

Room temperature synthesis of coinage metal (Ag, Cu) chalcogenides†

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Coinage metal chalcogenides in their nanoregime have been synthesized in aqueous medium at room temperature by mixing the nanoparticles of silver or copper with selenium nanoparticles which are authenticated by UV-vis, XRD and TEM analyses.

In recent years, the impetus for considerable research into the synthesis of semiconductor nanostructures emanates from their potential applications in various fields, such as solar cells, pigments, IR detectors, luminescence devices and optical fiber communication.^{1,2} The binary chalcogenide semiconductors have received attention due to their size-dependent optical properties³ in addition to other physical and chemical properties^{4,5} as a consequence of the quantum size effect. In this context, coinage metal chalcogenide nanoparticles exhibit a number of interesting and useful characteristic properties different from the corresponding bulk compounds. These binary semiconductors are the basic materials for Schottky barriers, solar cells and electronic engineering. Bulk metal selenides have been prepared from the elements at high temperature and from the reaction of alkali metal halides by solid state metathesis.^{6,7} Parkin *et al.* studied silver sulfide and silver selenides formation in liquid ammonia at room temperature in a pressure vessel.⁸ There the elements intermix to form the corresponding chalcogenides. But the reaction was not studied when the components are in the nanoregime. In the nanostage as the particle dimension decreases the ratio of the number of internal atoms to that of the surface atoms becomes larger. Therefore, surfaces become active and surface reaction processes occur predominantly at low temperature.⁹

During the last few decades, a variety of synthetic strategies *e.g.*, vacuum deposition, sonochemical methods, ultrasound irradiation, laser ablation, template synthesis *etc.* have been described in the literature for the preparation of silver selenide nanoparticles.^{10–13} These protocols employ a number of stabilizing agents, like ethylenediamine and surfactants which contaminate the products with high levels of carbon impurity, that affect the magnetoresistivity (MR) of the products.¹⁴ Solution phase alloying of gold with selenium has already been reported from our group in aqueous micelles under UV.¹⁵ In this paper we report a novel method for the synthesis of metal chalcogenides. The diffusion of

silver and copper nanoparticles into the selenium nanoparticle in dispersed phase is reported with simple aqueous solution leaving behind contaminants. Surface energy and interparticle affinity for size-dependent diffusion have been shown elegantly leading to the evolution of Ag₂Se in the nanometer size regime. Again, the size of the particles can readily be tuned simply by varying the concentration of preformed silver. To the best of our knowledge, this is the first report of the preparation of silver and copper selenides at room temperature that too in aqueous solution by mixing preformed silver and selenium nanoparticles in definite proportions.

Silver nanoparticles were prepared by the reduction of aqueous silver(I) ions by sodium borohydride solution following the procedure reported by Creighton *et al.*¹⁶ To an aliquot of AgNO₃ (0.33 mmol, 3 ml) an ice-cold aqueous solution of NaBH₄ was added all at once and shaken vigorously. The resulting solution showed an absorption maximum at 397 nm indicating the formation of silver nanoparticles. Copper nanoparticles were prepared from CuSO₄ solution by using glucose as a reducing agent. Glucose (0.5 g) was dissolved in 6 ml CuSO₄ (0.33 mmol) solution, to it 0.01 ml of NaOH (1 M) was added and the mixture warmed to ~70 °C. The solution turned yellow showing an absorption maximum at 528 nm. Again, selenium has been synthesized wet chemically by refluxing the mixture of H₂SeO₃ and sodium borohydride at ~70 °C. The brick red color of the solution appears instantaneously indicating the formation of selenium nanoparticles.¹⁵ The as-prepared silver(0) were kept for 24 h for complete removal of excess BH₄[–] ions. Now, preformed silver and selenium particles were mixed together in different volume ratios. The color of the mixture changes from yellow to brown. Upon addition of selenium to the silver nanoparticles the absorption maximum of silver is blue shifted and shows an absorption maximum at 387 nm. On standing, the plasmon peak of silver disappears gradually and after ~3 h has died down completely. However, the color changes towards black as the concentration of silver(0) increases.

