

Solution phase evolution of AuSe nanoalloys in Triton X-100 under UV-photoactivation†

Sudip Nath, Sujit Kumar Ghosh and Tarasankar Pal*

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India.

E-mail: tpal@chem.iitkgp.ernet.in

Received (in Cambridge, UK) 31st October 2003, Accepted 26th February 2004

First published as an Advance Article on the web 16th March 2004

A solution phase UV-irradiation technique has been exploited to produce an AuSe nanoalloy through fusion of preformed Au (photoproduced) and Se (chemically prepared) in a micellar (TX-100) medium.

In recent years, multicomponent nanoalloys have been the subject of increased scientific interest because of their outstanding electronic, optical and catalytic properties which are strikingly different from either of the parent constituents.¹ The combination of two kinds of constituents results in the evolution of fine structures and has given birth to new physicochemical properties.

It is now well known that among the semiconductors, selenium is an important element in view of its various applications, especially for its photoelectrical and semiconducting properties.² A high reactivity of Se towards a wealth of chemicals has stimulated researchers to convert selenium into functional materials such as ZnSe and CdSe.³ In the case of metallic nanoparticles gold is the most important one to study. Gold particles have been found to be particularly useful for cell labelling in biology and formation of a modified surface for surface enhanced Raman scattering.

During the last few decades, a variety of synthetic strategies⁴ have been described in the literature for the preparation of gold nanoparticles whereas very few synthetic approaches⁵ have been adopted to design nanoscale selenium particles. In this communication, we have elegantly demonstrated a solution phase approach to fuse gold and selenium nanoparticles in a micellar environment to prepare AuSe nanoalloys through UV-photoactivation. To the best of our knowledge, there exists no other report of AuSe alloying in solution through UV-activation.

Gold nanoparticles were prepared photochemically by the reduction of aqueous Au(III) ions in Triton X-100 (polyoxyethylene isooctylphenyl ether, TX-100, Aldrich) surfactant. On the other hand, selenium has been prepared chemically by the reduction of aqueous Se(IV) solution with NaBH₄ using TX-100 as the stabilizing agent. In a typical set, an aliquot of HAuCl₄ (0.33 mM, Aldrich) was taken in 3 mL of TX-100 solution (10 mM) and photoirradiated for 30 min under UV-light of 340 lux to obtain small (~5 nm) spherical particles (ESI 1†). Absorbance measurement of the resultant pink solution showed a λ_{max} at 521 nm indicating the formation of a gold hydrosol (ESI 2). For the preparation of selenium nanoparticles, selenious acid (0.33 mM, Merck) was treated with freshly prepared NaBH₄ (2.7 mL, 10 mM, Aldrich) and shaken continuously. The colorless solution changes to brick red during the first 15 min of reaction indicating the formation of amorphous (*a*-) Se existing in the form of spherical (~25 nm) colloids⁶ (ESI 3). The TX-100 was added within this period and the stabilized Se nanoparticles were freed from NaBH₄ by keeping the solution overnight on a water bath.

Now, preformed Au and Se particles in TX-100 were mixed together in different ratios (v/v) in a 1 cm quartz cuvette. Irradiation of the solution for 1 h under UV-light (340 lux, 365 nm) resulted in the formation of AuSe nanoalloys in solution. Prolonged irradiation of the solution (~3 h) with a higher flux of UV-light (840 lux)

facilitates agglomeration of AuSe nanoalloys and renders the isolation of solid AuSe particles⁷ (ESI 4). By varying the proportion of the constituents in the mixture, the composition of the AuSe alloy particles becomes tunable. It is important to mention that the evolution of nanoalloy does not take place if chemically prepared Au and Se particles are taken in an aqueous solution for UV-irradiation devoid of TX-100. The co-reduction of HAuCl₄ and H₂SeO₃ either by chemical or photochemical means also fails to produce any AuSe nanoalloy. Therefore, it is reasonable to assume that in the present study, the nonionic surfactant, TX-100 plays a triple role. It helps in the photoevolution of gold nanoparticles by acting as a reducing agent,⁸ imparts stability to the gold and selenium particles preventing possible agglomeration through the capping action, and in addition, promotes the fusion of constituent gold and selenium particles to form AuSe nanoalloys.

Fig. 1 presents the UV-visible spectra of selenium and gold nanoparticles, the spectrum of their physical mixture (*i.e.*, a gold-selenium mixture) and gold-selenium nanoalloys. From the spectra, it is clearly evident that the nanoalloy traces a distinctly different spectral profile from the physical mixture of the constituents and obviously from the individuals (ESI 5). To substantiate the formation of nanoalloys, a fluorescence study (ESI 6) and typical complexation reaction with sodium cyanide have been carried out. The solutions become colorless (representative spectra vanished) within a few minutes when gold or selenium particles are shaken separately in the presence of NaCN solution under ambient conditions. The generation of a colorless solution in both cases signifies the formation of [Au(CN)₄]⁻ and [SeCN]⁻ ions respectively.^{9,10} Similar observations were noted for the gold-selenium mixture but under the same conditions the nanoalloy typically resisted cyanide attack (no dissolution) and the peak due to the alloy particles remains unaltered on long standing (~5 days). These observations confirm the formation of a stable Au-Se alloy.

It is well documented that the peak position of the surface plasmon absorption due to gold nanoparticles in the nanoalloy is composition dependent.¹¹ The characteristic UV-visible band of gold in the nanoalloy becomes affected by changing the gold mole fraction in the alloy as compared to only gold. In the present case, the absorption maximum varies with the composition of AuSe alloy nanoparticles (ESI 7). Thus the maximum of plasmon absorption (~610 nm) can provide some indication of the evolution of AuSe alloys with tunable composition for optical applications.

