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Self-cleaning and spectral attributes of erbium doped sodium-zinc-tellurite glass: Role of titania nanoparticles

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ABSTRACT

Highly transparent and durable self-cleaning materials became demanding for diverse applications. To attain such goals, glass system with composition $(69 - x)TeO_2$-$20ZnO$-$10Na_2O$-$1Er_2O_3$-$(x)TiO_2$, where $x = 0.0$, 0.1, 0.2, 0.3 and 0.4 mol% were synthesized using the conventional melt quenching method and characterized. For the first time, the influence of embedded TiO_2 (Titania) nanoparticles (TNPs) concentration variation on the self-cleaning and spectral properties was examined to establish their correlation. TEM micrograph revealed the nucleation of spherical TNPs (average size ≈ 14 nm) inside the amorphous matrix. Reduction in the optical band gap energy (from 3.08–3.03 eV) and water contact angle (from 68° to 43°) both were evidenced with the increase in TNPs contents, wherein the later one (reduced contact angle or enhanced wettability) was attributed to the enhanced hydrophilicity of the glass samples. Conversely, a slight increase in the methylene blue (MB) degradation rate with the increase of TNPs contents up to 0.2 mol% indeed indicated an improved photocatalytic activity of the synthesized glass. The absorption spectra exhibited ten significant bands of Er^{3+} ions in the wavelength range of 407 to 1532 nm. The emergent three prominent photoluminescence (PL) emission bands of the glass sample (with 0.2 mol% of TNPs) positioned at 535 nm, 555 nm and 670 nm were enhanced by a factor of 6.77, 4.56 and 2.00, respectively. Surface plasmon resonance (SPR) band of the embedded TNPs inside the glass was detected around 581 nm. Furthermore, Raman band of the glass (containing 0.4 mol% of TNPs) centred at 845 cm^{-1} displayed an intensity enhancement by a factor of 3.58 times, which was ascribed to the TNPs localized SPR field mediated effect. It is established that the measured enhanced hydrophilicity (self-cleanliness) and improved spectral features of the present glass composition was steered by the TNPs surface plasmon assisted effects.

1. Introduction

Inspired by the sustained natural acts shown by lotus leaf and butterfly wings, the self-cleaning technology received a great attention in late 20th century. Lately, extensive research efforts have been dedicated to develop highly efficient and durable self-cleaning coating surfaces with enhanced optical qualities [1–4]. The optical qualities of material are signified in terms of excellent transmittance of incident light [5], high refractive index [6], unique up-conversion (UC) ability to facilitate electronic transition and wide absorption capacity from UV to visible region [7]. These qualities are advantageous for multi-functional applications in optoelectronic and bio-photonic fields [8]. Glass systems having such attributes also may be useful for solar cell application where the efficiency of energy conversion can be enhanced via Er^{3+} ions doping inside the host glass [9]. Sustainable materials such as tiles [10], textiles [11–13] plastic [14] and glass [15,16] with self-cleaning properties were greatly demanded and thereby became commercially available (e.g. BalcoNano™ from Balcony Systems Solutions, Rain Racer™ from Rain Racer Developments, ClearShield™ from Ritec International) [1,17,18]. To protect glass surface from pollutants contamination empowered transparency lose various strategies were adopted [4,6]. Such taints on glass surface not only causes vision opacity but also accountable for considerable aesthetic damages of cultural heritage unless averted. In fact, the complex mechanism involving the clinging of ultrafine dirt particulates on wetting layers is poorly understood.

It is needless to say that among various self-cleaning materials, glass system owing to their extreme durability, thermal stability, and

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transparency have gained special attention in the building and construction industries, automotive sectors, optical devices, fuel-cells and solar panels [18,19]. Usage of these self-cleaning glass is rather interesting since it would lessen both the cleanliness maintenance time and cost, leading to more economical and environmental amiable material [18]. Besides, self-cleaning glass systems are viewed as innovative and efficient material for pollutant removal and energy production [20,21]. Earlier, self-cleaning glass systems were made by coating the glass surface with Titania (TiO_2) nanoparticles (TNPs) to induce photocatalytic activity and promote self-cleanliness. However, such glass is unable to maintain the prolonged self-cleanliness due to leaching problem associated with the coating material that often gets rid of easily from the glass surface. Meanwhile, TNPs in powder form can draw impurities into water during the photocatalytic reaction and thus additional extraction process is prerequisite to retrieve the TNPs in water treatment. To surmount such limitation, embedment of TNPs inside the glass matrix via chemical composition optimization appears more advantageous for large-scale pollutant removal and water purification applications. In-depth literature review revealed that development of self-cleaning glass system using a method other than coating of TNPs above the host surface is lacking [21].

Generally, the self-cleaning capability of materials is achieved by controlling their surface wettability [18], where the photocatalytic properties of the material play a paramount role [1,22]. Material's surface is considered as super-hydrophilic when the water contact angle (WCA) is below 50°. Conversely, the surface is categorized as super-hydrophobic when WCA is above 150° [23]. Instead of super-hydrophobic trait, super-hydrophilic characteristic is recognized as new way to create self-cleaning glass since a minimum angle of inclination is essential for a droplet to roll off the surface [4]. Photocatalysis being a chemical reaction between organic species and free radicals upon irradiation with UV–visible or near-infrared (NIR) light can easily degrade the harmful pollutant on to the glass surface [24]. Over the years, most common photocatalysts that are used to degrade organic pollutants are TiO_2 [25,26] ZnO [27] CdS [28] and Bi_2WO_6 [29]. Among these photocatalysts, TNPs are widely used for self-cleaning purpose due to their cost-effectiveness and strong photocatalytic property that can decompose dye pollutants such as Methylene Blue (MB), Methyl Orange (MO), Ethyl Violet and some other air pollutants [17].

