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Morphology dependent change in photovoltage generation using dye-Cu doped ZnO nanoparticle mixed system

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ABSTRACT

The present report deals with the studies on hybrid photoelectrochemical cell containing a commonly used dye, phenosafranine and Cu doped ZnO nanoparticles/nanoflakes for conversion of solar energy to electrical energy. The cell consisting nanoflakes yielded voltage of high magnitude (~784 mV), good storage duration (~60 h) and better energy conversion efficiency (3.82%) compared to other similar cells. The particle size and morphology of the nanomaterials were determined with X-ray diffraction and electron microscopy studies. Absorption spectra of the dye-nanomaterial mixed system indicated that the absorbance of dye molecules increased with addition of nanomaterials due to adsorption of dye molecules on the surface of nanomaterials, which facilitated incident photon absorption. Presence of planar lipid membrane hindered the back recombination of photoexcited charges causing radical increase in voltage generation, efficiency and storage duration.

1. Introduction

The possibility of regulating chemical and physical properties of materials in nanoscale has currently attracted widespread scientific and technological interest. Along with many imperative applications, the use of different nanomaterials in photovoltaics has been a highly interesting field in recent years. M. Gratzel first introduced DSSC (dye sensitized solar cell) with nanocrystalline TiO_2 and Ru bipyridl [1]. There after tailored nanomaterials has become the focal point of research in energy conversion in order to get enhanced light absorption [2], to reduce recombination losses [3], to address the problem of mismatch between the incident solar spectrum and the spectral absorption properties of the material [4]. Thus use of nanomaterials potentially leads to higher solar energy conversion efficiencies which provide innovative strategies for designing new and more effective light energy harvesting devices [5]. Different metal and metal oxide nanoparticles like TiO_2 [6], ZnO [7], SnO_2 [8] CeO_2 [9], Cr_2O_3 [10], Au [11] and Ag [12] are being extensively used as basic materials for low cost production of electrical energy from solar energy. Among these binary valance metal oxides, ZnO attracts attention due to its amazing physical and chemical properties [13,14]. Low cost production and environmental stability of ZnO along with its band gap value 3.37 eV, binding energy 60 eV and band edge position very similar to that of TiO_2 [15] makes it a promising semiconductor which can be extensively used in conversion of solar energy [16–18]. Moreover, ZnO nanostructures exhibit varieties of different size and morphology which is important for its better performance as light energy conversion material [7,19]. Doping ZnO with transition metals like Cu, Al etc showed better efficiency [20,21]. The solar energy conversion efficiencies for Al doped ZnO nanofibers and Sn doped spindle shaped ZnO nanoparticles were reported to be 0.54–0.55% and 1.82% respectively [22,23]. Efficient energy harvesting has also been observed by using multi-walled carbon nanotubes in the counter electrode of a dye-sensitized solar cell [24].

The aim of the present work is to increase the efficiency and storage duration of the hybrid PEC (photoelectrochemical cell) using low cost suitable materials that guided us to choose

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nanostructure Cu doped ZnO. This report describes a simple, less hazardous and efficient method to synthesize Cu doped single wurtzite phase ZnO nanoparticles (CZNPs) of two different morphologies which were subsequently mixed with a photosensitive dye, namely, PSF (phenosafranine). The aqueous suspension of PSF-CZNPs complex was then used for solar energy conversion in a cost effective way. The efficiency of photovoltage generation changed with the change in morphology of CZNPs.

2. Experimental

2.1. Materials

Zinc acetate dihydrate [$(CH_3COO)_2Zn\cdot 2H_2O$] from Merck, India, Cupric acetate monohydrate [$(CH_3COO)_2Cu\cdot H_2O$] and Lithium hydroxide monohydrate [$Li(OH)_2$, H_2O] from Loba Chemie, India and n-hexane from Merck, Germany were used for CZNPs preparation without any further purification. Cholesterol (Eastman Organic Chemicals) was oxidized and recrystallised from n-decane (Merck, Germany). The dye phenosafranine (3,7-diamino-5-phenazinium chloride) [$C_{18}H_{15}ClN_4$] was purchased from Loba chemie, India for PV (photovoltage) study.

2.2. Preparation of Cu doped ZnO

Nanomaterials of Cu doped ZnO have been synthesized according to the procedure described by Spanhel and Anderson [25] with some modification. As in previously reported paper, it had been found that doping concentration of Cu of 3 mM gives best results [26], so the present study is preceded with this concentration. The CZNPs were then fired at 120°C for 6 h and Cu doped ZnO nanoflakes (CZNFs) were obtained.

