ZrO₂ incorporated TiO₂ based solar reflective nanocomposite coatings on glass to be used as energy saving building components

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Abstract

Single layer design ZrO₂ incorporated TiO₂ based transparent hard reflecting nanocomposite coatings on glass substrates were developed by sol-gel dip-coating technique using zirconium (IV) *n*-propoxide (ZP) and titanium (IV) isopropoxide (TTIP) followed by heat treatment at 500 °C for 1 h. The above nanocomposite based TiO₂-ZrO₂ coated glass could be used as component for efficient energy saving building materials with esthetic beauty. The TZ85:15 coated glasses (dimension: 200 × 200 mm²) with coating thickness 90 ± 10 nm having refractive index value of 1.985 ± 0.002 were found to be flawless with good hardness ~ 5H and adhesion properties. GIXRD and Raman analysis of specimens revealed the crystalline nature of the heat-treated coatings, whereas the formation of Ti-O-Zr network was observed by XPS and FTIR. Coated glass showed > 28% of average reflection (within wavelength range of 350–2500 nm) and ~ 31% (within wavelength range of 400–800 nm). It also revealed the golden yellow reflected color under tube-light exhibiting enhanced aesthetic beauty making suitable candidate for heat reflecting component.

Keywords Nanocomposite · TiO₂-ZrO₂ · Reflective coating · Sol-gel · GIXRD

1 Introduction

Solar energy gives a lot of benefit to the earth, but its radiation also causes temperature rise inside houses and buildings [1–3]. In the solar spectrum approx 50% energy is in the UV-visible region and the rest of the total solar energy is in the infrared radiation region which is absorbed by the earth surface. Hence, absorption of this rays is responsible for the heating up of the surfaces [1, 3] leading to rise in temperature and increases the demand of cooling within the conditioned buildings. As a consequence, development of effective energy storage system, especially prevention of loss of stored energy, particularly those are harvested from renewable sources are most important and critical in terms of commercial applications [4]. Several R&D are carried out to arrest the energy loss, caused by several means [5–8]. Here, the application of reflective coatings on the surface of building components could be

one of the preventive measurements. Such component with reflective coating could minimize the temperature on the surface as well as inside the room of the building by enhancing reflectance of near IR radiation.

Thus, reflective coating becomes a key interest of work for the researchers to promote energy efficient technologies along with energy conservation in buildings [2]. In respect to this, materials with high solar reflectance and high thermal emittance are mostly desirable. Transparent heat reflecting (THR) coating shows a wide opportunity in this field, specially when they possess high reflectance at the near infrared (IR) radiation and a high transmittance at the visible region which is a great alternative in solving the purpose [9, 10]. For this purpose different metal/metal oxides like SiO₂ [11], ZrO₂ [1, 6, 9], Al₂O₃ [1], Cu₂O [8], MgO [1], Fe [12], Ni [13], ZnO [1, 14] are generally used as dopants in TiO₂ matrix for high reflecting material to enhance IR radiation for various applications. In addition,

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thin film of silver, gold and copper used as the metal in dielectric/metal/dielectric structures are studied as a potential material to reduce surface or inside room temperature by enhancing reflectance at the IR radiation solar spectrum for encourage energy saving building applications [8–10]. But most of these THR coatings are reported multilayer structure mainly by using highly expensive coating deposition technique, as a consequence not cost effective.

Metal oxide, specifically ZrO_2 and TiO_2 thin films, particularly a combination of TiO_2 – ZrO_2 has been used to develop such reflecting coatings because TiO_2 has unique UV-resistant and self-cleaning property while ZrO_2 has high mechanical strength with chemical resistant property [2, 15]. Moreover, properties of the composite can be easily tailored by a simple control on the composition of the systems. Beside this, reflective coatings made from TiO_2 – ZrO_2 composites are also widely investigated for various optical applications such as filters, lenses, waveguides, optical adhesives and anti-reflective coatings etc. [16–20]. So, metal oxide, specifically using TiO_2 – ZrO_2 composite sol for the formation of great quality reflective coatings is quite a practiced topic in this field. But best of our knowledge from literature, the formation of single layer TiO_2 – ZrO_2 composite based coating for the development of heat reflecting in NIR region is not yet reported.

