STRUCTURAL, MORPHOLOGICAL AND OPTICAL PROPERTIES OF BIMETALLIC NANOPARTICLES IN TELLURITE GLASS SYSTEM FOR IMPROVEMENT IN SURFACE-ENHANCED RAMAN SCATTERING

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DECLARATION

I hereby declare that the work presented in this thesis entitled "Structural, Morphological and Optical Properties of Bimetallic Nanoparticles in Tellurite Glass System for Improvement in Surface-Enhanced Raman Scattering" is of my own effort, except for the materials, excerpts and equations referred to as cited in the reference section.

2 October 2020

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DEGREE	:	**MASTER OF SCIENCE (PHYSICS WITH ELECTRONICS)**
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ABSTRACT

Combining bimetallic nanoparticles (NPs) with rare-earth ions in tellurite glass is an interesting field for researchers due to the amplification in surface-enhanced Raman scattering (SERS). To ensure the SERS effect to occur, a selection of SERS substrate is very crucial as their plasmonic properties and nanostructured metallic surface will stimulate the plasmonic excitation for Raman scattering to take place. Determining the SERS enhancement in tellurite glass with addition of bimetallic NPs is the main focus of this research. Four series of glass are prepared via melt-quenching method. Glass containing monometallic titanium NPs with erbium content are prepared with composition of $(70\text{-}x\text{-}y)TeO_2–20ZnO–9Na_2O–1Er_2O_3–(x)TiO_2–(y)Al_2O_3$, where x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 mol% and y = 0 mol%. Glass containing monometallic titanium NPs without erbium content are prepared with composition of $(70\text{-}x\text{-}y)TeO_2–20ZnO–9Na_2O–0Er_2O_3–(x)TiO_2–(y)Al_2O_3$, where x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 mol% and y = 0 mol%. In contrary, glass containing bimetallic titanium and aluminium NPs with erbium content are prepared with composition of $(70\text{-}x\text{-}y)TeO_2–20ZnO–9Na_2O–1Er_2O_3–(x)TiO_2–(y)Al_2O_3$ where x = 0.0 and 0.3 mol% and y = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mol%. Glass containing bimetallic titanium and aluminium NPs without erbium content are prepared with composition of $(70\text{-}x\text{-}y)TeO_2–20ZnO–9Na_2O–0Er_2O_3–(x)TiO_2–(y)Al_2O_3$ where x = 0.0 and 0.3 mol% and y = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mol%. In-depth characterization are performed by using X-Ray Diffraction (XRD), Ultraviolet-Visible Spectroscopy (UV-VIS) Fourier-Transform Infrared Spectroscopy (FTIR), Transmission Electron Microscopy (TEM), Photoluminescence Spectroscopy (PL), Atomic Force Microscopy (AFM) and Raman Spectroscopy. XRD spectra confirms the amorphous nature of glass samples with the appearance of broad hump between 25° to 35° and the absence of sharp peak. A weak plasmon band is observed at 550 nm for glass containing monometallic titanium NPs. Meanwhile, a weak plasmon band is observed at 554 nm and 827 nm for glass containing bimetallic titanium and aluminium NPs. The variations in the direct optical band gap, indirect optical band gap and Urbach energy is due to the contribution of metallic NPs. FTIR spectra shows the appearance of Zn–O tetrahedral bond, symmetric stretching vibrations of Te–O in Te, Te–O–Zn linkages, vibrations of water molecules and fundamental stretching of hydroxyl group for glass containing monometallic NPs. Glass containing bimetallic NPs display the Zn–O tetrahedral bond, stretching vibrations of Al–O, Te–O bending vibrations in TeO_3 units, Al–O stretching, vibrations of water molecules and fundamental stretching of hydroxyl group. TEM image display the increasing size of NPs following the Ostwald ripening process and coalescence process. AFM image illustrates the formation of scattered island due to NPs. PL emission spectra display the two significant peaks centred at 547 nm and 668 nm with enhancement in intensity due to the surface plasmon resonance (SPR) effect. Raman spectra illustrate the amplification in Raman signal with Raman enhancement factor of 1.55, 1.45, 1.51 and 1.61 for TZNETiAl0.6 glass. The amplification in Raman signal due to excitations of surface plasmon from titanium and aluminium NPs. TZNETiAl0.6 glass shows optimum properties to be used in molecular detection application due to favourable surface roughness value which is suitable for substrate properties and highest enhancement intensity in PL and Raman spectra attribute to the plasmonic effect from titanium and aluminium NPs.

