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Development of Modified Glasses by Transparent, Functional Hybrid Sol-Gel Nano-Ceramic Coatings, a Comparative Study

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Abstract

This paper concentrates on the development of glasses with self-cleaning surfaces exhibiting high water contact angles. In this study, we prepared super-hydrophobic nano-ceramic coated glass based on titania & silica using simple sol-gel & dip coating methods and studied the best composition of the coatings by altering ratios of titanium tetraisopropoxide (TTIP)/tetraethyl orthosilicate (TEOS) with different homogenizing agents. We characterized the coatings by surface roughness measurement, percentage of optical transmission, static contact angle, near-infrared (NIR) transmission, and diffuse reflectance. The fabrication of coatings on glass substrates played an important role in increasing the water contact angle of about 95˚ and visible & NIR transmission of about 90%. We compared our modified glass substrate with commercial low emissivity (Low E) glass using X-ray diffraction (XRD) analysis, which showed pure amorphous surface claiming excellent wettability and thus the prepared glass substrate could have a variety of applications in different fields.

Keywords

Sol-Gel, Nano-Ceramic Coatings, Self-Cleaning Glass, Water Contact Angle, Optical Transmission

1. Introduction

The use of glasses becomes more prominent and extraordinary when these have been modified with excellent transparent coatings, giving amusing self-cleaning surfaces [1]. Recent works have identified significant interactions between surface modifications with water contact angles. Hydrophobic surfaces, usually having a water contact angle greater than 90˚, have vast applications as self-cleaning objects [2]. The wettability of glass substrates depends on different contact angles and roughness of the surfaces. Such surfaces inhibit contamination, giving water droplets a spherical shape, rolling off over the surfaces, and then picking up the dirt particles [3]. That is why the surface is often the most important part of any engineering structural component like glass substrate. Hydrophobicity and surface morphology are the deciding factors for the self-cleaning property of a solid glass surface [4].

Nano-ceramic coatings have revolutionized progress in the development of energy-efficient coatings on glass called "smart-glass" with special functional coatings that can have excellent self-cleaning properties [5]. Smart glasses modified by nano ceramic coatings are considered attractive because they are visibly transparent and can intelligently control visible and near-infrared (NIR) transmission with good self-cleaning properties. Commercially important nano-ceramic materials are metal oxides such as silica, titania, alumina, ceria, zirconia, zinc oxide, iron oxide, and mixed metal oxide, where silica and titania offer great potential for various applications due to their superior characteristics that are not typically found in conventional coatings [6]. Nano-ceramic coatings having photocatalytic properties [7] are able to degrade organic material, causing stains adsorbed on the surface into volatile molecules, leading to "self-cleaning" [5].

A variety of methods are available for metal oxide coatings. Wet chemical processing, also known as sol-gel technique, is the most important method for coatings in industrial application purposes and also from both technical and scientific viewpoints [8]. Coatings deposited by the sol-gel method can have different characteristics of compositional distribution and phase stability [9]. It has several advantages over the conventional surface derivatization method. It has control of homogeneity on the molecular level and good compositional control [7]. Sol-gel is a simple and economical method without homogeneity problems encountered in the processing of powders. It can maintain a lower crystallization temperature [10] and is used to deposit coatings over a large area with a very uniform thickness [11].

Jean-Denis Brassard *et al.* used solutions of mono dispersive spherical fluorinated silica nanoparticles of ~120 nm which have been prepared by sol-gel processes and have been used to prepare thin films on flat aluminum, silicon, and glass substrates by spin-coating processes. The water contact angle values were found to increase with increasing numbers of layers until a critical number of layers: three in the case of the as-prepared solution used for coating and seven in the case of the diluted solution used for coating. When applied on other substrates, like silicon or glass, super hydrophobicity was obtained by tuning the number of layers of deposition. The transparency of the coating has been demonstrated on glass substrates, which showed the great potential of such coatings in industrial use on large scale, such as on windows and car windshields as well as for aesthetic purposes on opaque substrates [6].

