ISSN: 0976-3031

Available Online at http://www.recentscientific.com

CODEN: IJRSFP (USA)

International Journal of Recent Scientific Research
Vol. 9, Issue, 7(A), pp. 27756-27759, July, 2018

International Journal of Recent Scientific Research

DOI: 10.24327/IJRSR

Research Article

BLUE LIGHT EMISSION FROM TITANIA QUANTUM DOTS SUPPORTED ON CARBOXYLATED SINGLE WALLED CARBON NANOTUBES

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DOI: http://dx.doi.org/10.24327/ijrsr.2018.0907.2324

ARTICLE INFO

Article History:

Received 4th April, 2018
Received in revised form 18th May, 2018
Accepted 16th June, 2018
Published online 28th July, 2018

Key Words:

Photoluminescences, Titania, SWCNTs

ABSTRACT

A novel titania quantum dots supported on Carboxylated Single-walled carbon nanotubes (SWCNTs) is prepared by a simple wet chemical route and characterized by TEM (transmission electron microscope), EDS (energy dispersive spectroscopy), Raman Spectroscopy and thermal analysis(TG-DTA). Finally their luminescent properties are investigated. A strong photoluminescence emission with a maximum at 450 nm was observed. The titania nanoparticles supported on SWCNTs possess interesting luminescence characteristics and may have potential applications as a fluorescence probe. The titania quantum dots are considered as important sources of the observed luminescence.

INTRODUCTION

Semiconductor nanocrystals, also called quantum dots (DOS) exhibit novel properties different from those of their corresponding bulk materials [1]. Particle size has a significant effect, also called quantum size effect on the electronic, magnetic and optical properties of semiconducting solids when their size, in at least one dimension, becomes comparable with the exciton (Bohr) radius (1-10 nm) [2]. Semiconductor crystallites with colloidal dimensions display an intriguing quantum size effect in their photoluminescence properties, which have been investigated because of their use in biological labels.

Titania (Titanium dioxide, TiO_2) is one of the most important semiconducting material, has researched for photo-assisted degradation of a variety of toxic chemicals [3-5] as a promising electrode material in dye-sensitized solar cells [6-8], as a gas sensors [9, 10] etc. Moreover, TiO_2 is non-toxic, safe and can be used in pharmaceuticals [11]. The electronic structure and luminescence of nanosrtuctured titania have been actively researched [1, 2, 12, 13]. Luminescence at room temperature, which is impossible for bulk titania, was found for nanostructured titania.

The present study deals with nanostructured titania supported on carboxylated SWCNTs. Carbon nanotubes (CNTs) have been considered as a good support for nanomaterials because of their high specific area and chemical stability [14]. The TiO_2/SWCNTs composite have been obtained by simple chemical route. The resultant TiO_2/SWCNTs composite were characterized by different techniques including transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), Raman spectroscopy and Thermo gravimetric-Differential Thermal analysis (TG-DTA). Study of room temperature photoluminescence (PL) behavior of TiO_2/SWCNTs composite is reported.

MATERIALS AND METHOD

Purification/oxidation of Pristine SWCNTs

SWCNTs [ASP-100 F, Iljin Nanotech. Co. Ltd. Korea] was used. Other chemicals ethylene glycol (EG), HNO_3, titanium (IV) oxide bis (acetylacetone) (Ti-OBA) all are AR grade and used as received.

A sample of raw SWCNTs was initially sonicated in 3 M HNO_3 for about 15 mins to disperse the nanotubes. Then the reaction mixture was subsequently refluxed for 16 hours. The black mixture was cooled to room temperature and filtered using 0.2 μm polycarbonate membrane and dried at 100 ^oC in vacuum. As a result of this purification/oxidation process, the oxidants attack graphene structure by electrophilic reactions

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and significant density of oxygenated functional groups is introduced on the end caps as well as in sidewalls of SWCNTs. The presence of oxygen-containing functional groups facilitates the exfoliation of CNT bundles and increases the solubility in polar media [15] and increase the possibility of further functionalization.