ABSTRAK

SIFAT STRUKTUR, MORFOLOGI DAN OPTIK ZARAHNANO DWILOGAM DALAM SISTEM KACA TELURIT UNTUK KESAN PENINGKATAN PENYERAKAN PERMUKAAN RAMAN

Gabungan zarahnano dwilogam dengan ion nadir bumi dalam kaca telurit adalah bidang kaji yang menarik bagi para penyelidik disebabkan kesan peningkatan penyerakan permukaan Raman (SERS). Untuk memastikan kesan SERS berlaku, pemilihan substratum SERS adalah sangat penting di mana sifat plasmonik dan struktur permukaan logam nano akan membantu dalam pengujaan plasmonik untuk penyerakan Raman. Penentuan peningkatan penyerakan permukaan Raman dalam kaca telurit dengan penambahan zarahnano dwilogam ialah fokus utama dalam kajian ini. Empat siri kaca disediakan melalui kaedah perlindapan leburan. Kaca mengandungi monologam zarahnano titanium dengan kandungan erbium disediakan dengan komposisi $(70-x-y)TeO_2–20ZnO–9Na_2O–1Er_2O_3–(x)TiO_2–(y)Al_2O_3$, di mana x = 0.0, 0.1, 0.2, 0.3, 0.4 dan 0.5 mol% dan y = 0 mol%. Kaca mengandungi monologam zarahnano titanium tanpa kandungan erbium disediakan dengan komposisi $(70-x-y)TeO_2–20ZnO–9Na_2O–0Er_2O_3–(x)TiO_2–(y)Al_2O_3$, di mana x = 0.0, 0.1, 0.2, 0.3, 0.4 dan 0.5 mol% dan y = 0 mol%. Sebaliknya, kaca mengandungi dwilogam zarahnano titanium dan aluminium dengan kandungan erbium disediakan dengan komposisi $(70-x-y)TeO_2–20ZnO–9Na_2O–1Er_2O_3–(x)TiO_2–(y)Al_2O_3$ di mana x = 0.0 dan 0.3 mol% dan y= 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 dan 0.6 mol%. Kaca mengandungi dwilogam zarahnano titanium dan aluminium tanpa kandungan erbium disediakan dengan komposisi $(70-x-y)TeO_2–20ZnO–9Na_2O–0Er_2O_3–(x)TiO_2–(y)Al_2O_3$ di mana x = 0.0 dan 0.3 mol% dan y= 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 dan 0.6 mol%. Pencirian lanjut dijalankan menggunakan Pembelauan Sinar-X (XRD), Spektroskopi Ultraungu-Cahaya Nampak (UV-VIS), Spektroskopi Inframerah Transformasi Fourier (FTIR), Mikroskopi Penghantaran Elektron (TEM), Spektroskopi Pendarkilau (PL), Mikroskopi Daya Atom (AFM) dan Spektroskopi Raman. Spektra XRD mengesahkan sifat amorfus sampel kaca dengan kemunculan bonggol pada 25° sehingga 35° dan ketidakhadiran puncak tajam. Kepelbagaian pada jurang jalur optik langsung, jurang jalur optik tak langsung dan tenaga Urbach disebabkan sumbangan zarahnano logam. Jalur plasmon lemah didapati pada 550 nm bagi kaca mengandungi monologam zarahnano titanium. Manakala, jalur plasmon lemah didapati pada 554 nm dan 827 nm bagi kaca mengandungi dwilogam zarahnano titanium dan aluminium. Kepelbagaian pada jurang jalur optik langsung, jurang jalur optik tak langsung dan tenaga Urbach disebabkan sumbangan zarahnano logam. Spektra FTIR menunjukkan kemunculan ikatan tetrahedron Zn-O, getaran regangan simetri Te-O pada Te, rantaian Te-O-Zn, getaran molekul air dan regangan asas kumpulan hidroksil bagi kaca mengandungi zarahnano monologam. Kaca yang mengandungi zarahnano dwilogam menunjukkan ikatan tetrahedron Zn-O, getaran regangan Al-O, getaran lengkungan Te-O dalam unit TeO_3, regangan Al-O, getaran molekul air dan regangan asas kumpulan hidroksil. Imej TEM menunjukkan peningkatan saiz zarahnano melalui proses pematangan Ostwald dan proses pergabungan. Imej AFM menunjukkan pembentukan serakan pulau-pulau disebabkan zarahnano. Spektra sinaran PL menunjukkan dua puncak ketara berpusat pada 547 nm dan 668 nm dengan peningkatan pada keamatan disebabkan kesan resonans plasmon permukaan (SPR).

