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A facile chemical synthesis of a novel photo catalyst: SWCNT/titania nanocomposite

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Abstract. A simple chemical precipitation technique is reported for the synthesis of a hybrid nanostructure of single-wall carbon nanotubes (SWCNT) and titania (TiO_2) nanocrystals of average size 5 nm, which may be useful as a prominent photocatalytic material with improved functionality. The synthesized hybrid structure has been characterized by transmission electron microscopy (HRTEM), energy-dispersive X-ray analysis (EDAX), powder X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. It is clearly revealed that nearly monodispersed titania nanocrystals (anatase phase) of average size 5 nm decorate the surfaces of SWCNT bundles. The UV-vis absorption study shows a blue shift of 16 nm in the absorbance peak position of the composite material compared to the unmodified SWCNTs. The photoluminescence study shows a violet-blue emission in the range of 325-500 nm with a peak emission at 400 nm. The low temperature electrical transport property of the synthesized nanomaterial has been studied between 77-300 K. The DC conductivity shows semiconductor-like characteristics with conductivity increasing sharply with temperature in the range of 175-300 K. Such nanocomposites may find wide applications as improved photocatalyst due to transfer of photo-ejected electrons from TiO_2 to SWCNT, thus reducing recombination, with the SWCNT scaffold providing a firm and better positioning of the catalytic material.

Keywords: SWCNT; titania; photoluminescence; DC conductivity; photocatalytic material

1. Introduction

The processing of carbon nanotubes (CNTs) by surface modification and hybridization with other nanostructures can drastically change their physical properties and transform them into novel functional materials which may find applications in useful devices. Hybridizing semiconductor quantum dots on CNT surfaces can modify their optical absorption and luminescence characteristics significantly and such hybrids have been used to tailor light-emitting diodes (Tessler *et al.* 2002), to organize sensor systems and to fabricate electrochromic devices (Bechinger *et al.* 1996). TiO_2 is one of the most investigated semiconducting material which finds demanding applications as a semiconductor photocatalyst (Anderson *et al.* 2002, Sung and Lee

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2004, Sung *et al.* 2006), as well as in optical devices (Appell 2002), gas sensors (Rothschild *et al.* 2003) and solar cells (Park *et al.* 2000). The photocurrent or photochemical efficiency of TiO_2 is greatly influenced by its crystal structure and phase, particle size, surface area and porosity (Lee *et al.* 2006). The design and development of highly efficient photocatalytic materials is of interest because of 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 (Byrappa *et al.* 2008). Recently, attention has been focused on remarkable enhancement in electrical properties of CNT- based composites (Barrau *et al.* 2003). TiO_2 has excellent transparency to visible light due to its wide forbidden bandgap. But its electrical conductivity at room temperature is less than 1 $(\Omega\ \text{cm})^{-1}$ (Diebold 2003, Yildiz *et al.* 2007) and its photocatalytic activity is limited by the photo ejected electrons getting lost due to recombination. A TiO_2–SWCNT composite reduces recombination and enhances photocatalytic ability. Earlier (Kongkanand *et al.* 2007) dispersed titanium dioxide nanoparticles on SWCNT films to improve photoinduced charge separation and transport of carriers. (Kalbac *et al.* 2007) deposited electrochemically TiO_2 nanocrystals of average size 8 nm on SWCNTs and studied their application in Li-ion batteries. But we propose a simpler chemical route to prepare the desired nanocomposite.

We report a wet chemical method to prepare the hybrid nanostructure of SWCNT and TiO_2 nanoparticles. The hybrid material shows interesting optical properties with violet-blue emission under UV excitation. The electrical transport property of the hybrid material is studied in the temperature range of 77-300 K with DC conduction showing semiconductor-like behavior. This nanocomposite may act as an improved photocatalytic material.

