Enhanced photovoltaic properties in graphitic carbon nanospheres networked TiO₂ nanocomposite based dye sensitized solar cell

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Abstract:

In this work, we report a novel carbon based TiO₂ nanocomposite electron injection layer (photoanode) towards the improved performance of DSSCs. Graphitic carbon nanospheres (GCNSs) were synthesized by a unique acidic treatment of multi-wall carbon nanotubes. GCNS-TiO₂ nanocomposites with different concentrations of GCNSs (ranging from 5-20 μ L) were prepared to use as photoanodes in DSSCs. Structural and morphological properties of GCNS-TiO₂ nanocomposites were analyzed by Raman spectroscopy and ultra-high resolution transmission electron microscopy techniques, respectively. A systematic increment in the short circuit current density (J_{SC}) and open circuit voltage (V_{OC}) of DSSC was observed by increasing GCNS concentration up to an optimal value, possibly due to the combined effect of slight rise in quasi-Fermi level and higher carrier transport rate in the resultant composite. Thus, a significant enhancement of $\sim 47\%$ in the efficiency of DSSC containing GCNS-TiO₂ photoanode was observed as compare to DSSC with pure TiO₂ photoanode.

Keywords: Graphitic Carbon nanosphere, Dye-sensitized solar cell, Raman spectroscopy, TEM.

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1. Introduction

Fossil fuel resources are being used from ancient time but these are finite. Their collection and combustion also poses great hazards to our natural ecosystems. Renewable energy sources can provide valuable services to meet increasingly energy demands. Photovoltaic cells are most adaptive, inexpensive and sustainable form of green and renewable energy. A number of options are being explored in this locus. Silicon wafer-based solar cell (first generation of photovoltaic) is the most popular in the photovoltaic market. Highest efficiency reported for monocrystalline Silicon solar cell is 25% [1-3]. Thin film based solar cell (second generation of photovoltaic), reaching to new record efficiency up to 21.7% [4], have been developed to reduce the production cost and complication in manufacturing steps, but still make use of expensive materials and intricate techniques [5-9]. Dye-sensitized solar cell (DSSC), one of the third generation solar cells, represents a whole new era of added functionality and thrifty technologies [10-13]. However, DSSC does not hold a promise of higher photo-conversion efficiency (PCE) comparable to other thin film technologies, but their overall performance and lowered cost makes them adorable for further growth. A modern version of dye-sensitized solar cells was firstly introduced by O'Regan and Grätzel in 1991 [14]. Solar energy conversion in a typical DSSC is achieved through a photo-electrochemical process [15-18]. Conventional DSSC includes photoanode based on high band gap semiconducting materials such as TiO_2

nanoparticles deposited on a conducting glass substrate. However, inorganic-organic lead halide perovskite materials are being used to design low cost and highly efficient photovoltaics [19].

A few recent studies have shown the effect of addition of carbon allotropes [20-36], such as carbon nanotubes (CNT) [23-26], graphene [27-29], graphene oxide [30, 31], fullerene [32], graphenized carbon nanofiber [33], and carbon black [34] on the enhanced performance of photovoltaic cells. Excellent structural and mechanical properties, high surface to volume ratio, low resistivity, and high electrochemical stability of such carbon nanostructures have been found to be advantageous for improved DSSCs performances^{25, 27,}[35, 36]. These carbon allotropes have been implemented either in ionic liquid electrolyte [32] or in working electrodes [21-31] of a cell to enhance photon absorption efficiency, charge injection efficiency and/or charge transport efficiency.

In this report, we demonstrate a comparative study on photovoltaic properties of DSSCs based on (i) TiO₂ and (ii) graphitic carbon nanospheres (GCNS)-TiO₂ nanocomposite photoanodes. A significant rise in the photo-conversion efficiency of DSSC was observed at an optimal concentration of GCNS in photoanode. Further, the origin of improved photoresponse of DSSC due to the addition of GCNS was also discussed.

