

Visible Photoluminescence Emission from Chemically Synthesized MWCNT/TiO₂ Hybrid Nanostructure

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ABSTRACT

TiO₂ nanoparticles of average size 3.5 nm have been attached to multi-walled carbon nanotubes (MWCNTs) following a very simple wet chemical process. The hybrid structure has been characterized by high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDAX), powder X-ray diffractometry (XRD), Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy. The photoluminescence (PL) study shows violet emission from the MWCNT/TiO₂ hybrid material in the range 325-500 nm with peak emission around 400 nm, which is absent in the case of pristine MWCNT. The PL emission has been obtained for 220-270 nm UV excitation wavelength and can be attributed to the charge transfer between TiO₂ nanocrystals and MWCNTs.

Keywords: MWCNT, TiO₂, nanohybrid, photoluminescence

1 INTRODUCTION

Modification of carbon nanotube (CNT) surfaces with organic, inorganic and biological compounds can significantly influence their physical properties and yield novel materials for potential applications [1]. As semiconducting nanomaterials are capable of emitting and/or absorbing light and possess fascinating optical properties [2, 3], attaching semiconductor nanocrystals onto the CNT surfaces can modify their optical characteristics and luminescent properties significantly. The combined properties of two functional nanoscale materials can stimulate a wide range of applications [4, 5]. TiO₂ nanocrystals find demanding applications related to semiconductor photocatalysts [6-8], optical devices [9], gas sensors [10] and solar cells [11]. On the other hand, CNTs can be used as catalytic support materials due to their high aspect ratio and their ability to disperse catalytically active metal particles [12]. Authors here report a simple wet chemical technique to coat MWCNT surfaces with TiO₂ nanocrystals. The synthesized MWCNT/TiO₂ hybrid

nanomaterial exhibited violet emission in the range of 325-500 nm with peak emission around 400 nm. This type of hybrid material can be utilized in several optoelectronic devices that extend from nanotube based sensors to solar energy conversion. Moreover, the hybrid structure may render it useful for catalytic applications.

2 EXPERIMENTAL DETAILS

The procured MWCNTs were purified through acid treatment, washed with water and ethanol and eventually dried under infrared (IR) lamp. 12 mg of purified MWCNT was taken in 20 ml of TiCl₃ and stirred using a magnetic stirrer (REMI 2MLH) for 10 min. 4.8M NH₄OH solution was then added drop wise to the solution containing MWCNT till the pH became 7 and further stirred for 18 h. The product colloidal solution was centrifuged for 15 min at rpm 4500 at 5°C. The precipitate was then washed thoroughly with de-ionized water followed by 2-propanol and left for drying at room temperature. TiO₂ nanoparticles were also synthesized following similar method. Chemicals from Merck (GR grade) were used throughout, at room temperature and without any further purification.

The prepared samples were characterized for their nanostructure and compositional properties, using microscopy and spectroscopy analyses. The hybrid structure was revealed in the HRTEM (JEOL JEM 2100, operating voltage 200 KV) and SEM (HITACHI S 3000N) micrographs. EDAX (HITACHI S 3000N) and FTIR (Nicolet iS10) were used for compositional analysis of the samples. XRD patterns were obtained using Philips PANalytical X-Pert Pro diffractometer. 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.

The dried samples were dispersed in sodium dodecyl sulphate (SDS) solution to study their optical properties using UV-vis (HITACHI U-3010) spectrophotometer and FL spectrofluorimeter (HITACHI F-2500).

3 RESULTS AND DISCUSSIONS

Figure 1 shows the HRTEM micrograph which clearly reveals that TiO₂ nanocrystals are uniformly coated on the MWCNT surfaces. The inset shows the TiO₂ nanoparticles size distribution histogram. It has been calculated that TiO₂ nanoparticles of average size 3.5 nm decorated the MWCNT walls.

