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Tailoring the size of gold nanoparticles by electron beam inside transmission electron microscope

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ABSTRACT

Au nanoparticles (NPs) embedded in silica matrix were synthesized by atom beam co-sputtering and investigated in detail by transmission electron microscopy (TEM). A study on electron beam induced tailoring of size of Au nanoparticles has been performed in an in-situ TEM experiment as a function of electron irradiation time. This study concludes that electron beam irradiation can result in a controlled growth of NPs in proportion to irradiation fluence. Analytical calculations for electron energy loss in Au NPs and fused silica have been performed, which indicate that the observed growth of Au NPs in present case is due to rise in temperature of Au NPs and surrounding silica.

Keywords: Gold nanoparticles; electron beam; transmission electron microscopy

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Introduction

Plasmonic nanocomposite materials are of immense interest due to their potential application in plasmonics, nanophotonics and biomedical engineering [**1-3**]. They exhibit extra-ordinary optical, electrical and magnetic properties, when their dimension is reduced to nanoscale region [**4-6**]. Particularly, the noble metal nanoparticles (NPs) embedded in dielectric matrices exhibit interesting surface plasmon resonance (SPR) absorption in UV-visible region due to itinerant electron oscillations when excited by electromagnetic radiation [**4**]. The surface plasmon resonance absorption depends on the size, shape of nanoparticles and the dielectric constant of the medium in which they are embedded. Playing with different parameters (i) size, (ii) shape and (iii) matrix one can synthesize nanocomposite with tunable SPR which have significant importance in biomedical engineering and nanoelectronic applications [**1-3**]. One can also synthesize nanocomposites with tunable SPR by selection of appropriate synthesis conditions like temperature and environment etc [**5**]. Noble metal nanoparticles also exhibit interesting thermodynamic features due to their large surface to volume ratio which inculcate them as the promising candidates in catalytic reactions. These versatile technological applications demand the controlled synthesis of metal-dielectric nanocomposites using different techniques. Several physical and chemical methods [**6-12**] have been employed for synthesizing metal nanostructures. Ion beams exhibit a unique role in controlled engineering of nanostructures in terms of size and shape [**13-15**].

Recent investigations on electron beam irradiation of nanocomposites [**16-19**] have reported that electron beam can also be used for tailoring the size of nanoparticles in a controlled manner. Since during TEM measurements, the nanocomposite specimen is exposed to energetic electrons therefore an in-situ study on the effect of electron beam irradiation of the nanoparticles in the nanocomposite film is of interest. The in-situ TEM studies on CdS nanocrystals [**16**] and submicron Al-Si alloy particles [**17**] have been reported but in-situ TEM study on gold nanoparticles has not been reported so far. In this paper we would like to emphasize the role of electron beam irradiation on the gold nanoparticles, which could be beneficial to achieve further control on the size already synthesized gold nanostructures. A qualitative explanation of increase in the size (diameter) of Au nanoparticles with electron irradiation time has been discussed in the light of electron interaction with matter as subsequent rise in temperature. The study reveals that the electron irradiation can be used to further increase of size of gold nanoparticles embedded in silica.

Experimental

Au nanoparticles embedded in silica matrix (thickness ~ 45 nm) were deposited on carbon coated Cu grids by atom beam co-sputtering [**6, 8-11**] of Au and silica target with 1.5 keV neutral Ar atoms. TEM micrographs were recorded in-situ after irradiating the NPs by converting the electron beam on the sample for 5 minutes. For this a TECNAI G^2 20-TEM, equipped with LaB6 filament, operating at 200 keV, was used. Five different such micrographs were recorded after each time exposing the same area for 5 minutes exactly under the similar electron beam conditions. The electron beam current density was 1.78×10^8 A/m^2. The average size of the Au nanoparticles was analyzed manually at each step using image J.

Results and discussion

Fig. 1 shows the TEM images of pristine and electron beam irradiated Au-SiO_2 nanocomposite film. TEM micrograph of pristine nanocomposite film is shown in **Fig. 1a** and the circular section (**b**) inside (**a**), shows the electron beam modified area of the nanocomposite film after exposure of 10 minutes. The selected area electron diffraction pattern is shown in (**c**), which confirms the face centred cubic structure of the gold NPs. The TEM images corresponding to pristine as well as that of the final irradiation fluence (after 25 minutes cumulative exposure) are shown in **Fig. 1d** and **e**, respectively. The electron beam was kept at the same spot during the entire measurement to monitor the growth. **Fig. 1e** clearly demonstrates that there is growth in size (diameter) of gold NPs after 25 minutes electron beam irradiation. Analysis of the average size (diameter) of nanoparticle from TEM image at each step confirmed an average increase in size of nanoparticles from ~3.8 nm to ~7.0 nm after 25 minutes irradiation. The size distributions of gold nanoparticles corresponding to pristine and irradiated at different times are shown in **Fig. 2a-f**. These size distributions were obtained by line profiling on the diameter of each nanoparticles in the TEM images and they clearly elaborate the growth of nanoparticles after electron beam irradiation. The growth of nanoparticles under electron beam irradiation occurs due to the thermal energy deposition by energetic electrons into the nanocomposite film and the resulting phenomenon is discussed in the next section.

