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Tuning structural and wettability properties of glass using ellipsoidal TiO_2 nanoparticles

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Self-cleaning glasses became demanding for various advanced applications due to their manifold advantages. In this view, some tellurite glasses containing TiO_2 nanoparticles with varying concentrations were synthesized using the standard melt-quenching. These glasses were transparent with a reddish appearance. The HRTEM images of the glasses showed the presence of ellipsoidal TiO_2 NPs with sizes ranging from 9–22 nm and 5–9 nm along the major and minor axis, respectively. The lattice fringe pattern of the selected TiO_2 NPs confirmed their anatase structure with a lattice spacing of 0.36 nm. The observed reduction in the water contact angle from 67.5° to 43.0° of the glasses indicated their hydrophilic nature. The high work of adhesion (0.101– 0.126 $N.m^{-1}$) of the glasses revealed the strong interfacial attractive force between water and glass. It was demonstrated that by adjusting the TiO_2 NPs contents the hydrophilic traits of the glassed can be tailored, indicating the suitability for self-cleaning applications.

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1. Introduction

Emerging issues of difficulties in handling, high consumption of energy and chemical detergents, and high costs have been aroused due to the surface cleaning of building materials such as tiles, facades, and glass panes [1]. Recently, materials including TiO_2, SiO_2, ZnO, VO_2, Ag and polydopamine-encapsulated octadecylamine have been reported as potential candidates to produce superhydrophilic self-cleaning surfaces [2]. TiO_2 offers a beneficial feature in the self-cleaning application prior to surfaces utilizing sunlight and natural rainfall to keep the surface clean. This feature becomes one of the most interesting and attractive, drastically reducing time, cost, and energy for maintenance [3]. In the case of superhydrophilic self-cleaning coating under the right conditions such as frequent rain and in the presence of sunlight during a hydrophilic sheating stage, water plays an important role to wash away the airborne pollutants and other organic contaminants in the form of hydrophilic coating evenly spread water over the surface. Hence, the process that occurs contributes to fewer cleaning cycles and is found to be more stable with a longer life span as compared to hydrophobic self-cleaning coating [4].

The superhydrophilicity can be achieved by process conditions such as concentration and pH or the proper nanoparticles (NPs) size [5]. However, TiO_2 NPs must be immobilized onto a substrate. Various coating techniques have been reported such as sputtering, chemical vapor deposition, and thermal spraying. Despite these techniques, it comes with their own drawbacks such as high-temperature requirements probably changing the TiO_2 microstructure and these techniques are economically nonviable [6]. Yusof et al. [7] fabricates glass containing TiO_2 NPs and demonstrates an extensive study on the thermal, optical, structural, and wettability properties. By using TiO_2 NPs concentration in the range of 0.1 to 0.4 mol%, they found the wettability properties are strongly dependent on the photocatalytic properties of glass.

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In the present study, a new type of tellurite glass system at various contents of the TiO_2 NPs doping (0.05 to 0.20 mol%) was prepared. The presence of erbium ions in the close vicinity of TiO_2 NPs experiences stimulated optical interaction. Water is the most abundant and freely available liquid system that possesses optimal density as well as polarity. Therefore, we utilize water as an essential medium to demonstrate the process of removal of dust or contaminants from the glass surface containing TiO_2 NPs and evaluate the self-cleaning features of prepared glass. We found the hydrophilicity and adhesion of low surface energy varied with the addition of TiO_2 NPs into the glass matrix.

2. Experimental details

2.1. Fabrication of glass

The tellurite glass system with the composition of (79–x)TeO_2 – 20ZnO – 1.0Er_2O_3 – (x)TiO_2, where x = 0.00, 0.05, 0.10, 0.15 and 0.20 mol% were synthesized using a melt-quenching technique. Starting materials of TeO_2, Er_2O_3, and TiO_2 from Sigma Aldrich and ZnO from R&M Chemicals are mixed thoroughly. A platinum crucible containing the glass constituents is placed in a furnace at 950 °C for 30 min and the melt is poured into a brass mold after the desired viscosity is attained. Subsequently, the sample is transferred to an annealing furnace and kept for 3 h at 300 °C to remove the thermal and mechanical strains. The samples are then cooled down to room temperature. The samples are subjected to a cutting and polishing process for further structural and wettability characterizations. Table 1 summarizes the details of the glass code and glass composition of all prepared glass.

