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Metal oxide based Natural Dye-sensitized solar cell

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ABSTRACT

Natural Dye-sensitized solar cells (DSSCs) have attracted considerable attention in recent years due to the possibility of low-cost conversion of photovoltaic energy. The DSSCs-based Natural Dyes as sensitizers show high efficiency and excellent stability, implying potential practical applications. A WO_3-TiO_2 and CeO_2-TiO_2 nanomaterials were synthesized for the modification of conventional porous TiO_2 photoanodes for dye-sensitized solar cells (DSSCs). As a result, a compact thin film was superimposed on ITO surface and bridging gaps between TiO_2 nanoparticles, which was confirmed by scanning electron microscope (SEM). The network facilitates the electron transfer in the DSSC process by removing the dead ends of electron pathways, connecting gaps along the electron pathways, and physically enlarging electron pathways, which can be demonstrated by the performance improvement of photocurrent and open-circuit potential. The open-circuit voltage of dye coated WO_3-TiO_2 and dye coated CeO_2-TiO_2 are found to be 435 mV, 680 mV respectively.

1. INTRODUCTION

The dye sensitized solar cell (DSSC) is a photovoltaic device for the conversion of visible light into electricity, based on the sensitization of wide band gap semiconductors. (Balraju 2009) Light is absorbed by the dye sensitizer, which is anchored to the surface of a wide-band-gap semiconductor. Charge separation takes place at the interface via photoinduced electron injection from the dye into the conduction band of the nanocrystalline solids which are metal oxides, especially titanium dioxide. The performance of the cell mainly depends on the dye used as sensitizer. The absorption spectrum of the dye and the anchorage of the dye to the surface of TiO_2 are important parameters determining the efficiency of the cell. (Otaka 2004)

Another crucial parameter in the fabrication of DSSCs is the sensitizing dye. Due to the dye significant role, considerable interest has been directed towards the development and improvement of new families of organic dyes and of metal complexes. So far, the most efficient dye is found to be Ru(II) (Nazeeruddin 2001, Wang 2005) and Os(II). (Altobello 2005) These complexes have a number of interesting features such as good absorption, long excited lifetime, and highly efficient metal-to-ligand charge transfer. The disadvantages of these complexes are high cost and sophisticated

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preparation techniques. Therefore, alternative organic dyes such as natural dyes have been studied intensively. The main features of natural dyes are their availability, environmental friendly and low in cost. (Garcia 2003)

Recently studies deals with transition metal and rare earth elements like Ln, Nd, Ce mixed with TiO_2 showing activity in the visible region have been reported. (Wang 1999, Lee 2005) Rare earth elements mixed with TiO_2 show a red shift due to doping leading to the formation of inter band states. (Xu 2002) Moreover addition of rare earth elements is found to reduce recombinationof electrons and holes effectively by trapping them as well as by facilitating there faster movement along the surface of TiO_2. (Xi 2005) Among the various reare earth Ce has been reported to consistently show activity in the visible region when mixed with TiO_2. The advantage associated with Ce is that it is one among the four most abundant rare earth element. CeO_2 is widely used in fuel cells and pollution control applications due to its redox behavior, oxygen defects and catalytic activity. (Carrettin 2004) CeO_2 is n-type semiconductor whose band gap is varying between 2.7-3.4 eV depending upon the method of preparation. (Ozer 2001)

In this work, natural betacyanin dye was obtained from fresh and dried roots of beta vulgaris plant. The betacyanin dye was characterized by UV–VIS absorption spectra. The photovoltaic properties of the fabricated DSSCs using betacyanin dye coated photoelectrodes were investigated.

