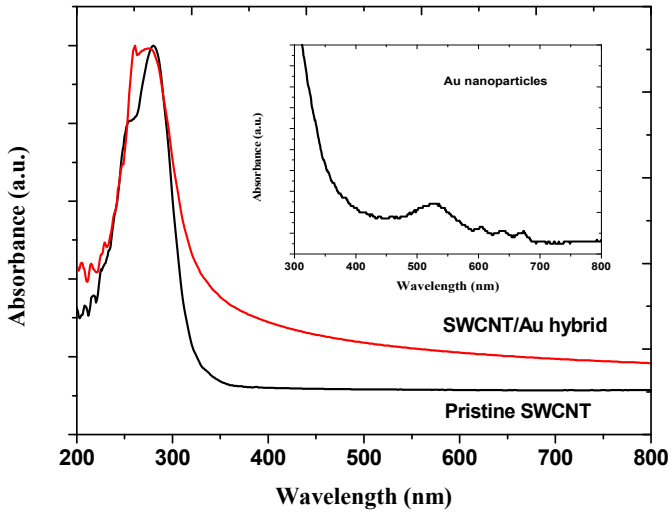

Fig. 5 UV-vis absorption spectrum of pristine SWCNT and SWCNT/Au nanohybrid; the inset shows the absorption spectrum of as prepared Au colloidal solution.

The SWCNT/Au nanohybrid sample has not shown any plasmon absorption hump for Au NPs, due to complete utilization of gold source in the dispersion [17] and masking of Au SPR absorption band in the nanohybrid.

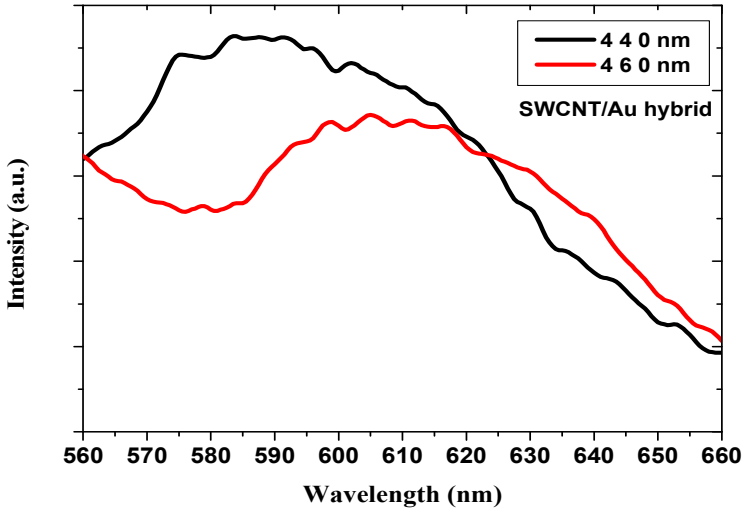

Fig. 6 PL emission spectra of SWCNT/Au hybrid at excitation of 440 nm and 460 nm.

Photoluminescence (PL) emission spectra of SWCNT/Au nanohybrid at plasmon absorption excitation wavelength is shown in Fig. 6. PL emission has been studied in the 220-520 nm excitation wavelength range, but the SWCNT/Au nanohybrid sample has not shown any significant emission except when excited with the plasmon absorption wavelengths. Thus, the PL obtained is attributed to the plasmon emission of the Au NPs only and no significant change in emission pattern is observed due to hybridization and charge transfer although there is some quenching of the emission intensity.

The DC conductivity of pristine SWCNT and SWCNT/Au nanohybrid with varying temperature of 303 K to 473 K is shown in Fig. 7. On treating Au NPs to SWCNT surfaces, the conductivity of SWCNT has appreciably increased.

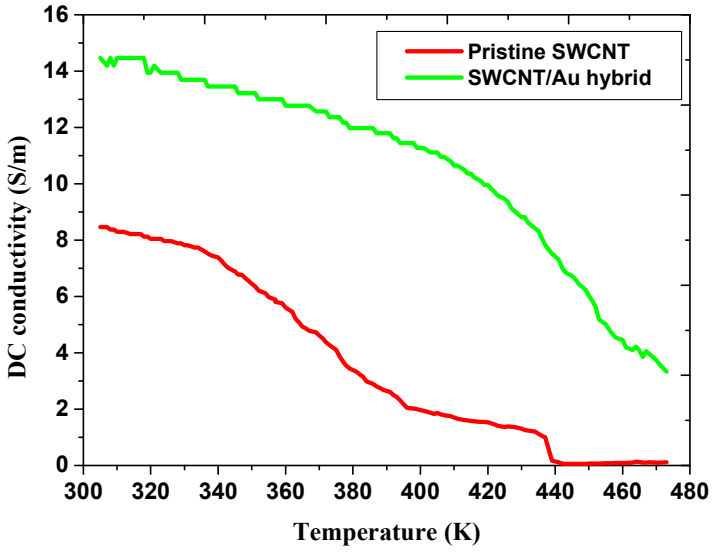

Fig. 7 DC conductivity of pristine SWCNT and SWCNT/Au nanohybrid with varying temperature of 303 K to 473 K.

High temperature DC conductivity measurement of the SWCNT/Au nanohybrid samples from 303-473 K showed the total metal-like temperature dependence of conductivity. The increase in electrical conductivity is attributed to the influence of Au NPs.

Conclusions

Using a very simple wet chemical technique, Au NPs of average size of 3.0 nm have been attached onto SWCNT surfaces. The PL emission intensity of the nanohybrid decreased on increasing the excitation wavelength in the plasmon absorption region. High temperature DC conductivity increases appreciably when pristine SWCNT is treated with Au NPs. High temperature DC conductivity measurement from 300-473 K showed a metal-like temperature dependence. Such SWCNT/Au nanohybrid material may find application in industrial catalysis, medical diagnostics and in fabrication of polymer composites using functionalized carbon nanotubes.

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