Layer-by-layer deposition of $\text{TiO}_2\text{--ZrO}_2$ electrode sensitized with Pandan leaves: natural dye-sensitized solar cell

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Received: 19 July 2018 / Accepted: 25 June 2019 / Published online: 18 July 2019
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Abstract

TiO_2 , ZrO_2 and layer-by-layer $\text{TiO}_2\text{--ZrO}_2$ films were prepared by doctor blade method followed by sensitization with natural dye for dye-sensitized solar cell application. The structural and optical, morphological and compositional properties were investigated by X-ray diffraction and UV–Vis spectroscopy, scanning electron microscopy, BET, surface profilometer and energy-dispersive X-ray analyzer, respectively. Dye-sensitized solar cells were fabricated using the prepared electrodes of TiO_2 , ZrO_2 and layer-by-layer $\text{TiO}_2\text{--ZrO}_2$ films sensitized with natural dye extracted from Pandan leaves (*Pandanus amaryllifolius*). The $J\text{--}V$ characteristics were recorded to measure photo-response of fabricated devices and electrochemical impedance spectroscopy to study the electron behavior, series resistance and lifetime. Photovoltaic parameter like short-circuit current, open-circuit voltage, fill factor, and power conversion efficiency were evaluated for fabricated solar cell under artificial light supplied from white LED ($15\text{ mW}\cdot\text{cm}^{-2}$). The average values of power conversion efficiency of DSSCs fabricated with TiO_2 , ZrO_2 and layer-by-layer $\text{TiO}_2\text{--ZrO}_2$ photoanodes were found to be 0.65%, 3.04% and 3.13%, respectively.

Keywords $\text{TiO}_2\text{--ZrO}_2$ · Layer by layer · Pandan leaves · Natural dye-sensitized solar cells · EIS

Introduction

Today, due to the increasing global warming and energy crisis worldwide, it is important to find renewable and green energy source, which are cost effective and reliable. Solar energy is one of the most gifted sources for producing environmentally friendly energy. Compared to first- and second-generation solar cells, dye-sensitized solar cells (DSSCs) can be considered as one of the most favorable photovoltaic devices because of the low-cost, simplicity in fabrication

along with moderated efficiency. In general, TiO_2 and/or ZnO are used as a wide band gap semiconductor material in DSSCs [1–3]. Still there is a need to search for alternative materials towards the enhancement in device efficiency. In this direction, one can look for alternative semiconductor such as ZrO_2 and its bilayered structure with routine TiO_2 . ZrO_2 is a wide band gap semiconductor with direct band gap values ranging from 2.5 to 3.8 eV [4], which may be an attractive candidate for dye-sensitized solar cell application [5].

Doping in TiO_2 can modified optical and electrical properties leads to increase the performance by providing more active sites on the surface that can play a significant role for adsorption of dye molecules, improvement in light absorption, and also enhance the electron collection in the conduction band [6, 7]. On the contrary, one can enhance the performance of DSSC using multi-layered or composite photoanodes [8, 9]. Recently, Mohamed et al. reported the improvement in efficiency from 1.61 to 4.51% of DSSC fabricated with doping of ZrO_2 in TiO_2 nanofibers photoanode sensitized using N719 dye [7]. Jin et al. observed that the efficiency of DSSCs with a $\text{TiO}_2\text{--ZrO}_2$ composite electrode was 6.2%, an increase of 26.5% than pure TiO_2 electrode

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(4.9%) for N719 dye as sensitizer. This is because, the addition of ZrO_2 in TiO_2 increased dye loading, thereby improving the electron recombination times than for a pure TiO_2 electrode results in the decreased electron recombination at the TiO_2 /electrolyte interface, increasing electron transfer [10]. The highest efficiency of 6.5% was achieved for N719 dye-sensitized ZrO_2 nanofiber-doped TiO_2 photoelectrode prepared by squeeze printing [11]. Furthermore, the significant enhancement in power conversion efficiency can be ascribed for TiCl_4 -treated TiO_2 nanosheets film coated with ZrO_2 and the highest efficiency of 7.33% is achieved for N719 dye [12].