Table 1. Glass code and glass composition of prepared glass samples.

Glass code	Glass composition (mol%)			
	TeO_2	ZnO	Er_2O_3	TiO_2
TZE	79	20	1.0	0
TZETi0.05	78.95	20	1.0	0.05
TZETi0.10	78.90	20	1.0	0.10
TZETi0.15	78.85	20	1.0	0.15
TZETi0.20	78.80	20	1.0	0.20

2.2. Characterization of glass

2.2.1. Geometry of nanoparticles

High-resolution transmission electron microscopy measurement is performed using Hitachi HT7700 operating at 120 kV. Aspect ratio describes the ratio of the maximum to the minimum dimension of a particle as follows:

$$R = \frac{L}{D} \tag{1}$$

where *L* represents the diameter in the longitudinal axis and *D* represents the diameter in the transverse axis [8].

2.2.2. Wettability properties

The water contact angle measurement is performed using OCA15EC equipped with SCA20 software. All measurements are performed at room temperature. The work of adhesion W_A is defined as the reversible work to separate a solid and a liquid (water) initially at contact and to bring them at a distance where they no longer interact [9]. The unit of work of adhesion is $J.m^{-2}$ ($N.m^{-1}$) [10]. Work of adhesion is expressed in terms of surface and interfacial tensions as follows [9,10]:

$$W_A = \gamma_S + \gamma_L - \gamma_{SL} \tag{2}$$

where γ_S is the solid surface tension and γ_L is the liquid surface tension, whereas γ_{SL} is the solid-liquid interfacial tension. The shape of a droplet is measured through the contact angle θ and surface tension of the liquid (water) which relates to W_A through the equation of Young-Dupré below [7,9,10]:

$$W_A = \gamma_L(1 + \cos\theta) \quad (3)$$

The surface tension of water at room temperature (25 °C) was estimated to be ≈ 0.073 $N.m^{-1}$ [7,11].

3. Results and discussion

3.1. Physical properties

Figure 1 shows the physical appearance of all prepared glass samples that appeared to be transparent in nature and reddish in color. The TZE glass samples without TiO_2 NPs exhibited reddish color due to the creation of ions in rare-earth sites of the host glass material which are capable of absorbing certain wavelengths in the visible spectrum [12]. Nevertheless, the addition of TiO_2 NPs to the glass composition does not contribute to the significant changes in the color appearance of glass samples.

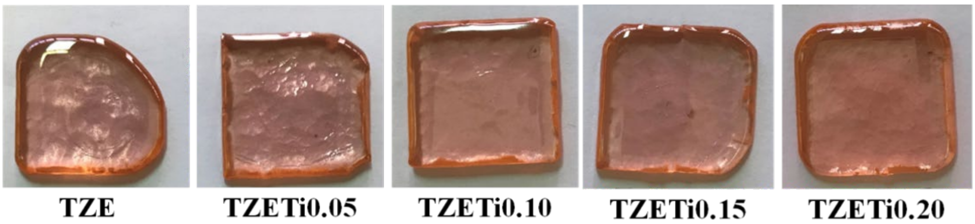

Fig. 1. Physical appearance of the prepared glasses.

3.3. Geometry of nanoparticles

Figure 2(a) shows the high-resolution transmission electron microscopy (HRTEM) image of the TZETi0.20 glass sample. The black spots as indicated by the arrow represent TiO_2 NPs. The appearance of smaller NPs shows a homogeneous contrast within one nanoparticle. Meanwhile, the larger NPs clearly show the inhomogeneous contrast regions within one nanoparticle, indicating their polycrystalline structure [13]. The distribution of TiO_2 NPs is observed to appear as a long rod or "ellipsoidal" shape without any branches and without a sharp end. The appearance of nanostructures ellipsoidal NPs possessing different symmetry axes has been reported by various researchers [14–16]. In another study conducted by Bai and co-workers [17], they found that the ellipsoidal NPs enhanced the light-harvesting features of materials compared to the spherical NPs. This is driven by the oscillations of the polarization charges along a certain direction in the multifold symmetry of ellipsoidal particles [14].