2. Experimental

2.1 Synthesis of graphitic carbon nanospheres (GCNSs)

30 wt% Fe-Co-Mo (1:1:1)/MgO was used as catalyst for the growth of multi-walled carbon nanotubes (MWCNTs) and harsh acidic conditions were then employed to synthesize graphitic carbon nanospheres (GCNSs). The catalyst was prepared by impregnating stoichiometric

amounts of 0.5 M aqueous solutions of ferric nitrate, cobalt nitrate and ammonium molybdate with MgO powder at 70 °C for 6 h followed by calcination at 400 °C for 6 h and reduction at 450 °C for 3 h under H₂. The catalyst was then used for the growth of carbon nanotubes in a horizontal tube furnace. Briefly, 80 mg of catalyst powder was uniformly dispersed on a quartz boat and placed in the central region of tube furnace. There, the catalyst was activated at 800 °C for 1 h in a 100 sccm H₂ flow and MWCNTs were synthesized by flowing 10/100 sccm C₂H₂/H₂ for 30 min. The furnace was then cooled to room temperature under H₂ atm.

The as-grown MWCNTs were subjected to multiple steps in order to remove metallic impurities completely and synthesize pure GCNSs. Typically, 1 gm of as-grown MWCNT powder was first treated with 500 ml of 37% HCl to dissolve MgO, washed with de-ionized water and then dried. The collected material was then refluxed with concentrated HNO₃ (70%) at 110 °C for 48 h to remove amorphous carbon and metallic impurities, washed with water/methanol, and dried overnight at 100 °C. Finally, the resulting material was mixed with 8 M HNO₃ + 8 M H₂SO₄ and ultrasonicated (130 W, 20 kHz) for 6 h at 70-80 °C. It was then filtered, washed with de-ionized water until neutrality, dried at 80 °C, and heat-treated at 500 °C for 1 h under Ar/H₂ (9:1).

2.2 TiO₂ and GCNS-TiO₂ photoanode preparation and characterization

The TiO₂ nanopowder (~ 10 nm, Sigma-Aldrich) slurry was prepared based on the reported method²⁴. GCNS (1 mg) were dispersed in isopropanol (1 ml). Both mixtures were treated in an ultrasonic bath for 1 hour. GCNS mixture was added to TiO₂ slurry in various concentrations. This paste was spin-coated (2000 rpm) on the ITO-glass (Dyesol) substrate (active area of 0.16 cm²). The substrate was sintered at 400°C for 30 mins.

2.3 Photoanode sensitization, DSSC preparation, and its characterization

TiO₂ and GCNS-TiO₂ photoanodes were imbued into solution of commercial 0.3mM N719 dye (Aldrich) for 8h. Counter electrode was prepared by coating Platinum nanoparticle solution (Dyesol) on ITO substrate and then it was annealed at 400°C for 15min. Photoanodes were taken out from the dye and sealed with counter electrodes using thermal sealant (Dyesol). Few drops of iodine based electrolyte were added to the assembled DSSC by capillary action.

Raman measurements were performed using Horiba- T64000 micro-Raman system with 514.5 nm argon ion laser as excitation source. Photovoltaic measurements were done using Keithley-2401 electrometer under solar simulator. The morphological characterization of pure GCNS and GCNS-TiO₂ composite photoanodes were carried out using ultra-high resolution transmission electron microscope (UHRTEM, JEOL JEM-2200FS with Cs corrector and Omega Energy Filter).

3. Results and discussion

Fig. 1 UHRTEM images of GCNS synthesized from chemically modified CVD grown MWCNTs, at different magnifications. Inset to Fig. 1 (d) shows interlayer separation in GCNS.

