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Synthesis and characterization of a binary oxide ZrO_2–TiO_2 and its application in chlorophyll dye-sensitized solar cell with reduced graphene oxide as counter electrodes

ASHA R PAI* and BIPIN NAIR
Amrita School of Biotechnology, Amrita Vishwa Vidyapeetham, Amritapuri, Kollam 690 525, India

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Abstract. **Natural dyes have been used to sensitize TiO_2 nanocrystalline solar cells, but they still require pigment purification and co-adsorption of other compounds. In this study, nanocrystalline ZrO_2–TiO_2 films sensitized with the bioorganic dye, chlorophyll extracted from green leaves of *Chromolaena odorata* were investigated. The nanocrystalline ZrO_2–TiO_2 films were synthesized by the precipitation synthesis. The samples were characterized using X-ray diffraction, UV–vis absorption spectroscopy, Fourier transform infrared spectroscopy and scanning electron microscopy. The photoelectrodes were prepared using ZrO_2–TiO_2 sensitized with the chlorophyll dye and the counter electrodes using reduced graphene oxide. The shift in the absorption wavelength of chlorophyll showed an increase of adsorption of dye. The conversion efficiency was also studied.**

Keywords. **Dye-sensitized solar cells; ZrO_2–TiO_2; films; chlorophyll; nanocrystalline; reduced graphene oxide.**

1. Introduction

Solar cells based on dye-sensitized TiO_2 nanoparticles were first developed by Grätzel and co-workers.[1] Regenerative photoelectrochemical cells are composed of nanocrystalline TiO_2 films sensitized with a dye. Under a light beam, the dye absorbs photons and injects electrons into the semiconductor's conduction band. The charge carriers then scatter to the external circuit. The dye is reduced by a redox pair, which, in turn, is also regenerated in the counter electrode.[1–3] The use of natural products such as organic dyes in solar cells offers promising prospects for the advance of this technology, since the photoexcitable dyes are substances that cede electrons easily, while the use of synthetic dyes involves several problems, such as their synthesis, purification and use, as well as the fact that they require rare metals.[4–7] Further the sensitization of TiO_2 with single or cocktail of dyes, which has been adopted for attaining higher levels of efficiency, introduces a problem as the dye-sensitization process on TiO_2 differ as the adsorption kinetics of different dyes are widely different and the unfavourable electron transfer between the dyes themselves can result in lowering of the cell efficiency. This problem can be solved by either step by step dye sensitization by introducing Al_2O_3 layer between the dyes, etc. The selection of suitable cocktails of dyes is also a major issue. This makes the device fabrication more complicated. Most importantly the performance of the dye-sensitized solar cell (DSSC) depends on the sensitization of the dye for the improvement of the solar spectrum, which can be done by adding various dopants such as transition metal elements, non-metal element – nitrogen, sulphur, boron, carbon nanotubes, etc. In this work we report the use of binary oxide ZrO_2–TiO_2 for improving the sensitization of natural dye chlorophyll dye.

Chlorophyll (figure 1) an organic dye found in leaves of plants has been studied as a sensitizer in the present work.[8] All green plants contain *chlorophyll a* and *chlorophyll b* in their chloroplasts. *Chlorophyll b* differs from *chlorophyll a* by having an aldehyde (–CHO) group in place of a methyl group ($–CH_3$).[9] The structural formula of *chlorophyll a* is $C_{55}H_{72}O_5N_4Mg$ (see figure 1a) with a molecular weight of 893.48 g mol^{-1}. *Chlorophyll b* has a structural formula of $C_{55}H_{70}O_6N_4Mg$ (see figure 1b) and a molecular weight of 907.46 g mol^{-1}.[10] The differences in these structures cause the red absorption maximum of *chlorophyll b* to increase and lower its absorption coefficient.[11,12] Both molecules are hydrophobic in the $C_{20}H_{39}OH$ region and the remaining region is hydrophilic. Chlorophyll pigments strongly absorb in the red and blue regions of the visible spectrum, which accounts for their green colour.