Usually, Ru-metal complexes and metal-free organic dyes are used as sensitizer due their good stability and light harvesting property with high molar extinction coefficient [13, 14]. However, application of these types of sensitizers also faced problems regarding complicated synthetic routes and most importantly use of environmentally non-benign chemicals [15]. Hence, dyes obtained from nature having similar characteristic were used with the advantages such as availability, low-cost, environmental friendliness and as a green alternative to commercially available dyes [16–20]. To the best of our knowledge; it is observed that not many reports are available on natural dye-sensitized TiO_2 – ZrO_2 bilayer electrode for DSSC application. Win et al. reported sensitization of Rose extract over TiO_2 – ZrO_2 film prepared by rolling method of DSSC and observed 0.23% efficiency [21]. DSSC fabricated using nanocrystalline ZrO_2 – TiO_2 film prepared by doctor blade method and sensitized with the bioorganic dye, chlorophyll extracted from green leaves of *Chromolaena odorata* shows 0.1% efficiency. Recently, Tomar et al. reported improvement in efficiency of DSSC

using Zn-doped TiO_2 – ZrO_2 prepared by hydrothermal method with juice of pomegranate as natural sensitizer. The efficiency of DSSC fabricated with TiO_2 – ZrO_2 is 1.97% and that of the Zn-doped TiO_2 – ZrO_2 nanocomposites were found 4.58%. The enhancement in efficiency is because the Zn doping has introduced new energy levels and lowered the recombination [22].

From literature survey including recent reports, very few reports are available on sensitization of chlorophyll dye with different metal oxides for dye-sensitized solar cell. The comparison of photovoltaic performance of chlorophyll dye-sensitized photoanodes for DSSC application under different light intensities with reported literature is summarized in Table 1 [21, 23–36].

In this article, we promote to use natural dyes as sensitizer towards the development of attractive, colorful and low-cost DSSCs. Hence, attempt has been focused in this direction to develop the low cost and eco-friendly source of green energy by using inexpensive and naturally available dye extracted from Pandan leaves as sensitizer over TiO_2 , ZrO_2 and layer-by-layer TiO_2 – ZrO_2 photoelectrodes towards the fabrication of DSSCs.

Experimental

Material and chemicals

Fluorine-doped tin oxide (FTO)-coated glass with a sheet resistance of $\sim 15 \Omega \text{ cm}^{-2}$ was used as substrate. Nanocrystalline powder of TiO_2 (particle size $\sim 7 \text{ nm}$ with anatase phase), zirconium oxide powder (particle size $\sim 45 \text{ nm}$ from

Table 1 Summary of photovoltaic performance of chlorophyll dye-sensitized with various photoanodes for DSSC application

Photoanode	Source	Intensity of light (mW cm^{-2})	PEC (%)	References
TiO_2 – ZrO_2	Rose dye	–	0.23	[21]
TiO_2	Pandan leaves	100	0.1	[23]
TiO_2	Anthocyanin:chlorophyll	100	0.062	[24]
TiO_2	Pandan leaves	100	0.35	[25]
TiO_2	Papaya leaves	100	0.36	[26]
TiO_2	Rosella extract	100	0.57	[27]
TiO_2	Chlorophyll derivative	100	2.25	[28]
TiO_2/ZnO	Papaya leaves	100	0.07	[29]
TiO_2	Papaya leaves	100	0.094	[30]
TiO_2	Chlorophyll	–	0.049	[31]
TiO_2	Pandan leaves	100	0.0006	[32]
TiO_2 – ZrO_2	<i>Chromolaena odorata</i>	10	0.1	[33]
TiO_2	Shisonin leaves	100	0.59	[34]
TiO_2	Chlorophyllin (<i>Cu-Chl-e6</i>)	100	1.81	[35]
TiO_2	<i>Undaria pinnatifida</i> (Wakame)	100	4.6	[36]
TiO_2 – ZrO_2	Pandan leaves	15	15	Present work

SRL Chem. India), ethyl cellulose (SDFCL, India), ethanol (AR, 99.9%, Changshu Yangyuan Chemical, China), α -terpineol (LR, 98%, HPLC, India), acetyl acetone (98%, Merck, India), potassium iodide (99.8%, SRL, India), iodine (99.5%, Fisher Scientific, UK), *t*-butyl pyridine (96%, Acros organics, USA), acetonitrile (AR, 99.5%, SDFCL, India) were used as it is without any further purification.