UHRTEM investigations are carried out to study the morphology and structure of GCNS and GCNS-TiO₂ composites. It is evident from Fig.1 that GCNS are of uniform shape and size (within a size distribution of 25 ± 5 nm), where the interlayer separation is found to be 0.2 nm. It may be further noticed that these spheres are not isolated and we anticipate that they are attached together either by van der Waals forces or physically attached by a thin layer of graphene [37]. Fig. 2 show the UHRTEM images of GCNS-TiO₂ composite, where the TiO₂ nanoparticles of diameter $\sim 10\pm 5$ nm are found to be nicely decorated on the surface of GCNS and demonstrates the GCNS interconnections between TiO₂ nanocrystals. UHRTEM image and histogram showing the TiO₂ particle size distribution has been included in the supplementary information, Fig. S 1. As shown in inset of Fig. 2 (b), the clear lattice fringes of the side face of a single TiO₂ nanocrystal corresponds to (211) lattice plane with a d-spacing of ~ 0.166 nm.

Fig. 2 UHRTEM images of GCNS-TiO₂ composite at (a) low magnification, and (b) high magnification image shows the GCNS interconnecting different TiO₂ crystals in the composite.

Electron energy-loss spectroscopy (EELS), performable within a UHRTEM probe is a very powerful tool to carry out the chemical bonding analysis of a specimen, by finding the interaction details of a high-energy beam (200keV) with a specimen [38].

Fig. 3 EELS mapping performed in GCNS-TiO₂ composite for (a) Ti and (b) C (c) EELS spectra of the GCNS-TiO₂ composite performed in the selected region shown in the inset. Spectra in green color show the data after background correction.

Fig. 3 represents the EELS mapping and the EEL-spectra of GCNS-TiO₂ composite. Fig. 3 (a) shows the mapping of TiO₂ and Fig. 3 (b) shows the mapping of GCNS in the composite. EELS mapping was performed in a selected area of composite shown in the inset Fig. 3 (c). In a carbon nanostructure, the curvature and/or interlayer coupling between different stacks of graphene layers can influence the electronic states of carbon nanostructures, and so the carbon profile in the EEL spectra [39]. It can be further depicted from the Fig. 3 (c) that carbon K-edge signal in higher energy-loss region consists of signal due to $1s \rightarrow \pi^*$ excitation (around 285 eV) as well as $1s \rightarrow \sigma^*$ excitation (around 290-310 eV). Further the peak occurring at around 455.5 eV can be identified as $L_{2,3}$ edges of Ti and the peak at 532 eV corresponds to O-K edge. Any significant impurity peak was not observed in EEL spectra. Quantitative estimation of atomic ratio of O/Ti peak was observed to be ~ 2 so it further confirms the presence of TiO₂ [40].

Fig. 4: Raman spectra of GCNS-TiO₂ composite at room temperature. Characteristic Raman peaks of carbon material has been observed for GCNS, shown in the inset.

Raman spectroscopy is a commonly used technique to characterize TiO₂ nanoparticles and carbon nanostructures. Room temperature Raman spectra of the GCNS-TiO₂ and pure TiO₂ nanocomposite have been shown in Fig. 4 and supplementary information; Fig. S2 (a), respectively. The spectral analysis depicts the distinct phonon peaks at 143, 396, 517, 632, 1348, 1580 cm⁻¹, which is in agreement with previously reported results, suggesting that our TiO₂ nanoparticles show pure Anatase phase [41]. Moreover, the broad line shapes of the Raman peaks indicate nanocrystalline nature of the TiO₂ sample. The full width half maximum (FWHM) of the phonon peak at 143 cm⁻¹ is found to be 23.31 cm⁻¹ which is almost 3 times larger than its bulk value (7.5 cm⁻¹) [42]. This abrupt increase in the FWHM is the consequence of phonon

confinement in TiO₂ nanocrystals [43]. However, some other factors, such as defects and size distribution might have significant contribution to the line shape broadening [44].

More importantly, the presence of two distinct Raman peaks in the higher frequency region of the spectra (1000-1600 cm⁻¹) are the characteristics phonon peaks related to carbon materials [45]. The peak at 1350 cm⁻¹ is known as the D-peak which is otherwise a Raman inactive mode becoming active due the presence of defects [46]. The peak at 1577 cm⁻¹ is the zone center Raman active mode of carbon and is associated with in-plane vibration of the carbon atoms [47]. It is worth mentioning that the relative intensity ratio (I_D/I_G) of the D and G-peak is a measure of defect concentration in carbon materials [48] i.e., higher is the value of the ratio, larger is the defect concentration in the sample. The I_D/I_G ratio was determined to be ~1.44 (>1), as seen from the inset of Fig.4. The higher value of I_D/I_G ratio signals towards the presence of larger defect concentration in our GCNS sample. It is anticipated that during the harsh chemical synthesis process there could be a significant breakdown of the carbon-carbon bond owing to the appearance of D-peak.

