SELF CLEANING CHARACTERIZATION WITH THE INCORPORATION OF TITANIUM DIOXIDE AND AURUM BIMETALLIC NANOPARTICLES IN TELLURITE GLASSES

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ABSTRACT

This study emphasizes the fabrication of glass containing bimetallic TiO_2 and Au nanoparticles (NPs) which potentially exerts the self-cleaning effect. A series of glass with a composition of (70−x−y)TeO_2–20ZnO–9Na_2O–1Er_2O_3–(x)TiO_2–(y)Au where x = 0, 0.3 mol% and y = 0, 0.03, 0.05, 0.10, 0.15, 0.20 mol% were fabricated by employing the melt-quenching technique. Another series of glass samples without erbium content were fabricated with a composition of (70−x−y)TeO_2–20ZnO–9Na_2O–(x)TiO_2–(y)Au where x = 0, 0.3 mol% and y = 0, 0.03, 0.05, 0.10, 0.15, 0.20 mol% by using the melt-quenching technique to investigate the plasmon peak for TiO_2 and Au NPs. Various characterizations were performed to investigate the optical, structural, and wettability features of glass with the addition of varying concentrations of bimetallic TiO_2 and Au NPs. X-ray diffraction spectra affirm the amorphous nature of glass with the appearance of a broad peak located at 25°−35°. High-resolution transmission electron microscopy images reveal the formation of lattice fringes with a value of 3.6 Å and 2.3 Å representing the TiO_2 and Au NPs, respectively. Atomic force microscopy illustrates enhancement in surface roughness of glass ranging from 4.86 nm to 8.70 nm with the incorporation of higher concentrations of NPs. Ultraviolet-visible spectra show the emergence of plasmon bands in the range of 550 – 560 nm and 595 – 624 nm due to the contribution of Ti and Au atoms. The formation of thin film water on the glass surface from the anti-fogging testing, reduction in the dust deposition rate of the glass sample, and decrement in the water contact angle value of glass samples indicate the hydrophilic nature of glass. Degradation of methylene blue affirms the photocatalytic activity of the glass containing varying concentrations of TiO_2 and Au NPs. The favorable features of the current glass composition contribute to the self-cleaning application.

ABSTRAK

KACA DENGAN SIFAT PEMBERSIHAN SENDIRI SERTA SIFAT ANTI-KABUS DENGAN PENGLIBATAN ZARAH NANO DWILOGAM

Kajian ini melaporkan penggabungan zarah nano dwilogam TiO_2-Au dalam meningkatkan ciri-ciri kaca dengan sifat pembersihan kendiri. Satu sistem kaca dengan komposisi $(70-x-y)TeO_2-20ZnO-9Na_2O-1Er_2O_3-(x)TiO_2-(y)Au$ di mana x = 0, 0.3 mol% dan y = 0, 0.03, 0.05, 0.10, 0.15, 0.20 mol% telah disediakan melalui kaedah perlindapan leburan. Satu siri kaca yang lain dengan komposisi $(70-x-y)TeO_2-20ZnO-9Na_2O-(x)TiO_2-(y)Au$ di mana x = 0, 0.3 mol% dan y = 0, 0.03, 0.05, 0.10, 0.15, 0.20 mol% telah disediakan menggunakan kaedah perlindapan leburan untuk mengkaji puncak plasmon zarahnano TiO_2 dan Au. Pelbagai pencirian telah dilakukan bagi mengkaji ciri optik, struktur dan kebolehbasahan kaca setelah penambahan kepekatan yang berlainan bagi nano dwilogam TiO_2 dan Au. Spektra XRD mengesahkan sifat amorfus sampel kaca dengan kemunculan bonggol pada 25° – 35°. Imej TEM mengesahkan kehadiran zarah nano TiO_2 dengan kekisi 3.6 Å manakala Au mempunya kekisi 2.3 Å. Imej AFM mengesahkan peningkatan kekasaran permukaan sampel kaca dari 4.86 nm kepada 8.70 nm apabila kandungan zarahnano meningkat. Spektra UV-Vis sampel kaca menunjukkan jalur plasmon lemah yang dikesan pada julat 550 – 560 nm dan 595 – 624 nm disebabkan oleh kesan sumbangan daripada atom Ti dan juga atom Au. Sampel kaca menunjukkan sifat hidrofilik berdasarkan pembentukan air yang dilihat seperti filem nipis pada permukaan kaca hasil daripada ujian pengabusan, pengurangan kadar pemendapan debu terhadap sampel kaca dan penurunan nilai sudut sentuh air. Penurunan metilena biru mengesahkan aktiviti fotokatalitik kaca mengandungi pelbagai kepekatan zarah nano TiO_2 dan Au. Hasil dalam kajian ini menunjukkan bahawa komposisi bagi sistem kaca terkini dapat menyumbangkan dalam aplikasi kaca dengan sifat pembersihan kendiri.