Substrate cleaning

Prior to deposition FTO substrates were cleaned by using soap solution followed by double distilled water and then with acetone in ultrasonic bath for 10–15 min.

Preparation of TiO₂ and ZrO₂ paste

In detail, 0.5 g TiO₂ nanoparticles powder was ground in mortar pestle with addition of 7 ml ethanol and kept in ultrasonic bath for 15–20 min. Afterwards 0.3 g ethyl cellulose was ground in same mortar pestle in 2 ml ethanol. Then the sonicated paste of TiO₂ was subsequently added and ground with ethyl cellulose in mortar pestle for uniform mixing. Then the mix solution was transferred in the borosilicate glass bottle for sonication with the addition of 1.3 g α -terpineol for 3 h followed by addition of 3 drops of acetyl acetone to the above mixture and allowed to sonicate for another 1 h. Finally, for the evaporation of ethanol; the prepared solution was placed in incubator at 60 °C till it becomes more viscous. Similar procedure was repeated for the preparation of ZrO₂ paste.

Preparation of photoelectrodes

Pre-cleaned FTO substrate was covered at the edges by using scotch tape of ~30 μ m thickness and layer of prepared TiO₂ paste was then coated on FTO substrates using doctor blade method at room temperature. The as-prepared films of pristine TiO₂ were dried at 60 °C in incubator for 10–15 min. The above procedure was repeated four times to get optimized thickness of ~12 μ m measured by using surface profilometer. Similar route is employed for the preparation of ZrO₂ films followed by drying at 60 °C for 10–15 min.

Layer-by-layer approach was utilized for the preparation of TiO₂–ZrO₂ bilayered films. Briefly, pre-cleaned FTO substrate was covered at the edges by using scotch tape and first layer of prepared TiO₂ paste was coated on FTO using doctor blade method. Then the as-prepared film was dried at 60 °C for 15 min followed by the coating of second layer of ZrO₂ on putting scotch tape over TiO₂ in similar way. Again the as-prepared bilayered film was dried at 60 °C for 15 min. The above procedure was repeated one more times to get optimized thickness of ~12 μ m for layer-by-layer TiO₂–ZrO₂ films. Finally, all the prepared films of pristine TiO₂, ZrO₂

and TiO₂–ZrO₂ bilayered structure were air annealed at 450 °C for 1 h to remove the organic solvents as well as to improve the crystallinity of the film and the interfacial structures.

Preparation of natural dye

Firstly, natural chlorophyll dye was prepared from 3 g fresh leaves of fragrant screw pine (*Pandanus amaryllifolius*) or locally known as Pandan leaves. The leaves were cleaned with distilled water, rinsed with ethanol, and were cut into small pieces and immersed in 5 ml ethanol followed by grinding in mixer for 10 min and the same was repeated at least for 3–4 times. Again 5 ml of ethanol was then added in the above mixture and kept on a magnetic stirrer at room temperature for 1 h. Finally, the above mixture is kept for around 24 h in a closed bottle in dark at room temperature. The filtrate of the above solution was used as natural dye for sensitization of photoelectrodes towards the fabrication of DSSCs.

Sensitization of photoelectrodes

The annealed films of pristine TiO₂, ZrO₂ and TiO₂–ZrO₂ bilayered structure were then immersed in naturally prepared dye for 72 h at room temperature. Subsequently, the films were dipped in ethanol for 5–10 s to remove the excess of dye, followed by drying at room temperature.