Furthermore, Raman spectra of N719 dye sensitized GCNS-TiO₂ composite photoanode for long immersion time has been shown in supplementary information; Fig. S2 (b). The obtained peaks for the dye have been identified as reported in literature [49, 50].

Fig. 5: Raman mapping of GCNS-TiO₂ composite layer at room temperature showing (a) distribution of D-peak and (b) distribution of relative intensity ratio between G to D-peak.

Furthermore, we carried out Raman mapping to verify the homogeneity of the composite film and the distribution of GCNS in the GCNS-TiO₂ composite layer. Fig. 5 (a) shows the mapping of carbon D-peak intensity (over a sample area of 8×8 μm) that corresponds to the GCNS. It can be seen from the Fig. 5 (a) that the intensity mapping is very uniform with a narrow dispersion in intensities. These results are consistent with TEM mapping results of composite. Fig. 5 (b) shows

the Raman mapping for the intensity ratio of G to D peaks over the above mentioned scan area defined in Fig. 5 (a). The uniform distribution of the intensity mapping indicates that the defects generated in these structures are very uniform.

Fig. 6: Schematic representation of the dye-sensitized solar cell.

DSSCs were fabricated using the photoanode of (i) pure TiO_2 and (ii) GCNS- TiO_2 composites with different concentrations of GCNS (0-20 μL). The schematic representation of DSSC containing GCNS- TiO_2 composite photoanode was depicted in Fig. 6. Photocurrent densities (J) versus voltage (V) characteristics for these cells were shown in Fig. 7 (a). The various important parameters, such as open circuit voltage (V_{OC}), short circuit current density (J_{SC}), fill factor (FF), and efficiency (η) were calculated for each cell to compare the photovoltaic responses, which are tabulated in Table 1. A rise in J_{SC} was observed as the concentration of GCNS increased,

whereas V_{OC} attained a maximum value of ~ 0.72 V at an optimal concentration of 5 μL . The maximum value of J_{SC} was found to be ~ -15.43 mA/cm^2 for the cell containing GCNS concentration of 10 μL with an increment of $\sim 62\%$ as compared to pure TiO_2 photoanode. The highest value of efficiency $\sim 5.46\%$ was achieved for GCNS- TiO_2 photoanode containing 10 μL of GCNS. On the other hand, the DSSC having pure TiO_2 as photoanode showed an efficiency of $\sim 3.72\%$, which is quite less as compared to DSSC with composite photoanode. A significant enhancement of $\sim 47\%$ in efficiency of DSSC containing GCNS- TiO_2 (10 μL of GCNS) as photoanode was observed as compare to conventional DSSC with TiO_2 photoanode, clearly indicate the role of GCNS to improve the photovoltaic properties of DSSC. However, it has been noticed that the J_{SC} was remarkably decreased with further addition of GCNS concentration above 10 μL . Furthermore, transient photocurrent characteristics were also measured by several on-off cycles every 15 seconds, of incident light from solar simulator at zero-biasing, as represented in Fig. 7 (b)-(e). Rise and decay curves were consistent over several cycles [51, 52]. Similar to J-V data, a higher value of J_{SC} has been observed for the DSSC containing composite photoanode (with GCNS concentration up to 10 μL) as compared to DSSC with photoanode of pure TiO_2 .

Fig. 7: (a) J-V characteristics and (b)-(e) Transient photocurrent characteristics of DSSCs based on pure TiO_2 and GCNS- TiO_2 composite photoanodes with different GCNS concentrations.