Inset in Figure 2(a) illustrates the selected area electron diffraction (SAED) image of the TZETi0.20 glass sample. The image taken from one of these areas indicates the existence of a polycrystalline structured component representing TiO_2 NPs. Figure 2(b) reflects the lattice image with a lattice spacing of 0.36 nm corresponds to the anatase TiO_2 NPs. The lattice spacing which is obtained in the current study is in good agreement with the study conducted by Yang and co-workers [18]. The appearance of lattice fringe is observed due to the respective zone axis orientation superimposed to a certain extent of darkening due to diffraction and mass absorption of TiO_2 NPs in contrast to the uniform appearance of the surrounding glass matrix [19].

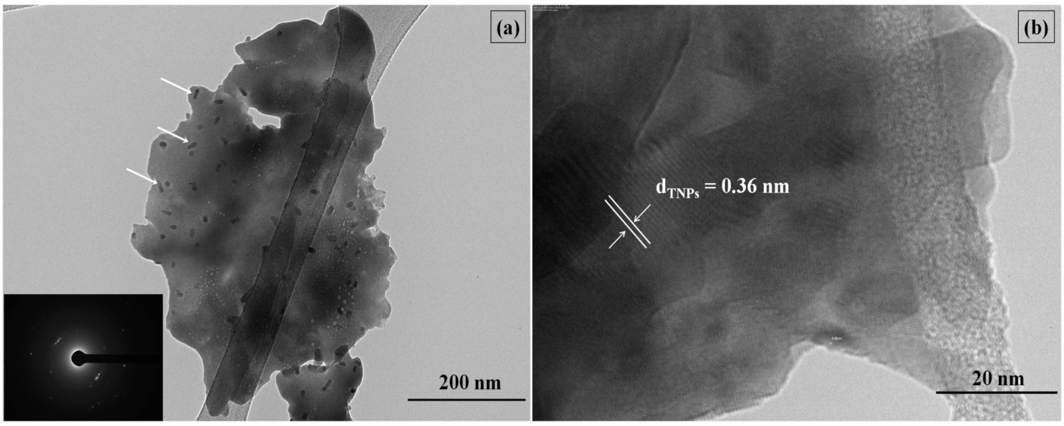

Fig. 2. (a) HRTEM image. The inset shows the SAED pattern and (b) lattice fringe pattern of the TZETi0.20 glass.

Determination of diameter in the longitudinal and transverse axes of NPs is a prerequisite to investigating the size distribution of nanostructures in the glass matrix. Table 2 summarizes the size of TiO_2 NPs on the longitudinal and transverse axis and the aspect ratio of each detected particle. Figure 3(a) and Fig. 3(b) show the histogram of the size distribution in the longitudinal and transverse axis obtained by measuring the diameters of 40 NPs. The size distribution of TiO_2 NPs illustrates the diameter of the longitudinal and transverse axis in the range of 9–22 nm and 5–9 nm, respectively. The aspect ratio of TiO_2 NPs in glass samples lies between 1.29 to 3.14. Each of the NPs possesses different values of aspect ratio, in which particles with high aspect ratio are prerequisites for optical interaction [20]. The higher value of the aspect ratio indicates a much-increased surface area signifies the increase in surface interaction and activity [21, 22].

Table 2. The aspect ratio and the size of the TiO_2 NPs along the longitudinal and transverse axis obtained from the TZETi0.20 glass.