The leaf extract containing chlorophyll dye has been previously used to sensitize TiO_2 nanocrystalline solar cells, resulting in high J_{sc} (short-circuit current density),

*Author for correspondence (asharp@am.amrita.edu)

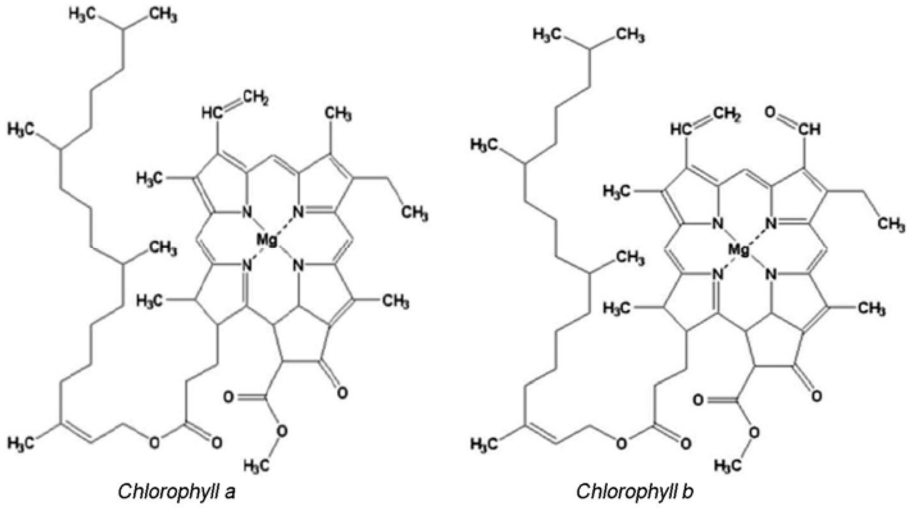

Figure 1. Molecular structure of *chlorophyll a* and *chlorophyll b*.

but these dyes still require pigment purification and the co-adsorption of other compounds on the TiO_2 surface.[7,8,13] The *chlorophyll a* hardly gets adsorbed on to the TiO_2 film and hence the efficiency of the cells is considerably low though the J_{sc} obtained is usually high. In this work, we have been able to achieve a considerable increase in the adsorption of the chlorophyll dye on to the binary oxide ZrO_2–TiO_2 layer.

Zirconia (ZrO_2), a ceramic oxide, occurs as a white pigment in tetragonal, monoclinic and cubic phases. Being a wide bandgap metal oxide similar to TiO_2, it has been used in the preparation of DSSCs.[14–17] ZrO_2 nanoparticles were chosen mainly because of their good biocompatibility in retaining the native structure and bioactivity of biomacromolecules.[18] A binary oxide was developed by doping TiO_2 with ZrO_2. The presence of ZrO_2 in TiO_2 not only decreases the particle size and effects the surface area but also improves the surface acidity in the form of –OH groups,[19] thus modifying the surface of the photoelectrode. Reduced graphene oxide-coated counter electrodes have also been used.

2. Experimental

2.1 *Synthesis of nanocrystalline ZrO_2–TiO_2 using precipitation synthesis*

Five grams of $ZrCl_4$ and 5 ml of $TiCl_4$ were diluted with ice-cold distilled water. To this aqueous solution, ammonia was added dropwise under continuous stirring by magnetic stirrer until the pH of 10–10.5 was attained. After the hydrolysis, the gel was washed free of anions and dried in oven at 110°C for 12 h as well as vacuum (50 mbar pressure) at 70°C temperature in a Rotavapor. After this, sample was calcined at 600°C for 12 h in a static air atmosphere.[20]

2.2 *Extraction of chlorophyll*

The pigments were extracted from the leaves of *Chromolaena odorata* as shown in figure 2, with acetone/petroleum ether. Using a column of silica gel and mixture of petroleum ether and acetone as the eluting solvent, the chlorophyll was separated from the rest of the components. The separated chlorophyll was protected from direct sunlight and stored in refrigerator.[21,22]

2.3 *Preparation of ZrO_2–TiO_2 with chlorophyll photoelectrode*

ZrO_2–TiO_2 binary oxide powder was grounded using a mortar and pestle. Then dimethyl formamide was added to the powder and a paste was prepared. The film was prepared by doctor blading and further annealing at 480°C for about an hour. The chlorophyll dye was adsorbed on to the oxide semiconducting surface by dipping the substrate into the dye solution. After deposition, the films were dried and its UV–vis absorption spectra was studied.[5,23]

2.4 *Preparation of counter electrode using reduced graphene oxide*

Reduced graphene oxide was prepared using the pencil graphite and coated on to the ITO glass plate.[24]

2.5 *Fabrication of DSSC*

A DSSC was developed using the photoelectrode using ZrO_2–TiO_2 binary oxide layer dipped in chlorophyll dye and reduced graphene oxide as the counter electrode. The electrolyte solution was prepared using 0.05 M I_2, 0.5 KI

Figure 2. Tropical weed – *Chromolaena odorata*.

in ethanol and PEG 500 and injected between the two electrodes.