Characterizations

The structural and optical analysis was carried out using X-ray diffractometry (XRD) (model: XRD, Rigaku ‘D/B max-2400’, CuK α with $\lambda = 1.54$ Å) and UV–Vis spectrophotometer (model: JASCO V-670) was used to record optical absorption spectra of photoelectrodes using diffused reflectance (DRS) mode in wavelength range 310–800 nm at room temperature, respectively. Surface profilometer (Dektak 150) was used for the measurement of thickness of annealed photoelectrodes. The morphological properties and elemental composition was done by using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) (model: JEOL-JSM 6360-A), respectively. The BET method was used for the measurement of surface area of all samples using Quantachrome Autosorb-iQ unit. The cell performance was measured by a semiconductor characterization unit (Keithley 2420 source meter) under illumination of artificial LED light (15 mW cm⁻²). The electrochemical impedance spectroscopy (EIS) measurements for DSSCs were carried out using potentiostat/galvanostat (IVIUM:Vertex) in the frequency range of 1 MHz to 1 Hz under dark.

Results and discussion

Structural studies

XRD patterns of the TiO_2 , ZrO_2 and $\text{TiO}_2\text{-ZrO}_2$ bilayered films were recorded using X-ray diffractometer with 0.1° s^{-1} step size and scan rate of $1^\circ/\text{step}$ as shown in Fig. 1. The characteristic along (101) and (004) peaks at 25.27° and 37.8° , respectively, were clearly observed and confirm the growth of tetragonal structure (JCPDF card No. 21-1272) of TiO_2 having anatase phase (a) on FTO substrate. XRD pattern of ZrO_2 on FTO substrate by doctor blade method is depicted as (b). The strong diffraction peaks along ($\bar{1}11$) and (111) were indexed to monoclinic structure (JCPDF card No. 37-1484). The XRD pattern (c) for $\text{TiO}_2\text{-ZrO}_2$ layer-by-layer film represents the combination of two sets of patterns: one from TiO_2 and the other originating from the ZrO_2 . Thus the formation of layer-by-layer TiO_2 with ZrO_2 is confirmed from the XRD. Asterisk (*) shown in the pattern assigned to the FTO-coated glass substrate.

Optical absorption spectroscopy

A UV–Vis spectrophotometer (model: JASCO V-670) was used to record optical absorption spectra of photoelectrodes in diffused reflectance (DRS) mode and ethanolic solution of dye under transmission mode in the wavelength range 310–800 nm at room temperature. Figure 2 shows the absorption spectra of pristine TiO_2 , ZrO_2 , $\text{TiO}_2\text{-ZrO}_2$ films, and chlorophyll dye solution. It is observed that all the films exhibit low absorbance in the visible region of the solar

Fig. 1 XRD pattern of pristine TiO_2 (a), ZrO_2 (b) and layer-by-layer $\text{TiO}_2\text{-ZrO}_2$ (c) films

Fig. 2 Optical absorption spectra of TiO_2 (—), ZrO_2 (—), $\text{TiO}_2\text{-ZrO}_2$ (—) films and ethanolic solution of dye (—)

spectrum. Usually, TiO_2 shows the characteristic spectrum with its fundamental absorption of Ti–O bond in UV region between 320 and 400 nm [37] with characteristic peak around 350 nm (band edge) for TiO_2 [38]. Whereas naturally prepared chlorophyll dye exhibits maximum absorption at 413 and 665 nm in visible region. Chlorophylls, which act as an effective photo-sensitizer in photosynthesis of green plant, has absorption maximum at 670 nm, thus, it is an attractive potential compound as a photo-sensitizer in the visible region [39]. The values for amount of dye adsorbed over different photoelectrodes used for the fabrication of DSSCs along with the thickness of photoanodes are summarized in Table 2. Chu et al. reported the enhancement of dye absorption for layer-by-layer photoelectrode and observed the improvement in performance of DSSC [40].

