Studies on the effect of temperature on Au Nanoparticles

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Abstract: ***This work report the temperature dependence UV-Visible (UV-Vis) Spectroscopy, Photoluminescence (PL) spectroscopy, Surface Plasmon Resonance (SPR), current change and electrochemical studies of gold nanoparticles (AuNPs). The UV-Vis, PL, SPR, current and redox potential of AuNPs strongly depends on temperature. The SPR band of AuNPs shows at 534 nm. The PL emission band of AuNPs shows at 421 nm, when excited at 350 nm. The UV-Vis of AuNPs was studied between the temperature range 180-800 C. The PL emission of AuNPs was studied between the temperature range 160-830 C. The observed temperature raise effects the red shift along with broadening of SPR band and PL emission intensity of AuNPs. The redox potential (verses Ag-AgCl reference electrode) of AuNPs was measured by cyclic voltammetry technique between the temperature range12o_80o C. The observed redox potential -0.956Volt at 12oC shifts anodically with raising the temperature to -0.904Volt at 40oC and the redox potential remains unchanged at -0.904Volt up to 80oC. Temperature induced effects on AuNPs appeared between the temperature range 38o-45o C and beyond this temperature range no significant influence of temperature on SPR, PL emission intensity, current change and redox potential were found. The temperature dependent effects may be attributed due to the electron-phonon scattering, thermal expansion of AuNPs.***

Keywords: Photoluminescence, Surface plasmon resonance, Redox potential, Cyclic voltammetry.

1. Introduction

The electronic and optical properties of nanoparticles are determined by both their size and shape. Metal nanoparticles have mainly been studied because of their unique optical properties [1-13]. Noble metal nanoparticles exhibit unique optical properties such as resonant absorption and scattering of light which is not found in bulk metals. Collective coherent excitations of free electrons in the conduction band, also known as surface plasmon resonance are responsible for strong absorption and scattering of light by the particles [5,9,14]. The noble metal nanoparticles have gained much attention recently due to a wide range of potential applications in surface enhanced Raman scattering, surface enhanced fluorescence, bio-chemical imaging, cancer treatment and sub wavelength optical waveguides. An influence of the temperature on the SPR in metal nanoparticles is crucial for pure and applied science of the nanoparticles. The temperature and size dependence of the SPR is important because of the recent applications of noble metal nanoparticles in thermally assisted magnetic recording, thermal cancer treatment, catalysis and nanostructure growth and computer chips [14,15]. Moreover temperature dependence of SPR is widely studied for its desirable application in thermal sensing. In this paper, we report the temperature dependence UV-Vis, PL, SPR, current change and electrochemical studies of AuNPs.

2. Experimental

2.1 Instruments and Reagents

UV-Vis spectra were recorded with double beam UV-1800 Shimadzu UV Spectrophotometer. PL spectra were recorded with Hitachi F-2500 FL Spectrophotometer. Electrochemical experiments were performed with Model 600D Series Electrochemical Analyzer Workstation CH Instruments, Inc. with a conventional three electrode system. Temperature control was performed by using TCC-240A Shimadzu corporation temperature controller device. Temperature dependence current change experiment was performed with fabricated potentiostat connected with TCC-240A Shimadzu temperature controller. Gold (III) chloride hydrate (HAuCl4.xH2O) 99.99% metal basis was obtained from Aldrich and used as such. The morphology of the AuNPs was analyzed using HR-TEM. HR-TEM images were obtained by using TEM, JEM-2100, 200KV, Jeol.

2.2 Preparation of AuNPs by using Camellia Sinensis (Tea) extract

The AuNPs was prepared by using Camellia Sinensis as published procedure [16]. The average size of AuNPs is 13.14 nm.

3. Result and Discussions

3.1 Temperature dependence UV-Vis Spectroscopy of AuNPs

From Figure 1a, it is found that red shift along with broadening of SPR band at 534 nm is observed in AuNPs with increase of temperature from 18o to 80oC. The exponential decay of absorption intensity at 534nm with increase of temperature is shown in Figure 1b. The exponential decay of absorption at 534nm continues up to 45oC and thereafter it remains unchanged

