Hydrophobic zinc-tellurite glass system as self-cleaning vehicle: Interplay amid SiO2 and TeO2

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INTRODUCTION

Inspired by natural lotus leaf effects, scientists in late 1980s were attracted towards self-cleaning technology. Soon, it was realized that materials’ surface wettability governed by the surface roughness (SR) and water contact angle (WCA) played significant role in the self-cleaning mechanism. Thus, man-made self-cleaning materials were achieved by controlling the surface wettability, where various coating techniques were exploited to get improved surfaces with both hydrophilicity (water loving or wettable) and hydrophobicity (water resistant or repellent) (Prathapan et al., 2014; Beniamin et al., 2017; Jijo et al., 2017). A surface is said to be wettable (hydrophilic) if WCA is below 90º, otherwise (WCA > 90º) called hydrophobic (less wettable) or super-hydrophobic (WCA > 135º). The self-cleaning property can belong to any of these categories namely hydrophilic and hydrophobic, however with different cleaning mechanism.

Glasses having photocatalytic titania (TiO2) coating on the surface act as hydrophilic system, wherein the self-cleaning can be achieved by forming a layer of water on the glass surface and utilizing the sunlight to carry away the deposited dust and other impurities (Kazuhito et al., 2005; Adriana et al., 2008; Kazuya et al., 2012; Ismail et al., 2016; Nurhafizah et al., 2017; Yusof et al., 2017). Meanwhile, hydrophobic glasses can be attained by controlling the SR with low surface energy. In hydrophobic glasses self-cleaning is attained by forming perfectly spherical water droplets on textured surfaces which subsequently roll off to carry away the deposited dust and dirt on it (Yusof et al., 2015; Yelda et al., 2010). Instead of using conventional surface coating strategy, modifying the surface texture (roughness, water-resistant tendency, hydrophobicity and energy) by controlling the bulk properties is relatively a new idea.

The optical qualities of zinc-tellurite glasses such as high refractive index and excellent transmittance are advantageous for applications in self-cleaning, optoelectronic and microfluidic devices, biomedical sciences, ships, automobiles, skyscraper windows, buildings, oven, solar panel and so forth. Recent advancement in the self-cleaning technology led to the discovery of several commercial products including tiles, textiles, paint for traffic marking and buildings (Ampornphan et al., 2014; Mridul et al., 2014; Haleh et al., 2016; Linda et al., 2011; Maryam et al., 2017; Fei et al., 2017). Therefore, the materials’ self-cleaning coatings on the surfaces could remarkably contribute towards sustainability and green environment by minimizing the usage of detergents, solvents and water. On top, it could save large volumes of traditional paints generally used as coatings to protect the buildings from UV radiations. Looking at these notable benefits of self-cleaning system we prepared new type of zinc-tellurite glasses via melt-quenching method by carefully compromising the proportions of SiO2 and TeO2 contents. As-quenched glasses were characterized using atomic force microscopy (AFM) and video contact angle (VCA) measurements. The effects of SiO2 concentration on the glass SR, surface energy and hydrophobic properties were evaluated. Glass 0.06 mol% of SiO2 revealed the optimal WCA of 112.39º and SR of 7.806 nm. It was established that a trade-off between SiO2 and TeO2 contents in the studied glasses could produce super-hydrophobic surface (WCA over 90º), leading to great opportunities for diverse self-cleaning applications.

Keywords: Hydrophobic surface, surface energy, self-cleaning, zinc-tellurite glass

Abstract

Cost-effective, environmental amiable and maintenance free glasses with improved hydrophobic activity are needed for diverse industrial applications. Pollutant and dirt depositions on glasses that cause the visual obscurity and damages of the cultural heritages require inhibition. The underlying mechanism of hydrophobic interactions assisted self-cleaning traits of glass is poorly understood. It has been shown that excellent hydrophobic glass with water contact angle (WCA) above 90º and very low surface wettability can be achieved by controlling the surface roughness (SR), where liquid droplets remain perfectly spherical on such surfaces (literally without touching) before being self-cleaned (rolls off). Moreover, selection and optimization of constituent materials composition as well as the preparation technique play a significant role towards such success. Most of the previous attempts for the self-cleaning glass preparation were made via coating strategy on glass surface. Yet, preparation of super-hydrophobic glass surfaces with self-cleaning attributes remains an open challenge. Driven by this idea, we prepared a new glass system of composition (80 – x) TeO2-20ZnO-(x)SiO2 (x = 0, 0.03, 0.06, 0.09 and 0.12 mol%) by melt-quenching method, where the proportions of SiO2 and TeO2 were interplayed. As-prepared samples (thin pellet without coating) were characterized using atomic force microscopy (AFM) and video contact angle (VCA) measurements. The effects of SiO2 concentration on the glass SR, surface energy and hydrophobic properties were evaluated. Glass 0.06 mol% of SiO2 revealed the optimal WCA of 112.39º and SR of 7.806 nm. It was established that a trade-off between SiO2 and TeO2 contents in the studied glasses could produce super-hydrophobic surface (WCA over 90º), leading to great opportunities for diverse self-cleaning applications.
EXPERIMENTAL

