Violet-Blue Emission from TiO_2/SWNT Hybrid Synthesized Following a Very Simple Technique

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ABSTRACT

Modification of CNT surfaces by hybridization with other nanostructures can drastically change their physical properties and transform them into useful functional nanomaterials. We report here a chemical precipitation process to synthesize a heterostructure of single walled carbon nanotubes (SWNT) and TiO_2 nanoparticles of average size 5 nm. The hybrid structure is characterized by high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDAX), powder X-ray diffractometry (XRD) and Raman spectroscopy. It is clearly revealed that titania nanocrystals of anatase phase and of nearly uniform size are attached to the surfaces of SWNT bundles. The UV-vis absorption study shows a blue shift of 16 nm in the absorbance peak position of the hybrid structure with respect to the pristine SWNT. The photoluminescence study shows violet-blue emission in the range 325-500 nm with peak emission at around 400 nm.

Keywords: SWNT, titania, nanohybrid, photoluminescence

1 INTRODUCTION

The carbon nanotube (CNT) since its discovery in the year 1991[1], has been continuously drawing attention of the researchers due to its fascinating physical and chemical properties [2]. The modification of the CNTs by surface functionalization and hybridization with other nanostructures can drastically change their physical properties to transform them into functional nanomaterials with desired properties and can find several novel applications in useful devices. Hybridizing semiconductor nanoparticles on CNT surfaces can modify their optical absorption and luminescence properties significantly and such composites have been used to tailor light-emitting diodes [3], to organize sensor systems and to fabricate electrochromic devices [4]. TiO_2 is one of the most investigated semiconductor which finds demanding applications related to semiconductor photocatlysts [5-7], optical devices [8], gas sensors [9] and solar cells [10]. The photocurrent or photochemical efficiency of TiO_2 is greatly influenced by its crystal structure, particle size, surface area and porosity [11]. The design and development of highly efficient photocatalytic composites have attracted the interest owing to their potential application for the degradation of toxic organic dyes and industrial effluents. CNTs can be used as catalytic support materials due to their high aspect ratio and their ability to disperse catalytically active metal particles [12]. There are several techniques to decorate CNT walls with TiO_2. Here we report one of the easiest methods to prepare TiO_2/SWNT hybrid. The hybrid material showed violet-blue emission at excitation wavelength of 250 nm and may find applications in sensor based devices. Also, the hybrid structure may render it useful for catalysis applications.

2 EXPERIMENTAL DETAILS

We procured SWNTs (1-2 nm outer diameter, length: 1-3 μm and purity > 95%) from Chengdu Organic Chemicals Co., Ltd. Chinese Academy of Sciences and further purified them by high temperature oxidation, acid treatment, ultrasonication, pH control and filtration [13]. To obtain TiO_2/SWNT hybrid structure, 30 mg of purified SWNT was taken in 20 ml of $TiCl_3$ and stirred using a magnetic stirrer (REMI 2MLH) for 10 min. 4.8M of NH_4OH solution was then added drop wise to the solution containing SWNT till pH became 7 and again stirred for 18 h using magnetic stirrer. The product colloidal solution was centrifuged for 15 min at rpm 6000 at 9^{o}C. The precipitate was then washed thoroughly with de-ionized water followed by 2-propanol and left for drying at room temperature. We also synthesized TiO_2 nanoparticles following similar method. For our experiments, chemicals from Merck (GR grade) were used at room temperature and without further purification.

The prepared samples were then characterized for their nanostructural as well as compositional properties. The hybrid structure was revealed in the HRTEM (JEOL JEM 2100, operating voltage 200 KV) micrograph. SEM and EDAX spectroscopy (HITACHI S 3000N) were used for compositional analysis of the samples. XRD patterns were obtained using Philips PANalytical X-Pert Pro diffractrometer. Raman spectroscopy was performed using TRIAX550 JY Horiba USA (provided with edge filter and a CCD detector). Argon ion laser of wavelength 488 nm was used as excitation source.

To study the optical properties, the dried samples were dispersed separately in sodium dodecyl sulfate (SDS) solution and their optical absorbance spectra were observed using UV-visible (HITACHI U-3010) spectrophotometer. Photoluminescence (PL) spectrum of the samples were studied using FL spectrofluorimeter (HITACHI F-2500) over a wide range of excitation wavelength from 220-400 nm.

3 RESULTS AND DISCUSSIONS

The HRTEM micrograph of TiO_2/SWNT hybrid is shown in figure 1. The micrograph clearly reveals that TiO_2 nanocrystals adhered uniformly onto the SWNT surfaces. The inset shows the particle size histogram of the TiO_2 nanocrystallites. The average size of TiO_2 nanocrystals is found to be 5 nm as obtained by fitting the particle size distribution from HRTEM micrograph.