2. Experimental

We procured SWCNTs (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 (Suri *et al.* 2008). To prepare TiO_2/SWCNT nanohybrid, 30 mg of purified SWCNT was taken in 20 ml of $TiCl_3$ and stirred using a magnetic stirrer (REMI 2MLH) for 10 min. 4.8M NH_4OH solution was then added drop wise to the solution containing SWCNT 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°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. In our experiments, chemicals from Merck (GR grade) were used at room temperature and without further purification.

The prepared samples were characterized for their nanostructural as well as compositional properties. The hybrid structure was revealed in the high resolution transmission electron microscope (HRTEM) (JEOL JEM 2100, operating voltage 200 KV) micrograph. Energy dispersive X-ray analysis (EDAX) using HITACHI S 3000N and Fourier transform infrared spectroscopy (FTIR) using Nicolet iS10 were used for compositional analysis of the samples. X-ray diffractometry (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.

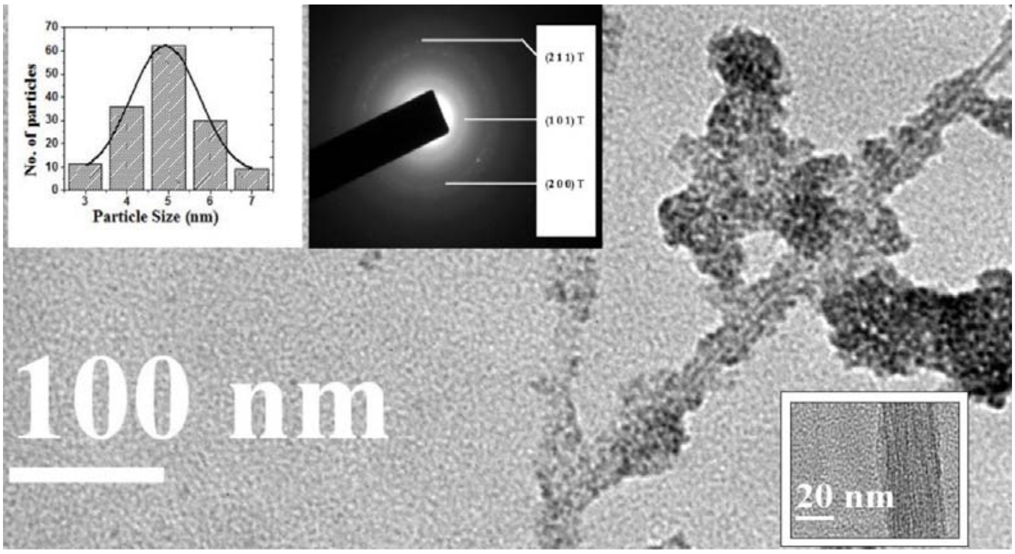


Fig. 1 HRTEM micrograph of TiO_2/SWCNT hybrid; insets show the HRTEM micrograph of pristine SWCNTs, SAED pattern of the hybrid material and the particle size distribution of TiO_2 nanocrystals

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 was studied using FL spectrofluorimeter (HITACHI F-2500) over a wide range of excitation wavelengths from 220-400 nm. DC conductivity of the samples was measured by two- probe method using 6514 Keithley Electrometer.

3. Results and discussion

The HRTEM micrograph of TiO_2/SWCNT hybrid is shown in Fig. 1. The micrograph clearly reveals that TiO_2 nanocrystals adhere uniformly over the surfaces of the SWCNT bundles. The insets show the HRTEM micrograph of pristine SWCNT, SAED pattern of the hybrid material and the particle size histogram of the TiO_2 nanoparticles. The electron diffraction pattern shows the reflections of zinc blende crystal structure corresponding to (1 0 1), (2 0 0) and (2 1 1) planes of anatase phase of TiO_2. The average size of TiO_2 nanocrystals is found to be 5 nm as obtained by fitting the particle size distribution from HRTEM micrograph.

Fig. 2 shows the EDAX spectrum of TiO_2/SWCNT hybrid. From the spectrum, the presence of titanium (Ti) and oxygen (O) with carbon (C) of SWCNT 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.