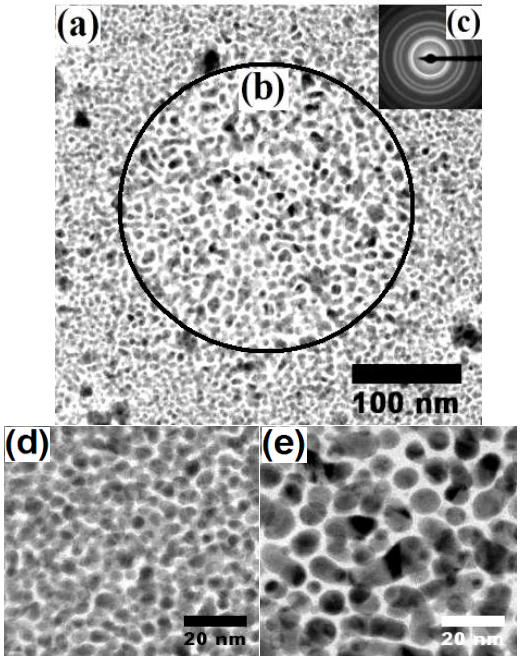

Fig. 1. Bright field TEM image of (a) pristine sample and (b) section of (a) irradiated with electron beam. Picture (c) shows the electron diffraction pattern. (d) and (e) are the magnified view of TEM images of pristine and electron irradiated sample up to 25 minutes, respectively.

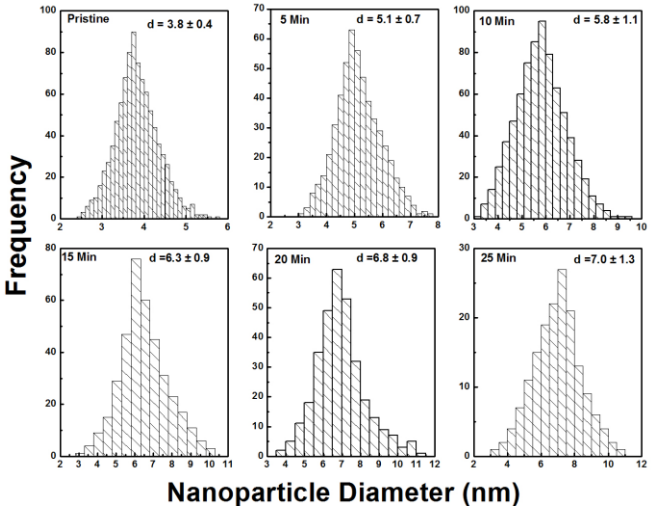

Fig. 2. Size distribution (a-f) of Au nanoparticles for (a) pristine and (b-f) irradiated for different times. Frequency is in arbitrary unit.

When a stream of electrons penetrates into a solid target, electrons get scattered and lose their energy either elastically with nuclei or inelastically with electrons [**16-17, 20**]. The inelastic collisions with atomic electrons result in either excitation or ejection of atomic electrons however the elastic collisions result in displacement. The energy lost by electrons is deposited within the material in the form of thermal energy resulting in increase of temperature of nanocomposite film. The increase in temperature of the system results in increase in diffusion and agglomeration of the constituent atoms and the small clusters. Due to poor solubility of gold in silica, the diffusion [**21**] results in growth of the Au nanoparticles. The growth of NPs under e-beam irradiation is proposed to be due to radiation-enhanced diffusion caused by rise in temperature. It is also likely to be due to the displacement of atoms caused by incident energetic electrons. Therefore we determine (i) the displacement caused by incident electrons, (ii) the temperature rise in the matrix and (iii) finally the growth due to temperature rise. The displacement cross-section σ_d for an electron with energy E_p, is given by

$$\sigma_d = K[E' + 2\pi\alpha\beta\sqrt{E'} - (\beta^2 + \pi\alpha\beta)\ln E' - (1 + 2\pi\alpha\beta)] \quad ----(1)$$

where, $K = 4\pi(a_0 z U_R)^2[(1-\beta^2)/(mc\beta^2)^2]$, and $E' = E_{max}/E_d = 2E_p(E_p+2mc^2)/E_d Mc^2$, M is the mass of the nucleus, a_0 is the average Bohr radius (5.29×10^{-11} m), U_R is the Rydberg energy (13.6 eV), Z is the atomic number of the nucleus (79 for Au), α = Z/137 and β = v/c, the ratio of velocity of electrons (energy 200 keV) and light.