Particle formation was studied through UV-vis spectral analysis. Fig. 1A exhibits the UV-vis spectra of Ag₂Se nanoparticles: Ag : Se (v/v) (a) (2 : 1) and (b) (3 : 1). In both the cases, the silver plasmon peak is not observed indicating the absence of free silver nanoparticles. Fig. 1B shows the gradual disappearance of the silver plasmon peak upon the addition of selenium nanoparticles for Ag₂Se (2 : 1) formation. In Fig. 1B, trace a shows the absorption spectrum of selenium nanoparticles whereas, trace b shows the surface plasmon absorption of silver nanoparticles. The surface plasmon absorption is due to the collective oscillation of the conduction electrons when those are in resonance with the incident electromagnetic radiation. Upon addition of selenium

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† Electronic supplementary information (ESI) available: ESI 1, UV-vis spectra of the formation of Cu₂Se; ESI 2, PL spectra of Ag₂Se; ESI 3, XRD of Cu₂Se; ESI 4, TEM images of Ag and Se nanoparticles; ESI 5, HRTEM image of Ag₂Se (3 : 1); ESI 6, UV-vis spectra of gold selenium interaction; ESI 7, Effect of heat studied by UV-vis spectra. See DOI: 10.1039/b606681j

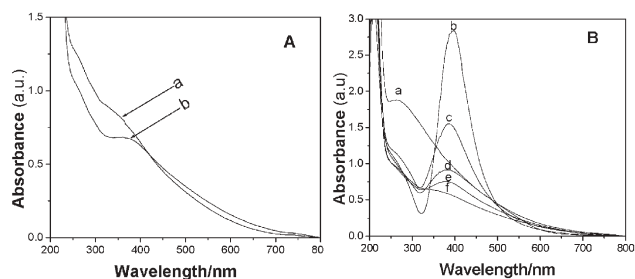


Fig. 1 (A) UV-vis spectra of (a) Ag_2Se (2 : 1) and (b) Ag_2Se (3 : 1) nanoparticles. (B) UV-vis spectra of (a) Se, (b) Ag, and gradual decrease of Ag plasmon peak after addition of Se at times (c) 0, (d) 1 h, (e) 2 h and (f) 3 h.

nanoparticles, the absorbance value gradually decreases (traces c–e) and after about 3 h the silver plasmon peak vanishes completely (trace f).

The disappearance of the silver plasmon peak upon the addition of selenium may be due to the change in the electronic environment of silver for its binding with selenium. Even at higher concentrations of silver Ag_2Se (3 : 1), the plasmon peak of silver is not observed in the UV-vis spectra. The same thing occurs in the case of copper (ESI 1).[†] After mixing with selenium the plasmon peak of copper shifts from 528 nm to 494 nm. On leaving the mixture to stand, the plasmon peak of copper gradually shifts towards blue and the absorbance dies down. After 5 h, the plasmon peak vanishes completely.

The band gap of silver selenide is 2.32 eV, calculated from the photoluminescence spectra (ESI 2).[†] Here, due to quantum confinement silver selenide semiconductor particles experience a larger band gap as compared to that of the bulk materials and there is a blue shift in the absorption spectra. The approximate particle size is 8 nm calculated from the band gap using the formulation by Brus:¹⁷

$$\Delta E_g = \frac{h^2 \pi^2}{2R^2 \mu} \quad (1)$$

where, ΔE_g is the change in the band gap due to quantum confinement, R is the particle radius and $1/\mu = (1/m_e + 1/m_h)$ is the combined effective mass of electron and hole. The change in band gap is inversely proportional to the particle radius. The effective mass of $\beta\text{-Ag}_2\text{Se}$ is $\sim 0.1\text{--}0.3$ Me for electrons and 0.75 Me for holes, respectively. The calculated particle size agrees well with the AFM results.