3. Results and discussion

3.1 *Characterization of binary oxide ZrO_2–TiO_2*

3.1a *Powder X-ray diffraction (PXRD):* The powdered samples where characterized using an X-ray powder diffractometer (Bruker AXS D8 Advance) using CuKα radiation (λ = 1.5406 Å). The samples were scanned in a 2θ range of 0–80° at a scanning rate of 0.05° s^{-1}.

The characteristic peaks (figure 3) of both ZrO_2 tetragonal (2θ = 30.487° for (111) and 35° for (002) and monoclinic (2θ = 32° for (111)) and TiO_2 anatase (2θ = 24.4° **(**101) and 54° (211)) were present in the pattern. The TiO_2 exists in the anatase phase and the presence of ZrO_2 prevents the phase transformation from anatase to rutile.[19] The absorption spectrum of the ZrO_2–TiO_2 samples is shown in figure 4.

3.1b *UV–visible absorption spectroscopy:* The absorption spectra show that ZrO_2–TiO_2 can absorb UV light below 380 nm, which is lesser than that of pure component of Titania.

3.1c *FTIR spectroscopy:* Figure 5 shows the infra red absorption spectra of ZrO_2–TiO_2 binary oxide. The peak at 2920 cm^{-1} results from the adsorption of H_2O molecules. The band around 667 cm^{-1} is attributed to the vibration mode of Ti–O–Ti bond (figure 5). The peak at 1653 cm^{-1} corresponds to the bending vibrations of the water molecule.

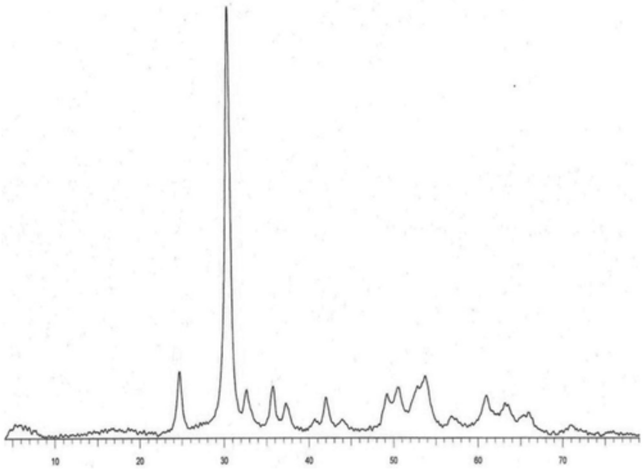

Figure 3. XRD pattern of ZrO_2–TiO_2 binary oxide sample treated at 600°C.

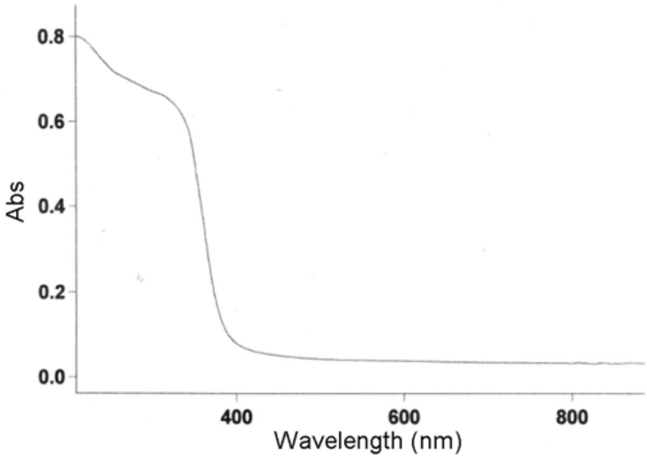

Figure 4. UV–vis absorption spectra of ZrO_2–TiO_2 binary oxide.

