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# Synthesis and application of zinc/tin oxide nanostructures in photocatalysis and dye sensitized solar cells

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## ABSTRACT

Zinc oxide (ZnO), tin oxide (SnO<sub>2</sub>) and zinc–tin oxide (ZnO–SnO<sub>2</sub>) nanostructures were successfully synthesized from vapor phase by heating well mixed various ratios of ZnO and/or SnO<sub>2</sub> powders with carbon in the temperature range of 1000–1200 °C in a loosely closed porcelain crucibles. The prepared samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Various morphologies including tetrapods, nanorods, nanowires, nanobelts and nanoparticles in the size range of 150–350 nm were microscopically observed. The photocatalytic activity of the prepared samples was tested toward the degradation of 2-chlorophenol (2-CP) in water. The photo-intermediate products were determined by high performance liquid chromatography (HPLC). The produced chloride and acetate ions during the degradation process were also monitored by ion chromatography. The results showed that ZnO was the most photoactive prepared nanostructures. The order of the photoactivity is ZnO > SnO<sub>2</sub> > ZnO–SnO<sub>2</sub>. Light-harvesting nanohybrids (LHNs) systems composed of the ZnO, SnO<sub>2</sub> and ZnO–SnO<sub>2</sub> nanostructures associated with the Rose Bengal as an organic dye has been employed to improve the light-harvesting performance of the cell. The open circuit-voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ) and conversion efficiency ( $\eta$ ) are found to be 715 mV, 17.52 mA/cm<sup>2</sup> and 6.74% for ZnO electrode, respectively. It is observed that the photoelectrochemical outputs for ZnO electrode increased by ~10% in  $J_{sc}$  and 30% in  $\eta$  compared with that obtained for SnO<sub>2</sub> and ZnO–SnO<sub>2</sub> electrodes, respectively. The use of branched tetrapods ZnO nanostructures improved the efficiency of DSSC significantly in presence of a low cost Rose Bengal dye compared with the commonly used N719 one. The results of DSSCs application are compatible with that obtained from photocatalysis. We believe that surface-to-volume aspect ratio, morphology and type of combination have a great effect on the photoelectrochemical properties.

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## 1. Introduction

Currently, the research work on transparent semiconducting oxides such as ZnO, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, CdO, In<sub>2</sub>O<sub>3</sub>:Sn and Cd<sub>2</sub>SnO<sub>4</sub> has been gaining much interest due to their high quality of electrical and optical properties [1,2]. In recent years, many efforts have been made to control the sizes and shapes of materials on nanoscale, because these parameters affect their properties [2]. The materials based on zinc and/or tin oxide have been extensively studied because they have many applications in solar energy conversion, catalysis, gas sensing, antistatic coating and transparent electrode preparation. Zinc oxide (ZnO) is n-type, wide band gap (3.37 eV at 298 K) semiconductor with a large exciton energy of 60 meV. Its nanoscale structures have attracted extra ordinary attention for their promising potential applications as a short-wavelength light emitting transport

conductor, interconnect integration in nanoelectronics, molecular electronics and in optoelectronic devices [3]. Tin oxides (SnO<sub>2</sub> and SnO) are n-type wide band gap semiconductors ( $E_g=3.6\text{--}3.97$  eV) and their electrical properties critically depend on their stoichiometry with respect to oxygen, on the nature and the amount of impurities or dopants present and on their nanostructure forms [4].

Besides these applications, ZnO is a very attractive semiconductor for use in photocatalysis and solar cells due its abundance and low cost, nontoxicity, high electron mobility, low crystallization temperature and easy synthesis. The biggest advantage of ZnO in comparison with the commonly studied TiO<sub>2</sub> is that it absorbs a larger fraction of UV spectrum and the corresponding threshold of ZnO is 425 nm. Upon illumination, valence band electrons are promoted to the conduction band leaving a hole behind (Eq. (1)). These electron–hole pairs can either recombine (Eq. (2)) or interact separately with other molecules. The holes at the ZnO valence band can oxidize the adsorbed water molecules or hydroxide ions to produce hydroxyl radicals (Eqs. (3) and (4)). Electrons in the conduction band on the catalyst surface can reduce molecular oxygen to superoxide anion

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(Eq. (5)). This radical may form organic peroxides or hydrogen peroxide in the presence of organic scavengers (Eqs. (6) and (7)). The hydroxyl radical is a powerful oxidizing agent and attacks the organic compounds and formed intermediates. These intermediates again react with hydroxyl radicals to produce final products (Eq. (8)). The mechanism of heterogeneous photocatalysis is presented as below [5,6]



ZnO has emerged to be a more efficient catalyst concerning water detoxification because it generates  $\text{H}_2\text{O}_2$  more efficiently [7], with high reaction and mineralization rates [8]. Also it has more number of surface active sites with high surface reactivity [9].

Nanocrystalline ZnO of different morphologies has also been found to be a promising material for dye sensitized solar cells because of its high photoactivity and transparency to visible light [10,11]. Dye-sensitized solar cells have gained widespread attention in recent years because of their low production costs, ease of fabrication and tunable optical properties, such as color and transparency. There are several important issues which are of great research interest that aim to improve the performance of the DSSC, efficient transportation of photoexcited electron. The use of ZnO nanocrystal layer is one of such key issues.

