INVESTIGATION ON THE GOLD NANOPARTICLES CONCENTRATION EFFECTS TO THE OPTICAL AND STRUCTURAL PROPERTIES OF NANOSTRUCTURE GLASS

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JUDUL: **INVESTIGATION ON THE GOLD NANOPARTICLES CONCENTRATION EFFECTS TO THE OPTICAL AND STRUCTURAL PROPERTIES OF NANOSTRUCTURE GLASS**

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DECLARATION

I hereby declare that the work in this thesis is my own except for quotation, equations, summaries and references which have been acknowledged.

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ABSTRACT

Achieving enhancement of photoluminescence and Raman spectra of glasses containing rare-earth ions and metallic nanoparticles are prerequisite. Many studies only reported the effect of concentration of the nanoparticles on structural and optical properties of the glasses instead of the variation in size and shape of nanoparticles. Thus, the current study aims to investigate effect of concentration of the gold (Au) nanoparticles on structural and optical properties of the glasses. Further, their geometric effect on photoluminescence and Raman enhancement with varying concentration of the gold nanoparticles for optimizing photoluminescence and Raman enhancement are addressed. A series of glass with composition of $70TeO_2$-$20ZnO$-$10Na_2O$-$0.5Er_2O_3$-(x)Au where x=0.0, 0.1, 0.2, 0.3 and 0.4 mol% were examined with X-ray diffraction (XRD), ultraviolet-visible (UV-Vis) spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), photoluminescence spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy and Raman spectroscopy. Modification in UV-Vis spectra was observed due to non-bridging oxygen created by gold nanoparticles with increasing concentration of gold nanoparticles. TEM images verified the presence of non-spherical gold nanoparticles. Photoluminescence spectra revealed luminescence enhancement caused by the effect of surface plasmon resonance (SPR) and energy transfer from the gold nanoparticles to erbium ions as concentration of the gold nanoparticles was increased up to 0.3 mol%. However, when the concentration of the gold nanoparticles exceeded 0.3 mol%, luminescence quenching occurs due to energy transfer from erbium ions to gold nanoparticles. Amplification of Raman spectra was attributed to the effect of SPR. The concentrations of the gold nanoparticles for maximizing photoluminescence and Raman spectra were found to be 0.3 and 0.4 mol%, respectively. Non-spherical shaped nanoparticles were found to optimize photoluminescence and Raman enhancement. The results demonstrated the effect of varying concentration of nanoparticles on the properties of the glasses due to the geometric effect of the nanoparticles especially on the enhancement of photoluminescence and Raman spectra.

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ABSTRAK

KAJIAN KESAN KEPEKATAN ZARAH NANO EMAS TERHADAP SIFAT OPTIK DAN STRUKTUR BAGI KACA BERSTRUKTUR NANO

Peningkatan spektra fotoluminesen dan Raman bagi kaca yang mengandungi ion-ion bumi nadir dan zarah nano logam adalah sangat penting. Kebanyakan kajian hanya melaporkan pengaruh kepekatan zarah nano terhadap sifat-sifat struktur dan optik kaca tersebut tetapi tidak melaporkan kepelbagaian pada saiz dan bentuk zarah nano. Maka, kajian ini bertujuan untuk mengkaji kesan kepekatan zarah nano emas pada sifat struktur dan optik kaca. Tambahan pula, kesan geometri pada peningkatan fotoluminesen dan Raman dengan kepelbagaian zarah nano emas untuk mendapatkan peningkatan fotoluminesen dan Raman yang optimum dibincangkan. Satu siri kaca yang mempunyai komposisi $70TeO_2$-$20ZnO$-$10Na_2O$-$0.5Er_2O_3$-$(x)Au$ di mana x=0.0, 0.1, 0.2, 0.3 dan 0.4 mol% telah dikaji menggunakan teknik pembelauan sinar-X (XRD), spektroskopi ultraungu-cahaya nampak (UV-Vis), mikroskopi pancaran elektron (TEM), mikroskopi pengimbasan elektron (SEM), spektroskopi serakan tenaga sinar-X (EDX), spektroskopi fotoluminesen, spektroskopi Inframerah Pengubah Fourier (FTIR) dan spektroskopi Raman. Perubahan pada spektrum UV-Vis disebabkan oleh ikatan oksigen tidak bersambung yang dihasilkan oleh zarah nano emas apabila kepekatan zarah nano emas ditingkatkan. Imej TEM membuktikan kehadiran zarah nano emas yang mempunyai bentuk bukan sfera. Spektrum fotoluminesen menunjukkan peningkatan daripada kesan resonan plasmon permukaan (SPR) dan pemindahan tenaga daripada zarah nano emas kepada ion-ion erbium apabila kepekatan zarah nano emas ditingkatkan sehingga 0.3 mol%. Bagaimanapun, apabila kepekatan zarah nano emas melebihi 0.3 mol%, penurunan pada keamatan fotoluminesen berlaku disebabkan pemindahan tenaga daripada ion-ion erbium kepada zarah nano emas. Peningkatan spektrum Raman disebabkan oleh kesan SPR. Didapati kepekatan zarah nano emas untuk mengoptimumkan peningkatan fotoluminesen dan Raman ialah 0.3 dan 0.4 mol%. Zarah nano berbentuk bukan sfera mengoptimumkan peningkatan fotoluminesen dan Raman. Keputusan tersebut menunjukkan kesan kepekatan zarah nano terhadap sifat-sifat kaca disebabkan kesan geometri terutamanya pada peningkatan spektra fotoluminesen dan Raman.

