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Enhanced performance of porphyrin sensitized solar cell based on graphene quantum dots decorated photoanodes

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ABSTRACT

Porphyrin sensitized solar cells (PSSC) has been successfully fabricated composed of graphene quantum dots (GQD) functionalized ZnO photoanodes, zinc tetrakis (4-carboxy phenyl)porphyrin (TCPPZn) as sensitizer and polypyrrole coated oxidised multiwalled carbon nanotubes (PPy/OMWCNT) as counter electrode. The effect of the concentration of GQD on the structural, morphological, photophysical and photovoltaic properties of GQD@ZnO, and GQD@ZnO/TCPPZn nanocomposites has also been investigated. Studies indicate that TCPPZn adsorbed on the surface on GQD@ZnO. Hot electron injection mechanism and multiple exciton generation from GQD to ZnO were mainly responsible for the photoexcitation response in PSSC. This study indicates that GQD can play role of sensitizer to some extent. The time decay measurements reveals the evidences of FRET mechanism, and synergistic interaction between GQD and TCPPZn. The J_{sc}, Voc, PCE of the corresponding PSSC devices enhanced initially and then decreased. Among all the devices fabricated, the PSSC with a 40% amount of GQD (GQD@ZnO/TCPPZn 40%) attains the best performance with the $J_{sc} = 10.1\ mA/cm^2$, $V_{oc} = 0.48$, PCE = 2.45% FF = 0.507 higher than ZnO@TCPPZn device fabricated without GQD. Overall, this design provides a new concept for the development of photoanodes which derive better efficiency for dye sensitized solar cell (DSSC) and PSSC at economical low cost.

1. Introduction

The Dye sensitized solar cells (DSSC) have garnered much attention as an attractive, light weight, low cost solar energy conversion technology [1]. DSSC solar cell design involves photo-electrode comprises of mesoporous wide band gap semiconductor oxide (TiO_2, ZnO) inner connected with the dye are packed on a coated transparent conducting glass such as ITO/FTO, in contact with electrolyte usually a redox couple and a counter electrode [2]. Dye sensitizers play an important role as it injects electrons into the conduction band of TiO_2, ZnO etc. Porphyrin sensitizers are capable to cover wide spectral range are considered to be cheaper and environmental friendly potentially replacing the expensive ruthenium based metal complex sensitizer [3,4]. Porphyrin has four meso and eight β positions for functionalizations and thus their optical and electrochemical properties can be easily tuned. Photo-electrode is the core of photon electron conversion process, hence play a vital role in determining the overall performance of the cell. A device with appropriate HOMO-LUMO levels, wide absorption profiles influence the light harvesting, electron injection and electron collection efficiencies of DSSC and hence affects the overall performance of the device [5]. Therefore, it is crucial to modify the photoanode by advancing the light harvesting properties with some scatters so that the enhanced efficiency of DSSC can be achieved [6]. ZnO has been widely used as photoanode and is good alternative to TiO_2 because of its similar energy band structure and photophysical properties as TiO_2, with better electron mobility (205–300 $cm^2\ V/s$), higher electron diffusion coefficient (104–106 cm^2/s) [7–9]. The large exciton binding energy of ZnO (approx 60 meV) allows efficient excitonic emissions even at room temperature, non toxicity and feasible synthesis of 1D nanostructures makes it a promisable candidate for low threshold and high efficiency photonic devices [10–12]. Modifications with carbon structures such as graphene, carbon nanotubes, carbon nano fibres, carbon quantum dots, graphitic carbon nitride gives significant results. Recently, graphene based materials has also been explored in DSSC for catalytic counter electrodes, non transparent anodes and sensitizers [13–15]. The high visibility, young modulus of graphene, ultrafast electron mobility, tunable band gap and photon absorption strengthens every aspects of photoanode [16]. Graphene, a single layer of carbon atoms in a two dimensional honeycomb lattice has given enormous attention owing to its high carrier transport mobility, superior mechanical flexibility and good thermal stability. Incorporation of graphene into semiconductor oxide can enhance electron

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transport while reducing charge recombination and thus increases the DSSC performance [17]. However, their direct application in nanodevices is restricted because graphene sheet do not have an energy band gap which can be explored by converting 2D graphene sheet into zero dimensional quantum dots [18]. GQDs are graphene sheets with size smaller than 100 nm have high surface area grafting by using π-π conjugated network [19]. Graphene quantum dots (GQDs) with quantum confinement, high mobility, tunable band gap, high loading of oxygen atoms, superior photoluminescence (PL) and edge effects have drawn great attention which can be utilized in bio imaging, LEDs, electrocatalysis, and light absorbers in photovoltaics, biosensing and bioimaging [20–22]. Likewise, other carbonaceous structure, carbon nanotubes have been widely used as fillers with conducting polymers due to their high electrical conductivity, chemical stability, low mass density and large surface area. Conducting polymer/carbon nanotubes composites possess superior electronic and optical properties as compare to individual components. Consequently, multiwalled carbon nanotubes (MWCNT), a kind of novel nanostructure from of carbon materials with large specific surface area, highly porous and hollow structures, have attracted intense interest as an ideal matrix for depositing PPy [23–25]. PPy/MWCNTs has many benefits over Pt, MWCNTs provide ballistic conductance, strength, stability and also enhances the charge transfer kinetics.

