Solar Energy 149 (2017) 188–194

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

A simple strategy for the anchoring of anatase titania on multi-walled carbon nanotubes for solar energy harvesting

Valmiki Koli [a,b,1], Ananta Dhodamani [a,1], Krantiveer More [a], Steve F.A. Acquah [c,*], Dillip Kumar Panda [c], Shivaji Pawar [b], Sagar Delekar [a,b,c,*]

[a] Department of Chemistry, Shivaji University, Kolhapur 416 004, MS, India
[b] Center for Interdisciplinary Research, D.Y. Patil University, Kolhapur 416 004, MS, India
[c] Department of Chemistry and Biochemistry, Florida State University, Tallahassee 30306-4390, FL, United States

ARTICLE INFO

Article history:
Received 26 September 2016
Received in revised form 27 January 2017
Accepted 12 March 2017
Available online 13 April 2017

Keywords:
A. Sol-Gel
B. Nanocomposites
C. Photoelectrochemical cell
D. Energy harvesting

ABSTRACT

Pure anatase titania (TiO_2) nanoparticles were anchored on the surface of functionalized multi-walled carbon nanotubes (MWCNTs) using a solution-based synthetic method at room temperature. X-ray diffraction and Raman patterns were used to analyze the structural and phase composition of these nanocomposites, highlighting the formation of anatase TiO_2 nanoparticles with MWCNTs up to 0.5 wt.%. The non-spherical particles of TiO_2 in the order of 7–12 nm, were confirmed through transmission electron microscopy analysis and these particles were well dispersed on the MWCNTs. The optical absorption spectra of these structures were studied by diffuse reflectance UV–visible spectroscopy. The optical energy band gap of the various nanocomposites was observed from 3.2 to 2.6 eV with an increasing amount of MWCNTs, up to 0.5 wt.%. The generation of ·OH species in nanocomposites in the presence of visible light irradiation was investigated by photoluminescence spectroscopy. Photoelectrochemical cell performance of TiO_2-MWCNTs for 0.5 wt.% content of MWCNTs under light intensity 100 mW/cm^2 showed a significant improvement of short-circuit current density from 1.23 to 12.1 mA/cm^2 and a cell efficiency (0.090–3.46%) that is better than many reported anatase-based compositions without sensitizer.

1. Introduction

The looming energy crisis is a concern for economic stability and has the potential to seriously affect sustainable human development. There are two main forms of energy, renewable and non-renewable. Most of the energy is generated from non-renewable energy sources, which include oil, natural gas, and coal. The excess use of these sources cause pollution and are not sustainable (Ardo and Meyer, 2009). Renewable energy sources, mainly sunlight, wind, water, tides, waves, geothermal heat, are abundant. Thus, there is need to harvest renewable energy sources for production of energy (Guldi and Sgobba, 2011). Among all of renewable energy sources, sunlight attracts most attention due to its abundance, which is converted to electricity by various photovoltaic (PV) devices (Scholes et al., 2011). The fossil fuels contribute maximum fraction of current annual energy consumption whereas solar energy usage is well below 1% (Wong and Ho, 2010). Hence, it is necessary to capture as much as solar energy and convert it into the electricity by using various technologies; which prove to be promising routes for renewable energy harvesting (Huang et al., 2013). In the solar energy harvesting, the main strategy is based on the use of PV technology; which become dominated by silicon materials either in crystalline or amorphous form; however, the overall cost is one of the barriers for its use. Thin film PV devices are popular, but stability with efficiency of these thin film based solar devices is the major limitations in energy conversions. Some of these issues can be addressed with the use of nanomaterials (NM); due to their excellent physical and chemical properties. NM such as titanium dioxide (TiO_2), zinc oxide (ZnO), cadmium sulfide (CdS), cadmium selenide (CdSe) and indium selenide (In_2Se_3) are useful for harvesting solar energy (Appierot et al., 2009).