Keeping the above views in mind, main motivation of this work is to investigate the sol–gel deposited (dip coating technique) TiO_2 – ZrO_2 single layer coating on glass substrate for the development of low cost THR windows. In this paper we have described the development of stable TiO_2 – ZrO_2 nanocomposite sol compositions capable of producing highly transparent, protective and reflective hard-coatings (single/one layer) on glass substrates. The detailed synthetic process for the formation of TiO_2 – ZrO_2 nanocomposite coating is discussed as a function of sol processing and thermal heating (500 °C) steps supported by systematic analysis of Fourier-transform infrared spectroscopy (FTIR), Raman, X-ray photoelectron spectroscopy (XPS), optical measurement and Grazing Incidence X-ray Diffraction (GIXRD) studies. The adhesion (coating material to the substrate), hardness, reflection and chemical endurance characteristics of the coatings have also been investigated.

2 Experimental

2.1 Materials

All chemicals were used as received. Titanium (IV) isopropoxide (TTIP), Zirconium (IV) *n*-propoxide (70% in 1-propanol) (ZP), were supplied by Sigma-Aldrich. While, acetylacetone (acac), 1-propanol and HNO_3 (~ 71%) were

supplied by MERCK Specialties Pvt. Ltd. Mili-Q (Millipore) water (18.2 M Ω) was used throughout the study.

2.2 Preparation of coating solution (sol)

TiO_2 , ZrO_2 and TiO_2 – ZrO_2 based nanocomposite coatings on glass substrates were prepared by sol–gel dip-coating technique using zirconium (IV) isopropoxide (ZP) (70% in *n*-propanol) and titanium (IV) isopropoxide (TTIP) followed by heat treatment at 500 °C. For the preparation of only TiO_2 and ZrO_2 coating sols TTIP and ZP precursor was used, respectively. Different TiO_2 – ZrO_2 based nanocomposite sols were prepared by varying mole ratio of TTIP and ZP. For the preparation of TiO_2 – ZrO_2 coating solution (sol), TTIP (0.0682 mol) and ZP (0.01049 mol) were mixed with 1-propanol (0.3244 mol) followed by refluxed for 1 h and then cooled to room temperature (RT) (25 ± 2 °C). To this, acac (0.5 mol per mol of (Ti + Zr)) and 1-propanol (0.1696 mol) mixture was added and kept for 45 min under stirring. Finally, a mixture of acid (2×10^{-4} mol)-water (0.17 mol) and propanol (0.366 mol) was added and kept another 2 h under stirring at RT to get coating sol. The mol ratio of TTIP: ZP was kept 85:15 and this sol was designated as TZ85:15. At this stage the equivalent amount of (TiO_2 + ZrO_2) in the sol was 8 wt%. The equivalent amount of (TiO_2 + ZrO_2) in the final coating solution was maintained 4 wt% by diluting with 1-propanol. The sol was filtered through Millipore 0.22–0.5 μm filter paper and left 24 h in refrigerator (4 ± 1 °C) or at ambient temperature (25 ± 2 °C) for aging before used for coating deposition on glass substrates. In similar way different coating sols were prepared by varying equivalent TiO_2 and ZrO_2 components as shown in Fig. 1.

2.3 Preparation of coatings

Prior to coatings deposition, glass substrates were cleaned with neutral detergent followed by washing with tap water and rinsing with distilled water and ethanol. The coatings

Fig. 1 Mol ratios of titanium (IV) isopropoxide (TTIP) and zirconium (IV) *n*-propoxide alkoxides used to prepare TiO_2 , ZrO_2 and TiO_2 – ZrO_2 nanocomposite sols

were prepared using the dipping technique (Dip-master 200, Chemat Corporation) with withdrawal speed in the range of 4–6 inches/min. The as-prepared films were first dried at 60 °C in an air oven for 1 h followed by heat treated at 500 °C (ramp 2 °C/min) for 1 h. Similar coatings were deposited on silicon wafers (both side polished, intrinsic, IR transparent) as well as single side polished silicon wafers and soda-lime glass substrates for the FTIR studies, RI (refractive index) with thickness measurements, and GIXRD, XPS and Raman analysis, respectively.