The displacement cross-section (σ_d) for Au atoms by energetic electrons at various E_d is shown in **Fig. 3**. The maximum energy transferred to Au, Si and O atoms from 200 keV electrons has been estimated, which reveals that matrix is more strongly affected by energetic electron in comparison to Au atoms because of the larger mass of Au atoms. The consequential displacement in the matrix identities definitely contributes in enhancing the diffusion of Au atoms and thus growth of Au NPs occurs.

Rishbud et al. [**16**] have given the formulation to calculate the rise in temperature (ΔT_e) of any system under electron beam irradiation in terms of electronic excitations and Coulomb encounter energies, electron beam parameters (current density and energy) and the matrix parameters. As the energetic electrons pass through the nanocomposite matrix, they create thermal spikes. The energy loss occurs mainly via two processes: (i) from electronic excitations (Q_e) and (ii) Coulomb encounter with nuclei (Q_c) as given below:

$$Q_e = \Theta\left[\log\left(\frac{m^2c^4\beta^2}{Z^2I^2(1-\beta^2)}\right) - \beta^2 + 0.198\right] \quad ----(2)$$

$$Q_c = \frac{\Theta}{1837.5A}\log\left(\frac{T_m}{T_a}\right) \quad ---(3)$$

where, constant $\Theta = 2\pi n Z^2 r_e^2\, m\, c^2/\beta^2$, T_m = (560.8/A) X (X+2), ($X = E_p/mc^2$ =0.2 MeV/0.511 = 0.391), T_a = (m/M) (1+ $Z^{2/3}$) R_h, β = v/c = 0.694 for the case of E_p= 200 keV electrons, Z=79 for Au. r_e (=2.818 x 10^{-15} m) is the classical electron radius, Rydberg energy for hydrogen atom is R_h= 13.6 eV, A (=197) is the atomic mass for Au, n is the number density of atoms in the particle, IZ (=13.54 eV) is the average ionization potential for Au atom [**18**].

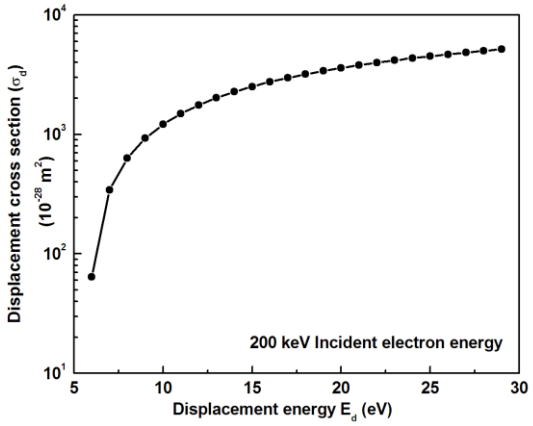

Fig. 3. Variation of displacement cross-section for different displacement energies for 200keV electron beam irradiation.

The total thermal energy gained by the matrix can be expressed by $Q= Q_e + Q_c$, which results in a rise in temperature (ΔT_e) of the matrix. The temperature rise (ΔT_e) of silica matrix due to electron beam irradiation in (current density J) for time t_e seconds is given by

$$\Delta T_e = \frac{3JQ}{8ec_v Dd} R_e^2 \log\left(1+\frac{4Dt_e}{R_e^2}\right) ----(4)$$

Where $D=k_t/c_v$ d (k_t is the thermal conductivity, c_v is specific heat and d is the density), $e=1.6x10^{-19}$ eV, J ($=1.73x10^8$ A/m^2) be the current density and R_e (=140 nm) is the effective beam radius, in which electron beam was falling. The rise in temperature (ΔT_e) of the nanocomposite silica matrix as a function of irradiation time (t_e) has been calculated using k_t = 130 J/m s K, Z=30, d=2200 Kg/m^3, c_v= 740 J/Kg K for silica matrix. The calculations reveal that the temperature of silica raises upto 512 K after electron beam irradiation for 25 minutes as shown in **Fig. 4**. It is evident from **Fig. 4** that there is rapid increase in temperature of silica during initial stage of electron beam irradiation. Further electron irradiation results in only slight increase in temperature which might be due to effect of radiation losses.