2. EXPERIMENTAL

The WO_3 and CeO_2 admixed TiO_2 nanopowder were prepared in the form of a sol-gel by the hydrolysis process. For WO_3-TiO_2 preparation, first $Ti[OCH(CH_3)_2]_4$ was added slowly to propanol drop by drop. Deionized water was slowly added under vigorous stirring conditions for the duration of 10 min. Then conc. HNO_3 solution was added under magnetic stirring. Then Na_2WO_4 solution was added dropwise into above mixture under continuous stirring. The resulting mixture was stirred at room temperature for 6 hrs. The resulting solid was centrifuged, washed, dried and calcined to get WO_3-TiO_2 oxides. For CeO_2-TiO_2 preparation, first $Ti[OCH(CH_3)_2]_4$ was added slowly to propanol drop by drop. Deionized water was slowly added under vigorous stirring conditions for the duration of 10 min. Then ceric ammonium nitrate solution was added dropwise into above mixture under continuous stirring. The pH of the solution was adjusted to 10-11 using aqueous ammonia. The resulting suspension was stirred at room temperature for 6 hrs. Then washed, dried and calcined to get CeO_2-TiO_2 nanopowder.

The roots of beta vulgaris were washed with distilled water and dried. After drying and crushing, they were immersed in absolute ethanol at room temperature in the dark for one week to extract the dyes. The solids were filtered out, and the filtrates were concentrated at 40°C and purified through column chromatography. After that, the natural betacyanin dye use as sensitizers.

ITO conductive glass with a sheet resistance of 15–20 Ω/cm^2 were first cleaned in a detergent solution using an ultrasonic bath for 15 min, rinsed with water and ethanol, and then dried. TiO_2-WO_3 and CeO_2-TiO_2 nanopowder pastes were deposited on the ITO conductive glass by doctor-blading technique in order to obtain thin film. The film

on the substrate was fired in air (oven) at 150^{o}C for 5-10 minutes. The nano-crystalline version of the material generally leads to high quantum efficiency. The photoelectrodes were sensitized by immersing them in betacyanin dye for 24 h. The immersed photoelectrodes in natural dye was removed and rinsed with ethanol and dried at room temperature for 1 h. The dye-coated photoelectrodes and Pt counter electrodes were assembled into sealed sandwich-type cells applying 2-3 drops of a redox (I^-/I_3^-) electrolyte solution. The electrolyte solution was composed of 0.5 M KI, 0.05 M iodine in acetonitrile.

The structural characterization of WO_3-TiO_2 and CeO_2-TiO_2 nanopowders were carried out through X-Ray Diffraction (XRD) by employing a Philips PW 1710 Diffractometer equipped with a graphite monochromater and SEM (Scanning Electron Microscope) with a ZEOL-JXA-8100 EPMA scanning electron microscope.

In order to explore the spectral response, the absorption spectra of betacyanin dye coated photoelectrodes on ITO glass substrate were carried out through double beam spectrophotometer (Systronics 2201).

3. RESULT AND DISCUSSION

Fig. 1 shows XRD patterns (CuKα radiation) of the WO_3-TiO_2 and CeO_2-TiO_2 nanomaterials. Analysis of XRD patterns revealed that on alloying ns-TiO_2 with WO_3 and CeO_2 did not lead to the formation of any new composite material. However, a slight change in the lattice parameter was invariably found.