2.3. Preparation of PSF-CZNPs & PSF-CZNFs system

The stock solution of CZNPs, CZNFs and PSF were prepared by dispersing them in water separately of concentration 1 mg/L for both nanomaterials and 2×10^{-1} M for dye. Desired concentration of CZNPs, CZNFs and PSF solution for UV and PV study were prepared after further diluting the stock solutions. Both these solutions were then mixed with dye solution and sonicated in an ultrasonic bath for 1 h at room temperature.

2.4. Characterization of the samples

Both samples were identified with powder X-ray diffraction (XRD) method. The crystalline size and the phase purity of the samples were measured by a Bruker AXS-type diffractometer using Cu Kα radiation at wavelength 1.5405 Å ($2\theta = 10°–70°$, scan speed = 0.2 s/step, increment = 0.02).

Raman spectroscopic measurements of the samples were performed in Raman spectrometer model LabRAM HR (Jobin YVON) with laser of wavelength ~488 nm.

The morphologies of the samples were examined with FESEM (Field Emission Scanning Electron Microscopy) (Model. FEI- Inspect F50).

PERKIN ELMER Lambda 25 UV/VIS Spectrometer (Shelton, CT064844794) was used to record absorption spectra of PSF-CZNPs and PSF-CZNFs systems.

2.5. Photovoltage generation study

Photoelectrical studies using PSF-CZNPs and PSF-CZNFs were performed in a specially designed easy to assemble photo-electrochemical cell (Fig. 1). It consisted of two L shaped glass tubes.

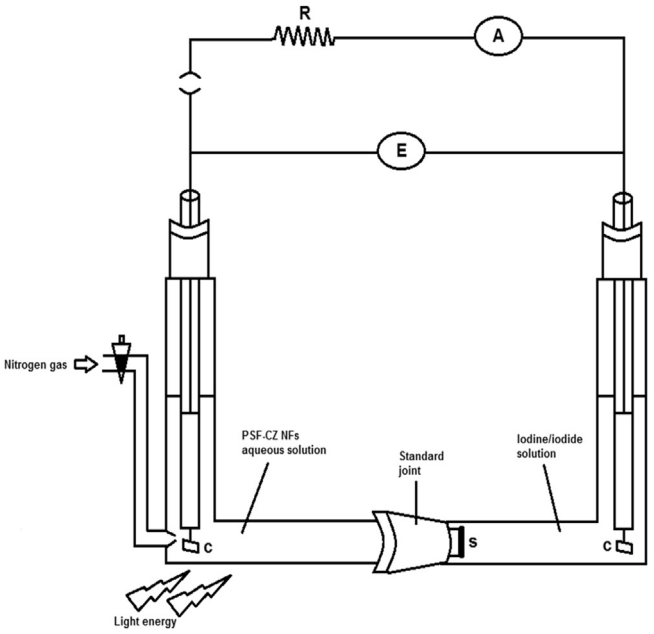

Fig. 1. Schematic diagram of the electrochemical cell; C – Platinum electrode; A – Multimeter; E – Electrometer; R – variable resistance; S – Sintered disc with PLM.

A micropore glass filter of ~10 μm porosity was mounted on one tube which was fitted into the other by means of a standard joint. A saturated solution of oxidized cholesterol in n-decane was brushed on to the glass filter to ensure a stable PLM (planar lipid membrane) formation which acted as barrier between the two compartments of the cell. One side of the PLM was filled with aqueous suspension of PSF-CZNPs or PSF-CZNFs and the other side with iodine/iodide (I^-/I^{3-}) solution. Before illumination the dye solution was deoxygenated by passing nitrogen gas through the solution in order to reduce surface oxidation of PSF [27].

A pair of platinum electrodes was placed symmetrically across the barrier. Photo induced 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 with a Lux-meter (D & L Instrument, MS6610).

3. Result and discussion

It is quite evident from the XRD patterns of CZNPs and CZNFs as shown in Fig. 2 (a) and (b) respectively, all the d-values of XRD peaks indicated the presence of wurtzite phase of ZnO [28]. No signal corresponding to Cu related secondary or impurity phase was detected in the samples. It may be attributed to the incorporation of Cu ion into the Zn lattice site rather than interstitial ones [20,29]. The grain sizes were obtained by fitting the XRD data to the Debye Scherrer formula ($D = 0.9\lambda/\beta \cos\theta$, where D is the crystallite diameter, λ is the radiation wavelength and θ is the incidence angle) and the average crystalline size for CZNPs (25–35 nm) was calculated from the FWHM (full-width at half maximum) of the XRD lines.

Particle size and morphology of the samples were determined by using FESEM micrographs (Figs. 3 and 4), which indicated that the CZNPs were almost regular spherical in shape and the particle sizes lied between 28–40 nm and the average length and width of CZNFs lied between 150–200 nm and 30–45 nm respectively. By using EDAX (energy dispersive X-ray spectroscopy) the elemental compositions of CZNPs (in our previous study [26]) and CZNFs (Fig. 5) were studied which indicated the presence of no other