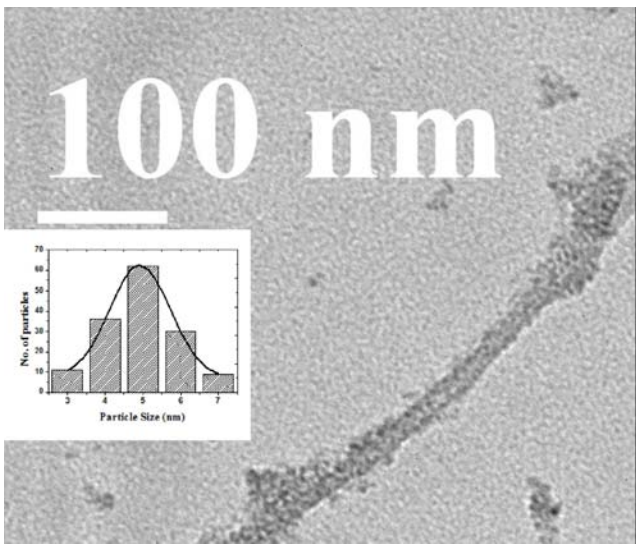

Figure 1: HRTEM micrograph of TiO_2/SWNT hybrid; inset shows the particle size distribution of TiO_2 nanocrystals.

Figure 2 shows the EDAX spectrum of TiO_2/SWNT hybrid.

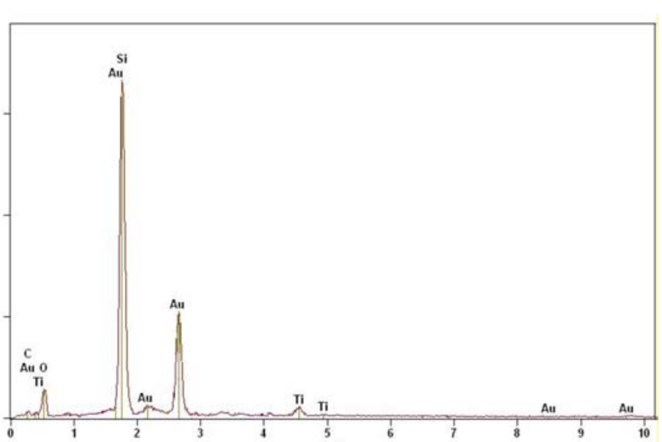

Figure 2: EDAX spectrum of TiO_2/SWNT hybrid

From the spectrum, the presence of titanium (Ti) and oxygen (O) with carbon (C) of SWNT are confirmed.

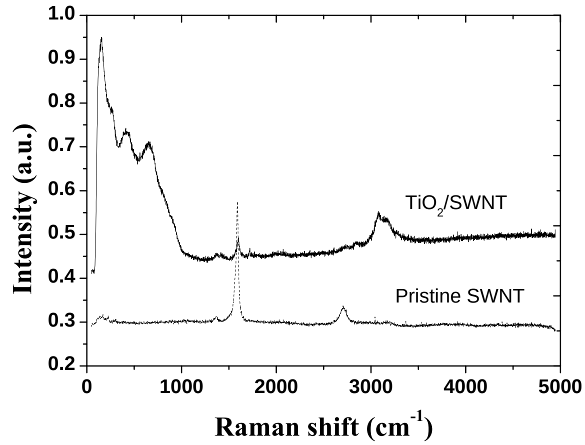

Figure 3: Raman spectrum of pristine SWNT and TiO_2/SWNT hybrid.

Figure 3 shows the Raman spectrum of pristine SWNT and that of TiO_2/SWNT hybrid. Additional peaks in the range 150-700 cm^{-1} of the hybrid sample are found which indicate that radial breathing mode (RBM) of SWNT has been influenced on decorating SWNT walls with TiO_2 nanocrystals. There is an up-shift by 12 cm^{-1} in the position of G band indicating charge transfer to SWNTs from TiO_2 nanocrystals. This type of up-shift of G band upon modification of CNT surfaces has been reported earlier by several authors [14, 15]. I_D/I_G for pristine SWCNT is 0.546 while that for TiO_2/SWNT hybrid has been found to be 0.939. This increase in I_D/I_G factor indicates that TiO_2 nanocrystals adhered to the SWCNT surfaces via chemical bonding. Figure 4 shows the XRD pattern of pristine SWNT and TiO_2/SWNT hybrid. For pristine SWNT, the peaks centered at 26°, 42° and 44° correspond to (002),