Spektra Raman menunjukkan penggandaan pada isyarat Raman dengan faktor peningkatan 1.55, 1.45, 1.51 dan 1.61 bagi kaca TZNETiAl0.6. Penggandaan pada isyarat Raman disebabkan pengujaan plasmon permukaan daripada zarahnano titanium dan aluminium. Kaca TZNETiAl0.6 menunjukkan ciri-ciri optimum untuk digunakan dalam aplikasi pengesanan molekul disebabkan nilai kekasaran permukaan yang sesuai untuk dijadikan sebagai sifat substrat dan peningkatan keamatan tertinggi pada spektra PL dan Raman disebabkan oleh kesan plasmonik daripada zarahnano titanium dan aluminium.

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LIST OF ABBREVIATIONS

AFM	-	Atomic Force Microscopy
BO	-	Bridging Oxygen
EFAD	-	Electric Field Assisted Diffusion
ET	-	Energy Transfer
FTIR	-	Fourier-Transform Infrared
GSA	-	Ground State Absorption
LSPR	-	Localized Surface Plasmon Resonance
NBO	-	Non-Bridging Oxygen
NPs	-	Nanoparticles
NR	-	Non-Radiative Decay
PL	-	Photoluminescence
RE	-	Rare Earth
SAED	-	Selected Area Electron Diffraction
SERS	-	Surface Enhance Raman Scattering
SP	-	Surface Plasmon
SPR	-	Surface Plasmon Resonance
SR	-	Surface Roughness
TEM	-	Transmission Electron Microscopy
UC	-	Up-Conversion
UV	-	Ultra-violet
UV-VIS	-	Ultraviolet-visible
XRD	-	X-Ray Diffraction

LIST OF SYMBOLS

%T	-	Transmittance
Δx	-	Length of deflection
B	-	Constant for extended tailing band
$\mathbf{c_a}$	-	Concentration of absorption
$\mathbf{E_{dir}}$	-	Direct band gap energy
$\mathbf{E_{ind}}$	-	Indirect band gap energy
$\mathbf{E_U}$	-	Urbach energy
F	-	Force
I	-	Incident beam
$\mathbf{I_O}$	-	Transmitted beam
$\mathbf{T_C}$	-	Cooling temperature
$\mathbf{T_G}$	-	Glass transition temperature
$\mathbf{T_M}$	-	Melting point temperature
b	-	Path length
d	-	Spacing of crystal plane
e	-	Natural logarithms base
$h\omega$	-	Function of photon energy
i	-	Square root of -1
k	-	Constant
n	-	Order of reflection
t	-	Time
v	-	Frequency
$\alpha\omega$	-	Absorption coefficient
θ	-	Angle
λ	-	Wavelength
ω	-	Photon frequency

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Glass architectural is plain and simply aesthetically in human eyes. This versatile material is used in everyday applications, from homes to kitchenware, automobiles, decorations and down to several unseen applications such as electronics, medical equipment, insulator and reinforcement material. Types of glass are made according to their specific needs and applications. The engineering of glass is made to exhibit different kind of structural, optical, thermal and chemical properties (Shelby, 2005).

The most common glasses used in the commercial glass industry are borosilicate and soda-lime silicate. Borosilicate-based glass are commonly found in the exterior lighting, industrial and lab equipment as they are high durability and its superior thermal shock resistance (Hasanuzzaman *et al.*, 2016). Food and drinks beverage and container, accessories and decorative tableware are made from soda-lime silicate-based glass, basically almost 80% of world-wide production due to its inexpensive cost and easy to be made as they have relatively low melting point (Ashby, 2012). Meanwhile, there is another type of glass which an interesting smart material in non-crystalline solids research has been reported. Tellurite glass as the most stable oxide 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 more applications (El-Mallawany, 2018). The trigonal bipyramid structure of tellurium dioxide gives it the advantage to form different bonds with different ions which enable it to be tune to favourable material properties for photonic application (Gulenko *et al.*, 2014).