XRD pattern of the as-prepared Ag_2Se synthesized from Ag : Se (2 : 1) and (3 : 1) are shown in Fig. 2 A and B, respectively. For

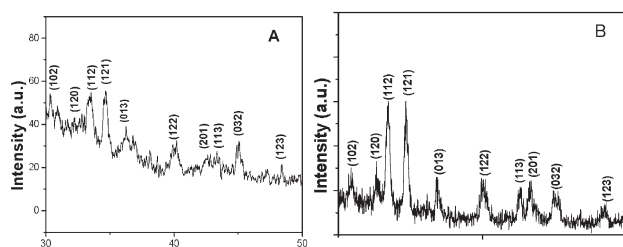


Fig. 2 X-ray diffraction pattern of (A) Ag_2Se (2 : 1) and (B) Ag_2Se (3 : 1).

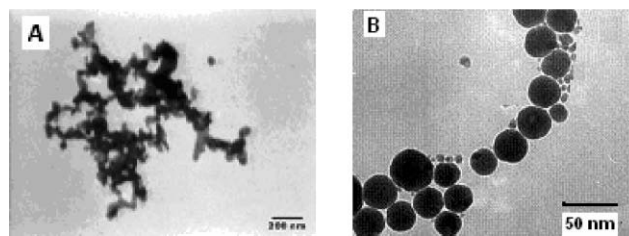


Fig. 3 TEM images of (A) Ag_2Se (2 : 1) and (B) Ag_2Se (3 : 1).

both cases, the accepted crystal structure is orthorhombic with the $P2_12_12_1$ space group. The measured lattice parameters are $a = 0.434$ nm, $b = 0.706$ nm and $c = 0.778$ nm, which agrees well with the JCPDS data. The peak positions in Fig. 2B are the same as those of Fig. 2A which confirms the compound formation rather than alloying. Also, the absence of any peak at 38° authenticates that no free silver is present in the system and the extra silver atoms anchor the particle surface due to preferential coalition.¹¹

The as-prepared copper selenide was amorphous in nature and heated on a water bath for 1 h and then centrifuged and mounted over a glass slide for XRD analysis (ESI 3).[†] The average crystalline size was calculated from the Debye–Scherrer equation to be 13 nm. The peaks at 43.9 and 39.6° corresponds to the (100) and (090) planes of the Cu_2Se particles.

The transmission electron micrographs of neat silver (10 ± 2 nm) and selenium (60 ± 5 nm) nanoparticles are presented in ESI 4.[†] The TEM images of the Ag_2Se (2 : 1) and Ag_2Se (3 : 1) are shown in Fig. 3A and B respectively.

The size of the as-prepared particles are calculated as ~ 7 nm for Ag_2Se (2 : 1) and ~ 30 nm for Ag_2Se (3 : 1). The TEM of the particles shows that the size increases from 7 nm to 30 nm with the increase in silver concentration above the stoichiometric ratio. Due to the very high sensitivity of the compounds towards the electron beam we could not notice clear images for Ag_2Se (2 : 1).¹⁸ AFM imaging for the Ag_2Se (2 : 1) particles corroborated that the size of the particles are ~ 7 nm (Fig. 4A) as was obtained from TEM. Clear lattice planes were visible from the high resolution TEM image (Fig. 4B) indicating good crystallinity of the particles.

However, with higher silver concentration monodispersed spherical particles of Ag_2Se were observed due to the adsorption of excess silver atoms on the surface of Ag_2Se particles as has been seen in the HRTEM (ESI 5).[†] The HRTEM image shows the attached planes of two different entities are in the closest

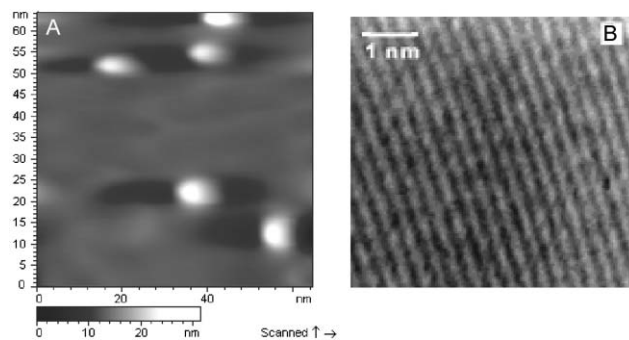


Fig. 4 (A) AFM and (B) HRTEM images of Ag_2Se (2 : 1) nanoparticles.

proximity. Analysis of the interplanar spacing again authenticates this fact. This confirms the affinity of silver nanoparticles to Ag_2Se . The HRTEM shown in Fig. 4B demonstrates that Ag_2Se are single crystalline in nature. The fringe spacing (0.28 nm) observed in this image agrees well with the separation between (102) lattice planes. The XRD and HRTEM data help us to conclude that the particles are single crystalline with orthorhombic crystal structure.