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LIST OF ABBREVIATIONS AND SYMBOLS

TeO_2	-	Tellurium dioxide
Na_2O	-	Sodium oxide
ZnO	-	Zinc oxide
Er_2O_3	-	Erbium (III) oxide
Au	-	Gold element
Te	-	Tellurium element
Zn	-	Zinc element
Na	-	Sodium element
Er	-	Erbium
O	-	Oxygen element
C	-	Carbon element
SPR	-	Surface plasmon resonance
XRD	-	X-ray diffraction
n	-	Order of diffraction based on Bragg's law of XRD
d	-	Spacing between two successive lattice planes of a crystal based on Bragg's law of XRD
θ	-	Angle of incidence of X-ray based on Bragg's law of XRD
λ	-	Wavelength of an electromagnetic wave (for the case of spectroscopy) or an electron (for the case of de Broglie equation for operation of TEM) or a characteristic X-ray emitted by an atom (for the case of analysis of EDX)
2θ	-	Angle between an X-ray source and an X-ray detector
β	-	Full-width at half-maximum (FWHM) of XRD peak due to

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crystallite based on Debye-Scherrer equation

Å	-	Angstrom
Cu	-	Copper
Kα	-	K alpha of X-ray emitted by copper atoms in copper anode in XRD of current study
$K\alpha_1$	-	K alpha 1 (One of K alpha X-ray doublets emitted by copper atoms in copper anode in XRD of current study)
$K\alpha_2$	-	K alpha 2 (One of K alpha X-ray doublets emitted by copper atoms in copper anode in XRD of current study)
nm	-	Nanometer
UV-Vis	-	Ultraviolet-visible obtained from ultraviolet-visible spectroscopy
A	-	Absorbance of a glass sample
T	-	Transmittance of a glass sample given by $T = I/I_0$
a.u.	-	Arbitrary unit (a unit used by absorbance for UV-Vis spectra, intensity of excitation and emission spectra of photoluminescence spectroscopy, and intensity of Raman spectra)
α	-	Absorption coefficient
d	-	Thickness of a glass sample
I_0	-	Intensity of incident light on a glass sample
I	-	Intensity of transmitted light through a glass sample
dI	-	The differential of intensity of light to represent the change of intensity of light as the light passes through the glass sample
dx	-	The differential of distance travelled by light inside the glass sample to represent the amount of distance travelled by the light inside the glass sample

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h	-	Planck's constant equal to 6.626 x 10^{-34} J s where J s is pronounced as Joule second
ΔL	-	Change in orbital angular momentum L during a transition between two energy levels
ΔS	-	Change in spin angular momentum S during a transition between two energy levels
ΔJ	-	Change in total angular momentum J during a transition between two energy levels where $J = L + S$
eV	-	Electron volt (a unit used to quantify optical band gaps of glass samples and Urbach energy for UV-Vis spectral analysis)
$\hbar$	-	Planck's constant h divided by 2π
c	-	Speed of light in vacuum equal to 3.0 x 10^{8} m/s
ω	-	Angular frequency of light, $\omega = 2\pi f$ with f representing frequency of light
E_{opt}	-	Optical band gap
n	-	Exponent of a factor $(\hbar\omega - E_{opt})$ that depends on type of optical transition based on Davis-Mott theory
E_{dir}	-	Direct optical band gap
E_{indir}	-	Indirect optical band gap
E_U	-	Urbach energy
B	-	Energy-independent constant in mathematical expression of Davis-Mott theory
cm^{-1}	-	Per unit centimeter (a unit of energy for energy level diagram in section of photoluminescence spectroscopy; a unit of wavenumber for FTIR, and a unit of Raman shift for Raman spectroscopy)
ATR	-	Attenuated total reflection

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FTIR	-	Fourier Transform Infrared spectroscopy
n_i	-	Refractive index of a first medium that an infrared light is incident on based on principle of ATR-FTIR
n_r	-	Refractive index of a second medium that an infrared light passes through based on principle of ATR-FTIR
θ_i	-	Angle of incidence of an infrared light based on principle of ATR-FTIR
θ_r	-	Angle of refraction of an infrared light based on principle of ATR-FTIR
TEM	-	Transmission electron microscopy
p	-	Momentum of an electron based on de Broglie's equation in physical principle of TEM
U	-	Electrostatic potential difference (or accelerating voltage) to accelerate electrons emitted by electron guns of TEM
μ	-	Location parameter of a lognormal distribution function
σ	-	Shape parameter of a lognormal distribution function
SEM	-	Scanning electron microscopy
EDX	-	Energy dispersive X-ray spectroscopy; an abbreviation with the same meaning as that of EDS
E_i	-	Energy of an initial state of an electron of a given atom based on physical principle of EDX
E_f	-	Energy of a final state that has lower energy than that of an initial state of an electron of a given atoms based on physical principle of EDX
E_0	-	Beam energy of an incident electron beam in SEM and EDX
keV	-	Kilo electron volt (used in EDX spectrum in the current study)

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