No. of particle	Size of NPs (nm)		Aspect ratio, *R*	No. of particle	Size of NPs (nm)		Aspect ratio, *R*
	Longitudinal axis, *L*	Transverse axis, *D*			Longitudinal axis, *L*	Transverse axis, *D*	
1	12	7	**1.71**	21	19	9	**2.11**
2	12	7	**1.71**	22	17	7	**2.43**
3	22	7	**3.14**	23	17	7	**2.43**
4	14	7	**2.00**	24	17	7	**2.43**
5	11	5	**2.20**	25	17	7	**2.43**
6	12	7	**1.71**	26	15	7	**2.14**
7	12	7	**1.71**	27	14	7	**2.00**
8	15	9	**1.67**	28	17	7	**2.43**
9	19	9	**2.11**	29	10	7	**1.43**
10	17	9	**1.89**	30	10	7	**1.43**
11	21	7	**3.00**	31	10	7	**1.43**
12	15	7	**2.14**	32	16	7	**2.29**
13	14	7	**2.00**	33	21	7	**3.00**
14	14	7	**2.00**	34	15	7	**2.14**
15	12	9	**1.33**	35	17	7	**2.43**
16	12	7	**1.71**	36	15	7	**2.14**
17	12	5	**2.40**	37	14	7	**2.00**
18	12	7	**1.71**	38	15	7	**2.14**
19	9	7	**1.29**	39	15	7	**2.14**
20	17	9	**1.89**	40	17	7	**2.43**

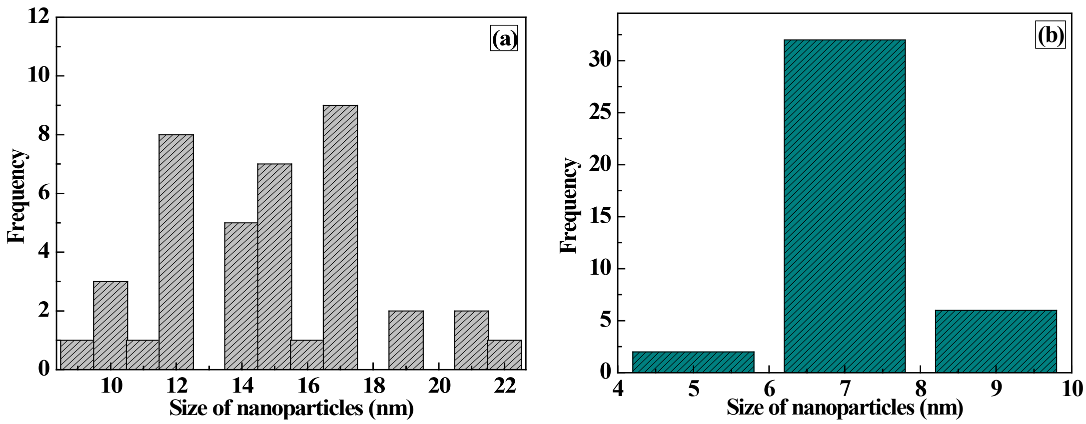

Fig. 3. Size distribution of TiO_2 NPs along the (a) longitudinal and (b) transverse axis obtained from the TZETi0.20 glass.

3.4. Wettability properties

Generally, super-hydrophilicity and super-hydrophobicity are the two main properties of self-cleaning materials. The ability of water to spread completely on the surface rather than remaining in the shape of droplets is stirred by the super-hydrophilic property of TiO_2 stimulated by UV light [3]. Thus, the formation of the small contact angle between the droplet and the surface facilitates the removal of particles on the surface due to the good contact between the surface and the droplet [2]. Meanwhile, the surface exhibits contact angles of about 100° illustrating the hydrophobicity with a low-wettability state. In this case, there is an extreme reduction in the adhesion of water, as well as particles on the surface. The formation of droplets is observed for the application of water on super-hydrophobic surfaces. Subsequently, the removal of contaminant particles from the rough surface occurred due to the adherence feature of contaminant particles to the droplet when the droplets roll off [3]. This process involved the rolling of water droplets due to the high contact angle between the surface and the droplet [2]. In the present work, the hydrophilic and hydrophobic nature of surface materials is determined by using water contact angle measurement. The key factor to achieving the self-cleaning properties depends on the wettability characteristic of the glass surface. Figure 4 shows the image of water droplets on the surface of TZE, TZETi0.05, TZETi0.10, TZETi0.15, and TZETi0.20 glass samples. The water spread is a prerequisite factor for self-cleaning and acts as a manual cleaning with water as an outside cleaning source [23].