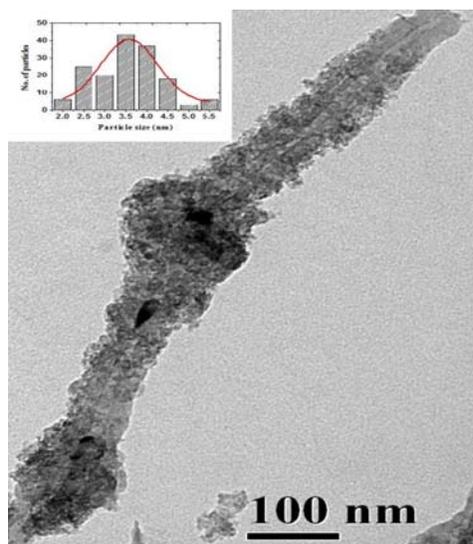


Figure 1: HRTEM micrograph of MWCNT/TiO₂ hybrid; inset shows the particle size distribution of the TiO₂ nanoparticles.

Figure 2 shows the EDAX spectrum of the MWCNT/TiO₂ hybrid material. In the inset, the SEM micrograph of the hybrid material has been shown. From the EDAX spectrum, the presence of titanium (Ti) and oxygen (O) with carbon (C) of MWCNT are confirmed. Si is due to glass substrate on which the film of the sample has been deposited and Au, due to gold coating of the film.

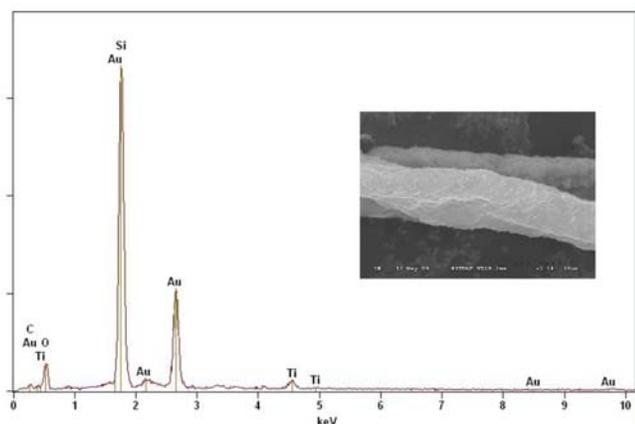


Figure 2: EDAX spectrum of MWCNT/TiO₂ hybrid; inset shows the SEM micrograph of the hybrid material.

Figure 3 shows the FTIR spectrum of pristine MWCNT and MWCNT/TiO₂ hybrid. The Ti-O bonding is confirmed from the stretch in the region 470-500 cm⁻¹ [12]. Stretches at 1630 and in the range 3173-3377 cm⁻¹ are deformation vibrations and stretching vibrations of H₂O, respectively, originated from the absorption of water by KBr matrix [13]. Stretch in the range 1400- 1600 cm⁻¹ is due to C=O bonding mode.

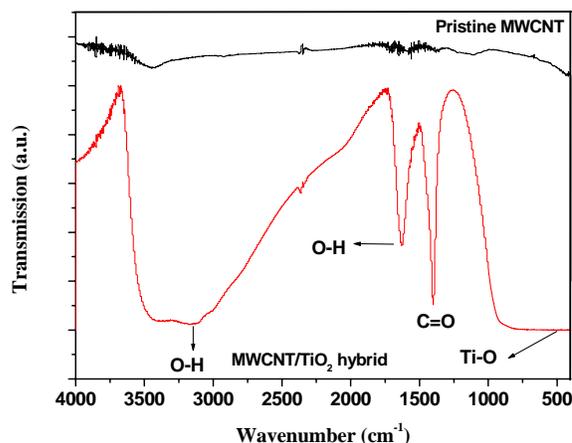


Figure 3: FTIR spectrum of pristine MWCNT and MWCNT/TiO₂ hybrid.

The Raman spectrum of pristine MWCNT and MWCNT/TiO₂ hybrid is shown in Figure 4. The peaks at 150, 414 and 638 cm⁻¹ of the hybrid sample correspond to the characteristic signal of anatase phase of TiO₂ [14].