Fig. 3 shows the FTIR spectrum of pristine SWCNT (a) and TiO_2/SWCNT hybrid (b). The Ti-O bonding is confirmed from the stretch in the region 470-500 cm^{-1} (Byrappa *et al.* 2008). Stretch at 1630 cm^{-1} is due to carboxylate anion. Stretches in the range 3173-3377 cm^{-1} are the stretching vibrations of H_2O, originated from the absorption of water by KBr matrix (Zhao *et al.* 2009). Stretches in the range of 1400- 1600 cm^{-1} are due to C-O bonding modes.

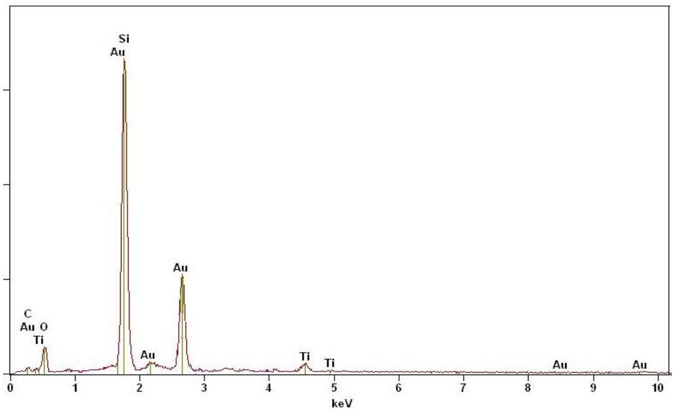


Fig. 2 EDAX spectrum of TiO_2/SWCNT hybrid

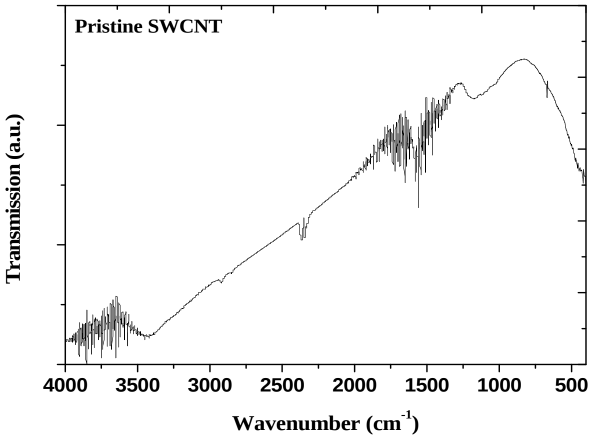


Fig. 3(a) FTIR spectrum of pristine SWCNT

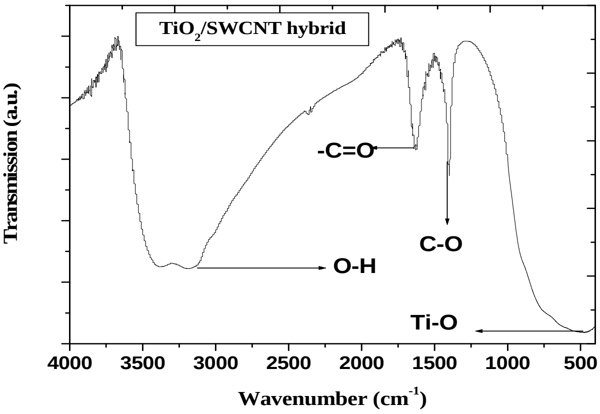


Fig. 3(b) FTIR spectrum of TiO_2 / SWCNT hybrid

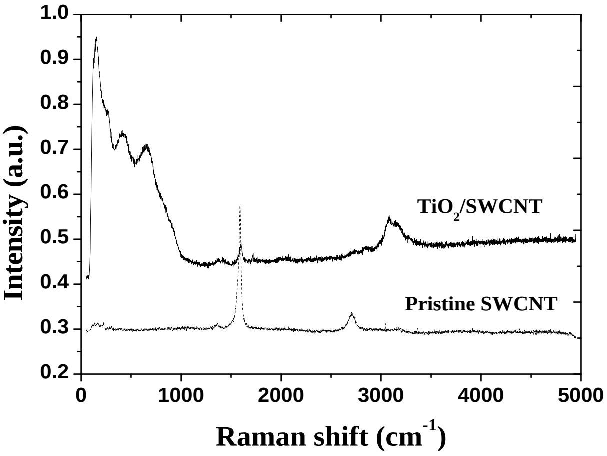


Fig. 4 Raman spectrum of pristine SWCNT and TiO$_2$/SWCNT hybrid

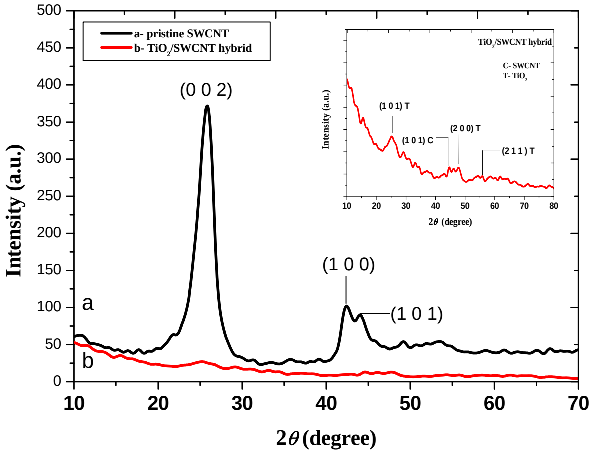


Fig. 5 XRD pattern of pristine SWCNT and TiO$_2$/SWCNT hybrid; inset shows the magnified XRD pattern of TiO$_2$/SWCNT hybrid

Fig. 4 shows the Raman spectrum of pristine SWCNT and that of TiO$_2$/SWCNT hybrid. The peaks at 150, 408 and 650 cm^{-1} of the hybrid sample correspond to the photoelectronically active anatase phase of TiO$_2$ (Zhao *et al.* 2010). There is an up-shift by 12 cm^{-1} in the position of G band indicating charge transfer to SWCNTs from TiO$_2$ nanocrystals. This type of up-shift of G band upon modification of CNT surfaces has been reported earlier by several authors (Rao *et al.* 1997, Sumanasekera *et al.* 1999). I_D/I_G for pristine SWCNT is 0.546 while that for TiO$_2$/SWCNT hybrid has been found to be 0.939. This increase in I_D/I_G factor indicates that TiO$_2$ nanocrystals are attached to the SWCNT surfaces via chemical bonding.

Fig. 5 shows the XRD pattern of pristine SWCNT and TiO$_2$/SWCNT hybrid. For pristine SWCNT, the peaks centered at 26°, 42° and 44° correspond to (002), (100) and (101) reflections of