Metallic nanoparticles (NPs) and tellurite glass have recently grown in research on the optical and luminescence enhancement properties. This glass preparation is study along with the presence of rare-earth ion due to the energy transfer mechanism from the metallic NPs to the rare-earth ion which will be contributed to the intensified local field and luminescence enhancement (de Almeida, 2008). The local field effect induced by the surface plasmon resonance (SPR) of metallic NPs which is yield in the vicinity of rare-earth ion is investigated extensively due to its stimulating effect in intensified Raman signal, or also known as surface-enhanced Raman scattering (SERS). These metallic NPs are called as the SERS substrate for which they possess the favourable properties as a plasmonic material.

SERS is initially founded in 1970 by Fleischmann and co-workers when they reported an unusually large Raman signal is obtained from pyridine adsorbed on a roughened silver electrode (Fleischmann *et al.*, 1974). Since then, SERS has been exploited mostly in biomedical and biochemical research which provide new combination and techniques for analytical applications. However, some issues should be taken into consideration before SERS is fully taken into bio-clinical practices such as reproducibility, background interference signal and qualitative analysis. The convergence of photonics and nanoscience creating more opportunities on producing SERS substrate that is significant on detecting wider range of biological or chemical analytes (Candeloro *et al.*, 2017).

Few experiments have been demonstrated with incorporation of monometallic NPs in tellurite glass. In previous work demonstrated by Amjad et al (2013), the embedment of silver NPs shows significant Raman signal up to the power of tenth along with enhancement in photoluminescence due to the local field effect of silver NPs (Amjad *et al.,* 2013). Another experiment is conducted with incorporation of gold NPs in tellurite glass resulting in SERS enhancement which is highly potential candidate for solid state lasers and other nanophotonic devices (Ghoshal *et al.,* 2015). A similar experimental work was performed by Saidi et al (2018), in which the enhancement of Raman signal is observed in the tellurite glass with the presence of bimetallic NPs of silver and titanium. Hence, it is proved the combination of bimetallic NPs potentially improves the absorption, optical and structure properties better than monometallic NPs due to the attributed localized surface plasmon resonance of Ag/Ti

which transferred the strong local electric field to the rare-earth ions positioned in their vicinity (Saidi *et al.,* 2018).

This current research proposed a new idea of producing a simple and cheaper nanostructured plasmonic glass which exerts the SERS capabilities for molecular detection application by using conventional melt-quenching technique. The direct embedment of metallic NPs into glass composition by using a melt-quenching technique provides facile glass fabrication which possesses beneficial features for SERS application. The other technique of fabricate nanostructured plasmonic glass such as ion-exchange, chemical vapour deposition and laser-induced plasma required multiple steps and involves an intricate process. In current research, the selection of titanium and aluminium as bimetallic NPs is prerequisite due to their plasmonic properties in the ultraviolet (UV) region which give rise to the Localized Surface Plasmon Resonance (LSPR) on the surface of metallic NPs.

1.2 Problem Statement

In order to identify the molecular structure of a molecule, the vibrational information of the molecule must be extracted. This is possible with the aid of Raman spectroscopy. Raman spectroscopy is a method to analyse the molecular and vibrational properties of a molecule in a non-contact and non-destructive ways (Vašková *et al.*, 2011). In this modern developing century, the established technique of Raman spectroscopy is constantly used in chemical and materials analysis (Ochsenkuhn *et al.*, 2012). However, Raman spectra signal is not strong enough to be applicable in wide biomedical field and biomolecular sensing application (El-Said *et al.*, 2017).

In order to overcome this limitation, this research proposes the embedment of metallic NPs in the glass matrix to allow the amplification of Raman spectra up to the factor of 10^5. The amplification in Raman spectra with the aid from metallic NPs is known as surface-enhanced Raman spectroscopy (SERS) (Sharma, 2012). In this research, two series of glasses containing monometallic and bimetallic NPs were prepared by using conventional melt-quenching technique. Further, the surface morphology, structural and optical properties of each glass is characterized in-depth