2.4 Characterization of the coatings

RI (n) and thickness of the coatings deposited on single side polished Si-wafer was measured using spectroscopic ellipsometer, J. A. Woollam Co., Inc., USA. Infrared absorption spectra of the film deposited on both side polished Si-wafers were recorded by FTIR spectrometry (Nicolet, 380) with a resolution of 4 cm^{-1} and 200 scans. Raman spectra of the materials were obtained by using Renishaw In Via Reflex Raman spectrometer with diode (514 nm) laser source by using 20 $\times$ objective lens. The percentage of reflectance spectra of the films synthesized with respect to wavelength was measured using a Perkin Elmer Lambda 900 UV/visible/NIR spectrometer with a Lab sphere of 150-mm integrating sphere. GIXRD of the heat treated coatings were recorded with a Rigaku Smart-Lab X-ray diffractometer operating at 9 kW (200 mA, 45 kV) using Cu-K α ($\lambda = 1.54059 \text{ \AA}$) radiation maintain 0.3° grazing incidence angle for all the measurements. XPS measurements were performed with a PHI 5000 Versa probe II XPS system having an AlK α source and a charge neutralizer at room temperature and the base pressure was maintained at 6×10^{-10} mbar with an energy resolution of 0.6 eV. To evaluate the mechanical strength and chemical resistant of the coatings different tests were carried out, viz., cross cut and adhesive tape test following ASTM D 3359 and hardness test using a lens coating pencil hardness tester following ASTM D 3363, thermal, boiling salt water and 40 h in isopropanol tests. The above standard test procedures are as follows [21]:

- i *Cross cut and adhesive tape test following ASTM D 3359:* Using a cutting device such as a razor blade, six parallel cuts $1.5 \text{ mm} \pm 0.5 \text{ mm}$ apart and approximately 15 to 20 mm in length are made in the coating. Another six parallel cuts $1.5 \text{ mm} \pm 0.5 \text{ mm}$ apart are made in the coating perpendicular to the first set. This forms a cross-hatched pattern of squares over which tape is applied, such as Birla 3 M Scotch Magic Tape #810. The tape then is pulled rapidly as close to an angle of 180° as possible, and the percent adhesion is quantified by the amount of coating removed from the squares

in the cross-hatched pattern. If no coating material is peeled off from the substrate, it is quantified as ASTM Class 5B (highest standard).

- ii *Abrasion test using pencil hardness tester following ASTM D 3363:* Pencil hardness of the coated surface was evaluated following ASTM D 3363 specifications using a pencil hardness tester (BYK Gardner instrument). The pencil hardness value is given according to grade of pencil such as 9B–9H. For testing the sample, first pencil is inserted into the machine then it must touch the test surface, and is tighten the lamping screw. Then pencil is moved over the surface about 6–12 mm under a fixed load of 750 g and a fixed angle of 45 degrees. The test is repeated using successive grade pencils where one does not scratch and next one does scratch. The pencil grade for which it does not scratch the sample is the value of hardness.
- iii *Boiling salt water test:* This boiling in salt solution test evaluates the ability of a hard-coat to adhere to a substrate and the susceptibility of the coating to crazing. A coated glass is subjected to five to ten cycles of thermal shock by submersing the coated substrate for 2 min in a boiling salt water solution which comprises 3.5 L of deionized water, 157.5 g of sodium chloride, and 29.2 g of sodium dihydrogen orthophosphate, followed by submersing the coated glass for 1 min in water at $24 \pm 2 \text{ }^\circ\text{C}$. Coating performance is quantified by whether or not coating layer detachment or complete delamination from the substrate occurs, and by whether or not crazing of the coating occurs.