Vinayak V. *et al.* prepared tetraethyl orthosilicate (TEOS) based hydrophobic, self-cleaning silica coatings on a glass substrate by single step sol-gel process with methyl trimethoxysilane (MTMS) as a co-precursor. The coating sol was prepared by keeping the molar ratio of TEOS, methanol, and water constant at 1:33.15:6.06, respectively, throughout the experiments with NH_4F (0.1 M) as a catalyst. The molar ratio (M) of the MTMS/TEOS varied from 0 to 7.84, and its influence on hydrophobicity was studied by static contact angle and sliding angle measurements. It was observed that, with an increase in the M value from 0 to 1.57, the contact angle increased respectively, and with a further increase in the M value, the contact angle reduced and remained nearly constant thereafter. For coatings prepared with M values 0.78, 1.18, and 1.57, petal effect (water sticking) was observed. The sliding angle for the coatings was reduced with a further increase in M values, leading to self-cleaning surface [2]. The above-mentioned authors used complex and expensive spin-coating process and obtained moderate hydrophobicity and self-cleaning properties.

In this paper, the surface of commercial float glass has been modified by simple and cost-effective sol-gel nano-ceramic coatings with different ratios of precursors and homogenizing agents. The effect of the treatment on the optical properties of the glass substrate has been studied by transmittance measurements, and the water contact angle has been investigated to identify the best composition for practical applications.

2. Materials and Methods

2.1. Materials

The chemicals used in this study for the preparation of coatings were titanium tetraisopropoxide (TTIP) (Sigma-Aldrich, USA) as the source of titania (Ti), tetraethyl orthosilicate (TEOS) (Sigma-Aldrich, USA) as the source of silica (Si); Isopropanol (IP)/2-Methoxyethanol (2ME)/Methanol/Acetyl acetone (AcAc)/Meth acrylic acid(MA) (Merck, Germany) as homogenizing agent for hydrolysis and condensation reactions. In some cases, ammonium fluoride (AF) (BDH, England) was used as a catalyst. The type of glass substrate used in the experiment was transparent Float Glass of 2.5 mm thickness.

2.2. Methods

2.2.1. Pretreatment of Glass Substrate

Air/tin side of float glasses were identified using UV lamp (C-65 Chromato-Vue cabinet, UVP, USA) of 254 nm by observing the fluorescence of the tin side of the float glass under the UV lamp. Pretreatment was given to the glass substrates before coating in order to remove any kind of grease or impurity present on the surface. Surface pretreatment of the substrate was carried out by cleaning the glass slides with liquid detergent. These slides were then treated with HCl and further cleaned with distilled water for 2 minutes, followed by deionized water and acetone rinsed in turn to remove the surface contamination and dust. At last, all the glass substrates were dried at 60˚C for 1 hour.

2.2.2. Fabrication of Sol-Gel Coatings on Glass Substrates

TTIP/TEOS was used as precursor for the preparation of coating alcosols using sol-gel techniques. The molar ratio of precursor to homogenizing agent was optimized to various ratios. Initially homogenizing agents were stirred for 30 min to homogenize the solution with magnetic stirrer (UC-152, STUART) and then TTIP or TEOS were added drop wise starting from 1 ml to promote the hydrolysis and condensation reactions and stirred for certain minutes. In some defined cases, ammonium fluoride was used as catalyst. Prior to gelation, stirring was turned stopped. The prepared alcosol was then transferred to a test tube and the glass substrate was coated using a Millimeter Grade Programmable Dip Coater (Model No; Controller: PTL MMB-01, Drying Oven: WHL-30B). The glass substrates were coated prior to gelation maintaining dipping and withdrawal rate of 50 mm/min. Dipping for certain cycles were carried out with 1 min dipping duration. The coated substrates were taken in aging process at room temperature (~27˚C) for 40 min to stiffen the network and thereby reducing the risk of fracture, then, sintered at 150˚C for 2 h at 1.5˚C/min ramping rate by Vacuum Oven (Thermo Stable OV-70, Witeg, Germany) maintaining the vacuum of 0.67 Pa. After cooling, the coated samples were washed with deionized water. Different coatings by altering the compositions of precursors and homogenizing agents were coded as showing in **Table 1**.