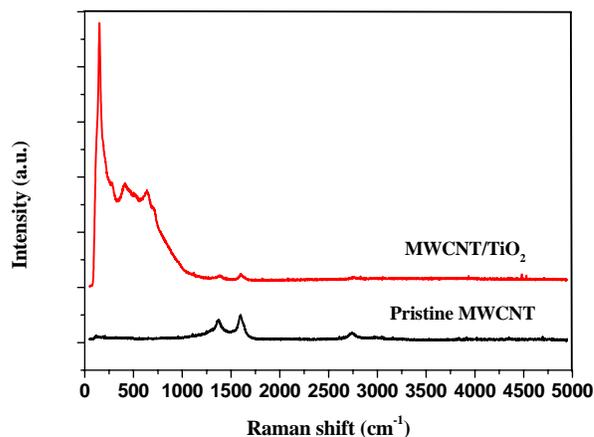


Figure 4: Raman spectrum of pristine MWCNT and MWCNT/TiO₂ hybrid.

There is an up-shift by 6 cm⁻¹ in the position of G band indicating charge transfer to MWCNTs from TiO₂ nanocrystals. This type of up-shift of G band upon modification of CNT surfaces has been reported earlier by several authors [15, 16]. Figure 5 shows the XRD pattern of MWCNT/TiO₂ hybrid material. The XRD pattern of

MWCNT/TiO₂ nanostructure gives the peaks assigned to (101), (200) and (211) planes of the reported data for TiO₂ (JCPDS card no. 21-1272) for its anatase phase.

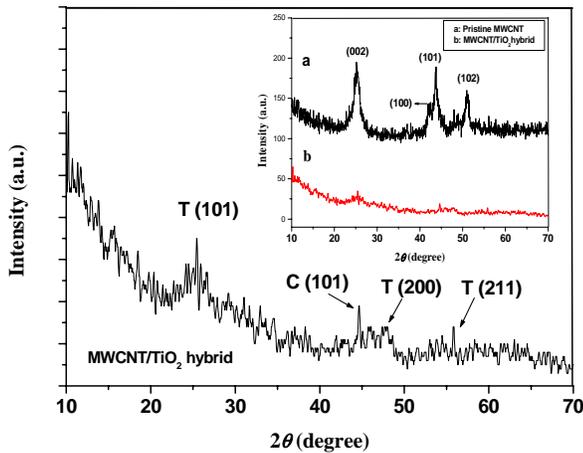


Figure 5: XRD pattern of MWCNT/TiO₂ hybrid ; inset shows XRD pattern of pristine MWCNT and MWCNT/TiO₂ hybrid.

Moreover, the hybrid structure also shows the (101) reflection from MWCNT surface. The inset of Fig. 5 shows the XRD pattern of both pristine MWCNT and MWCNT/TiO₂ hybrid structure. For MWCNT, the peaks centered at 26°, 42°, 44° and 50° correspond to (0 0 2), (1 0 0), (1 0 1) and (1 0 2) reflections of the graphitic planes of the CNTs respectively (JCPDS card no. 75-1621). The UV-vis absorbance spectrum of the samples is shown in Figure 6.