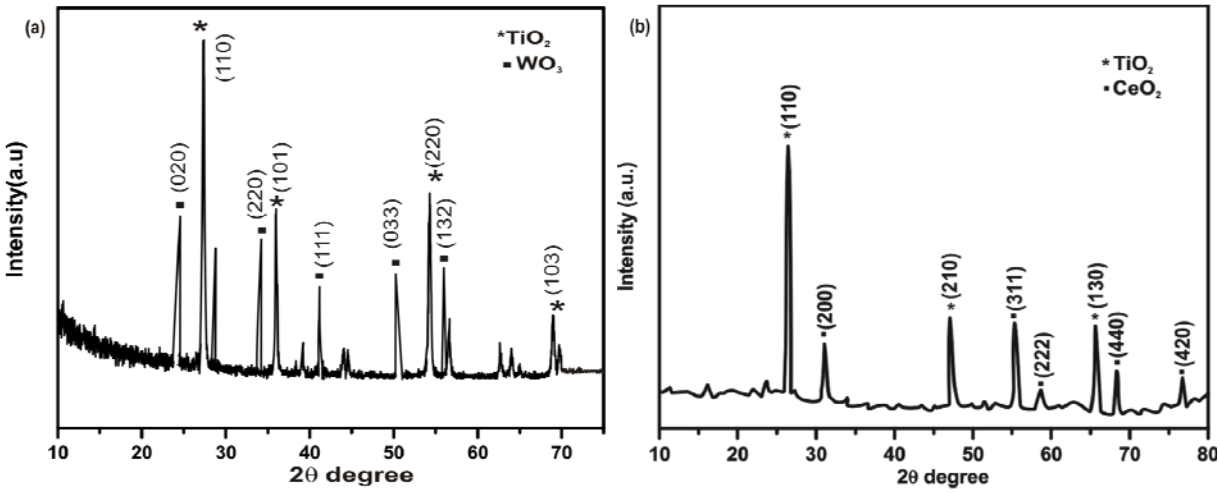
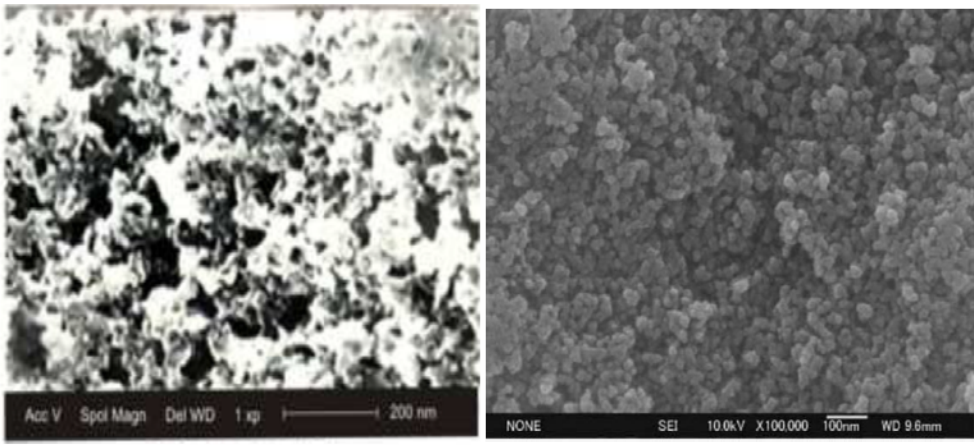


Fig. 1 XRD pattern of (a) WO_3-TiO_2 and (b) CeO_2-TiO_2 nanoparticles

With the help of scanning electron microscope (JEOL-JXA-8100 EPMA), the micro structural characteristics of the synthesized mixed oxide WO_3-TiO_2 and CeO_2-TiO_2 nanopowder were done (Fig. 2). The observed nanostructured characteristics showed a very fine grained structure suggestive of a nano-crystalline like matrix. By employing

the Scherer's equation for the powder diffraction peaks and SEM, the average grain size of the WO_3-TiO_2 and CeO_2-TiO_2 nanomaterial were found to be 20-40 nm, 20-35 nm respectively.



(a) (b)

Fig. 2 SEM diagram of (a) WO_3-TiO_2 and (b) CeO_2-TiO_2 nanoparticles

Fig. 3 shows UV-Vis absorption spectra of dye coated WO_3-TiO_2 and CeO_2-TiO_2 photoelectrodes. The difference in absorption peak is due to the binding of dye to the oxide surface and also to the band gap energy.