2.3. Characterization

The static contact angle θ (air side & tin side) of uncoated transparent Float Glass and glasses coated with different compositions of precursors & homogenizing agents were measured to study the wetting ability and self-cleaning property of the glasses before and after coating. Furthermore, compositions that gave best wetting ability were studied. In practice, a droplet was placed on the solid surface and the image of the drop was recorded by using a contact angle optical tensiometer with high definition camera (resolution: 1280 × 720) [12]. Measurement of the thickness and roughness of sol-gel coatings were performed using a surface profilometer (Dektak XT, Bruker) in nanometer range. The transmission (%) spectra were measured by using a UV-Visible spectrophotometer (UV-1800, Shimadzu, Japan) for optical characterization. To investigate the near infra-red transmittance, FT-IR/NIR spectrometer (Frontier, brand: Perkinelmer) was used. Wavelength range was selected from 1000 nm to 4000 nm. Diffuse reflectance of the coated and non-coated samples was carried out using UV-2600 UV-Vis-NIR spectrophotometer, Shimadzu, Japan, in the range of 220 to 1400 nm by attaching integrating sphere and by using barium sulphate as reference of 100% reflectance. X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a material. This was performed using GBC X-ray diffractometer having Cu Kα (1.5406 Å) radiation. The diffraction

Table 1. Compositions of different Sol-Gel Systems with coded name.

Coded Name	Compositions of Sol-Gel Systems	Coded Name	Compositions of Sol-Gel Systems
S1	TTIP: 1 ml IP: 30 ml AcAc: 20 ml	S11	TTIP: 3 ml 2ME: 30 ml MA: 20 ml
S2	TTIP: 2 ml IP: 30 ml AcAc: 20 ml	S12	TTIP: 1 ml 2ME: 30 ml AcAc: 20 ml
S3	TTIP: 3 ml IP: 30 ml AcAc: 20 ml	S13	TTIP: 2 ml 2ME: 30 ml AcAc: 20 ml
S4	TTIP: 1 ml IP: 30 ml 2ME: 20 ml	S14	TTIP: 3 ml 2ME: 30 ml AcAc: 20 ml
S5	TTIP: 2 ml IP: 30 ml 2ME: 20 ml	S15	TEOS: 1 ml 2ME: 30 ml MA: 20 ml
S6	TTIP: 3 ml IP: 30 ml 2ME: 20 ml	S16	TEOS: 2 ml 2ME: 30 ml MA: 20 ml
S7	TTIP: 3 ml IP: 40 ml 2ME: 10 ml	S17	TEOS: 3 ml 2ME: 30 ml MA: 20 ml
S8	TTIP: 3 ml IP: 10 ml 2ME: 40 ml	S18	TEOS: 2 ml IP: 30 ml Methanol: 20 ml AF: 8 drops
S9	TTIP: 1 ml 2ME: 30 ml MA: 20 ml	S19	TEOS: 2 ml IP: 40 ml 2ME: 10 ml AF: 8 drops
S10	TTIP: 2 ml 2ME: 30 ml MA: 20 ml		

patterns were recorded in the range of 20˚ to 90˚ having scanning speed 5˚/minute [13].

3. Results and Discussion

3.1. Contact Angles Measurements

The static water contact angle measurement was first performed on uncoated transparent float glass which was found as 35˚ in air side and 60˚ in tin side

(**Table 2**). It indicated that water drops didn't attain spherical shape on glass substrate (**Figure 1**). It claimed that the glass substrate noticeably had hydrophilic surface.

The variation of the contact angle with different coatings by changing in compositions of Sol-Gel systems is given in **Table 2**. After the surface treatment, from samples S4 to S10 and S15 to S19 films were quantified from measurements of the small water contact angles vary < 90˚ indicating hydrophilic surfaces (**Figure 2**).

These values increased with the changing compositions of homogenizing agents in the sols, reaching water contact angles ≥ 90˚ in the treatment with samples from S1 to S3 and S12 to S14 (**Figure 3**). The maximum water contact angle measured for sample S2 (TTIP: 2 ml, IP: 30 ml, AcAc: 20 ml) was 95˚ which was due to the enhancement of the adhesion force between water droplet and coated surface applied on to the glass substrate. This noticeable increase in water contact angle proved the wettability characteristics of the modified glass emitting excellent transition from hydrophilic to hydrophobic surface [12]

3.2. Thickness and Roughness of Coatings

An important factor that can improve the hydrophobicity and wettability of the glass substrate is the surface roughness [3]. The thickness and surface roughness values of sample coatings were measured (**Table 3**) where thickness didn't play any significant role on hydrophobicity of the coated surfaces. The viscosity of the sol and dipping time determined the variety of thickness of coatings on both air side and tin side. The coatings in sample S4 to S10 and S15 to S19 films showed average roughness in which cases water contact angles were also less than 65˚. On the contrary, samples from S1 to S3 and S12 to S14 had explicitly rougher surfaces and greater water contact angles. This confirmed that the surface properties of the substrates a were changed from hydrophilic to hydrophobic after the treatment [9]. Moreover, liquid in contact with a rougher surface can adopt several metastable configurations with apparently higher contact angle and tracking the dirt's away from the surface by exposing to water.