Different morphologies of ZnO,  $\text{SnO}_2$  nanostructured materials and various combinations with at least one of these compounds have been explored for energy and other applications by many authors. Among these nanostructures and combinations; nanoparticles [12–15], nanowires [16–18], nanotubes [19], aggregated beads [20], hollow spheres [21], nanopyramids [22], tetrapods [23,24], nanotrees [25], nanocones [26], ZnO/ZnO core-shell nanowire array [27], micro-flower [28], nanorods [29–31], as well as densely packed setose ZnO nanorod arrays [32] have been used as photoanode materials in dye-sensitized solar cells (DSSC) applications. Although various strategies have been applied to improve the ZnO-based solar cell's performance, the worldwide energy conversion efficiencies are still relatively lower than the commonly investigated  $\text{TiO}_2$  counterparts. This might be mainly due to the low electrical conductivity of Zn (II) ion-dye complexes formed on the ZnO surfaces. It leaves lots of research rooms for further improvement of the ZnO-based solar cell's performances via modifying the nanostructures of ZnO and varying many other parameters.  $\text{TiO}_2$ -ZnO-shell aggregate photoelectrodes have been studied to improve the DSSC performance. An improved efficiency ( $\eta$ ) 4.6% was obtained [33]. Recently, ZnO nanocones with exposed {10\_11} facets were prepared and used as photoanode material in a N719-sensitized solar cell, which displayed a better conversion efficiency (3.84%) than the devices fabricated with commonly used ZnO nanorods with predominantly exposed {10\_10} facets due to the significantly less dye aggregation on the ZnO {10\_11} facets as compared to the other ZnO facets [26]. Quantum dots-docrated ZnO nanorods- based dye sensitized solar cells have also been tested and the following photoelectrochemical properties have been obtained;  $V_{oc}$  (mV)=690,  $J_{sc}$  ( $\mu\text{A}/\text{cm}^2$ )=620, FF (%)=29.92, and  $\eta$  (%)=0.13 [34]. Also, doping with  $\text{SnO}_2$  was a way to improve the efficiency of ZnO [35]. The conversion efficiency was increased up to 4.2%. Kumara et al. [36] studied a cell consists of thin

shell of ZnO on  $\text{SnO}_2$  and a thin shell of  $\text{SnO}_2$  on ZnO. It was found that the first cell could effectively counteract recombinations of electrons with acceptors in the electrolyte and increase the efficiency. It was also stated that  $\text{SnO}_2$  and ZnO are individually not good materials for dye-sensitized photoelectrochemical cells.

In this paper we report on synthesis, characterization and evaluation for application of nanostructured zinc and tin oxides via a simple thermal reduction-oxidation route. The prepared materials were tested and evaluated for photocatalysis and dye sensitized solar cells applications using.

## 2. Experimental

### 2.1. Materials preparation and characterization

Zinc and tin oxide tetrapods, nanowires, nanorods, nanobelts were prepared by heating well-mixed powders of zinc or tin oxide (ZnO 99%,  $\text{SnO}_2$  99%) and carbon. The weight ratio oxide/carbon varied from 1 to 3. An inverted porcelain crucible over a porcelain lip containing the mixed powders was employed as a reactor in order to prepare oxide nanostructures. The crucible was introduced to a muffle furnace working at normal atmosphere. The reaction temperature ranged from 1000 to 1200 °C and the heating time changed from 30 to 240 min with a rate of 15°/min. The crucible containing the reaction mixture was introduced into the furnace before it was turned on. Once the furnace reached the desired temperature, the planned reaction time was adjusted. At the end of the experiment, the furnace was turned off and the sample was left inside to cool down to room temperature. After cooling down, the thermally treated powders were collected, packed and kept in a desiccator for further physicochemical investigations. Structural and phases identifications were done at room temperature by X-ray diffraction. Morphologies of the prepared structures were investigated by scanning electron microscopy.

### 2.2. Cell fabrication and solar cell measurements

#### 2.2.1. Working electrode preparation

Pastes of ZnO,  $\text{SnO}_2$  or ZnO- $\text{SnO}_2$  were coated onto ITO substrate ( $8\text{--}12 \Omega \text{sq}^{-1}$ ) through mixing with triton X-100 and acetic acid. The coated substrates were heated at 450 °C for 30 min. After cooling, the coated substrates (electrodes) were immersed in a dye bath containing Rose Bengal for 24 h. The used redox electrolyte was iodine solution.

#### 2.2.2. Counter electrode preparation

The counter electrode was carbon-coated ITO. The photocurrent density-voltage ( $J$ - $V$ ) measurement was performed using light intensity of  $10 \text{ mW cm}^{-2}$  calibrated using Radiometer (International Light Technologies).

### 2.3. Photocatalytic measurements

Quartz batch photoreactor of cylindrical shape, containing 500 ml of aqueous suspension, was used for performing the photoreactivity experiments. A magnetic stirrer guaranteed a satisfactory suspension of the photocatalyst and the uniformity of the reacting mixture. UV-vis lamp (365 nm) was axially immersed within the photoreactor and it was cooled by water circulation; the temperature of the suspension was about 300 K.

The initial concentration of 2-chlorophenol pollutant (2-CP) was 100 ppm. The polluted water was aerated using a bubble distributor. The experiments were performed at room temperature and at pH 5.5. Prior to irradiation, the slurry was aerated for 10 min in dark to reach adsorption equilibrium followed by light irradiation. Adequate 5 ml aliquots samples were withdrawn at various irradiation time intervals and analyzed after filtration using HPLC (PerkinElmer series

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