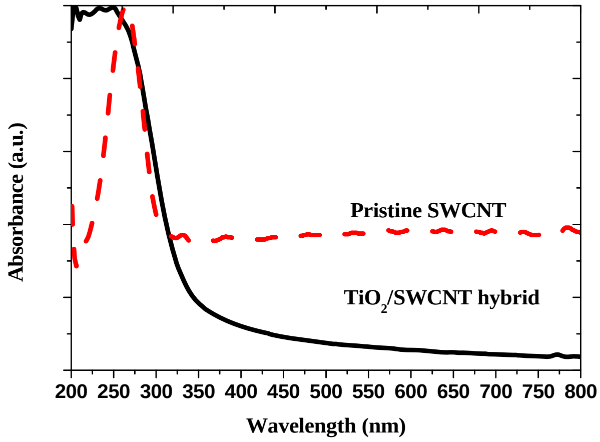


Fig. 6 Absorption spectra of pristine SWCNT and TiO2/SWCNT hybrid

graphitic planes of the SWCNTs (JCPDS card no. 75-1621). The XRD pattern of TiO_2/SWCNT composite gives the peaks assigned to (101), (200) and (211) planes of the reported data for TiO_2 (JCPDS card no. 21-1272) for its anatase phase. These are in good agreement with the observations from the HRTEM SAED pattern. Moreover, the hybrid structure also shows the (101) reflection from SWCNT surface. The inset of Fig. 5 shows the magnified image of the XRD pattern of the hybrid structure. The absorption spectra of pristine SWCNT and TiO_2/SWCNT nanostructure are shown in Fig. 6. The absorption peak position blue shifts by 16 nm from 264 nm to 248 nm on decorating SWCNT walls with TiO_2 nanocrystals and this will alter the catalytic properties of TiO_2/SWCNT nanostructure (Satoh *et al.* 2008).

Fig. 7(a) shows the PL spectrum of pristine SWCNT and TiO_2/SWCNT hybrid at 250 nm excitation wavelength. The hybrid structure shows violet-blue emission when excited by UV radiation of wavelength 220-260 nm. Beyond 260 nm excitation wavelength, no considerable photoluminescence has been observed.

Fig. 7(b) shows photoluminescence spectra of TiO_2/SWCNT hybrid at different excitation wavelengths. With the increase of excitation wavelength, the PL emission intensity increases. The spectrum covered a region from 325-500 nm with the peak position at around 400 nm. For 220 nm excitation wavelength, emission ceases at around 425 nm but extends upto 500 nm in the case of 250 and 260 nm excitations. The pristine SWCNT sample showed no luminescence in this region. The PL emission of the hybrid structure is attributed to the charge transfer between titania nanocrystals and carbon nanotubes. When excited by lower excitation wavelengths and hence higher energy values, transition of electrons from TiO_2 to SWCNTs takes place, but these highly energetic electrons transit instantly thereby causing emission. When excited by higher wavelength radiation, the number of electrons taking part in the transition process increases and hence increases the PL intensity (Paul *et al*. 2010).

Photocatalytic activity of anatase TiO_2 is largely enhanced when it is hybridized with SWCNT. The mechanism of this enhancement may be given as shown in the proposed scheme. When excited by UV-radiation, electrons e^- from the valence band (VB) are lifted to the conduction band (CB) of the anatase TiO_2, creating a hole (h^+) in the valence band. For isolated TiO_2, these charges

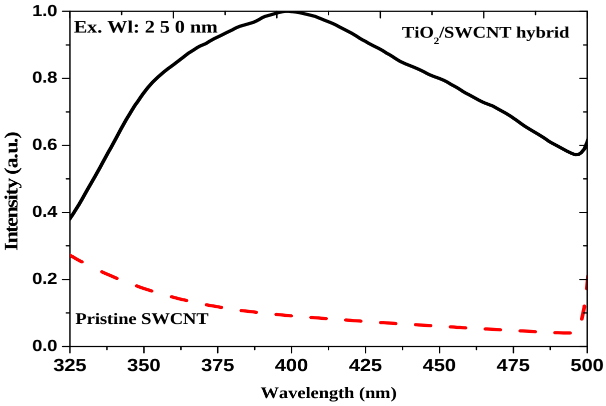


Fig. 7(a) PL spectra of pristine SWCNT and TiO$_2$/SWCNT hybrid at 250 nm excitation