3.3. Measurement of Optical Transmission

Considering all of the experiments, it was observed that there was no significant effect on UV light transmittance almost all of the cases rather there were change in visible light transmittance for the samples [11] [14]. **Figures 4(a)-(c)** showed the visible transparency value for samples S4, S5 & S6 giving transmission percentages from about 55 to 80. In the case of sample S5 where the amount of TTIP was increased from 2 ml to 3 ml exhibited golden reflective coating with greater transmission % than S4 & S6.

Figures 5(a)-(d) showed the visible transparency values for non-coated glass and samples S1, S2 & S3 giving exceptional transmission percentages about 90 noting that optical transmission of coated glasses remained near similar to the

Table 2. Effect of change in compositions of sols on static water contact angles at both sides of float glass.

Sample Name	Water contact angle before coating	Water contact angle at air side after coating	Water contact angle at tin side after coating
S1	Air side: 35˚ Tin side: 60˚	90˚	90˚
S2		90˚	95˚
S3		90˚	90˚
S4		30˚	65˚
S5		40˚	45˚
S6		50˚	65˚
S7		45˚	60˚
S8		55˚	65˚
S9		50˚	65˚
S10		50˚	55˚
S11		50˚	40˚
S12		85˚	90˚
S13		85˚	90˚
S14		90˚	90˚
S15		30˚	30˚
S16		25˚	40˚
S17		30˚	50˚
S18		60˚	65˚
S19		50˚	65˚

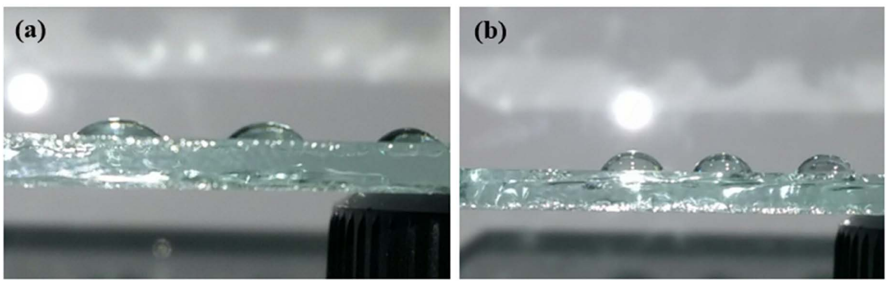

Figure 1. Water contact angles on non-coated sides of transparent float glass (a) on air side, θ = 35˚; (b) on tin side, θ = 60˚.

non-coated glass. Excellent transmission percentages suggested that the modified glasses could have good applications in energy-saving smart windows [15].

3.4. Measurement of NIR Transmittance

Glasses can delineate great energy saving effects by transmitting visible and near infra-red radiation through these and reflecting UV & long-wave infra-red

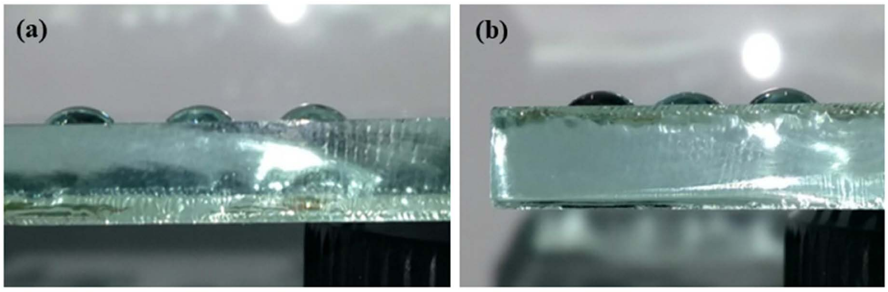

Figure 2. Water contact angle on coated air and tin sides for sample S5 (TTIP: 2 ml, IP: 30 ml, 2ME: 20 ml) (a) on air side, θ = 40˚; (b) on tin side, θ = 45˚.