Surface morphology and elemental analysis

The top-view of pristine TiO_2 , ZrO_2 and $\text{TiO}_2\text{-ZrO}_2$ bilayer films was examined using SEM to analyze the surface morphology (Fig. 3). The SEM results clearly illustrated nanoporous surface nature of TiO_2 , ZrO_2 and $\text{TiO}_2\text{-ZrO}_2$ films which is the basic requirement of photoelectrode in DSSC. At high resolution (inset), it is observed that the samples were granular in structure and porous in nature. Figure 3c shows the $\text{TiO}_2\text{-ZrO}_2$ film has uniform surface area than the pristine ZrO_2 and TiO_2 which leads to better dye adsorption and results in enhancing the overall performance of the DSSC for $\text{TiO}_2\text{-ZrO}_2$ bilayered photoanode. The layer-by-layer structure of $\text{TiO}_2\text{-ZrO}_2$ bilayered photoanode exhibit moderate surface area compared with the pristine bulk materials positive sign for amount of

Table 2 Structural and morphological properties of TiO₂, ZrO₂ and TiO₂-ZrO₂ photoelectrodes and their photovoltaic and electrochemical output parameters with natural dye-sensitized solar cells

Photoanode	Surface area multi-BET (m ² g ⁻¹)	Thickness (μm)	Crystallite size (nm)	Amount of dye adsorbed (nmole cm ⁻²)	τ _e (ms)	R _{ct} (Ω)	V _{oc} (mV)	J _{sc} (mA cm ⁻²)	FF	PCE (%)
TiO ₂	72.26	2.8	37	4.18	0.53	648	340 ± 3	1.69 ± 0.07	0.170 ± 0.008	0.65 ± 0.04
ZrO ₂	25.80	3.2	158	69.5	3.33	1184	341 ± 1	7.03 ± 0.14	0.190 ± 0.004	3.04 ± 0.02
TiO ₂ -ZrO ₂	33.39	12.5	50	82.4	1.32	1340	530 ± 5	4.80 ± 0.11	0.185 ± 0.006	3.13 ± 0.03

±, standard deviation

dye adsorption and also leads to the shortened collection length for charges results into increasing efficiency [41]. The values of surface area measure by BET technique for all the samples are summarized in Table 2 and found to be in accordance with the previously reported results [42].

The energy-dispersive X-ray (EDS) spectrum of TiO₂-ZrO₂ bilayer film is shown in Fig. 3d. EDS confirmed that the presence of titanium, zirconium and oxygen. The atomic percentages of elements are tabulated in the inset of Fig. 3d.

Solar cell assembly

The dye-sensitized photoanodes and platinum counter electrode was separated by spacer of 10 μm thickness over photoanodes and assembled into a sandwich-type open cell using binder clip. The active cell area for DSSC was regulated to 0.25 cm² using stainless steel mask covered from back side of photoanode over the glass side of the FTO. The mask is designed in such a way that it allowed entering the light through aperture and remains opaque for light over the remaining part of the cell. Figure 4a shows the schematic of device for chlorophyll dye-sensitized layer-by-layer TiO₂-ZrO₂ photoanode-based DSSC. A drop of prepared liquid electrolyte was introduced between the sensitizer and the counter electrode in such a way that no air bubble is formed. An electrolyte composed of 0.5 M potassium iodide (KI); 0.1 M iodine (I₂) and 0.5 M *t*-butyl pyridine (C₁₃H₂₁N) in an acetonitrile solvent was used.

Photovoltaic study

Photovoltaic measurements of the fabricated DSSCs using natural dye as sensitizers were performed by measuring the *J*-*V* measurement as shown in Fig. 4b. In present study we have measured the *J*-*V* characteristics of each DSSCs device 3 times for 2 sets of photoanodes to check the repeatability along with the reproducibility of the device and the average values of photovoltaic performance was reported. The cell performance was recorded by a semiconductor characterization unit (Keithley 2420 source meter) under illumination of artificial light (15 mW cm⁻²) supplied from white LED source. The current density-voltage (*J*-*V*) characteristics under illumination conditions were measured at room temperature (27 °C). The output photovoltaic parameters of natural dye-sensitized solar cell, i.e., the short-circuit current density (*J*_{sc}), open-circuit voltage (*V*_{oc}), fill factor (FF) and power conversion efficiency (PEC) of the devices with standard deviation are summarized in Table 2.