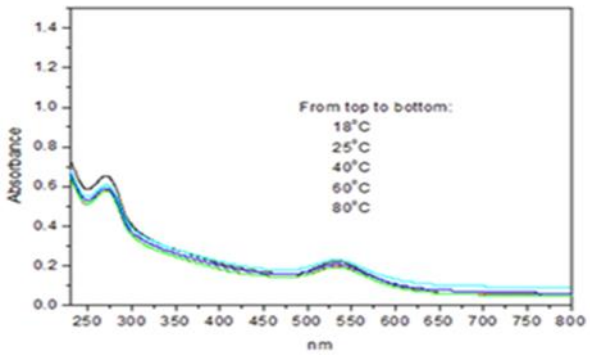

Figure 1a

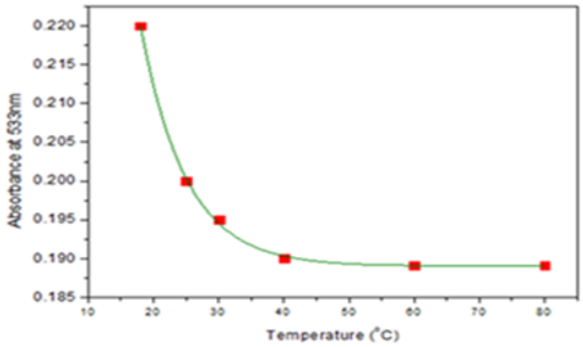

Figure 1b

Figure 1: UV-Vis spectrum of AuNPs with average size of 13.14nm in water and temperature dependence SPR absorption band at 534nm for AuNPs with gradual increase of temperature from 18 to 80oC.

The temperature dependence effects such as red shift and broadening of SPR band of AuNPs arises due to (i) damping parameters such as electron-electron scattering due to frequency dependent energy term hc^{v}, electron-phonon scattering and electron surface scattering. (ii) dielectric function of the AuNPs and immediate surrounding medium, which arises due to intra band transition of AuNPs and (iii) coefficient of thermal expansion of the AuNPs. With increase of temperature the separation between AuNPs decreases due to the lattice expansion and the dimer nearly touch at high temperature. As a result the electric field intensity between the gap of the dimer increases due to strong inter particle coupling of charges [1,14,15,17,18,19].

3.2 Temperature dependence photoluminescence of AuNPs

Figure 2a shows the PL emission spectra of AuNPs in water with gradual increase of temperature from 20o to 83oC. The PL emission was observed at 421nm for excitation at 350nm. The change of emission intensity at 421nm with increase in temperature is shown in Figure 2b.

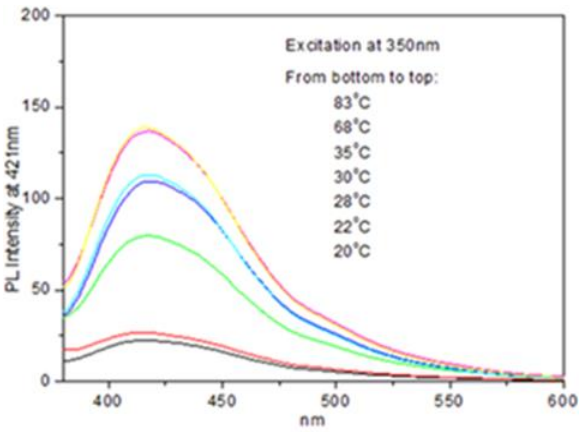

Figure 2a

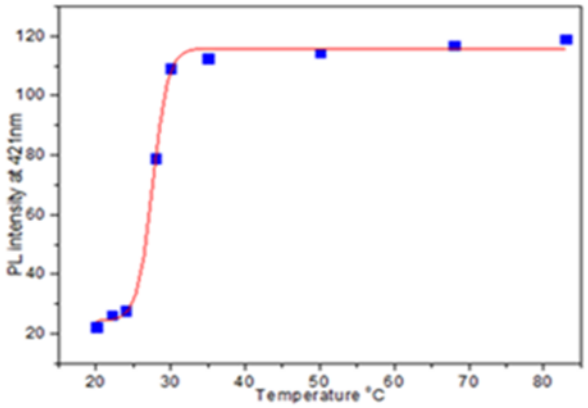

Figure 2b

Figure 2: PL emission spectrum of AuNPs with average size of 13.14nm and temperature dependence PL emission intensity at 421nm of AuNPs in water with increase of temperature from 20 to 83oC.

The emission intensity of AuNPs increases up to 38oC and thereafter it remains unchanged. The origin of temperature induced PL emission is caused by two physical mechanisms: (i) temperature induced electron-phonon scattering rate in the AuNPs and (ii) thermal expansion of AuNPs with increasing temperature.

The phonon population in the AuNPs increases with raising the temperature leading to an increase in the probability of electron-phonon scattering. As a result, increased in the electron phonon scattering rate with raising temperature would lead to an increase in the damping constant γα which in turn would decrease the local field enhancement factor and correspondingly PL quantum yield of the AuNPs [1,14,15,17,18,19].

The thermal expansion of AuNPs with raising temperature lead to an increase in the radius of the AuNPs, which results in decrease in free electron scattering rate of the AuNPs surface and surface plasmon damping constant. Therefore, the temperature induced decrease in the scattering rate of free electrons on the AuNPs surface would increase enhancement factor of PL. Thus, electron-phonon and free electron scattering rate on the AuNPs surface influence the temperature dependence PL quantum yield of the AuNPs [1,14,15,17,18,19].