Synthesis of Oxidized SWCNTs/TiO_2 composite

0.1 g of purified SWCNTs was well dispersed in about 40 mL of EG and 0.1 g of Ti-OBA (already dispersed in 10 mL EG) was added to well disperse SWCNTs. It was heated up to 120 ^{o}C with stirring and kept for about 4 hours. Then it was followed by filter, washing with D. I. water and vacuum drying.

Characterization

Transmission Electron Microscopy/Energy Dispersive Spectroscopy. All TEM images were taken at an accelerating voltage of 200 kV on a JEOL, JEM 2100F, equipped with EDS capabilities. The samples were obtained by drying sample droplets from an ethanolic dispersion onto Cu grid coated with carbon film.

Thermal analysis. *The* combined thermo gravimetric-differential thermal analysis (TG-DTA) was carried out on a SEIKO, INST., Seiko Exstar 6000 instrument. The analysis was performed at a heating rate of 10 ^{o}C/min over the temperature range, 50 -1000 ^{o}C, in an oxygen environment.

Raman Spectroscopy. Solid state Raman spectra of pristine, purified and TiO_2/SWCNTs composite were obtained on a RM 1000-inVia, Renishaw with excitation wavelength of 632.8 nm.

Photoluminescence Spectra. PL spectra of TiO_2/SWCNTs (Powder sample) composite were measured at excitation wavelength of 325 nm with He-Cd laser.

RESULTS & DISCUSSION

TEM Analysis

Figure 1 (a) represents the TEM images of oxidized/purified SWCNTs. After oxidation/purification many defects sites are produced, which can be seen in figure. These defect sites play an important role on attachment of oxygen functional group for attaching the metal nanoparticles. The signal of oxygen in the EDS shown in figure 1(b) is originated from these oxygen functional groups.

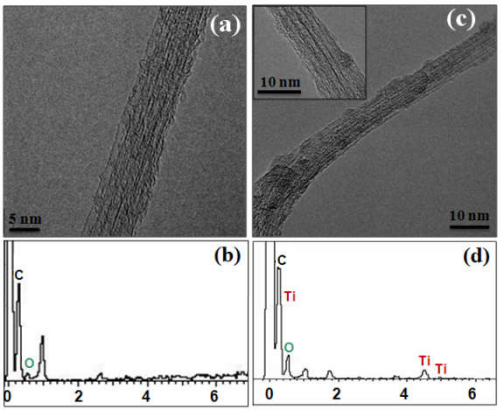

Fig 1 TEM images of (a) oxidized SWCNTs, (b) Ti-SWCNTs composite (c) EDS of oxidized SWCNTs and (d) EDS of Ti-SWCNTs composite.

The presence of defects sites is also confirmed by increase intensity of D band in Raman spectrum (Fig. 2) and lowering the burning temperature of nanotubes shown in thermal analysis (Fig. 3).

Figure 1 (c) represents the TEM image of TiO_2/SWCNTs composite. The TEM image shows the distribution of titania nanoparticles on the surface of acid treated SWCNT bundle. The presence of titania nanoparticles was confirmed from EDS spectra shown in fig. 1 (d). The average size of titania nanoparticles is about 3- 5 nm.

Raman Analysis

Raman spectroscopy has provided an exceedingly powerful tool for the characterization of pristine as well as their functionalized derivatives of SWCNTs. The characteristics Raman signals observed in SWCNTs are radial breathing mode (RBM) (between150 and 350 cm^{-1}) corresponds to the coherent vibration of the C atoms in the radial direction, D-band (around1300-1400 cm^{-1}) originating from defects, G- band (around 1600 cm^{-1}) associated with the C-C stretching tangential mode in graphite, and 2D band (around 2650 cm^{-1}) which is dominant feature in the second-order Raman spectra in SWCNTs.