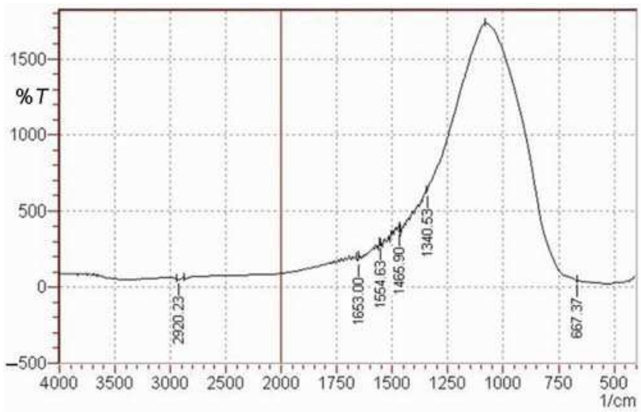

Figure 5. FTIR spectra of ZrO_2–TiO_2 binary oxide.

3.1d *SEM images of the ZrO_2–TiO_2 film annealed at 480°C:* The SEM images clearly indicate spherical grains covering the substrate. The film is highly nanoporous (figure 6).

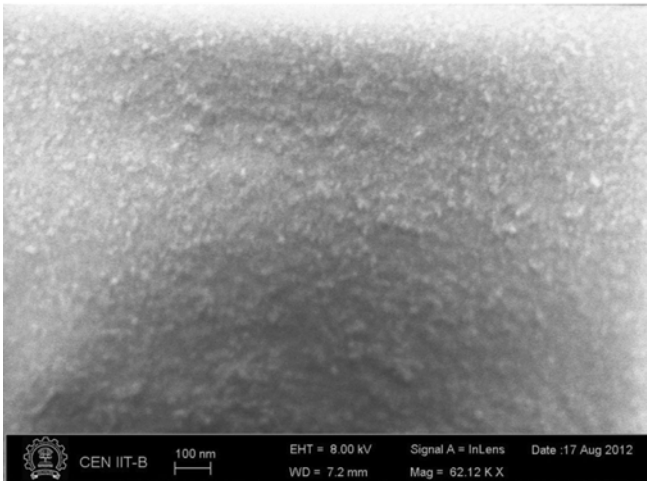

Figure 6. SEM images of the ZrO_2–TiO_2 thin film annealed at 480°C.

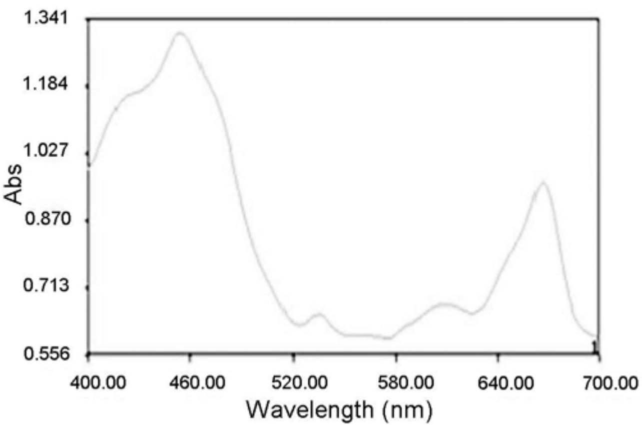

Figure 7. Absorption spectra of the chlorophyll extract in petroleum ether.

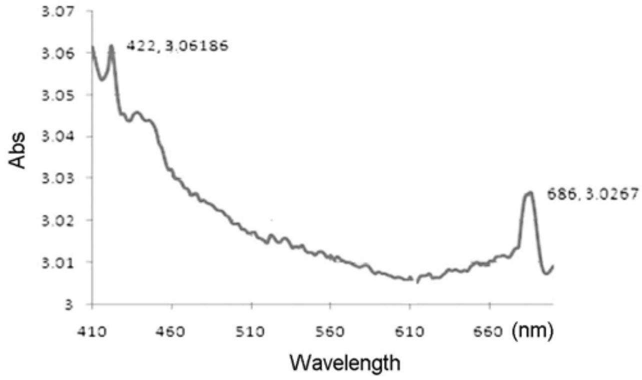

Figure 8. Absorption spectra of ZrO_2–TiO_2 thin film sensitized using chlorophyll.