TiO_2 attracts much attention due to its abundance, low cost, high absorption coefficient and structural stability (Yan et al., 2013a,b). Due to this unique properties, TiO_2 is applicable in environment remediation and solar energy conversion in the past decade (Li et al., 2015). However, due to the high band gap (~3.2 eV);

---

* Corresponding authors at: Department of Chemistry, Shivaji University, Kolhapur 416 004, MS, India (S. Delekar).

E-mail addresses: sacquah@chem.fsu.edu (S.F.A. Acquah), sdelekar@chem.fsu.edu, sddelekar7@rediffmail.com (S. Delekar).

[1] These authors contributed equally.

http://dx.doi.org/10.1016/j.solener.2017.03.036

it is active under the UV electromagnetic spectrum (Online, 2013). Additionally, the high rate of recombination of photo-generated electron-hole pairs in TiO_2 lower its photo conversion efficiency (Tang and Yin, 2015). TiO_2 needs to be modified for a low optical band gap as well as a decrease in the recombination rate of electron-hole pairs. Various strategies including doping with metal ions (Delekar et al., 2012; Yan et al., 2015) and non-metal ions (Barkul et al., 2016; Yang et al., 2009) have been used. Nanocomposites (NCs) with either metal oxides (Habib et al., 2013) or other precursors like dyads, carbon nanotubes, graphene oxide, etc. have been reported. Making NCs with different forms of carbon nanostructure, especially multi-walled carbon nanotubes (MWCNTs) are promising due to the unique optical, electrical, and mechanical properties of MWCNTs; which may result in better opto-electrical performance of the titania multi-walled carbon nanotubes (TiO_2-MWCNTs) NCs. In solar energy harvesting, MWCNTs has two roles plausibly. As per the literature, CNTs may acts as electron scavengers in the composites. This is due to its highly conductive nature; which accepts the excited electrons from the conduction band of TiO_2 resulting in the well separation of charge carriers. Su et al. (2013) reported the nature of MWCNTs, as an electron sinks, in combination with the other semiconductors and also shown the enhancement in life-time of photogenerated carriers due to their well separations as the Fermi level of MWCNTs is lower as compared to TiO_2. Another role of MWCNTs is concerned to the photosensitizer and hence itself absorbs the photon energy and thereafter the electrons are transferred to the conduction band of TiO_2. Rajasekar et al. (2013) prepared TiO_2/CNTs composites and these composites were tested for the degradation of rhodamine B in visible light. In the composites, the introduction of CNTs into TiO_2 remarkably increased the photocatalytic degradation efficiency. The synergetic effect, induced by a strong interphase interaction between CNTs and TiO_2, was ascribed to CNTs acting as photosensitizers rather than as adsorbent or dispersing agent in the composites. These two possible ways ultimately decrease the probability of the recombination of the electron-hole pairs and hence which may results the absorption of UV–visible light with efficient conversion of solar energy into electrical energy (Wen et al., 2013). Therefore, in the composites, MWCNTs act as absorber or sensitizer and hence which enhances the photo-conversion efficiency with separation of charge carriers. Therefore, in connection to its advantages in energy harvesting, MWCNTs are promising support materials for TiO_2 NPs to tune opto-electrical properties. NCs of TiO_2 with MWCNTs show different physical properties from TiO_2 (Li et al., 2007) which can be tailored towards solar cells, quantum memory elements, and semiconducting devices (Tettey et al., 2010).

Recently many researchers have prepared the TiO_2/CNT NCs using various methods. Ma et al. (2013) prepared TiO_2/CNT NCs film by *in-situ* chemical vapour deposition method. This method required highly expensive devices with high temperatures for fabricating the NCs. There are only a few examples of environmentally friendly organic precursors for direct coating of TiO_2 NPs on the surface of MWCNTs (Joshi et al., 2011). The photocatalytic performance for both liquid and gas phase environmental clean-ups was improved by using TiO_2/MWCNTs NCs; which was prepared by wet impregnation method; but this methodology ease suffering with improper composition of the NCs (Xu et al., 2010). In these earlier investigations, the photocatalytic reactions of TiO_2-MWCNTs NCs were carried in the presence of UV-light or visible light irradiation; but these results were not up to the mark related performance in solar energy harvesting.