3 Results and discussion

3.1 Properties of sols and its stability

In this work the different nanocomposite sols were prepared by varying TiO₂ and ZrO₂ mol ratio. Viscosity of the as prepared sols was in the range of 5–6 cPs. For example, initial viscosity of the TZ85:15 coating sol was of about 6 cPs having pH 3–3.5. Stability of the sol (usable condition for coating deposition) at (RT) ($25 \pm 2 \text{ }^\circ\text{C}$) was in the range 40–50 days and 170–180 days when stored at RT ($25 \pm 2 \text{ }^\circ\text{C}$) and refrigerator ($4 \pm 1 \text{ }^\circ\text{C}$), respectively.

3.2 FTIR spectra of sol and coatings

3.2.1 FTIR study

Figure 2 represents FTIR spectra of the as prepared and heat-treated (500 °C/2 h) TZ85:15 coatings. We have used acac to control the fast hydrolysis rate of Zr and

Ti-alkoxides. As-prepared coating (Fig. 1a) showed sharp pair of peaks at 1586 and 1533 cm^{-1} due to (C–C and C–O) stretching's arising from (Zr+Ti)-acac chelate [22]. All these peaks almost disappeared or decreased after heat treatment (Fig. 2b). Moreover, as-prepared (Fig. 2a) coating showed peaks at 1042 and 650 cm^{-1} due to Ti–OH and Zr–OH, respectively [22, 23]. Intensity of these peaks decreased with heat-treatment. Coatings also showed peaks at 665, 797 and 430 cm^{-1} attributed to Ti–O–Ti and peaks at 450 cm^{-1} was due to Zr–O–Zr. The appearance of the peaks at 457 and 535 cm^{-1} indicating the formation of inter linked Ti–O–Zr network.

3.3 Raman and XRD studies

Figure 3 represents the Raman spectrum of the TZ85:15 coating heat treated at 500 °C for 1 h. In general, anatase has six Raman active modes (A_{1g} , $2B_{1g}$, $3E_g$). Presence of well-defined Raman bands at 144 (E_g), 197 (E_g), 399 (B_{1g}), 513 (A_{1g}), 519 (B_{1g}), and 639 cm^{-1} (E_g) indicate the anatase phase of TiO_2 [24, 25]. However, no significant Raman peaks of crystalline ZrO_2 were observed may be due to use of 514 nm laser source. But crystalline nature of ZrO_2 from the TZ85:15 coating was observed by GIXRD analysis.

Figure 4 shows XRD patterns of TZ100:0 (TiO_2), TZ0:100 (ZrO_2) and TZ85:15 (TiO_2 - ZrO_2) coated glasses heated at 500 °C for 1 h. Heat-treated TZ100:0 coating showed diffraction peaks at $2\theta = 25.2, 37.8, 48, 55.1$ and 62.68° corresponding to the TiO_2 anatase phase (JCPDS Card 00-021-1272). Similarly for TZ0:100 coating, sharp and strong peaks at $2\theta = 30.26, 35.25, 50.37$ and 60.2° along with other related peaks at $62.96, 74.53, 81.9$ and 85.22° were observed due to the crystalline tetragonal phase of ZrO_2 (JCPDS Card 00-050-1089). In case of mixed composition

Fig. 2 FTIR spectra of the TZ85:15 coatings (a) as-prepared and (b) heat treated at 500 °C for 1 h. Coating was prepared from TZ (85:15)-sol on a both side polished intrinsic Si-wafer

Fig. 3 Raman spectra of TZ85:15 coating heated at 500 °C for 1 h

TZ85:15 coating, most of the peaks appeared similar to the TZ100:0 coating but three new peaks were observed at 37, 53.28 and 62.4° (showing by arrow) which may be due to mix phase at this temperature. Moreover, shifting in the diffraction angles of the anatase (101) peak towards lower values (25.35 to 25.2°) in TZ85:15 coating (shown in enlarge scale) also indicated the formation of inter-linked Ti–O–Zr network in the nanocomposites [26]. The crystallite size of TiO_2 in TZ85:15 composite was calculated from the Debye–Scherrer equation [27] using the (101) peak and estimated to be ~ 16 nm.

