

Increased quantum efficiency in hybrid photoelectrochemical cell consisting of thionine and zinc oxide nanoparticles

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ABSTRACT

In this paper we report our studies on hybrid photoelectrochemical cell made of thionine and zinc oxide nanoparticles. Nanostructured zinc oxide was synthesized in the laboratory by time and cost effective method. The photoelectrochemical cell yielded voltage of high magnitude (401.5 mV) and efficiency (1.21%) compared to other conventional photoelectrochemical cells. The morphology of the nanostructured zinc oxide was identified by X-ray diffraction and electron microscopy studies. Spectral studies indicated adsorption of the dye molecules on zinc oxide nanoparticles, the reason for efficient absorption of the incident photons. During photoexcitation the thionine molecules and the zinc oxide nanoparticles acted as donor–acceptor cluster which produced photovoltage.

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1. Introduction

The emergence of nanomaterials has opened up new ways to utilize them in construction of light energy harvesting assemblies [1]. The high photoelectric transfer efficiency obtained by Grätzel et al [2] in their ruthenium bipyridyl complex sensitized nanocrystalline TiO₂ solar cell, inspired many researchers to design solar cells by using nanocrystalline TiO₂ [3–6]. In this connection other nanocrystallites such as SnO₂ [7,8] and ZnO [9–11] were also explored by many other workers with quite encouraging results. An important advantage of nanocrystallite based solar cells was the tuning of the spectral properties of the cells through appropriate choice of nanostructure shape, size and organization [12].

For our studies we used nanostructured zinc oxide (ZnO) of two different morphologies, namely quantum dot (QD) and nanorod (NR). Stability of ZnO against photocorrosion and its similarity with TiO₂ in respect to band gap (3.2 eV) and band edge position [13] guided us to choose ZnO. We devised a photoelectrochemical cell consisting of two compartments, one of which was filled with a mixture of aqueous solution of thionine dye (TH) and aqueous suspension of ZnO QDs/NRs and the other compartment with iodine–triiodide solution (I⁻/I₃⁻). High values of photovoltage and

efficiency were obtained in both cases. Spectral studies indicated that ZnO QDs or NRs acted as dye adsorber and function basically in increasing the exposed surface area of dye molecules under illumination. Thus light absorption efficiency of the photosensitizer dye molecule increased via adsorption to the nanoparticle surface which in turn minimized thermal losses and increased the overall photon conversion efficiency of the cell.

2. Materials and methods

For nanoparticle preparation we have used zinc acetate dihydrate [Zn(OAc)₂·2H₂O] from Merck, India and lithium hydroxide monohydrate [LiOH·H₂O] from Loba Chemie, India. Absolute ethanol was purchased from Merck, Germany and all these chemicals were used without further purification. For photovoltage (PV) study the dye thionine [C₁₄H₁₃N₃O₂S] was purchased from Loba Chemie, Mumbai, India and was used after recrystallization.

ZnO NPs were prepared according to the procedure described by Spanhel and Anderson [14] with some modifications in the initial stage where, instead of refluxing the ethanolic zinc acetate solution for 3 h, we stirred it for 30 min at 60 °C. This took less time than standard method. The ZnO NPs were then characterized by using X-ray diffraction (XRD) spectra, recorded on Bruker AXS type diffractometer using CuKα radiation - 1.5409 Å (2θ = 10°–0°, scan speed 0.2 s/step, increment – 0.02). Particle size of the sample was determined by using high resolution transmission electron microscopy, HRTEM (JEM 2010, JEOL Ltd, Tokyo, Japan).

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The ZnO NPs were then fired in furnace at 200 °C with 2 h soaking and nanorods were obtained as identified by X-ray diffraction and field emission scanning electron microscopy, FESEM (JSM 6700F, JEOL Ltd, Tokyo, Japan).

The DTA-TG study of ZnO NPs within a temperature range of 100 °C to 300 °C was performed by using DTA-TG machine (DTG-60H, Shimadzu).

Photoelectrical study was performed by using both ZnO QDs and NRs. We devised a photo electrochemical (PEC) cell consisting of two compartments, one of which is filled with aqueous suspension of TH-ZnO QDs or TH-ZnO NRs and the other with iodine/iodide (I^-/I_3^-) solution. The two compartments of U-shaped PEC cell were separated by a platinum foil. A pair of platinum electrodes was placed symmetrically across the foil. Photoinduced voltages and currents were measured by using Keithley digital multimeters (DM196). A 60 W lamp was used for illumination and the light intensity was measured by using a Luxmeter with photodetector (D & L Instrument, MS6610).