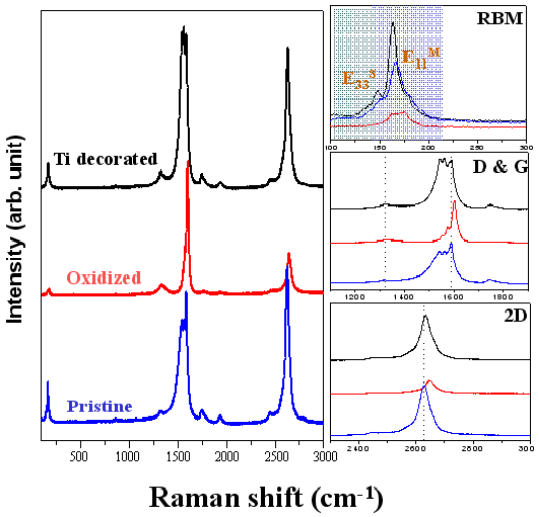

Fig 2 Raman Spectra of Pristine, Oxidized and TiO_2 supported SWCNTs

The RBM can be used to study the nanotube diameter, the G band frequency can be used to distinguish between metallic and semiconducting SWCNTs and also used to probe the charge transfer arising from doping SWCNTs, the intensity of 2D band is used to characterize the metallicity, and the relative intensity of the D-line is proportional to the number of such defects.

Fig. 2 shows Raman Spectra of solid samples of pristine, oxidized and Er-decorated SWCNTs taken at 633 nm excitation wavelength. Each of them consists of expected characteristic bands of SWCNTs.

The bands of the radial breathing mode appearing at 181, 167 and 149 cm^{-1} indicate the diameter distribution of SWCNTs. There was sharp decrease in intensity of the lowest energy RBM band (149 cm^{-1}) for oxidized SWCNTs as compared to that of pristine. This may be due to that the oxidation affects the large diameter SWCNTs.

The appearance of prominent Raman peak at 1340 cm^{-1} in oxidized SWCNTs showed increase in the number of defective sites. These defects include the conversion of sp^2-hybridized carbon to sp^3-hybridized carbon during the oxidation process, with the creation of carboxylic group, hydroxyl group etc.

The G-band of pristine SWCNTs show the typical feature expected for metallic tubes. The pristine SWCNTs show a broad asymmetric band at 1589 cm^{-1} with a BWF profile, the shape of which is due to coupling between phonon scattering and electronic scattering in the metallic tubes [16]. Oxidation and functionalization of carbon nanotube also affect the G band. This G band becomes more symmetric and the most intense after oxidation, which is more similar to the profile expected for semiconducting tubes i. e. Lorentzian lineshape.

The band at 2625 cm^{-1} is 2D band, the intensity of which is very prominent indicating presence of metallic tubules in pristine SWCNTs. After oxidation/purification, the intensity this 2D band was significantly suppressed because the metallic SWCNTs had been removed. Together with 2D and G band the CNTs shows semiconducting behaviour because the oxygen functional group can convert the metallic CNTs into semiconducting [17]. The intensity of this 2D band became prominent again in Ti/SWCNTs composite showing the presence of metallic tubules.

When the side walls of the SWCNTs are covalently modified the appearance of a prominent Raman peak at 1340 cm^{-1} is due to the sp^3 states of carbon demonstrates the disruption of the aromatic system of π electrons [18].

Thermal Analysis

TGA is a very valuable tool for determining the overall quality of the material, providing information on the various carbon structures in the sample due to differences in their decomposition temperatures. The TG-DTA measurement on the pristine-, oxidized- and Er decorated SWCNTs is shown in Fig. 3.

For pristine SWCNTs, a constant weight is maintained up to 450 ^oC. Then after this temperature their decomposition begins, and drastic mass (about 90 %) loss occurs between 450 - 750 ^oC. The decomposition starts with the burning of amorphous carbon with small exothermic peak at around 500 ^oC. Second strong exothermic peak is due to burning of SWCNTs. Almost all SWCNTs was burned out at this temperature range and the weight remaining about 10 % at above 750 ^oC corresponds to the weight of some impurities in pristine SWCNTs.