To harness the excellent properties of carbon materials, we have introduced carbon materials in photoelectrodes in the form of GQD and MWCNT. Zinc porphyrin has been used as sensitizer due to its higher short circuit current (J_{SC}) and its first oxidation potential usually lies around +0.8–1.2 V, the upper lying LUMO level of Zn(II) porphyrin lies in better overlap with the ZnO conduction band and increases the driving force for electron injection of the excited zinc porphyrin in the semiconductor. In present study, porphyrin sensitized solar cell (PSSC) has been fabricated which comprises GQD sensitized ZnO as photoanodes and PPY: MWCNT as counter electrode. All the components had been individually reported by many researchers in previous literature viz. Zamiri et al. investigated the role of GQD as photosensitizer as an alternative to N719 dye and achieved an efficiency of 1.077% [26]. Chen et al. investigated the GQD doped polypyrrole counter electrode for DSSC and found that GQDs doped PPy has porous structure and displays higher catalytic current density and lower charge resistance towards electrolyte and achieved the PCE of 5.27% for device PPy doped with 10% GQDs [27]. Foroushani et al. studied the role of ZnTCPP as a sensitizer in combination with ruthenium complexes in co sensitized solar cell and the efficiency of the device after co sensitization was improved to 6.35% [28]. GQDs sensitized PSSC with GQD decorated ZnO photoanode and PPy/MWCNTs as counter electrode and metalloporphyrin replaces dye in a single device is absolute novel concept having a synergistic effect of all the components. To understand the mechanism of GQD and the effect of its concentration on the optical and photovoltaic properties, different photoanodes with different concentrations of GQD were prepared.

2. Experimental

2.1. Materials

Solvents used in the synthesis and purification were supplied by Merck and freshly distilled prior to use. The multiwalled carbon nanotubes (MWCNT, 98%, OD: 40–50 nm, length: 0.5–500 Im), pyrrole monomer (Py, 98%) were obtained from Sigma Aldrich, USA. Anhydrous ferric chloride ($FeCl_3$, 97%), sodium hydroxide and citric acid were purchased from Fischer scientific. Tetrakis (4-carboxy phenyl)porphyrin (TCPP, 97%) was purchased from TCI Chemicals was used as received.

2.2. Synthesis of graphene quantum dots (GQD)

GQD was synthesized by direct pyrolyzing of Citric acid as reported in literature [29]. Citric acid (2.0 gm) was melted at 200–210 °C using silicone oil bath. After 5 min, its color changed from colorless to pale yellow and after 30 min color changed to orange color indicating the formation of GQD. Drop wise melt of citric acid was poured into 100 mL of 10 mg mL^{-1} NaOH solution with constant stirring. The pH of the solution was adjusted to 7.0 with NaOH solution. The light yellow color solution with blue emission under UV light was obtained.

2.3. Synthesis of GQD functionalized ZnO

GQD@ZnO composite were prepared by insitu method. To achieve the optimum efficiency and evaluate the effect of composition of GQD on photoanode, different percentage (v/v) of GQD as visible light sensitizer was added to prepare GQD@ZnO composite. Zinc acetate dihydrate [Zn $(CH_3COO)_2]\cdot 2H_2O$ was dissolved in isopropanol at 60 °C. After complete dissolution of zinc acetate dihydrate, different amount of GQD solution was added and thereafter NaOH also dissolved in isopropanol was added to the reaction mixture with constant stirring. After continuous stirring for another 2 h, the reaction mixture became turbid and pale yellow-whitish color solution was obtained. Stirring was continued for another 3 h, after that precipitate was collected by centrifugation and washed with distilled water and isopropanol for several times to dissolve other impurities. The precipitate was dried under vaccum for 6 h.

2.4. Synthesis of zinc porphyrin (TCPPZn)

The metallation process involves deformation of the TCPP ring, exchange of solvent molecule with first pyrrolenine nitrogen atom, chelate ring closure followed by deprotonation of nitrogen atoms which leads to the formation of TCPPZn. A mixture of porphyrin (TCPP) (79.07 mg, 0.01 mmol) in chloroform and zinc acetate dihydrate (Zn (ac) $_2.2H_2O$) (39.5 mg, 0.18 mmol) in methanol (10 mL) was stirred at room temperature for 4 h. After removal of solvent under reduced pressure, purple color precipitates were obtained.

2.5. Synthesis of GQD@ZnO@TCPPZn nanocomposite

GQD@ZnO@TCPPZn composites were prepared by insitu method. Zinc acetate dihydrate [Zn $(CH_3COO)_2]\cdot 2H_2O$ was dissolved in methanol. After complete dissolution of zinc acetate dihydrate, TCPPZn dissolved in chloroform was added to the reaction mixture and reaction was continued to stir for another 3 h. Precipitates was centrifuged washed with distilled water and ethanol for several times to dissolve the impurities. The precipitate was dried under vaccum for 4 h.

2.6. Preparation of Polypyrrole/OMWCNT composite

One dimensional hybrid PPY/OMWCNT nanocomposite was prepared by insitu chemical oxidative polymerization. This composite possess a core/shell structure in which, OMWCNT possess core and PPy acts as shell. To prepare PPy/OMWCNT composite, multiwalled carbon nanotubes were first purified by heating at 400 °C in air to remove any carbonaceous impurities and then refluxed for 16 h at 90 °C with 8 N HNO_3 to improve the adhesion between the polypyrrole and carbon nanotubes by π-π interaction. To get the neutral pH, product was washed with deionised water and final product was dried in vaccum. To prepare PPY/OMWCNT composites, OMWCNT was first dispersed in 20 mL deionised water and ultrasonication was done for 30 min. Subsequently, pyrrole monomer was added to this dispersion followed by slow addition of $FeCl_3$ which act as an oxidant. The reaction mixture was stirred overnight at room temperature. The black residue was filtered, washed with distilled water and acetone till all the oligomers