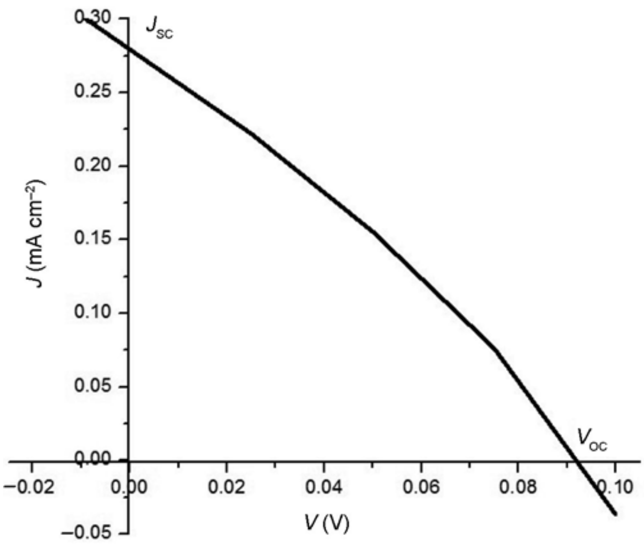

Figure 9. *J–V* characteristics of the dye-sensitized solar cell.

3.2 *Photosensitization study of chlorophyll dye on the photoelectrode using ZrO_2–TiO_2*

The absorption spectra show that ZrO_2–TiO_2 absorbs UV light below 380 nm, which is lesser than that of pure component of Titania.

The absorption spectrum of chlorophyll is shown in figure 7. *Chlorophyll a* has approximate absorbance maxima of 430 and 662 nm, while *chlorophyll b* has approximate maxima of 453 and 642 nm (figure 8). The concentration of each pigment (in μg ml^{-1}) of extract using the following equations was calculated to be approximately 10 μg ml^{-1} of the extract.

$$C_a = 12.21A_{663} - 2.81A_{646}, \quad (1)$$

$$C_b = 20.13A_{646} - 5.03A_{663}. \quad (2)$$

Here, C_a is the concentration of *chlorophyll a* and C_b the concentration of *chlorophyll b*.[25]

3.3 *J–V characterization of the DSSCs*

The characteristics (figure 9) of the obtained DSSCs were measured using a halogen lamp as a light source. The power was 10 mW cm^{-2}. The fill factor, P_{max}, J_{sc} and V_{oc} of the cell was calculated to be 38.1%, 9.6 μW, 0.279 mA cm^{-2} and 0.091 V, respectively. The conversion efficiency was obtained to be about 0.1%.

4. Conclusions

First, the ZrO_2–TiO_2 binary oxide has been synthesized and the adsorption of chlorophyll dye is studied. Based on the investigation on the structure and properties of the dye molecules, it was found that chlorophyll extracted from the green leaves of *C. odorata* showed good interactions with the ZrO_2–TiO_2 film. The blue shift of the absorption wavelength of the chlorophyll extract in the ether solution on ZrO_2–TiO_2 may be contributed to the solvent, aggregation state and ZrO_2–TiO_2. Although chlorophyll lacked the presence of carbonyl and hydroxyl groups for linkage to the substrate, the presence of OH acidic groups have contributed to the adsorption of the dye on the ZrO_2–TiO_2 substrate. The shift in the absorption maxima also indicates the broadening of the absorption spectra so that the film also readily absorbs more of UV light, which can contribute to the increase in the efficiency of the solar cells, developed using this material. This study shows how chlorophyll dye can be used to sensitize ZrO_2–TiO_2 to visible light, providing a very simple method to study dye sensitization of semiconductors. It is found that the presence of ZrO_2 with TiO_2 provides a microcrystalline nature to the surface and also the acidic surface with more OH groups help in the adsorption of dye on to the surface of the substrate. The reduced graphene oxide-coated ITO glass counter electrode was used for the DSSCs. Further studies are indicated to study the improvement of the conversion efficiency and fill factor of the cell by controlling the thickness of the layer of the substrate and more acidifying the substrate of the photoelectrode and varying the electrolytes.

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