Absorption spectra of TH-ZnO QDs/TH-ZnO NRs were recorded in a PERKIN ELMER Lambda 25 UV/VIS Spectrometer (Shelton, CT064844794).

3. Results and discussion

The DTA-TG curve (Fig. 1, top right) showed an endothermic peak at around 160 °C indicating a transition to another morphology and corresponding enthalpy change was calculated to be -117.96 J/g. When the same sample was scanned for the second time no such peak was observed indicating the transition to be irreversible one.

XRD spectrum (Fig. 1, top left, a) indicated that the prepared ZnO sample was in QD form. Large diffraction peaks of XRD spectrum gave a clear indication of QDs formation [15]. For the sample fired at 200 °C, a sharp diffraction peak appeared at 002 (Fig. 1, top left, b) which indicated the transformation of ZnO QDs to NRs [16].

The average particle size of ZnO QDs was calculated to be 7–10 nm by fitting its XRD data to the Debye–Scherrer formula [17]. In the HRTEM image (Fig. 1, bottom left) small, round shaped particles of ZnO QDs were clearly visible though agglomeration was present to some extent. The grain size estimated from the microscopic image was ~ 7 nm which is in good agreement with the size calculated from the XRD data. The FESEM image (Fig. 1, bottom right) of fired sample clearly indicated rod like structure at magnification 50×10^3 . Average length and width of NR estimated from FESEM image ranged between 100–150 nm and 25–40 nm respectively.

We studied the photovoltage generation in the PEC cell (Fig. 2 inset) using (a) TH solution, (b) TH-ZnO QDs suspension and (c) TH-ZnO NRs suspension. In all the three cases upon illumination voltage started rising with time and reached a saturation value after nearly 40 min (Table 1). The maximum saturation value remained constant as long as the light source was on. When the light was switched off the voltage decreased slowly and took nearly 6–7 h (Table 1) to reach to the initial value (Fig. 2). The photovoltage cycle was reproducible upon further illumination. The fill factor (FF) and the efficiency ($\eta\%$) of the cell were calculated from the I - V curves of the cell using the following equations [18]

$$FF = \frac{V_{pp} \times I_{pp}}{V_{oc} \times I_{sc}} \quad (1)$$

$$\eta\% = \frac{V_{oc} \times I_{sc} \times FF}{\text{power of incident photons}} \quad (2)$$

where V_{oc} = open circuit voltage, I_{sc} = short circuit current, $V_{pp} = V_{\text{powerpoint}}$, $I_{pp} = I_{\text{powerpoint}}$

The values of V_{oc} , FF and $\eta\%$ were summarized in the table. It was evident that the presence of ZnO nanoparticles caused increase in the values of V_{oc} , FF and $\eta\%$ whereas the cell consisting of ZnO NRs was the most efficient one.

In order to understand how the nanostructured ZnO tuned the photoelectric properties of the dye molecule we performed the