Materials

Series of glass samples with nominal composition of \( (80 - x) \) \( \text{TeO}_2 \)-
\( 20 \text{ZnO-(x)SiO}_2 \) \((x = 0, 0.03, 0.06, 0.09 \text{ and } 0.12 \text{ mol%}) \) were synthesized using melt-quenching method. The weight of each glass sample was 15 grams. Analytical grade powder constituents (purity 99.99\% from Sigma Aldrich) were weighed in Electronic Balance (Precisa 205A SCS) before being milled (for 30 minutes) to obtain homogeneous mixtures. Next, the mixture was placed in a platinum crucible and melted in an electric furnace at 950 °C for 1 hour 20 minutes. Upon achieving the required viscosity, the melt was poured on a preheated (300 °C) steel mould and quenched thermally to achieve solid pellet (2 mm thick). Later, the as-quenched sample was annealed at 300 °C for 3 hours inside an electric furnace and allowed to cooling down slowly to room temperature to eliminate thermal and mechanical stress. Soon, the sample was placed in a desiccator to prevent it from external contamination and moisture attack. Highly transparent bubble free glasses (light orange in color) were obtained. All samples were prepared using the same protocol. The SR of the glasses was analyzed by atomic force microscopy (AFM, SPI3800N) and the hydrophobicity was measured using optical contact angle (OCA) meter (Data Physics). The WCA was recorded using video contact angle (VCA) measurement system, wherein 0.500 µL of water was dropped from a 500 µL syringe onto the glass surface. All characterizations were made at room temperature.

RESULTS AND DISCUSSION

As aforementioned, for both hydrophilic and hydrophobic materials the surface self-cleanness is determined by WCA. Dust particles are easily rinsed off by water droplets formed on the hydrophobic surface (WCA > 90°) when exposed to rainwater, where capillary forces are significant for such self-cleaning. Dust particles are simply carried away with rolling water droplet. Strongly hydrophilic substances like soot can even be carried off by water (Prathapan et al., 2014). Table 1 enlists the glass composition (SiO\(_2\) and TeO\(_2\) content) dependent variation in the values of WCA, surface tension and surface roughness. Interestingly, the values of WCA were widened from (88.84 ± 0.01) to (112.39 ± 0.01 o) with the increase of SiO\(_2\) concentration from 0.0 to 0.09 mol%. At highest SiO\(_2\) content of 0.12 mol%, the value of WCA for the respective glass (TZS5) was dropped to (93.92 ± 0.01 o).

Glass with 0.06 mol% of SiO\(_2\) (TZS3) displayed the highest WCA of 112.39° (Figure 1a). Present glass composition produced superior hydrophobicity (wide WCAs over 90° meaning low wettability or highly water-repellent) than other reported glasses in the literature. Actually, the stronger attractive interaction (cohesive forces) between water molecules than the one (adhesive forces) between water molecule and glass surface allowed the formation of perfectly spherical water droplets. Accordingly, such droplets with large WCA rolled off by carrying away the dust and dirt to make the glass surface self-cleaned. Present glass composition produced superior hydrophobicity (wide WCAs over 90° meaning low wettability or highly water-repellent) than other reported glasses in the literature. Actually, the stronger attractive interaction (cohesive forces) between water molecules than the one (adhesive forces) between water molecule and glass surface allowed the formation of perfectly spherical water droplets. Accordingly, such droplets with large WCA rolled off by carrying away the dust and dirt to make the glass surface self-cleaned. The achievement of such reduced wettability (enhanced WCA) was majorly attributed to two factors such as surface energy and surface morphology (Mohamed et al., 2015). The enhancement of hydrophobicity with lower surface energy was determined by the chemical compositions that have great influence on the surface wettability. However, hydrophobic surfaces cannot be obtained only by lowering the surface energy. For instance, CF3-terminated surface was reported to possess lowest free energy and the best hydrophobicity wherein maximum contact angle (CA) on flat surfaces could only reach...
120°. In hydrophobic materials, the surface morphology plays a decisive role to control the wettability (Ganabve et al., 2011). In short, the self-cleaning property of solid surface is decided by the chemical composition and the surface morphology. Therefore, a roughened surface can not only enhance the hydrophobicity due to the enlargement in the solid-liquid interface wherein air can be trapped on rough textures (between the surface and the liquid droplet). Since air is an absolutely hydrophobic material with a CA of 180°, thereby air trapping can amplify the surface hydrophobicity via Cassie-Baxter mechanism.

Figure 1 depicts the typical WCA image (part a) of the droplet layed down on the TZS3 glass and the corresponding high resolution 3D AFM image (part b) of sample’s (containing 0.06 mol% of SiO2) surface (devoid of water droplet). The SR was measured over the sample cross-sectional area of 2.5 µm - 2.5 µm. The values of root mean-square (RMS) SR was found to be strongly sensitive to SiO2 contents. The TZS3 sample revealed highly irregular and widely scattered islands with estimated SR of 7.806 nm. The value of SR for TZS3 glass was highest compared to other samples. This observation was consistent with the Cassie-Baxter’s model, where a liquid droplet suspends on the top of a rough surface by leaving air pockets inside the texture (Ismail et al., 2016).

CONCLUSION

The SiO2 concentration dependent alterations in the WCA and SR of silicate-zinc-tellurite glass system were evaluated. The discerned significant enhancement of WCA and SR values of the proposed glass compositions with increasing of SiO2 contents indicated their hydrophobic (water repellent or low wettability) nature. Glass containing 0.06 mol% of SiO2 manifested the optimum WCA of 112.39° and best RMS SR of 7.806 nm. It was demonstrated that by manipulating the ratios of SiO2 to TeO2 contents glasses with super-hydrophobic surface (WCA > 90°) could be realized. Proposed glass system may be beneficial for diversified self-cleaning purposes.

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