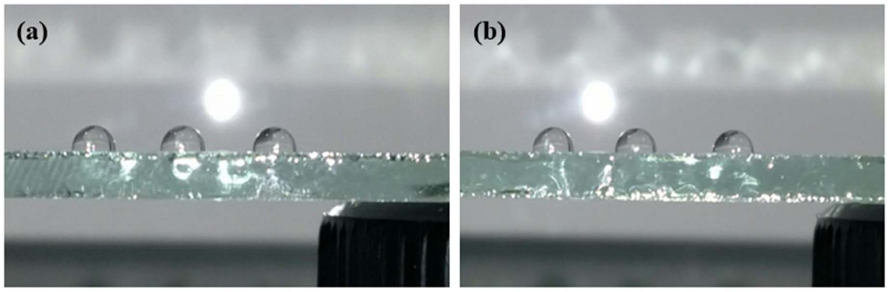

Figure 3. Water contact angle on coated air and tin sides for sample S2 (TTIP: 2 ml, IP: 30 ml, AcAc: 20 ml) (a) on air side, θ = 90˚; (b) on tin side, θ = 95˚.

Table 3. Thickness and roughness of coated surfaces of different compositions.

Sample Name	Surface thickness (mm)	Surface roughness (mm)
S1	A- 431 T- 128	A- 140 T- 103
S2	A- 460 T- 120	A- 151 T- 111
S3	A- 435 T- 115	A- 122 T- 120
S4	A- 193 T- 132	A- 79.707 T- 48.613
S5	A- 190 T- 120	A- 77 T- 46.3
S6	A- 215 T- 140	A- 85 T- 65
S7	A- 5.717 T- 116	A- 48.303 T- 66.959
S8	A- 213 T- 133	A- 80.029 T- 65.021
S9	A- 210 T- 130	A- 81 T- 62
S10	A- 200 T- 113	A- 78.88 T- 63

Continued

S11	A- 5.9 T- 110	A- 47 T- 65.4
S12	A- 273 T- 81.892	A- 91.7 T- 62
S13	A- 280 T- 80.9	A- 90.349 T- 60.223
S14	A- 275 T- 85	A- 89.9 T- 65
S15	A- 30.031 T- 115	A- 21.272 T- 47.73
S16	A- 41.538 T- 17.714	A- 20.069 T- 10.962
S17	A- 33.2 T- 114	A- 22.1 T- 47.3
S18	A- 106 T- 67.377	A- 54.905 T- 47.872
S19	A- 100 T- 66.99	A- 57 T- 45.6

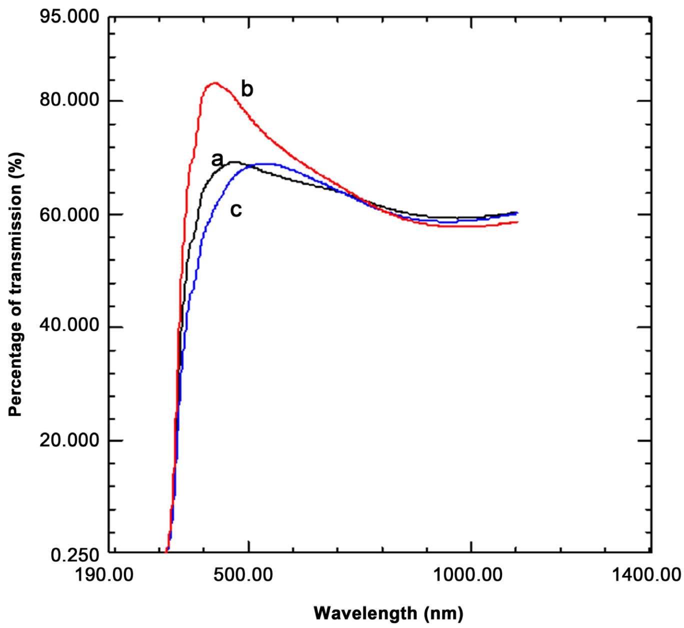

Figure 4. Transmittance spectra of coated samples S4, S5 & S6 (a-S4, b-S5, c-S6).

radiation by their reflective coatings [15]. From results of near infra-red (NIR) transmission experiments for different coated samples, it was noticeable that there was no significant change in NIR switching efficiency that was observed in any coated glass (**Figure 6**). It was almost similar for coated and non-coated