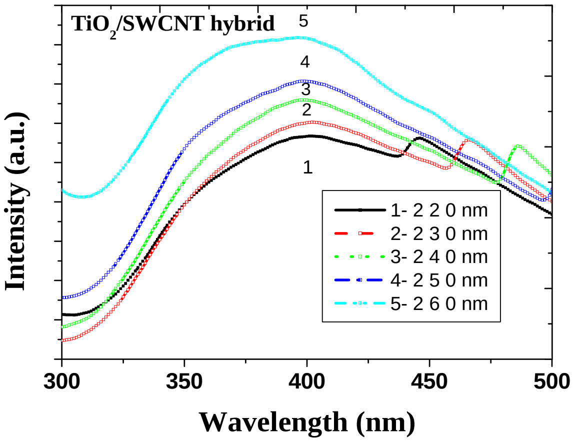
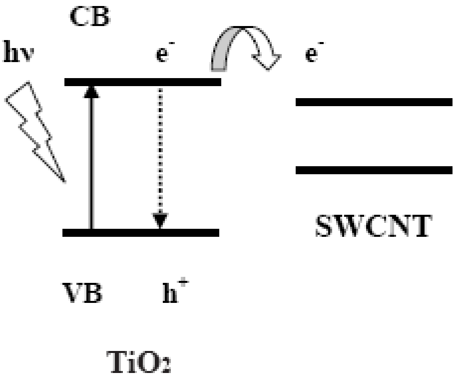


Fig. 7(b) PL spectra of TiO$_2$/SWCNT hybrid at different excitation wavelengths



Scheme: Charge transfer mechanism from TiO$_2$ to SWCNT quickly recombine without any contribution to the photocatalysis process, except only a small fraction participating in the photocatalytic reaction. In the TiO_2/ SWCNT hybrid, the conduction band edge of SWCNT is below the conduction band edge of anatase TiO_2, permitting transfer of electrons from TiO_2 surface to SWCNT. So, the hybridization causes charge separation and prevents recombination, enhancing the photocatalytic activity of the material. Photoluminescence takes place by electron- hole pair recombination on irradiating a photocatalyst. PL spectrum is often employed to study surface structure and other surface processes (Yao *et al.* 2008), but degrades the material as a photocatalyst.

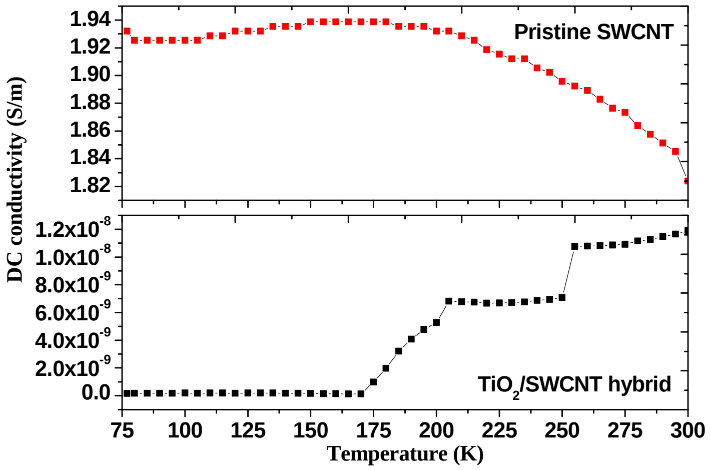


Fig. 8(a) Variation of DC conductivity of pristine SWCNT and TiO_2/SWCNT hybrid with temperature

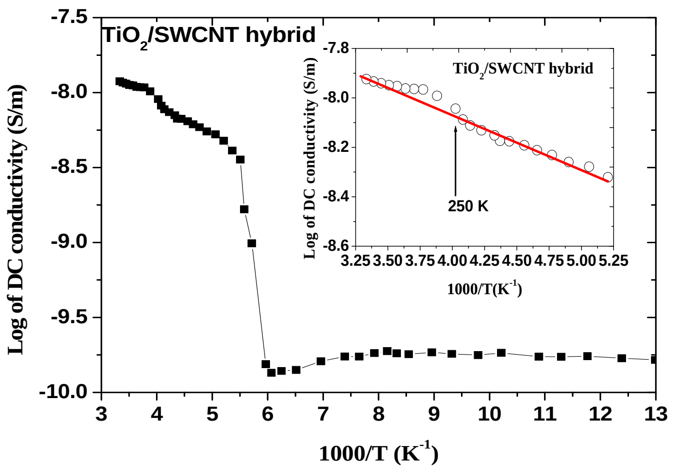


Fig. 8(b) Variation of log of DC conductivity of TiO_2/SWCNT hybrid with 1000/T (K^{-1}); inset shows the higher temperature plot of DC conductivity of the hybrid