Fig. 3 Surface morphologies of **a** pristine TiO_2 , **b** ZrO_2 and **c** TiO_2 - ZrO_2 bilayered films. Corresponding inset shows the images at high resolution. **d** EDS spectra of TiO_2 - ZrO_2 bilayered film and inset shows elemental constituent in tabulated form

Electrochemical impedance spectroscopy (EIS)

Figure 4c shows the Nyquist plots and Fig. 4d represents the Bode phase plots for all three devices sensitized with natural chlorophyll dye. It is observed that the radius of distorted semicircles increases as $\text{TiO}_2 < \text{ZrO}_2 < \text{TiO}_2$ - ZrO_2 which indicate the highest charge recombination resistance was observed for TiO_2 - ZrO_2 photoanode-based DSSC. The electron lifetime (τ_e) can be calculated by the peak frequency at the minimum phase angle (f_{peak}) from Bode phase plots using the relationship [$\tau_e = \frac{1}{2\pi f_{\text{peak}}}$] [43]. The shift in the phase angle maxima has been observed towards the low-frequency range as we move from the TiO_2 to ZrO_2 to TiO_2 - ZrO_2

photoanode. The values of τ_e found to increase from bare TiO_2 to TiO_2 - ZrO_2 photoanode-based DSSC. The substantial increase in the values of electron lifetime indicates the effective suppression of back reaction between the photogenerated electrons. Superior value for τ_e was recorded for the TiO_2 - ZrO_2 photoanode-based device as compare to the bare metal oxide-based devices, demonstrating the reduced charge recombination. This may be the reason towards getting higher efficiency with layer-by-layer TiO_2 - ZrO_2 photoanode-based DSSC. The value of charge recombination resistance (R_{ct}) was measured from Nyquist plots using second distorted semicircle in mid frequency region. Table 2 summarizes the values for τ_e and R_{ct} for all the three devices. As per literature, the larger value of R_{ct} is leads to the

Fig. 4 **a** Schematic of device, **b** current density–voltage (J – V) characteristics curve, **c** Nyquist plot and **d** bode phase plot for TiO_2 (open square), ZrO_2 (open circle), TiO_2 – ZrO_2 (open triangle) photoanodes-sensitized with natural dye

reduction in charge recombination rate which is favorable towards the enhancement in device efficiency [44]. The highest current density value is observed for ZrO_2 -based DSSCs which is may be due to the highest value of electron life time (τ_e) compared to other two devices.

Conclusion

Dye-sensitized solar cells (DSSCs) were assembled using extracts from fragrant screw pine (*P. amaryllifolius*) leaves as sensitizers with pristine TiO_2 , ZrO_2 and TiO_2 – ZrO_2 photoelectrodes. Photovoltaic parameters of the fabricated DSSCs were determined under illumination. It is found that the natural dye-sensitized layer-by-layer TiO_2 – ZrO_2 photoanode exhibits maximum power conversion efficiency of 3.13% than pristine ZrO_2 (3.04%) and TiO_2 (0.65%) which suggest that the anchoring of chlorophyll dye goes well with ZrO_2 as compared to TiO_2 . The improvement in efficiency is observed for TiO_2 – ZrO_2 bilayered structure, which is due to the high surface area available for dye adsorption. From EIS studies it is observed that the electron lifetime values for layer-by-layer photoanode-based DSSC is in between pristine photoanode-based DSSC. On the other hand, the charge recombination resistance for layer-by-layer photoanode is significantly greater than pristine ZrO_2 and TiO_2

photoanode-based DSSCs leads to the effective suppression of photo-injected electron recombination with the excited dye and I_3^- in the electrolyte resulted in the enhancement in efficiency for layer-by-layer TiO_2 – ZrO_2 photoanode-based DSSC. This opens the window for use of ZrO_2 as photo-electrode instead of routine metal oxides used as wide band gap materials and natural dye in spite of Ru-metal-based expensive dyes as sensitizer towards the fabrication of cost-effective and eco-friendly DSSC.

Acknowledgements Authors are thankful to University with Potential for Excellence (UPE)—II for partial financial support. PKB is thankful to University Grants Commission, New Delhi, India, for the award of Dr. D.S. Kothari Postdoctoral Fellowship and financial assistance (PH/16-17/0074).

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