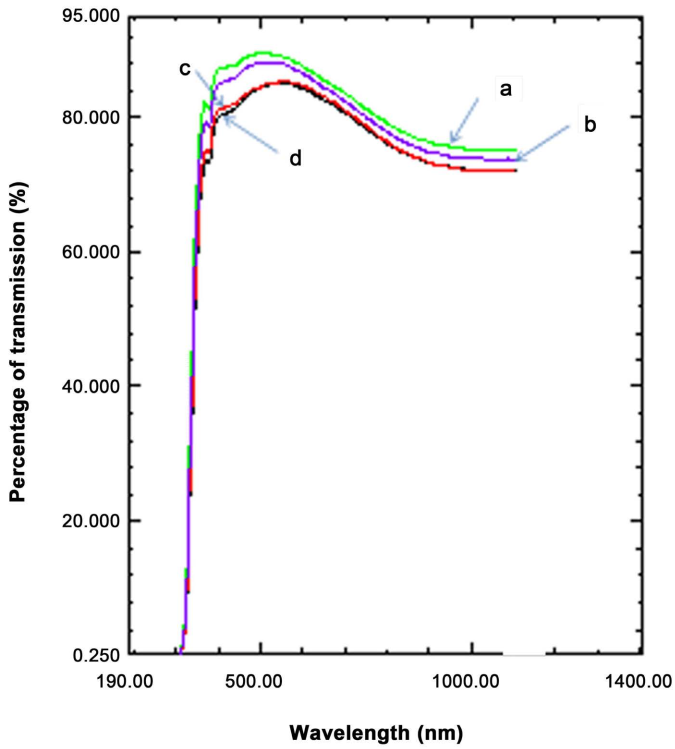

Figure 5. Transmittance spectra of non-coated glass and coated samples S1, S2 & S3 (a-non-coated glass, b-S1, c-S2, d-S3).

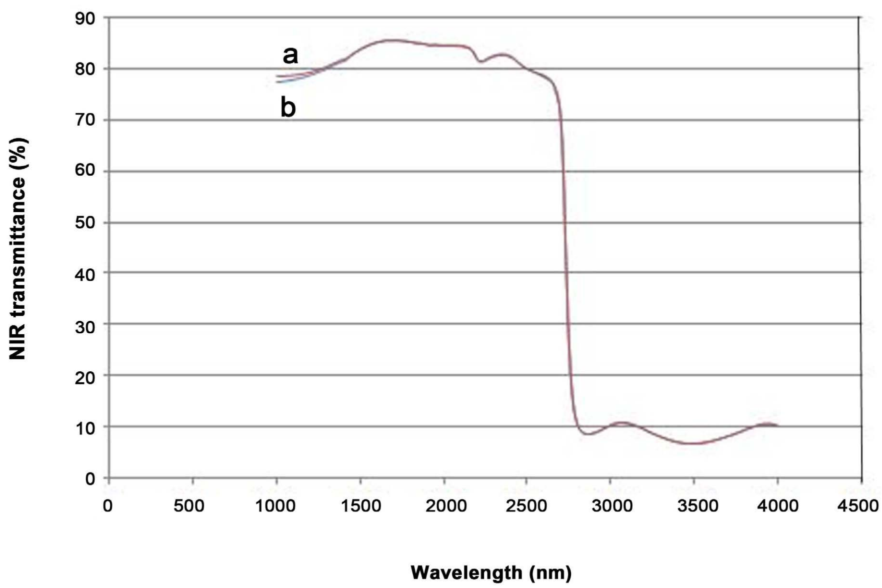

Figure 6. NIR transmittance of (a) before and (b) after coated glass (S2).

glasses. That means, the coated glasses could not block NIR significantly. It is rare for any coated glass showing both good percentages of visible transmittance and NIR switching efficiency. On the other hand, commercial low emissivity (low E) glass showed low transmission in NIR range than coated glasses (**Figure 7**).