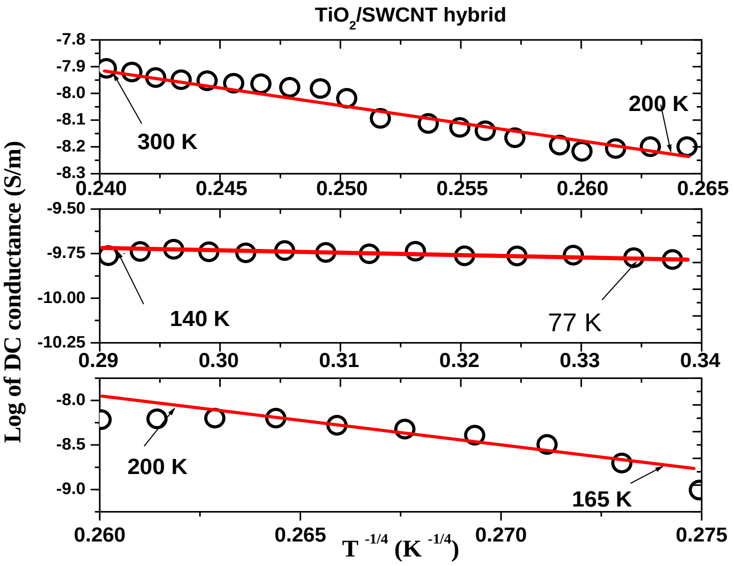


Fig. 8(c) Variation of log of DC conductivity of TiO_2/SWCNT hybrid with $T^{-1/4}$ ($K^{-1/4}$) in the range 77-300 K satisfying VRH model with d=3

Study of DC conductivity of pristine SWCNT has showed a crossover from a semiconductor-like temperature dependence of conductivity to a metal-like one with the increase of temperature, transition temperature being 180 K. The variation of DC conductivity of pristine SWCNT and TiO_2/SWCNT hybrid with temperature are shown in Fig. 8(a). When coated with TiO_2 nanoparticles, the whole material behaves as a semiconducting material. Its conductivity decreases by several orders of magnitude compared to that of the pristine SWCNT sample. So the contribution of SWCNT is overshadowed by the abundant presence of TiO_2 nanoparticles which are strong semiconducting materials.

Fig. 8(b) shows the variation of log of DC conductivity of TiO_2/SWCNT hybrid with 1000/T (K^{-1}). The inset shows the higher temperature plot of DC conductivity of the hybrid with 1000/T (K^{-1}).

The variation of log DC conductivity of TiO_2/SWCNT hybrid with $T^{-1/4}$($K^{-1/4}$) in the range 77-300 K which satisfies Mott's 3D variable range hopping (VRH) model with d=3 is shown in Fig. 8(c).

Mott's VRH model (Syed and Dinesan 1991) given by relation (1) may fit our experimental data for DC conductivity for temperature 77-300 K (as shown in Fig. 8(c)) with appropriate values of the constants.

$$\sigma = \sigma_0 \exp(-T_0/T)^{\gamma} \qquad (1)$$

where γ is the VRH exponent, which determines the dimensionality of the transport process via the equation $\gamma = 1/(1+d)$, where $d = 1$, 2 and 3 for one, two and three dimensional systems respectively. σ_0 is the conductivity when $T \rightarrow \infty$. T_0 is the Mott characteristic temperature, which depends on the electronic structure and the energy distribution of the localized states, as shown by relation (2).