Fig. 4 XRD patterns of TiO_2 , ZrO_2 and TZ85:15 coated glass heated at 500 °C for 1 h. Diffraction angles (2θ) of the anatase (101) peak is also shown in enlarged scale

3.4 XPS analysis

The XPS study (Fig. 5) of the cured coatings was performed in order to provide more evidence to the existence of Ti–O–Zr bonds in nanocomposite and chemical state of the elements. Figure 5a showed survey scan of coating TZ85:15, where binding energy corresponding to O, Ti and Zr were observed. The weak peak for C 1 s also appears which may be come from impurity. The Ti2p_{3/2} and Zr 3d_{5/2} peaks (Fig. 5c, d) corresponding to the binding energy of 458.4 and 182 eV represent Ti⁴⁺ and Zr⁴⁺ ions, respectively [25]. Shifting of Ti 2p_{3/2} towards lower energy region was observed for TZ85:15 coating compared to pure titania [28] coating due to the formation of Ti–O–Zr bond. Further, after deconvolution of O 1 s (Fig. 5b), peak localized at 531.38 eV can be attributed to Ti–O, while the peak at 529.8 eV is assigned to Ti–O and Zr–O indicating the interaction of Ti and Zr ions leading to the formation of Ti–O–Zr network. The above data also supports the results of the FTIR and GIXRD analysis regarding the formation of

Ti–O–Zr network. The experimentally observed elemental ratio of Ti:Zr was 84.4:14.6 in the heat treated coating, which was similar to the theoretically composition of equivalent Ti and Zr alkoxides (85:15) used for the preparation of the coating solution.

3.5 Physiochemical properties of the coatings

Figure 6 represents TiO₂–ZrO₂ (TZ85:15) coated float glass (dimension: 200 × 200 mm²). The thickness of the heat treated (500 °C/1 h) TZ85:15 coatings were in the range of 80–100 nm having refractive index value of 1.985 ± 0.002 (Table 1). Coatings were uniform, flawless and showed good hardness ≥ 5H with adhesion (ASTM class 5B) properties. Hardness value of the coating decreased with increasing of equivalent Ti-content in the TiO₂–ZrO₂ composite (Fig. 7). Hardness value was 2H and ≥ 7H for TZ100:0 and TZ0:100 coating, respectively. Figure 8 shows reflection spectra of TZ100:0 (TiO₂), TZ0:100 (ZrO₂), TZ85:15 (TiO₂–ZrO₂) coated and uncoated

Fig. 5 XPS of heat treated TZ85:15 nanocomposite coating: **a** survey scan and **b–d** high resolution scans in the region of O 1 s (**b**), Ti 2p (**c**) and Zr 3d (**d**)

Fig. 6 $\text{TiO}_2\text{-ZrO}_2$ (TZ85:15) coated float glass (dimension: $200 \times 200 \text{ mm}^2$) with showing golden yellow reflection colour (right) under tube-light

Table 1 Variation of refractive index (RI) values of the heat treated coatings having different titanium (IV) iso-propoxide (TTIP) and zirconium (IV) *n*-propoxide (ZP) content

Sample label	RI value of the heat treated coating (measured at 633 nm)
TZ100:0	2.192 ± 0.002
TZ90:10	1.992 ± 0.002
TZ85:15	1.985 ± 0.002
TZ60:40	1.965 ± 0.002
TZ50:50	1.920 ± 0.002
TZ0:100	1.855 ± 0.002

Fig. 7 Variation of pencil hardness values of the heat treated coatings having different TTIP and ZP content in $\text{TiO}_2\text{-ZrO}_2$ nanocomposite

soda lime glass substrates. It was clear that TZ85:15 coated glass showed $> 28\%$ of average reflection (in the wavelength region of 350–2500 nm) and $\sim 31\%$ (in the wavelength region 400–800 nm) whereas TZ100:0 (TiO_2) and TZ0:100 (ZrO_2) coated glass showed 25.5 and 18.2% average reflection, respectively in the wavelength region 350–2500 nm (Fig. 9). All above coated glasses showed