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LIST OF SYMBOLS

%	-	Percentage
°F	-	Degree Fahrenheit
°C	-	Degree Celcius
Å	-	Angstrom
λ	-	Wavelength
$h\omega$	-	The function of photon energy
k	-	Constant
$\alpha\omega$	-	Absorption coefficient
θ	-	Angle
ω	-	Photon frequency
h	-	Plank's constant
mg	-	Milligram
g	-	gram

LIST OF ABBREVIATIONS

AFM	-	Atomic Force Microscopy
Ag	-	Silver
Al_2O_3	-	Aluminium oxide
Au	-	Aurum
BO	-	Bridging oxygen
CO	-	Carbon monoxide
E_{dir}	-	Direct optical bandgap
E_{indir}	-	Indirect optical bandgap
Er_2O_3	-	Erbium oxide
Er^{3+}	-	Erbium ions
ErF_3	-	Fluoride
E_u	-	Urbach energy
eV	-	Electron volt
GaN	-	Gallium nitride
HF	-	Hydrofluoric acid
HRTEM	-	High-resolution transmission electron microscopy
LSPR	-	Localized Surface Plasmon Resonance
MB	-	Methylene blue
Na_2O	-	Sodium dioxide
NBO	-	Non-bridging oxygen
nm	-	Nanometre
NPs	-	Nanoparticles
PbO	-	Lead
PL	-	Photoluminescence
ppm	-	Part per million
RE	-	Rare earth
SAED	-	Selected Area Electron Diffraction
SCG	-	Self-cleaning glass
SERS	-	Surface-enhanced Raman spectroscopy
SPR	-	Surface plasmon resonance
SR	-	Surface roughness

Te	-	Tellurium
TEM	-	Transmission electron microscopy
TeO_2	-	Tellurium dioxide
TiO_2	-	Titanium dioxide
UC	-	Up-conversion
UV	-	Ultra-violet
UV-Vis	-	Ultraviolet-Visible
WCA	-	Water contact angle
XRD	-	X-ray Diffraction
Zn	-	Zinc
ZnO	-	Zinc oxide

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, the widespread use of glass in daily life can no longer be denied. Stimulated by the rapid development and increase in population, glass manufacturing emerged as one of the main elements in construction and industry. Glass fabrication was introduced as a craft in around 3500 B.C. across the world by sailors that originated from Egypt and Eastern Mesopotamia, and it was in the late nineteenth century that the glassmaking was industrialized (Surekha & Sundararajan, 2015). Generally, glass is defined as an amorphous solid that does not possess a complete long range of periodic atomic structure and exhibits behavior for a glass transformation (Shelby, 2005). In other words, glass is known as any material such as inorganic material that is formed by any technique that gives a transformation towards the glass with certain characteristics either transparent, translucent, hard, or impenetrable towards natural elements. Glass is classified according to their specific needs and applications. In the year 1950, large curtain walls in offices were typically made of glass. The engineering of glass is vital to producing final products that exhibit different structural, optical, thermal, and chemical properties (Shelby, 2005).

Tellurite glass is one of the types of glass that has been emerging as an interesting smart material in non-crystalline solids research. This type of glass is known as the most stable oxide and has opened a whole new photonics world to the interest of researchers such as optical amplifiers, lasers utilizing tellurite-based glass gain media, solar energy harvesting, biomedical applications, optical sensing, and diverse applications (El-Mallawany et al., 2008). The selection of materials in glass is vital to producing glass with desired properties. In the present study, the composition of glass was selected due to the beneficial features of the ternary glass system as reported by previous researchers (de Clermont-Gallerande et al., 2021; Al-Buriahi et al., 2022). Erbium oxide (Er_2O_3) as a rare earth dopant is a trivalent erbium ion that can enhance the photocatalytic activity of NPs through interfacial charge transfer and effective prevention of electron-hole pairs (Salama et al., 2017). However, the concentration of rare earth should be kept low to prevent adverse effects on the glass system (Ferodolin et al., 2022). Yusof et al. (2017) demonstrated tellurite-based glass containing 1 mol% of Er_2O_3 and varying concentration of TiO_2 NPs that exhibits self-cleaning features. It has been known that pure TeO_2 exhibits the highest nonlinear optical features among TeO_2-based glasses. However, the disadvantage of low glass-forming ability limits the practical application. Alternative methods can be employed to improve the glass-forming ability of TeO_2 glasses by incorporating modifier oxides such as ZnO and Na_2O (Al-Buriahi et al., 2022).

The incorporation of modifiers such as ZnO and Na_2O into the tellurite-based glass forms a heavy metal glass composition with enhanced structural, optical, thermal, and chemical properties (Dousti et al., 2015). In the present study, ZnO was used as a modifier as it can alter the composition of the host glass and generate unique physical, and good chemical stability and high photostability of glass (Lou, 1991; Novatski et al., 2019). Generally, ZnO is employed in the manufacturing field such as photocatalysts where it actively attacks microorganisms and facilitates photocatalysis reactions (Mirzaei & Darroudi, 2017). Meanwhile, Na_2O is a prerequisite because it can control the formation of the crystalline stages and lead to the generation of non-bridging oxygen and bridging oxygen (Kuo, 2014). In addition, the incorporation of Na_2O in the glass matrix lowers the melting temperature and improves the mechanical strength of glass (Udayashankar et al., 2014).