Table 3 enlists the glass code with varying values of contact angles. The variations in water contact angle of different materials (such as glass, glass-ceramic, and thin film) demonstrated by various researchers are included for comparison [23–26]. In the present study, the measured contact angle for glass without TiO_2 NPs (TZE glass) shows a high value of contact angle which is 67.5° which implies the weakly hydrophobic [27]. However, the contact angle for a glass containing TiO_2 NPs shows an abrupt change where the contact angle decreased to 44.7°, 43.7°, 43.1°, and 43.0° for TZETi0.05, TZETi0.10, TZETi0.15, and TZETi0.20 glass samples. The measured contact angles of glass containing TiO_2 NPs show hydrophilicity [27] and the values are in good agreement with a contribution from the anatase TiO_2 structure [23]. The anatase structure is favorable due to the large surface area [28]. The anatase structure of TiO_2 NPs in our glass is confirmed from the HRTEM image as discussed in the previous section. The hydrophilic properties of glass due to the incorporation of TiO_2 NPs in the glass matrix can be explained as follows: (1) the formation of oxygen vacancies on the TiO_2 surface stimulated by the UV-irradiation, (2) the oxygen vacancies provide a surface facilitates the adsorption of dissociative water and the generation of surface hydroxide groups, (3) the formation of hydrophilic TiO_2 surfaces with the aid of UV irradiation [28].

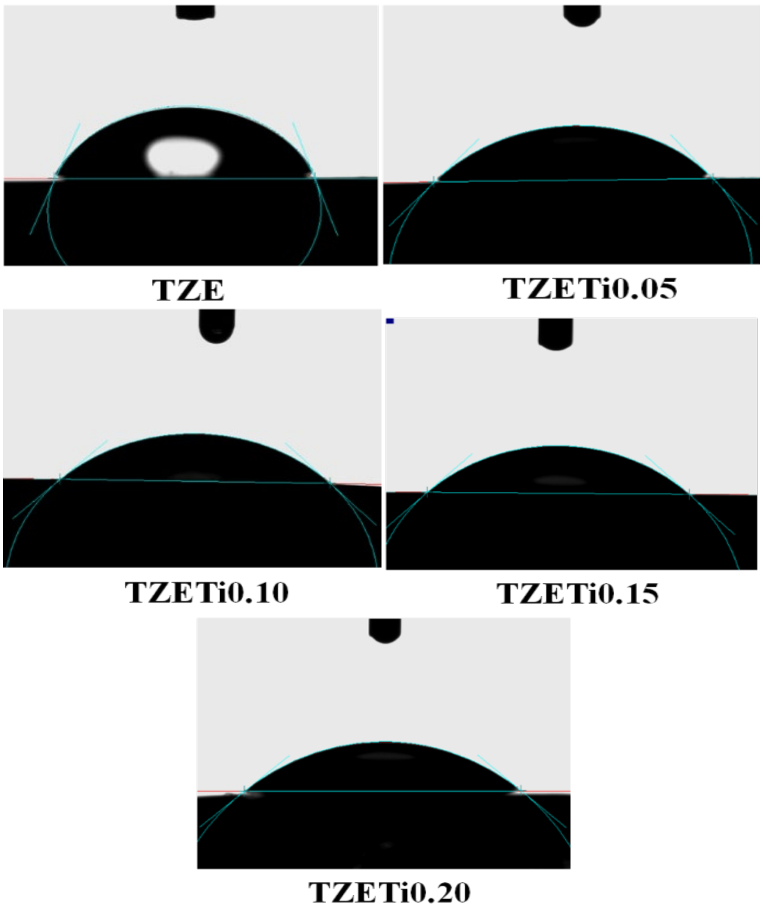

Fig. 4. Image of the water droplet revealing the formation of contact angle on the glass surface with varying TiO_2 NPs contents.