3.3 Temperature dependence current change of AuNPs

Figure 3 shows the temperature dependence current change of AuNPs in water with gradual increase of temperature from 27.6o to 61.6o C at applied potential 3.43Volt. The exponential decay of current continues up to 45oC and thereafter it remains unchanged. The exponential decay of current with increasing temperature arises from the thermal expansion of AuNPs. The concentration of free electron gas decrease on thermal expansion of AuNPs leads to decrease of current [1,14,15,17,18,19].

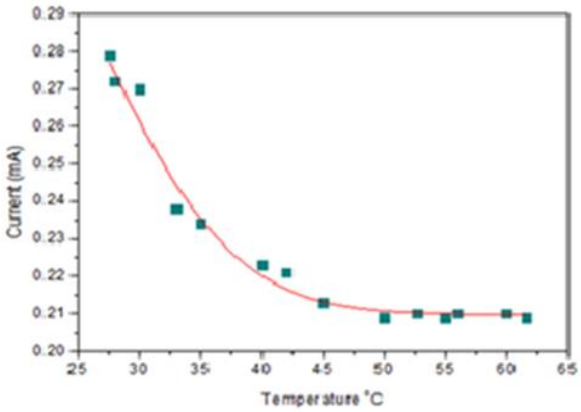

Figure 3: Temperature dependence current change for AuNPs with average size 13.14nm in water with gradual increase of temperature from 27.6 to 61.6oC (at applied potential 3.43Volt).

3.4 Temperature dependence cyclic voltammetry of AuNPs

Temperature dependence cyclic voltammogram of AuNPs in water with gradual increase of temperature from 12o to 80oC is shown in Figure 4a. The cyclic voltammogram of AuNPs in water at 12oC shows only a cathodic peak at -0.956 volt at scan rate 0.1 volt/second (versus Ag-AgCl reference electrode) due to irreversible oxidation of AuNPs to Au2O3 according to the redox reaction 3H2O+2Auo→Au2O3+6H++e-.

The redox potential -0.956 volt at 12oC shifts anodically to -0.904 volt up to 40oC and thereafter it

remains unchanged at -0.904Volt up to 80oC (Figure 4b).

At lower temperature the redox potential of AuNPs is more cathodic (-ve) in comparison with higher temperature. At higher temperature AuNPs is easier to oxidize to Au3+, which implies that electrochemically the net stabilization of AuNPs at lower temperature is greater than Au3+ at higher temperature. The anodic shift of redox potential in AuNPs arises due to thermal expansion of AuNPs. The concentration of free electron gas decrease on thermal expansion of AuNPs leads to anodic shift of the redox potential [1,14,15,17,18,19].

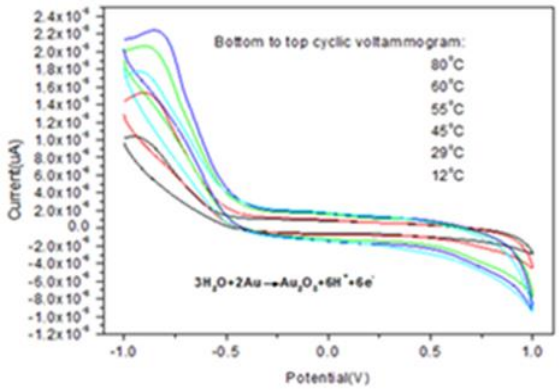

Figure 4a

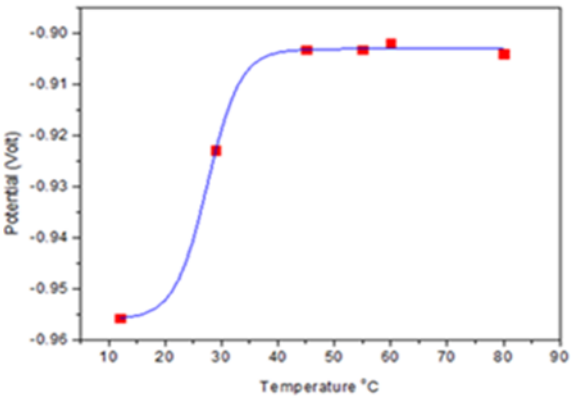

Figure 4b

Figure 4: Temperature dependence cyclic voltammetry and redox potential of AuNPs with average size of 13.14nm in water with gradual increase of temperature from 12 to 80oC. Supporting electrolyte: 0.1 NaNO3, Scan rate: 0.1Volt/second, Working electrode: GCE, Reference electrode: Ag-AgCl, Auxiliary electrode: Pt.

4. Conclusion

The temperature effect on AuNPs appeared from thermal expansion as well as surface damping and free electronic environment effects. From our experimental evidences it were observed that thermal expansion of AuNPs effects on the SPR, PL emission intensity, current and electrochemical redox potential between the temperature range 38o to 45oC. Beyond this temperature range no significant influence of temperature on SPR, PL emission, current and electrochemical redox potential were found.

Acknowledgments

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