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Synthesis and characterization of copper doped zinc oxide nanoparticles and its application in energy conversion

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ABSTRACT

Solar cells, in general, perform under light source of solar influx, while the heat energy of solar radiation remains unutilized. Using an aqueous suspension of copper doped zinc oxide nanoparticles in specially-designed electrochemical cells we have observed significant voltage (maximum 632.0 mV) and storage duration (~47 h) upon thermal excitation. The cells exhibit reasonable energy conversion efficiency (maximum 1.36%). These cells generate voltage even at room temperature (~30 °C) and the voltage increases gradually with increasing temperature. When the platinum foil separating the two compartments of the electrochemical cell is replaced by a planar lipid membrane, all the parameters e.g., thermovoltage, storage capacity and the energy conversion efficiency increase significantly.

1. Introduction

To provide sufficient energy for meeting human requirements is one of the challenges of 21st century and therefore emphasis is given on the development of alternative energy sources [1–4] in different cost effective ways. Nowadays varieties of nanoparticles (NPs) are used as the new building blocks to construct light energy harvesting assemblies [5–9]. New initiatives like use of biomimetic systems to simulate natural photosynthesis [10–13] and fabrication of hybrid solar cells by using nanoparticles have been very promising [14–16].

Owing to their photo luminescence properties, semiconductor nanocrystallites of titanium dioxide (TiO_2), silicon dioxide (SnO_2) [17,18] and zinc oxide (ZnO) [19,20] have attracted considerable attention and were explored by many workers showing quite interesting results. Specially ZnO NPs, an n-type semiconductor with wide band gap (3.3 eV at room temperature [21]) have widely been used in construction of light as well as heat energy harvesting assemblies [22,23]. Now doping TiO_2, ZnO etc. with transition metals like Cu, Co, Ni, Au etc. have created new materials which have potential application in semiconductor devices [24–26]. We have been working in developing biomimetic solar cells by using different photosensitive dyes [27,28] and different nanoforms of ZnO [29].

In the reported work we have doped ZnO NPs with copper (Cu) in different ratios, as Cu can suitably adjust the energy level in the surface states of ZnO NPs and the physical as well as the optical properties of doped nanomaterials can be tuned by changing the doping concentration [30,31].

Characterizations of these samples were done by using Powder X-ray Diffraction (XRD), Differential Thermal Analysis (DTA), Scanning Electron Microscopy (SEM) with Energy-dispersive X-ray Spectroscopy (EDAX), UV–Vis spectroscopy and Brunauer Emmett Teller (BET) surface analyzer. Heat induced voltage (thermovoltage) generation at different temperatures were recorded by using the samples in electrochemical (EC) cell, we have devised. Voltage of quite high magnitude ($V_{oc} = 632$ mV) and good energy conversion efficiency ($\eta\% = 1.36$) were observed within our experimental range (30 °C–50 °C). After withdrawal of the heat source the voltage decreased slowly indicating storage capacity of the cell. With insertion of planar lipid membrane within the cell, not only the voltage generation and efficiency increased, but also a radical increment in the storage duration was observed. Optical absorption measurement indicated decrease in the value of band gap with incorporation of Cu [32].

Since in this study the temperature required for voltage generation is not very high, the thermal excitation caused by solar radiation is enough to produce significant voltage. Moreover

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industrial waste heat may be suitably utilized in producing voltage after proper improvisation.

2. Materials and methods

Zinc acetate dihydrate [$Zn(OAc)_2$, $2H_2O$] from Merck, India, Cupric acetate monohydrate [$Cu(OAc)_3$, H_2O] from Loba Chemie, India, Lithium hydroxide monohydrate [$Li(OH)_2$, H_2O] from Loba Chemie, India and *n*-hexane from Merck, Germany were used for sample preparation without any further purification. Cholesterol (Eastman Organic Chemicals) was oxidized and recrystallized from *n*-decane (Merck, Germany).

Depending on the dopant concentration the prepared samples were designated as follows:

Sample a: ZnO NPs + 1 mM Cu.

Sample b: ZnO NPs + 3 mM Cu.

Sample c: ZnO NPs + 5 mM Cu.

Cu doped ZnO nanoparticles (Cu–ZnO NPs) were prepared following the procedure of Spanhel and Anderson [33] with some modifications. 0.1 M of [$Zn(OAC)_2$] was dissolved in 50 mL of absolute ethanol by vigorous stirring in a magnetic stirrer at 50 °C till the solution become transparent. Then $Cu(OAC)_3$ of different concentrations (1 mM, 3 mM and 5 mM respectively) were mixed with the solution separately and kept under vigorous stirring at same temperature (50 °C) until bluish transparent solution was formed. The precursor solution was then kept for cooling and at room temperature Lithium hydroxide of 0.14 M concentration was mixed with it. The mixture was then hydrolyzed in an ultrasonic bath (Model 229, Imeco Ultrasonic, India) for 30 min. By adding *n*-hexane into the resulting solution at 4:1 ratio, a bluish precipitate of Cu–ZnO NPs was obtained which was then separated by centrifugation (Model. Sigma 3–30 k) at 12,000 rpm. Finally the precipitate was collected, washed with distilled water and ethanol for several times and dried at 60 °C.