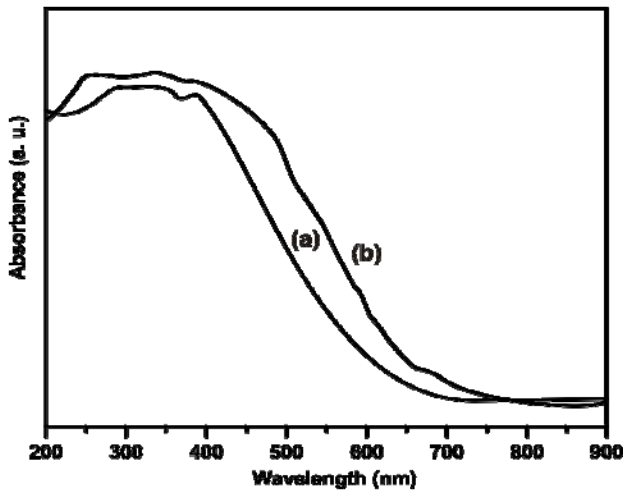


Fig. 3 UV diagram of (a) dye coated WO_3-TiO_2 and (b) dye coated CeO_2-TiO_2 photoelectrodes

The photoelectrochemical performance was made using Princeton Applied Research (PAR) model 173 Potentiostate/Galvanostate PAR 175 universal programmer coupled with a Housten 2000 X-Y/t recorder. A Xenon-Mercury lamp (Oriel Corporation, USA) was used as illumination source. The intensity of incident radiation

was adjusted and fixed at 100 mW/cm^2. The conversion efficiency (η) of DSSC were determined according to $\eta = I_{sc} \times V_{oc} \times FF /$ Intensity (mW/cm^2) based on *I-V* curve.

In Fig. 4 is photocurrent-voltage curve obtained for the DSSC fabricated with betacyanin dye coated WO_3-TiO_2 and CeO_2-TiO_2 photoelectrodes. The open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) of DSSC prepared from betacyanin dye coated WO_3-TiO_2 electrode are 435 mV, 9.86 mAcm^{-2} respectively with a conversion efficiency 2.2%. The open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) of DSSC prepared from dye coated CeO_2-TiO_2 electrode are 680 mV, 9.0 mAcm^{-2} respectively with a conversion efficiency 3.5%.

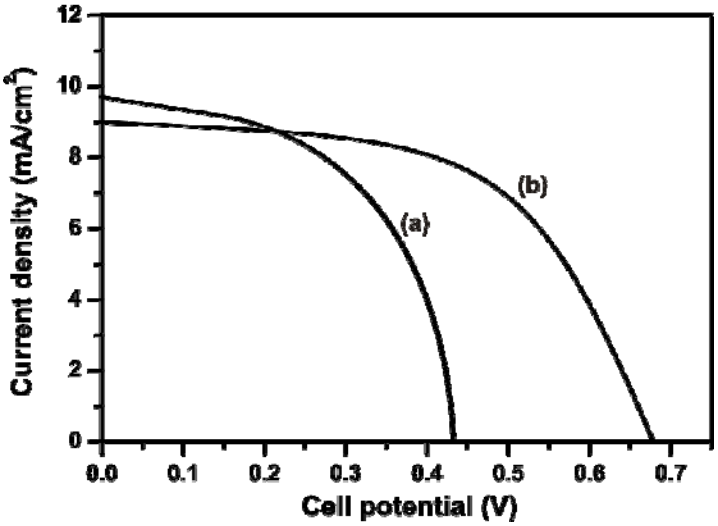


Fig. 4 *I-V* diagram of (a) dye coated WO_3-TiO_2 and (b) dye coated CeO_2-TiO_2 photoelectrodes

4. CONCLUSIONS

In summary, we have demonstrated a novel approach for fabricating efficient electronic devices by admixing metal oxides (WO_3 and CeO_2) into solution processable metal oxides as an interfacial layer. The nanocrystalline materials were synthesized using a sol–gel approach. The significant improvements in photovoltaic performances have also been obtained. We anticipate that this study will stimulate further research on metal oxides and salts as materials for combined functional layers to achieve efficient charge transport properties and reduce recombination.

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