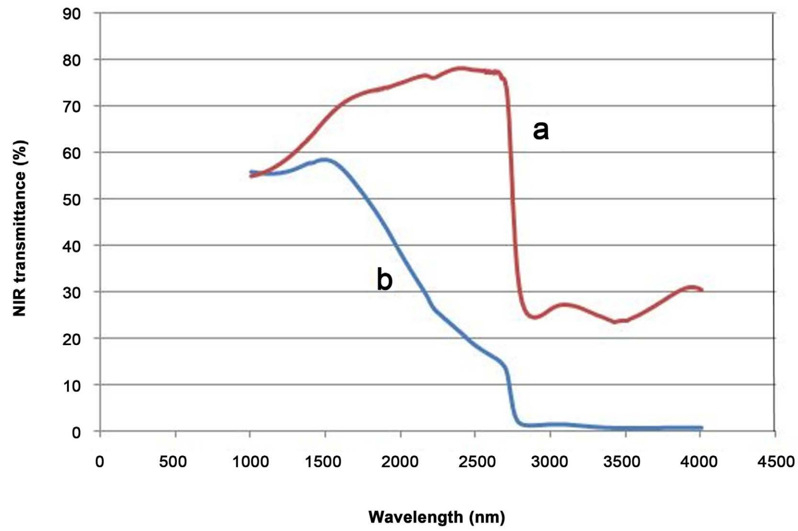

Figure 7. Comparison of NIR transmittance between (a) coated glass (S2) and (b) commercial low emissivity (Low E) glass.

3.5. Measurement of Diffuse Reflectance

Scattering of light upon reflection depends upon the roughness of the surface. The rougher the surface, the more diffuse the reflection and lower the transmittance. Results showed that the samples (S2) showing high transmittance percentages showed less diffuse reflectance and vice versa (**Figure 8**, **Figure 9**). It indicated that the coated glasses could be used as solar reflective glasses. These glasses with special coating could be designed to reduce the amount of heat entering a building. These could reflect and absorb heat as well as filtering light for reduced glare and can reduce the need for air-conditioning and blinds.

3.6. X-Ray Diffraction (XRD) Analysis

X-Ray diffraction patterns of coated glass (S2) from the experiments suggested that the coatings were amorphous on both air and tin sides (**Figure 10**, **Figure 11**). On the contrary, commercial low emissivity (low E) glass [16] showed one side as crystalline which was reflective and the other side as amorphous as shown in the **Figure 12**. Glass substrate with pure phase surface usually associated with hydrophobic sites showed greater wetting ability [17] and glass substrates with mixed phase surface associated with both hydrophobic and hydrophilic sites showed poor wetting character [13].

4. Conclusion

A comparative study between different ratios of different nano ceramic coatings on glass substrates based on Ti & Si was studied using simple sol-gel technique. Composition (TTIP: 2 ml, IP: 30 ml, AcAc: 20 ml) showed most promising results of dramatic increase in water contact angle up to 95˚ and excellent visible light transmission of about 90%. The appreciable NIR transmission with rougher surface and decreasing reflectance % ensured the more hydrophobicity of the

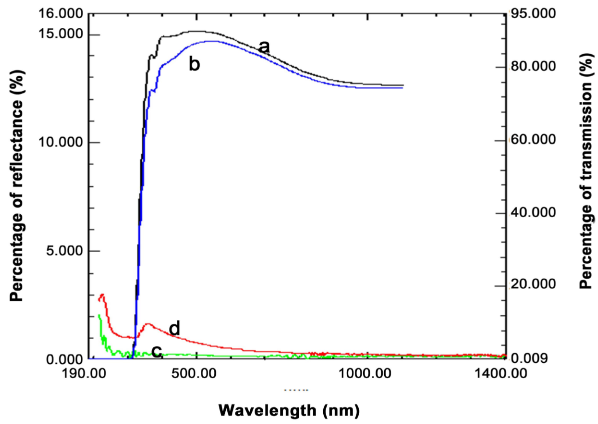

Figure 8. Diffuse reflectance and transmittance of before and after coated glass (S1) (a) transmittance before coating; (b) transmittance after coating; (c) diffuse reflectance before coating; (d) diffuse reflectance after coating.