The discovery of the photocatalytic properties of TiO_2 stimulates the deposition of TiO_2 thin films on the glass surface for diverse applications including self-cleaning glasses (Hosseini et al., 2022). The deposition of TiO_2 thin films on the glass surface elevates the conventional glass features to exhibit unique properties such as anti-fog, anti-bacterial, and anti-pollution (Zhao et al., 2015). It has been acknowledged that TiO_2 possesses photocatalytic degradation under various illumination conditions. However, transparent photocatalytic TiO_2 thin films exhibit a poor response to visible light that impedes their application under direct sunlight.

These drawbacks limit the potential application of TiO_2 thin films in the self-cleaning application (Uddin et al., 2008). Therefore, researchers come out with alternatives to combine TiO_2 with noble metals to solve the arising issue. Gold or aurum (Au) NPs is a noble metal. In a bulk form, Au NPs are extremely unreactive. In contrast, small clusters of Au NPs are catalytically active (Eustis & El-Sayed, 2006). Nowadays, the synthesis and in-depth investigation of the properties of noble metal NPs become prominent in different fields. Various researchers reported a significant enhancement in the photocatalytic activity of Au-modified samples that is beneficial for self-cleaning applications. In another study, the interaction between bimetallic TiO_2–Au NPs as membrane enhances the photocatalytic degradation that is advantageous for removing antibiotics and bacteria from water (Li et al., 2019).

Of late, bimetallic NPs have attracted attention among researchers. Bimetallic NPs consist of two different metal components which have more advantages compared to monometallic NPs, especially in the scientific and technology field. The structure of bimetallic NPs can be produced by the integration of two metals and can be placed in a random alloy, in which the alloy with the intermetallic mixture in the form of the cluster and the core-shell structures (Paszkiewicz et al., 2016). The glass application in the construction industry is diverse according to the elements that build up the glass. Recently, self-cleaning glass (SCG) has attracted more attention among researchers due to the emergence of unique superhydrophobic and superhydrophilic surfaces. The integration of glass as one of the elements in the building construction offers many advantages, particularly enhancing the efficiency of building energy such as reducing glare, preventing heat absorption, and having resistance to Ultraviolet (UV) light. However, the glass surface needs to be frequently cleaned and sometimes the cleaning and maintenance process can be very challenging (Fatemeh, 2016). In most fabrication techniques, SCG is usually coated with titanium oxide due to its multifunctional properties such as anti-abrasive, anti-pollution, and anti-reflective (Surekha & Sundararajan, 2015). However, not much work is reported for the direct embedment of the titanium oxide into the glass matrix to produce SCG. Therefore, this study emphasizes the direct embedment of bimetallic TiO_2 NPs and Au NPs into the glass matrix. In addition, further characterization is performed to evaluate the effect of TiO_2 NPs with varying Au NPs content on the self-cleaning properties of glass.

1.2 Problem Statement

Nowadays, glass is widely used in buildings and construction fields due to its many advantages and aesthetic value. Though, several arising issues need to be handled such as the requirement of dedicated manpower resources to keep the glass surfaces clean as this glass needs constant cleaning for maintenance activity. In addition, cleaning tasks were mostly done manually using cleaning agents, cloths, and wipers. These tasks are laborious, dangerous, and time-consuming, especially when cleaning in areas of certain heights (Bauchner et al., 2020). Thus, a new type of glass that utilized the unique features of metallic NPs to modify the glass surface had been invented known as self-cleaning glass (Surekha & Sundararajan, 2015). There were numerous studies on this new type of glass, for example, Yusof et al. (2018) reported that tellurite can be used as host glass with the incorporation of TiO_2 NPs to create the self-cleaning effect in the glass. Meanwhile, Salama et al. (2007) observed that the combination of Er^{3+} ions and TiO_2 NPs in tellurite glass improves the photocatalytic activity by controlling the incoming photon.

Aliofkhzraei (2014) conducted research regarding glass coated with SiO_2 to achieve a hydrophobic surface. However, weak adhesion between NPs and substrates decreases the lifespan of the coating since NPs detach easily from substrates (Syafiq et al., 2019). In another study, silicate-based glass containing bimetallic Ag and TiO_2 NPs was reported to possess a hydrophobic surface that leads to self-cleaning characteristics (Nazhirah et al., 2021). However, not much work is reported for the direct embedment of the NPs into the glass matrix to produce self-cleaning glass. In addition, controlling the shape and size of bimetallic NPs for beneficial features of self-cleaning in glass is challenging due to possible adverse effects such as agglomeration of NPs and crystallization of glass (Idris & Roy, 2023). Therefore, careful controlling and tuning of the concentration of metallic NPs are crucial to prevent the emergence of adverse effects in the glass system.