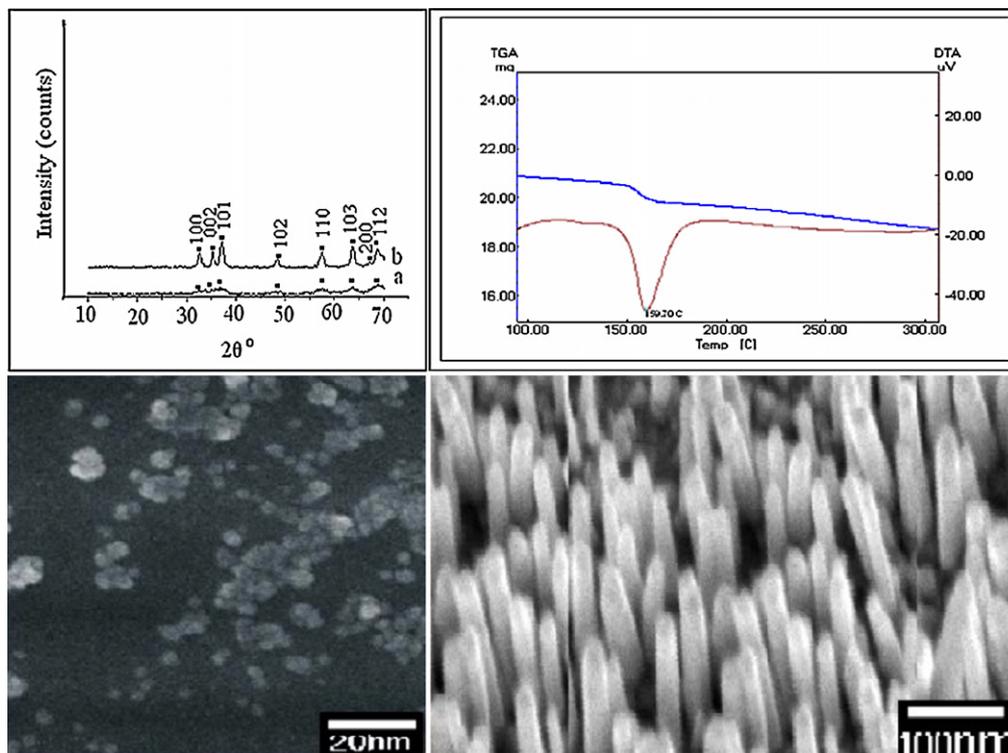


Fig. 1. Top left, X-ray diffraction patterns of ZnO QDs (a) and ZnO NRs (b); top right: DTA-TGA curve of ZnO QDs from 100–300 °C; bottom left: HRTEM image of ZnO QDs; bottom right: FESEM image of ZnO NRs.

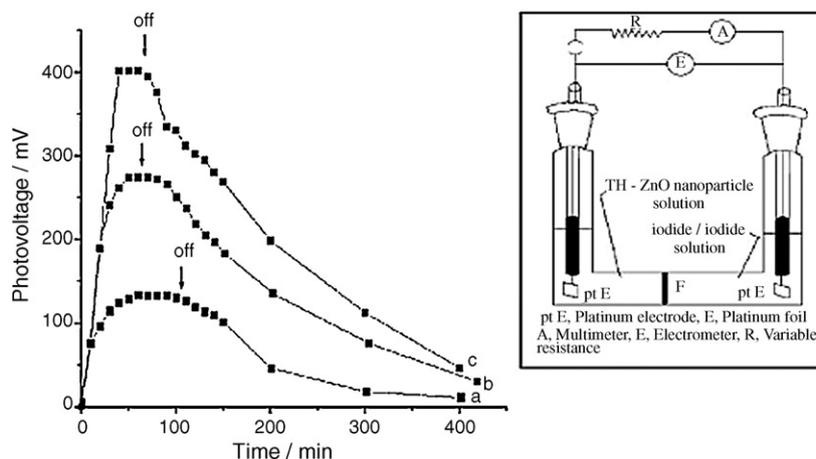


Fig. 2. Growth and decay curve for V_{oc} generation. (a) TH; (b) TH adsorbed on ZnO QDs and (c) TH adsorbed on ZnO NRs. Inset shows the model PEC cell.

Table 1

The characteristics of PEC cell using (a) thionine (TH), (b) TH–ZnO QDs and (c) TH–ZnO NRs.

Sample used	Open circuit voltage (V_{oc})	Time taken for V_{oc} (min)	Decay time (min)	Short circuit current (μA)	Fill factor (FF)	Efficiency ($\eta\%$)
TH	123.6	40	310	1.3	0.12	0.003
TH–ZnO QDs	272.6	54	420	12.8	0.31	0.72
TH–ZnO NRs	401.5	58	480	24.5	0.42	1.21

spectral studies. The absorption spectrum of TH (Fig. 3) in water exhibited two characteristic absorption bands, one in visible range around 598 nm with a shoulder at 565 nm and another at 280 nm in the ultraviolet region. The 598 nm band of TH is the characteristic feature of monomeric form, and the 565 nm shouldering can be attributed to the H-type dimer aggregate [19]. Photosensitivity of TH can be ascribed as a function of oxidation–reduction reaction of the nitrogen atom of its central heterocyclic ring [20]. Fig. 3 shows that with addition of ZnO QDs/NRs with thionine (4×10^{-4} M) the absorption efficiency of thionine increased remarkably. The peak positions remain unaltered but the overall intensity increased gradually with the increasing concentration of ZnO QDs/NRs (1.7×10^{-4} – 8.5×10^{-4} mg/L) which indicated adsorption of dye molecules onto the ZnO QDs/NRs surface [11,20,21], the adsorption processes being facilitated due to the high aspect ratio of the