It is established that TNPs possess high oxidative power, strong photo-stability, non-toxicity and antibacterial efficacy [1,17,30–34]. Furthermore, the empty d-shell of Ti^{4+} ions contributes to the large linear and nonlinear optical indices when incorporated inside glasses, indicating a very high oxygen hyperpolarizability of Ti—O pairs and large oxide ion electronic polarizabilities [35]. These are beneficial for broad array of technological purposes including biomaterials, photonic devices, semiconductors, and ionic conductors [36]. TNPs become super-hydrophilic under UV exposure, where a notable reduction in the WCA allows the formation of uniform water film on the surface and thereby prevents the deposition of the dirt above the surface layer [30]. Meanwhile, addition of sodium oxide (Na_2O) into glass help to increase the solubility of rare earth ions, which in turn improves the luminescence quantum yield of the glass [37,38] and enhances the electron excitation in TNPs with better photocatalytic action. Yet again, zinc oxide (ZnO) is an attractive compound that exhibits good photocatalytic activity, non-toxicity, superior chemical and thermal stability, good electrical and optical properties. It widely exploited for solar light activated photocatalysis, optoelectronic devices and sensor [33,39]. On the top, trivalent erbium ions (Er^{3+}) in erbium oxide (Er_2O_3) offer sharp up-conversion photoluminescence (PL) emission [40] in the visible region when doped inside glass [39], extend the absorption edge and provide extra photons beneficial for photocatalytic activity [39–41].

Currently, tellurite host based glass systems are greatly preferred because of their low phonon energy cut-off (600–700 cm^{-1}) that suppresses the non-radiative decay and provides optimum emission cross-section over the entire wavelength range [21]. Renewed interests towards the development of functional glass with synergism involving PL and self-cleanliness has resulted in valued materials as unconventional end-products [22]. Thus, embedment of self-cleaning photocatalytic agent (TNPs) into luminescent material (Er^{3+}-doped zinc tellurite glass) appear to be a synergistic strategy to customize the multi-functionality of binary/ternary inorganic glass system. However, a detail assessment of such synergism (self-cleanliness plus up-conversion luminescence) to realize tellurite glass system as prospective photoactive self-cleaning candidate is still lacking. Even though previous studies claimed that improved photocatalytic activity of glass can be achieved via the combined effects of Er^{3+} ions and TNPs by controlling the incoming photon [40,41], but a possible relationship between spectral and self-cleaning attributes of glass system is far from being developed. Specifically, the relation among WCA (wettability) and spectral (absorption and up-conversion emission) features of Er^{3+} ions doped tellurite glass embedded with TNPs is not clarified so far.

For the first time, we report the self-cleaning performance of Er^{3+} − doped (fixed contents of 1 mol%) tellurite glass system containing different TNPs concentration (varied from 0 to 0.4 mol%) in terms of WCA and degradation of MB [22]. The doping concentration of Er^{3+} is optimized by avoiding luminescence quenching [42]. Lower doping levels of Er^{3+} were maintained to avoid undesirable attenuations such as dipolar interactions and luminescence quenching [43]. Emission of Er^{3+} ion inside the sodium zinc-tellurite glass displayed optimum luminescence enhancement at 1.0 mol% of Er^{3+} doping before the luminescence quenching was likely to occur [44].Melt-quenching method is used to prepare Er^{3+}-doped tellurite glass with photocatalytic TNPs embedment. It is demonstrated that the present strategy of achieving hydrophilic self-cleaning glass is entirely different from conventional coating technique and is useful for practical outdoor applications [45]. A correlation between spectral modification and self-cleaning attribute of the proposed glass system is established. This approach may open up new avenues to fabricate multi-functional glasses with self-cleaning, anti-bacterial, energy conversion, and enhanced spectroscopic properties those are advantageous for sundry applications including buildings [46], solar modules [47] and optical devices [35].

2. Experimental procedures

2.1. Glass preparation

Series of glass samples with composition of (69-x)TeO_2-20ZnO-10Na_2O-1Er_2O_3-(x)TiO_2, where x = 0.0, 0.1, 0.2, 0.3 and 0.4 mol% were synthesized using the conventional melt quenching method. Table 1 summarizes the nominal compositions of the proposed glass system and their codes. About 15 g batch of analytical grade raw materials (powdered form) mixture (from Sigma Aldrich) including TeO_2 (purity 99.5%), ZnO (purity 99.9%), Na_2O (purity 80.0%), Er_2O_3 (purity 99.9%) and TNPs (purity 99.7%, anatase phase, size below 25 nm) were used as glass constituents and thoroughly ground. Then,

Table 1
Nominal compositions of the proposed glass system with respective codes.

Glass code	Glass composition (mol%)				
	TeO_2	ZnO	Na_2O	Er_2O_3	TNPs
TZNE	69	20	10	1	0
TZNE0.1Ti	68.9	20	10	1	0.1
TZNE0.2Ti	68.8	20	10	1	0.2
TZNE0.3Ti	68.7	20	10	1	0.3
TZNE0.4Ti	68.6	20	10	1	0.4
TZN	70	20	10	0	0
TZN0.4Ti	69.6	20	10	0	0.4