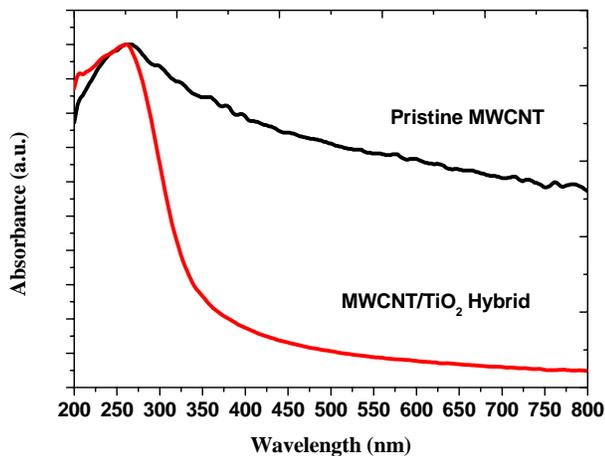
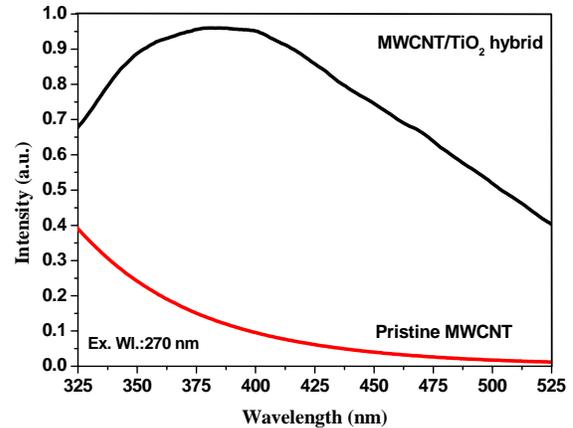
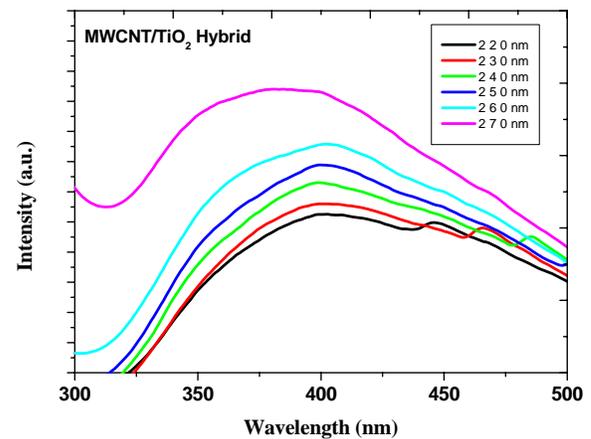


Figure 6: UV-vis absorbance spectrum of pristine MWCNT and MWCNT/TiO₂ hybrid.

The absorption peak position blue shifts by 5 nm from 267nm to 262 nm on decorating MWCNT walls with TiO₂ nanocrystals. This may affect the catalytic properties of MWCNT/ TiO₂ nanostructure [17], making way for their catalytic applications.



(a)



(b)

Figure 7: (a) PL spectrum of pristine MWCNT and MWCNT/TiO₂ hybrid at 270 nm excitation wavelength (b) PL spectrum of MWCNT/TiO₂ hybrid at excitation of 220-270 nm.

Figure 7 (a) shows the PL emission spectrum of pristine MWCNT and MWCNT/TiO₂ hybrid at 270 nm excitation wavelength. The hybrid structure showed violet emission when excited by UV radiation of wavelength 220-270 nm. Beyond 270 nm excitation wavelength, no considerable photoluminescence has been observed. Figure 7 (b) shows photoluminescence spectra of MWCNT/ TiO₂ hybrid at different excitation wavelength from 220-270 nm. With the increase of excitation wavelength, the PL emission

intensity increases. The spectrum covered a region from 325-500 nm with the peak position around 400 nm. The pristine MWCNT sample showed no luminescence in this region. The PL emission of the hybrid structure is attributed to the charge transfer between TiO₂ nanocrystals and MWCNTs. When excited by lower excitation wavelengths and hence higher energy photons, transition of electrons from TiO₂ to MWCNTs takes place, but these highly energetic electrons transit instantly thereby causing emission. The number of electrons taking part in the transition process increases and hence increases the PL intensity [18].

4 CONCLUSIONS

Authors reported a simple chemical technique to prepare MWCNT/TiO₂ nanostructures, where TiO₂ nanocrystals of average size 3.5 nm very beautifully decorated MWCNT surfaces. Visible violet photoluminescence emissions have been observed from the hybrid nanostructure, when excited by UV radiation in the range of 220-270 nm. The luminescence is proposed to be due to the charge transfer between TiO₂ nanocrystals and MWCNTs. This nanohybrid may find application as an optical material in optoelectronics or as a photocatalytic material.

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