In order to explain the observed trend in the photovoltaic performance with the variation in GCNS concentration, we divide our discussion into two parts: one for the increase and the other for the decrease in the efficiency trend. Comparative higher values of J_{SC} in composite photoanodes can be a consequence of the improved electron transport mechanism [53, 54]. Compared to the pure TiO_2 , the 5 μL GCNS mixed TiO_2 composite cell has shown 4.67% in efficiency accompanied by the increase in both J_{SC} as well as V_{OC} . An interesting and significant finding of our study is that the V_{OC} had increased from 0.67 to 0.72 V by adding GCNS in various concentrations (5-20 μL).

Table 1. (Photovoltaic Performance Parameters from J-V data measured from DSSC based on TiO_2 and GCNS- TiO_2 composite photoanode (active area 0.16 cm^2)

GCNS content	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	$\eta(\%)$
0	0.68	-9.53949	0.574	3.7235
5 μL	0.72	-14.35135	0.45257	4.67641
10 μL	0.72	-15.43357	0.4534	5.0383
20 μL	0.72	-11.23179	0.59871	4.7745

As for increase in V_{OC} , it has been reported that one can reduce the combination process by adding a thin layer (as conformal layer) of insulating material whose conduction band lies slightly above the conduction band of TiO_2 [55]. By doing so, generally it has been noticed that there is a little drop in J_{SC} which is accompanied by an increase in V_{OC} (probably due to the

uplift of the Fermi level of TiO_2), whereas in our case the J_{SC} values were found to increase up to a certain concentrations of GCNS. In view of this, if we assume that our GCNS particles retain the semiconducting characteristics of the parent multi walled carbon nanotubes (MWCNT) and the conduction band of MWCNT was lie slightly above its TiO_2 counterpart, as can be seen from the schematic band diagram of the GCNS- TiO_2 photoanode based DSSC. Band alignment of GCNS- TiO_2 system causes slight up rise in the quasi Fermi level of the composite and therefore, the net increment in difference between quasi Fermi level of GCNS- TiO_2 composite and redox potential of I^-/I_3^- occurs, which further results into an increase in V_{OC} [56]. Based on our results we believe that the band diagram presented in Fig.8 remains valid for different concentration of GCNS and this could be the reason why we observed a constant V_{OC} for all values of GCNS that we have used in our cells.

Fig. 8: Energy level diagram of a GCNS- TiO_2 composite photoanode based dye sensitized solar cell.

Now, we will discuss the variation of J_{SC} with different concentrations of GCNS. From Table 1, it can be seen that the value of J_{SC} increased with increase in GCNS concentration (up to 10 μ L) and then it decreased with further addition of GCNS. These results suggest that addition of small amount of GCNS in TiO_2 is enough to increase the injection as well as electron transfer rate in the cell, where the injection rate can be increased due to the ability of GCNS to improve the dye loading capacity in DSSC. Similar results have been reported in case of other carbon allotropes, such as graphene and CNT [57-61]. We believe that addition of high concentrations (> 10%) of GCNS acts as electron trapping sites centers resulting hindrance in the charge transfer in the dielectric medium (i.e., TiO_2).

4. Conclusions

We have fabricated GCNS- TiO_2 composite photoanode for dye sensitized solar cell that showed significant rise in overall photo-conversion efficiency. Graphitic carbon nanospheres (GCNSs) were synthesized by a unique acidic treatment of multi-wall carbon nanotubes. Detailed morphological studies of GCNS- TiO_2 composites were performed using Raman spectroscopy and ultra-high resolution transmission electron microscope (UHRTEM). Photovoltaic performances of the DSSCs containing GCNS- TiO_2 composite photoanode (with different GCNS concentrations) were investigated. A systematic increment in the short circuit current density (J_{SC}) and open circuit voltage (V_{OC}) of DSSC was observed by increasing GCNS concentration up to an optimal value. The increased values of both V_{OC} and J_{SC} can be understood on the basis of Fermi level modification and higher carrier transport rate in the resultant composite. Thus, a significant enhancement in the efficiency of DSSC containing GCNS- TiO_2 (10 μ L) was observed as compare to DSSC with TiO_2 photoanode.

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