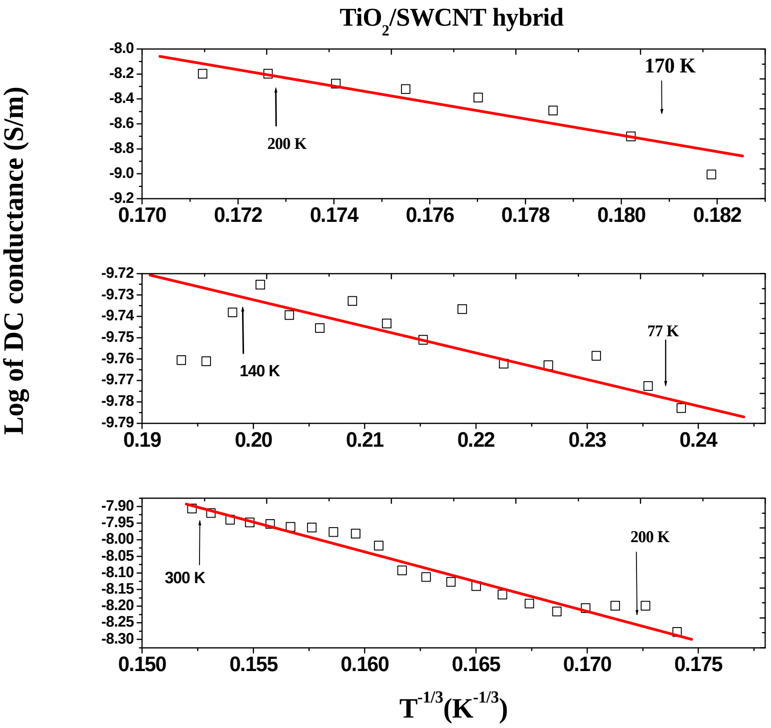


Fig. 8(d) Variation of log of DC conductivity of TiO_2/SWCNT hybrid with $T^{-1/3}$ ($K^{-1/3}$) in the range 77-300 K satisfying VRH model with d=2

$$T_0 = 16/\, k_B N(E_F)\, L_{loc}^3 \quad (2)$$

where k_B is the Boltzmann constant, N (E_F) is the density of states at the Fermi level and L_{loc} is the localization length. DC conductivity analysis shows that there are different conduction canals controlling the electron transport. This is because we used pellets of the considered sample for conductivity measurement and the alignment of SWCNTs within the pellet is random, leading to different slopes. In our analysis, in order to obtain the exponent γ with more accuracy, the experimental values of conductivity σ_i, and temperature T_i were fitted to a curve of the form of Eq. (1) using σ_0, T_0 and γ as adjustable parameters (Yildiz *et al.* 2007). We obtained the values of T_0 from the slopes of the linear variation of log σ with $T^{-1/4}$ and the estimated values of T_0 were 2.441 K, 6250X10^4 K and 1296 X 10^4 K for the three successive temperature ranges.

The variation of log DC conductivity of TiO_2/SWCNT hybrid with $T^{-1/3}$($K^{-1/3}$) in the range 77-300 K which satisfies Mott's variable range hopping (VRH) model with d=2 is shown in Fig. 8(d). But it is observed that in the low temperature region (77-160 K), two dimensional (2D) charge transport (γ = 1/3) VRH model does not fit well with the experimental values, although the fitting in the other two ranges is satisfactory. Thus 3D VRH model is responsible for the transport mechanism according to our investigation.

4. Conclusions

We reported a simple wet chemical process to synthesize a hybrid structure of SWCNT and TiO_2 nanoparticles. Titania nanocrystals of average size 5 nm uniformly decorated the walls of the SWCNT bundles and the hybrid 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 SWCNTs. Also the variation of DC conductivity with temperature was investigated. The conductivity of SWCNT decreased by several orders of magnitude when coated with titania nanocrystals. The experimental data obtained for DC conductivity fitted well with the Mott's three dimensional (3D) VRH model. Thus the hybridization of TiO_2 nanoparticles with SWCNT may render an advanced functional material with improved photocatalytic response due to reduced recombination of photoelectrons.

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