DTA of all the sample were performed within the temperature range 30 °C–400 °C (DTG-60H, Shimadzu) and the associated phase transitions were observed.

Powder XRD method was used to measure the crystalline size and the phase purity of the samples with different concentration of Cu. Measurements were done 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).

The surface morphology, size and the elemental analysis of the sample were observed by SEM fitted with EDAX (Model. FEI – Inspect F50). The sample was coated with gold using low voltage sputtering and then analyzed under SEM at operating potential 20 KV.

Absorption spectra of all the three samples were recorded in a PERKIN ELMER Lambda 25 UV/VIS Spectrometer (Shelton, CT064844794). For spectral studies, aqueous suspension of same amount of NPs (5.5×10^{-4} mg/L) of different materials were formed by sonication in an ultrasonic bath for 20 min.

Specific surface areas of the samples were determined by using Brunauer Emmett Teller (BET) surface analyzer (NOVA-4000e Quantachrome, USA) using nitrogen as a purge gas.

3. Experimental set-up

The electrochemical cell (EC) used in our experiment were of two types:

(A) Set-up A: The cell is consisted of an L-shaped glass tube with a platinum (Pt) foil separating the two arms of the tube.

(B) Set-up B: The cell is consisted of two L-shaped glass tubes. 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 (Fig. 1). For this set-up, a saturated solution of oxidized cholesterol in *n*-decane was brushed on to the glass filter to ensure a stable planar lipid membrane formation (PLM) [28]. One side of the PLM or Pt was bathed with HCL (0.1 M concentration), and the other side was bathed with aqueous suspension of Cu–ZnO NPs in 10 μg/ml concentration, which was prepared by dispersing the NPs in distilled water using an ultrasonic bath sonicator for 20 min.

We have recorded the thermo-voltage generation with the Cu doped ZnO nanoparticles in the EC cell for both set-ups where a pair of platinum electrodes was placed symmetrically across the barrier. The temperature was controlled by keeping the cells in a thermostatic chamber (model MDC-2901, INCON, India) and adjusted to different levels as required. Voltage generation was recorded at different temperature ranging from 30 °C to 50 °C. The voltages and currents were measured by means of Keithley digital multimeters (DM196).

4. Results and discussion

The DTA (Fig. 2) of Cu–ZnO NPs samples have showed two endothermic peaks at ~60 °C and ~150 °C and one exothermic peak at ~300 °C. The first endothermic peak was almost in the same position and this peak was reversible, indicating phase transition of the sample at that temperature. But the second endothermic and third exothermic peaks shifted slightly to lower temperature with

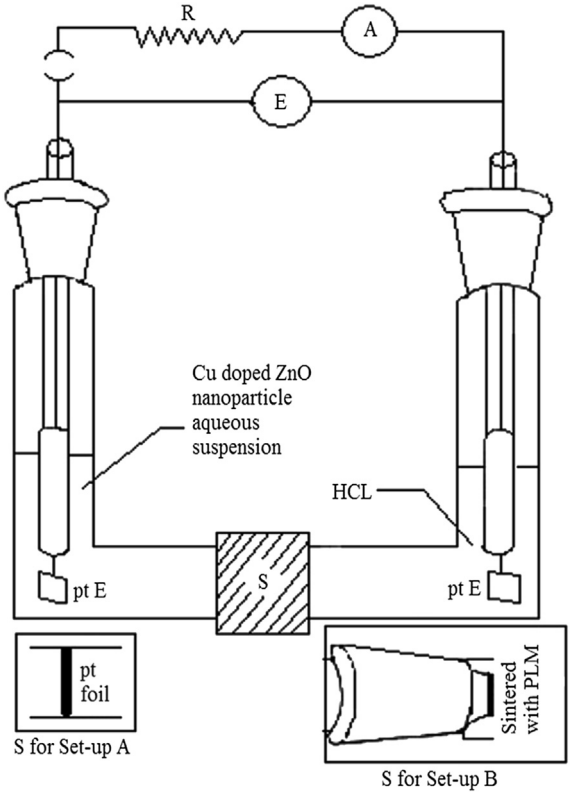

Fig. 1. Schematic diagram of the electrochemical cell; pt E – platinum electrode; A – multimeter; E – electrometer; R – variable resistance; S – separation.