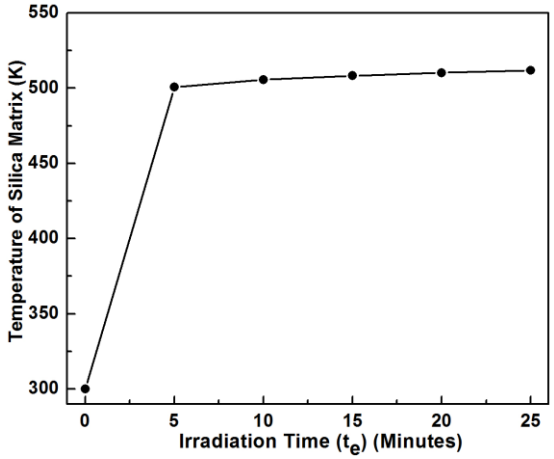

Fig. 4. Calculated curve for rise in temperature of silica matrix due to electron beam heating effect at current density $1.78x10^8$ A/m^2.

The increase in temperature of silica matrix plays a significant role in enhancement of the diffusion of Au atoms in the matrix and thus leads to the growth of nanoparticles. The growth of nanoparticles shows a cumulative behaviour with increase in irradiation time because of continuous agglomeration of gold atoms. The growth of Au NPs is determined on the basis of temperature dependent diffusion, as discussed in the following section.

The coarsening kinetics of NPs under e-beam irradiation can be described in terms of radiation induced

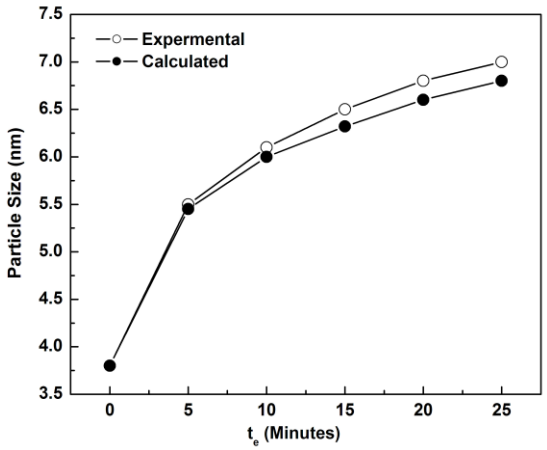

Fig. 5. Variation of theoretically calculated and experimentally observed growth of Au nanoparticles with electron irradiation time.

precipitation kinetics of metals in glass [**22**]. The coarsening rate can be modified according to Fick's law considering the effect of outward diffusion. The detailed investigation of this formulation has been discussed by Liu et al. [**16**] which give an approximate relation between the variation of average size (R_e) of NPs and irradiation time (t_e) as given below

$$R_{avg} = \left(\frac{4D\alpha t_e}{9}\right)^{1/3} ---(5)$$

where, D is the diffusion coefficient given by $D=D_0\exp(-\varepsilon_a/k_BT)$ and the parameter α is given by $2\sigma v^2 C_e/k_BT$. Using the values of surface energy (σ), volume (v) for gold atom and C_e be equilibrium concentration for gold, the value of α is found to be $2x10^{-19}$ m at temperature 500 K. Substituting all the experimental and theoretical parameters, it was observed that for activation energy ε_0=1.5 eV and $D_0=5x10^{-6}$ m^2/s of gold in silica, the results are in good agreement. The growth behaviors of Au nanoparticles under electron beam irradiation with time observed experimentally and with theoretical calculations, are shown in **Fig. 5**. The theoretically calculated growth of nanoparticles is slightly lower than the experimentally observed. This is attributed to that fact that electron irradiation results in creation of several point defects in silica, which assist in diffusion of gold atomic species. Since the displacement effects are very small, they have been ignored in the calculation for growth of size of nanoparticles.

A qualitative comparison of **Fig. 4**, the rise in temperature of silica and **Fig. 5**, the increase in particle size, after electron beam irradiations suggest that the trend

of increase in size is in agreement with rise in temperature. Due to large temperature increase (~200 ^{o}C) during initial 5 minutes, there is rapid growth (~3.75 nm to ~5.5 nm) in size of NPs. Irradiation after 5 minutes results in slight variation in temperature because of radiation losses but the growth of nanoparticles continues due to enhanced diffusivity. Thus the electron beam irradiation can result in growth of nanoparticles because of radiation enhanced diffusion. Also electron beam irradiation can be used to heat the selected area of sample precisely without affecting the surrounding however normal heating results in modification of whole sample. Electron beam irradiation can be used for engineering the size of nanoparticles in different areas of same sample which is difficult from normal heating.

Conclusion

In summary, an in-situ TEM study on 200keV electron beam induced growth of Au nanoparticles in silica matrix has been investigated. Electron beam irradiation result in the growth of Au nanoparticles, which can be controlled by irradiation time and thus controlled tailoring, is possible inside TEM. The temperature rise of silica matrix is estimated under the electronic energy deposition in silica film. Theoretical calculations explain the growth of Au nanoparticles due to enhanced diffusivity resulting from temperature rise induced by electron energy loss deposition.

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