Table 3. Variation in the water contact angle of the prepared glasses and comparison with previous studies.

Sample code	Sample nature	Type of NPs	Water contact angle (°)	Work adhesion, W_A ($N.m^{-1}$)	Sample properties	Reference
TZE	Glass	-	67.5	0.101	Weakly Hydrophobic	Present study
TZETi0.05	Glass	TiO_2	44.7	0.125	Hydrophilic	Present study
TZETi0.10	Glass	TiO_2	43.7	0.126	Hydrophilic	Present study
TZETi0.15	Glass	TiO_2	43.1	0.126	Hydrophilic	Present study
TZE0Ti0.20	Glass	TiO_2	43.0	0.126	Hydrophilic	Present study
TZNE0.4Ti	Glass	TiO_2	43.0	0.126	Hydrophilic	Yusof et al. [7]
TZS3	Glass	SiO_2	112.39	-	Hydrophobic	Mazlan et al. [24]
BBO	Glass-ceramic	Bi_2O_3	39	-	Hydrophilic	Sharma et al. [25]
TiO_2 (UV)	Thin film	TiO_2	43.0	-	Hydrophilic	Isaifan et al. [23]
TiO_2 600°C	Thin film	TiO_2	26.0	-	Hydrophilic	Jesus et al. [26]

The results obtained in the present study are in good agreement with the previous studies demonstrated by Yusof et al. [7] and Isaifan et al. [23]. The incorporation of TiO_2 NPs into the glass matrix leads to the decrement of the water contact angle. Yusof and co-workers [7] reported a lower value of contact angle 43.0° is obtained by using slightly higher TiO_2 NPs content which is 0.40 mol%. However, the significant findings in the current study show the contact angle value of 43.0° can be achieved by the incorporation of a lower concentration of TiO_2 NPs which is 0.20

mol%. Further, the diameter of the longitudinal and transverse axis of TiO_2 NPs (ellipsoidal shape) is observed in the range of 9–22 nm and 5–9 nm, respectively. Meanwhile, in the previous study conducted by Yusof et al. [7], the mean size of TiO_2 NPs (non-spherical shape) is reported in the range of 7 and 14 nm, which is smaller. We found the size and shape of TiO_2 NPs play a significant role in tuning the hydrophilicity of glass. The ellipsoidal shape of TiO_2 NPs is probable to enhance the light-harvesting features [17] and improve the hydrophilicity properties of glass which is evidenced by the drastic changes in water contact angle from 67.5° to 43.0°.

Since the work of adhesion affects cohesion and bonding between materials [29], it is worth noting that the work adhesion becomes prominent from 0.101–0.126 $N.m^{-1}$ with the addition of TiO_2 NPs signify the existence of strong attraction and causes greater forces required to separate the water from the glass surface [11]. The attractive forces between water molecules and the surface of the glass (adhesive force) are stronger than the cohesive force which is the attractive force between water molecules [1,7,9]. The hydrophilic properties are associated with a high surface tension value and have the ability to form hydrogen bonds with water [30]. Thus, glass with high hydrophilicity (exhibiting low water contact angle) allows the water to spread onto the surface and sweep the contaminants away resulting in a self-cleaning effect [31].

4. Conclusion

The self-cleaning properties of some ellipsoidal TiO_2 NPs-doped tellurite glasses were tuned by varying the NPs contents from 0.05 to 0.20 mol%. The HRTEM image verified the nucleation of the ellipsoidal shape of TiO_2 NPs with anatase structures. The SAED images illustrated the crystalline nature of the TiO_2 NPs. The observed decrease in the water contact angle of the glass surface from 67.5° to 43.0° indicated their hydrophilic nature. The TZETi0.20 glass made with 0.20 mol% of TiO_2 NPs disclosed the optimum self-cleaning properties with the lowest water contact angle of 43.0° and highest work of adhesion of 0.126 $N.m^{-1}$. The proposed glass composition with tunable hydrophilic characteristics is affirmed to be useful for self-cleaning applications.

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