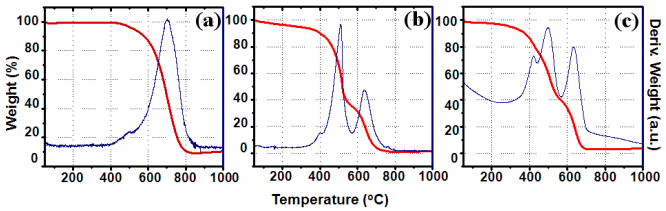

Fig 3 TG-DTA profile (a) Pristine- (b) Oxidized- and (c) Titania/SWCNTs

The thermal degradation of oxidized SWCNTs is a multistage process. Slight weight lost before 200 ^oC corresponds to the evaporation of adsorbed water because acid treated CNTs are hydrophilic in nature. The drastic weight loss was started from 350 ^oC and completed around 650 ^oC. Here weight loss occurs in two different steps; first in temperature range 350 - 520 ^oC and second in 520 - 660 ^oC. If we look very carefully from temperature range from 350 - 520 ^oC, we can see two exothermic peaks i. e weight loss occurs in two different steps. First step is the burning of several kinds of non-nanotubes (i. e different oxygen functional groups, amorphous carbon generated during acid treatment process) [19]. After removing all the oxygen functional groups, two types of SWCNTs remain there one having defects and another perfect SWCNTs. Second step is the removing of SWCNTs containing defects. Because decomposition of CNTs containing defects occurs at temperatures lower than that of perfect SWCNTs due to possible destruction of the CNTs structure during chemical oxidation. After temperature 550 ^oC, the sample contains only pure SWCNTs. And the thermal degradation on later case i. e in higher temperature range is due to burning of pure SWCNTs. The sample weight is reduced to approximately less than 1% after 660 ^oC i. e. all the carbonaceous materials have been removed and very little metal is left which was not removed even by acid treatment.

In TiO_2/SWCNTs, also the weight lost occurred in multistep as shown in TG curve, in fig 3. The figure showed that, there is small lost in weight before 200 ^oC, which may be due to loss of moisture. The major weight lost occurs in temperature range 300-450 ^oC and 500-630 ^oC. The weight lost in 300-500 ^oC is also occurs in multistep as shown by presence of many several DTA peaks. The weight loss here starts with the burning of several kinds of oxygen functional groups, amorphous carbon and completed before the combustion of CNTs. Then the weight loss is due to burning of CNTs containing defects. The weight lost in 500-630 ^oC is due to combustion of pure SWCNTs. After temperature 630 ^oC, weight was constant up to 1000 ^oC. The total residual weight of doped sample is estimated around 4%, mainly ascribed to titania.

Photoluminescence Study

The photoluminescence is the spontaneous emission of light from a material under optical excitation. The photoluminescence of TiO_2/SWCNTs composite was observed under excitation of the sample by UV light at 325 nm in air at room temperature. Figure 4 shows the powder PL spectra of TiO_2/SWCNTs composite. A strong emission band with a maximum at 450 cm^{-1} has been observed under excitation wavelength of 325 nm.

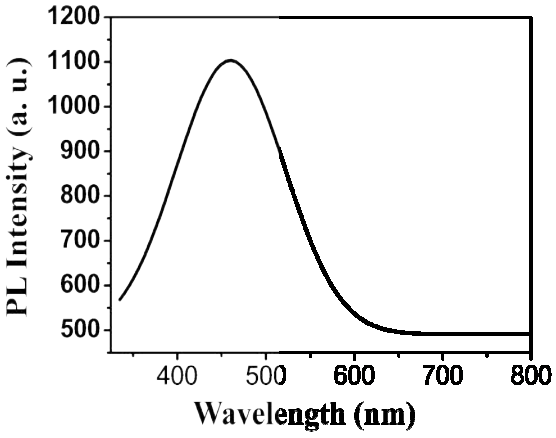

Fig 4 PL Spectrum of TiO_2/SWCNTs composite.

CONCLUSIONS

The titania nanoparticles are successfully decorated on the external surface of oxidized SWCNTs. The composite Ti/SWCNTs, exhibit photoluminescence in the visible range, with strong blue light emission at 450 nm and decrease to the green portion of the spectrum. Based on the above observations it can be synthesized blue-light emitting TiO_2 thin films and to characterize their photo luminescent and electroluminescent properties.

Therefore, it may potentially be used in the fluorescent lamps, display device or detector systems

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How to cite this article:

Sabita Shrestha.2018, Blue Light Emission From Titania Quantum Dots Supported on Carboxylated Single Walled Carbon Nanotubes. *Int J Recent Sci Res.* 9(7), pp. 27756-27759. DOI: http://dx.doi.org/10.24327/ijrsr.2018.0907.2324

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