Fig. 8 Reflection spectra of TZ100:0 (TiO_2), TZ0:100 (ZrO_2), TZ85:15 ($\text{TiO}_2\text{-ZrO}_2$) coated and uncoated soda lime glass substrates in the wavelength region 350–2500 nm

Fig. 9 Comparison of % reflection data of TZ100:0, TZ0:100 and TZ85:15 coated and uncoated soda lime glasses in the wavelength region 350–800, 800–2500 and 350–2500 nm

higher in reflection as compared to the uncoated glass, but in IR region better results was obtained from (TZ85:15) coated glass. Moreover, the TZ85:15 coated glass could resist up to 8 cycles of boiling in salt solution test [21] without any damage indicating its compatibility with the substrate and chemical inertness as well as thermal stability (Table 2). TZ85:15 coated glass also showed the golden yellow reflected color under tube light exhibiting enhanced aesthetic beauty (Fig. 6). For comparison, coating on glass substrates were also done using other nanocomposite sols (TZ50:50, TZ60:40 and TZ90:10) under similar condition. But in terms of adhesion, hardness, reflection properties, optimum result was obtained from TZ85:15 coated glass. So, the above nanocomposite based heat reflective coated glass could be useful as component for energy efficient building materials as well as it enhances aesthetic beauty

Table 2 Evaluation of the heat treated TiO₂–ZrO₂ (TZ85:15) coatings deposited on glass substrates having coating thickness 90 ± 10 nm

Name of the test	Specifications	Result
Visual appearance	–	Optically clear with a characteristic golden yellow reflection colour hue
Thickness		90 ± 10 nm (thickness increases with withdrawal speed)
Adhesion (coating material to the substrate)	DIN 53151 or ASTM D 3359	ASTM class 5B (highest standard)
Pencil hardness	ASTM D 3363	≥ 5H (TZ85:15); hardness decreases with increasing of Ti-content; ~ 2H (TZ100:0) and ≥ 7H (TZ0:100)
Boiling salt water	Chemical endurance test	Coating can resist ~ 8 cycles; with increasing of Ti-content resistance decreases
Thermal test	80 °C/6 h in an air oven	No cracking/crazing of the coating
Isopropanol test	Kept 40 h in isopropanol	Coating remains unaffected

of building from reflected color hue of the coating. In addition, coating containing anatase phase (titania) could be very used for self cleaning application due to its photocatalytic property.

4 Conclusions

In this work, ZrO₂ incorporated TiO₂ based transparent hard nanocomposite coatings (single/one layer) on glass substrates were developed by sol–gel dip-coating technique using ZP and TTIP followed by heat treatment at 500 °C. TZ85:15 coating composition was found to be optimum in terms of mechanical and optical properties. Large area such coating was developed on float glass substrate up to a dimension of 200 × 200 mm² in view of commercial application. The resultant coatings of 90 ± 10 nm in thickness having refractive index value of 1.985 ± 0.002 were found to be flawless, uniform, and showed good hardness ~ 5H (ASTM D 3363) and adhesion (ASTM class 5B; ASTM D 3359 specification). Formation of Ti–O–Zr network of the heat-treated coatings was confirmed by FTIR and XPS analysis whereas crystalline nature was revealed by GIXRD and Raman. Evaluation of optical properties showed > 28% of average reflection (in the wavelength region of 350–2500 nm) and ~ 31% (in the wavelength region 400–800 nm). In addition, coating also showed the golden yellow reflected color which could enhance aesthetic beauty from reflected color hue of the coating. So, the above nanocomposite based coated glass could be useful as suitable component for heat reflecting window for building materials with aesthetic beauty. Moreover, coating with crystalline anatase phase (titania) could be very used for self cleaning application due to its photocatalytic property.

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Compliance with ethical standards

Conflict of interest The authors declare no competing financial interest.

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