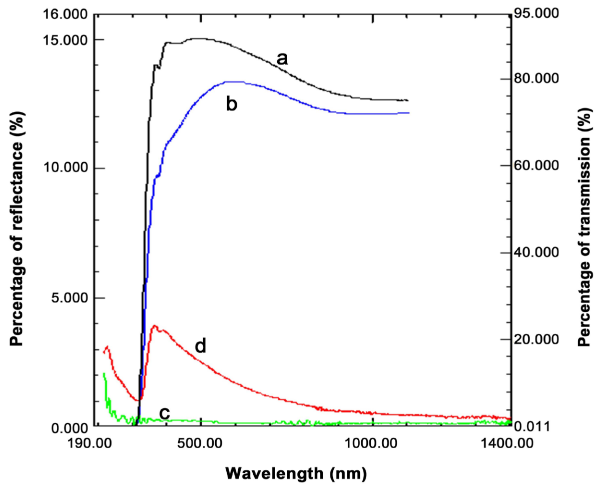

Figure 9. Diffuse reflectance and transmittance of before and after coated glass (S6) (a) transmittance before coating; (b) transmittance after coating; (c) diffuse reflectance before coating; (d) diffuse reflectance after coating.

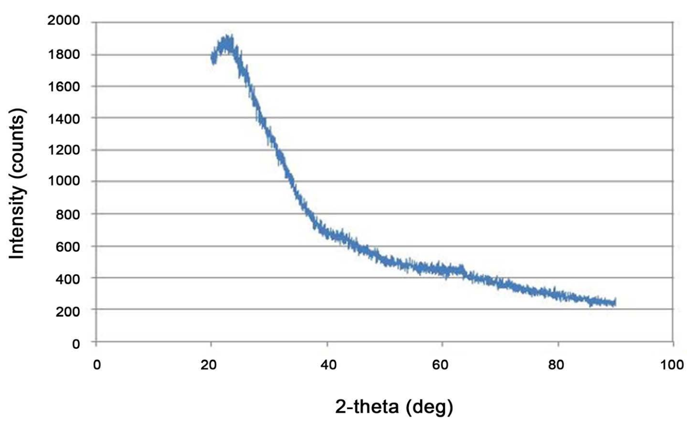

Figure 10. X-Ray diffraction patterns of coated glass (S2) facing the air side.

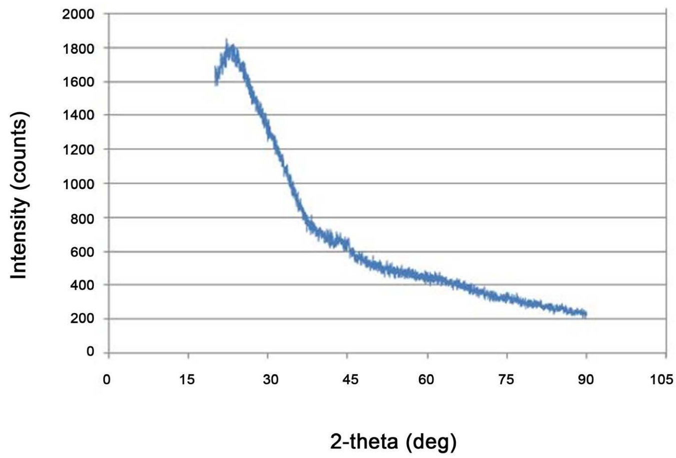

Figure 11. X-Ray diffraction patterns of coated glass (S2) facing the tin side.

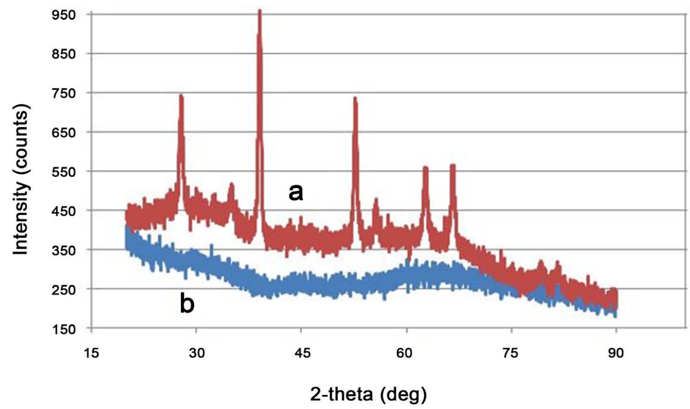

Figure 12. X-Ray diffraction patterns of commercial low E glass (a) for crystalline air side (b) for amorphous tin side.

glass substrates after coating which was responsible for self-cleaning performances. In comparison with commercial low E glass, our modified glass showed pure phase surface with greater wettability and could find potential & fruitful applications in a variety of fields.

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Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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