Here we report, a simple method for synthesizing TiO_2-MWCNTs NCs by an *in-situ* sol-gel method, resulting in pure anatase phase TiO_2 while varying the amount of MWCNTs from 0.1 up to 0.5 wt.% for efficient solar energy conversions without sensitizer.

2. Materials and methods

2.1. Materials

All chemicals used were of AR grade. MWCNTs were purchased commercially (CVD method, diameter: 20–45 nm, length: 10–40 μm and surface area: >500 m^2/g).

2.2. Fuctionalization of MWCNTs by acid treatment

MWCNTs were functionalized using earlier reported method (Ramar and Soundappan, 2012). The commercial MWCNTs were refluxed in mixture of H_2SO_4:HNO_3 (3:1 vol ratio) at 100 °C for 5 h. Then, the content was cooled, centrifuged, and washed with distilled water several times to maintain its neutralization. Further, it was dried at 80 °C in the electric oven for obtaining its functionalized form. These functionalized MWCNTs were dispersed in water with ultra-sonication for longer times.

2.3. Synthesis of TiO_2-MWCNTs NCs

The NCs of TiO_2-MWCNTs with optimum compositions of MWCNTs (0.1–0.5 wt.%) were prepared by an *in-situ* sol-gel method. Titanium (IV) tetra-butoxide was mixed with glacial acetic acid in a 250 mL round-bottom flask. The whole mixture was stirred followed by the addition of an aqueous solution of sodium dodecyl sulphate as a capping agent. The required amount of functionalized MWCNTs was dispersed in distilled water using ultra-sonication and it was added to the above titanium precursor at room temperature. The pH of the resulting solution was adjusted to 10.00 using ammonia solution. The solution was stirred at 60 °C for 3 h, and then cooled at room temperature. The precipitate was filtered, washed with ethanol, dried and calcinated in air at 400 °C for 5 h. The TiO_2 NPs were prepared by using method above without the addition of functionalized MWCNTs. The mechanism for forming TiO_2-MWCNTs NCs is shown in Scheme 1.

2.4. Fabrication of TiO_2-MWCNTs photoelectrode

0.2 g of TiO_2-MWCNTs NCs powders was dispersed in 5 mL ethanol by ultra-sonication. This was stirred with a mixture of 4 mL (10 wt.%) ethyl cellulose and 0.75 g of α-terpineol for 5 h at room temperature. Then, the mixture was grinded to evaporate excess alcohol. Then 'as prepared' paste was deposited on fluorine doped tin oxide (FTO) glass (with thickness 2 mm and surface resistivity ~7 Ω/sq cm^{-1}) substrates by doctor blading technique (Fadadu and Soni, 2013). The assembly was dried and calcinated at 400 °C for 1 h. These electrodes, in thin film form, were used for making a PEC device using a platinum deposited FTO as a counter electrode. The polysulfide/sulfide solution was used as electrolyte; which consists of 2.0 M Na_2S, 2.0 M S, and 0.2 M KCl solutions (Zhao et al., 2014).

2.5. Characterizations

X-ray diffraction (XRD) patterns of the TiO_2-MWCNTs NCs were recorded using the X-ray diffractometer (Bruker D8-advance) with Cu Kα (1.5406 Å) radiation in the 2θ range from 10 to 90°. UV–visible diffused reflectance (UV–visible DR.) spectra of the samples were measured using UV–visible spectrophotometer (Lab India UV-3092) in the range 300–700 nm. Raman spectra were recorded in the spectral range of 250–1700 cm^{-1} using the Raman spectrometer (Bruker Multi–RAM). Fourier transform infra-red (FTIR) spectra of the samples were recorded using Bruker Alpha FT9 in the range between 400 and 4000 cm^{-1}. The particle morphology