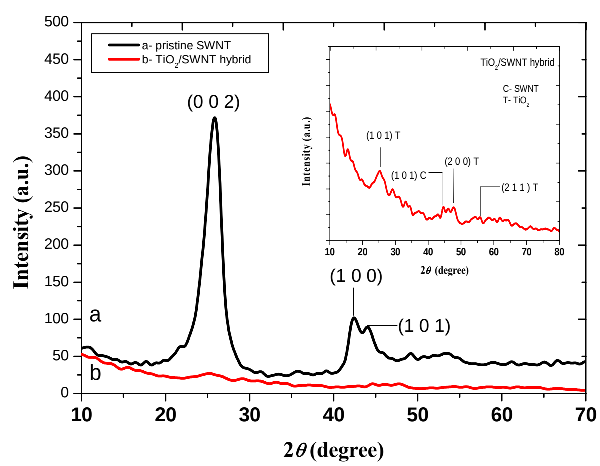

Figure 4: XRD pattern of pristine SWNT and TiO_2/SWNT hybrid

(100) and (101) reflections of graphitic planes from the SWNTs respectively (JCPDS card no. 75-1621). The XRD pattern of TiO_2/SWNT heterostructure gives the peak assigned to (101), (200) and (211) planes of the anatase phase of TiO_2. These are in good agreement with the reported data for TiO_2 (JCPDS card no. 21-1272). Moreover, the hybrid structure also shows the (101) reflection from SWNT surface. The inset of figure 4 shows the magnified image of the XRD pattern of the hybrid structure. The absorption spectra of pristine SWNT and TiO_2/SWNT nanostructure is shown in figure 5. The absorption peak position blue shifted by 16 nm from 264 nm to 248 nm on decorating SWNT walls with TiO_2 nanocrystals and this may also affect the catalytic properties of TiO_2/SWNT nanostructure [16], making their possible use in catalysis applications.

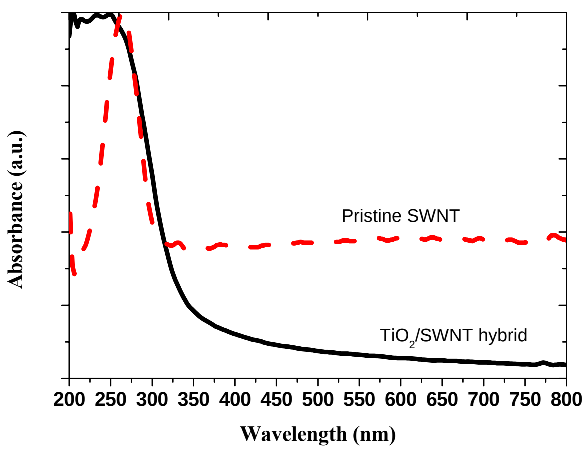

Figure 5: Absorption spectra of pristine SWNT and TiO_2/SWNT hybrid.

Figure 6 shows the photoluminescence spectrum of pristine SWNT and TiO_2/SWNT hybrid at 250 nm excitation wavelength. The hybrid structure showed violet-blue emission when excited by UV radiation of wavelength 220-260 nm. Beyond 260 nm excitation wavelength, no considerable photoluminescence has been observed. The spectrum covered a region from 325-500 nm with the peak position at around 400 nm. The pristine SWNT sample showed no luminescence in this region. The photoluminescence emission of the hybrid structure is attributed to the charge transfer between titania nanocrystals and carbon nanotubes.

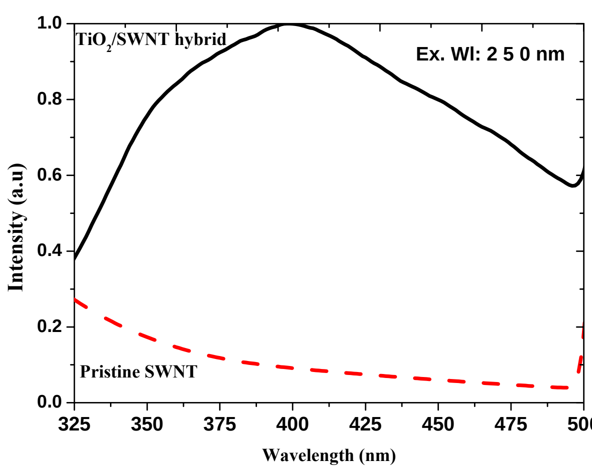

Figure 6: Photoluminescence spectra of pristine SWNT and TiO_2/SWNT hybrid at 250 nm excitation wavelength.

4 CONCLUSIONS

We reported a simple wet chemical process to synthesize a nanohybrid structure of SWNT and TiO_2 nanoparticles. Titania nanocrystals of average size of 5 nm uniformly decorated the walls of the SWNT bundles and the composite exhibited distinct optical properties, distinguished from individual components. A broad luminescence in the visible region in the range of 325-500 nm was observed which could be attributed to the charge transfer between the titania nanocrystals and SWNTs. This hybrid structure can find application as an useful optical material.

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