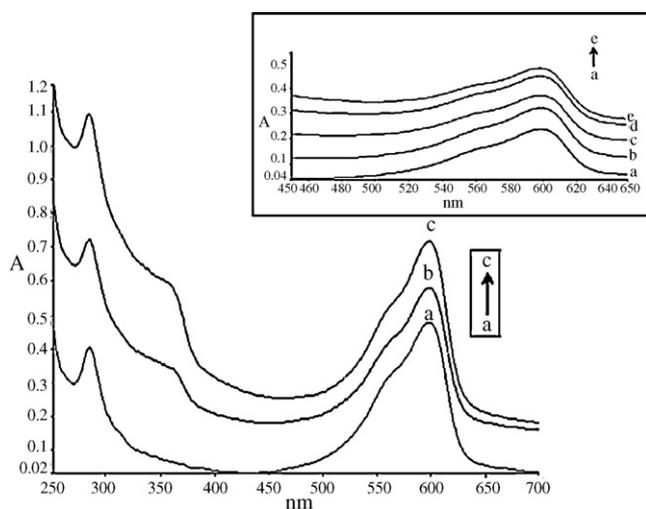


Fig. 3. The absorption spectra of TH–ZnO NRs system. Inset shows absorption spectra of TH–ZnO QDs system. Concentration of TH: 4×10^{-4} M; concentration of ZnO NRs ($\times 10^{-4}$ mg/L): (a) 1.7, (b) 3.4, (c) 5.1 and concentration of ZnO QDs ($\times 10^{-4}$ mg/L): (a) 1.7, (b) 3.4, (c) 5.1, (d) 6.8, (e) 8.5.

nanostructured ZnO. The NRs had higher aspect ratio as its surface morphology was different from that of QDs and adsorption of dye molecules was higher resulting in higher absorption of the incident photons. However, high ZnO nano-concentration (8.5×10^{-4} mg/L) was not effective for photovoltage generation. This can be explained as the availability of ZnO QDs or ZnO NRs surfaces limit the charge injection process thereby reducing the efficiency of charge transfer and may increase the rate of a reverse-electron-transfer process. [22].

The adsorption mechanism is based on an electrostatic attractive force between cationic TH molecules and ZnO nanocrystals as ZnO nanocrystal itself is negatively charged [23,24]. The photosensitizer TH acts in PEC cell as an electron acceptor and upon illumination generated voltage of 123.6 mV which increased to 272.6 and 401.5 mV by the addition of ZnO QDs and ZnO NRs respectively. Another notable feature is that the energy storage capability of cell also increased and it was 480 min (~ 8 h) in case of ZnO NRs and 428 min (~ 7 h) in case of ZnO QDs adsorbed with TH. Details of photoelectrical studies are mentioned in table.

The PEC cell performance significantly increased in case of TH–ZnO NRs system than TH–ZnO QDs which can be explained as more dye molecules adsorbed on NRs resulting in increasing photon absorption [25]. The best performance of PEC cell gave a maximum η of 1.21% in case of TH–ZnO NRs (when ZnO NRs conc was 5.1×10^{-4} mg/L) than TH–ZnO QDs (η of 0.72% when ZnO QDs conc was 6.8×10^{-4} mg/L) due to decreased number of grain boundaries in NRs that act as electron traps [26] in comparison to QDs.

The electrons required by the photoexcited dye molecules [27] were supplied from the conduction band of ZnO. The lost electrons were regenerated via a redox process within the iodide/triiodide couple. The nanostructured ZnO was potentially beneficial in two ways – (a) by providing the site for adsorption of dye molecules and (b) by accepting and shuttling the electrons. The production of a long-distance charge-separated state resulted into an enhancement in charge separation efficiency. This alongwith the vectorial transport of the charges which was casual otherwise increased the efficiency of the PEC by preventing back recombination of the photoinduced charges.

4. Conclusion

In our studies we synthesized ZnO QDs in the laboratory by methods which involved lesser time and cost compared to the existing methods. ZnO NRs were obtained by just soaking the QDs at 200 °C in furnace. The PEC cell made of the mixture of nanostructured ZnO and TH dye yielded photovoltage of appreciable magnitude and efficiency. Spectral studies indicated adsorption of the dye molecules on the nanoparticle surfaces which increased the light absorption efficiency thereby minimizing the thermal losses. The ZnO QDs/NRs–TH mixture acted as the donor–acceptor molecular assemblies and clusters where ZnO QDs/NRs acted in accepting the electrons which produced long-distance charge-separated states. This in turn increased the efficiency of the PEC cell by preventing back recombination of the carriers. Moreover the cells showed storage duration due to guided trajectory of electrons. Further studies are in progress to make the cell competitive with other solar cells.

The process adopted in our experiment is inexpensive as we used the well known thiazine group of dye thionine instead of costly ruthenium complex in our PEC cell and also improved efficiency as well as storage.

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