The diffusion process was studied earlier by McHardy and colleagues.¹⁹ They observed the diffusion of copper and silver metal at room temperature when those are in contact with amorphous germanium chalcogenides whether, the metals were vacuum deposited or deposited from silver nitrate solution. Also the silicon carbide was produced at room temperature by diffusion of carbon atoms into silicon particles.²⁰ Kaito *et al.* reported the diffusion of selenium particles into antimony film to form the Sb_2Se_3 .⁹ The chalcogenide formation has been studied in great detail taking bulk metal into consideration, but the situation is completely different when it comes to the nanostate. Parkin *et al.* reported the size effect on the rate of the reaction, with powders reacting faster than discrete pieces.⁸ In the present experiment, it is seen that the particle formation takes place only when the particles are in nanometer regime whereas no such reaction occurs for bulk metals. When the particle size decreases, the surfaces become active and surface reaction processes occur. Both the silver and selenium particles are dispersed in water as they are charged stabilized. Here, presumably smaller silver (~ 10 nm) particles diffuse into the selenium (~ 60 nm) particles owing to the smaller size of silver under dispersion. This diffusion is observed in the solution phase where the clusters exhibit Brownian motion. The coalescence release heat and the clusters get extra activation for diffusion. Hence, the particles diffuse due to sufficient energy available at the interface. When the silver particles diffuse into the selenium particles the silver plasmon peak disappears gradually. Due to the diffusion of silver nanoparticles the free motion of the electrons in the conduction band becomes restricted as a consequence of bond formation with selenium atoms. Therefore, the surface plasmon absorption of silver nanoparticles gradually vanishes. Again, the diffusivity scales inversely with the contact area of the surface.²¹ Thus, the diffusion of silver takes place up to a certain size limit after which the silver particles are precipitated. Under such a situation mixing the particles (silver and selenium) at room temperature or heating (~ 70 °C) the mixture results in no product being formed. However, we have not been able to obtain silver chalcogenides from the coreduction of AgNO_3 and H_2SeO_3 with NaBH_4 , instead we observe the selective silver surface plasmon band only due to reduction of AgNO_3 solution. Again, Ag_2Se was obtained even if the constituent particles, prepared by other reducing agents, are admixed together in solution. Interestingly when the same experiment was carried out taking gold nanoparticles into consideration the plasmon peak never vanished completely (ESI 6).[†] Also, separate peaks for gold and selenium in XRD analysis show there is no product formation due to the nobility of gold.

Heating the reaction mixture on a water bath at ~ 70 °C results in the disappearance of a silver plasmon peak in half an hour (ESI 7).[†] This amount of heat is sufficient to cross the activation barrier of the reaction and the product formation increases with

temperature. The diffusivity of the clusters depends on the temperature, T which follows Arrhenius behaviour:²²

$$D(T) = D_{00}\exp(-\varepsilon_d/kT) \quad (2)$$

where, ε_d is the effective activation energy of the process, k is the Boltzmann constant and D_{00} is a prefactor independent of size and temperature. So, with increase in temperature the diffusion is facilitated and product formation takes place within a few minutes.

The silver and copper selenide nanoparticles have been prepared by contact reaction of the constituent nanoparticles in solution phase. The silver and copper nanoparticles diffuse to form the compound whereas the gold nanoparticles could not diffuse at room temperature due to the high activation energy of diffusion. The method is simple and straightforward compared to other methods and substantiates the preparation of other metal chalcogenides. The material is supposed to have very useful magnetic, electrical and thermal properties because of the absence of trace carbon impurity on the surface of the nanoparticles that might alter the magnetic resistance of the particles.

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