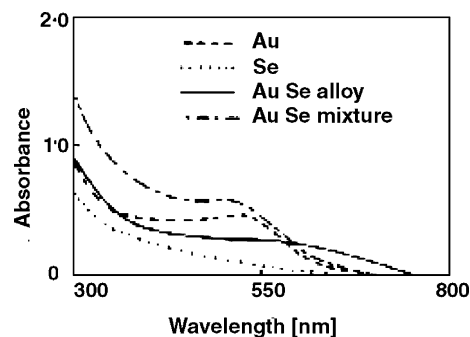


Fig. 1 UV-visible spectra of the samples.

† Electronic supplementary information (ESI) available: experimental procedure, TEM, UV-vis spectra, EDX data and brief explanation. See <http://www.rsc.org/suppdata/cc/b3/b313848h/>

AFM imaging (Fig. 2) was done for visualization of the alloy particles dispersed in the surfactant phase (ESI 8). The size of the alloy is found to be $\sim 30 \pm 4$ nm. The AFM image again corroborated the size of the particles ($\sim 30 \pm 6$ nm) as was obtained from TEM (ESI 9) analysis.

In Fig. 3 an SEM image of the nanoalloys is shown. The average composition of the AuSe alloys (deposited on carbon disks) was determined from EDX analysis attached with the instrument. The data analysis reveals that the alloy has almost same composition as expected from their preparatory composition (EDX data are presented in Table in ESI 10).

The XPS (Fig. 4) of the nanoalloy shows a band at 54.2 eV, which could be attributed to the peak due to resultant interaction of Au5p with the Se3d orbital. It is to be noted that for selenium the intense band is obtained at 57.6 eV due to Se3d orbital. For gold, the intense bands appear at 84.3 and 87.9 eV corresponding to $4f_{7/2}$ and $4f_{5/2}$ orbitals whereas a comparatively less intense band (54.0 eV)

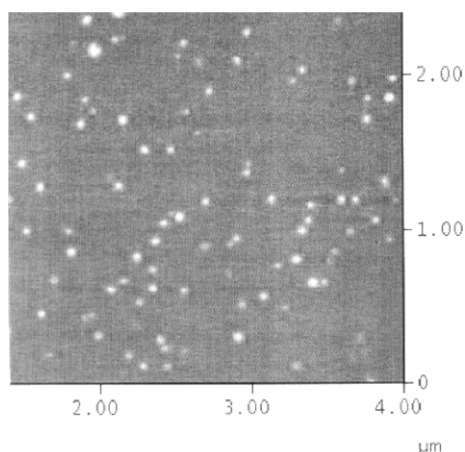


Fig. 2 AFM image of the AuSe alloy.

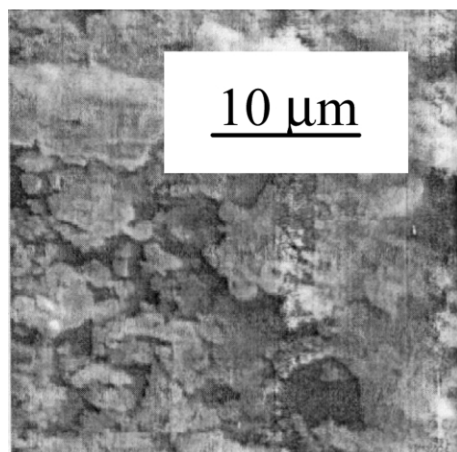


Fig. 3 SEM image of the solid phase AuSe alloy.

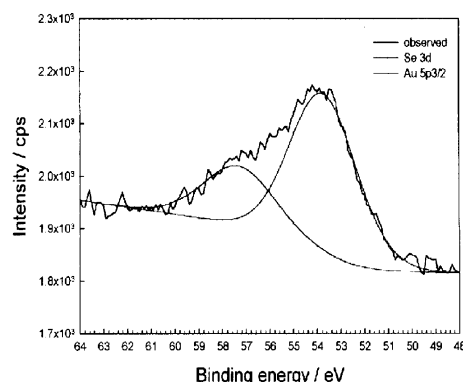


Fig. 4 XPS of the solid AuSe alloy.

is observed for the $5p_{3/2}$ orbital. Although the band due to Au5p is less intense with respect to the Au4f bands, a strong interaction of the Au5p with the Se3d orbital results from the formation of nanoalloy.

In conclusion, we have developed a UV-irradiation technique for the synthesis of AuSe nanoalloys and the particles have been characterized by several physical and chemical means. The method is simple to adopt, devoid of any hazardous chemicals and less time consuming. Synthesis of such multicomponent nanoalloys is of academic interest to find the nature of the interaction between the gold and selenium in the alloy from a theoretical perspective. These particles offer great scope for experimentation in the future to find how the photoelectrical, semiconducting and catalytic properties of Se are altered as a result of functionalization with a coinage metal. Moreover, the micelle-mediated fusion of two different nano-materials by UV-irradiation is the first example of its kind and it is determined that in a properly chosen environment interparticle fusion can be made possible for the preparation of exotic nanoalloys.

We sincerely thank CSIR and DST, New Delhi for financial assistance.

Notes and references

- 1 Y.-H. Chen and C.-S. Yeh, *Chem. Commun.*, 2001, 371.
- 2 B. Gates, Y. Yin and Y. Xia, *J. Am. Chem. Soc.*, 2000, **122**, 12582.
- 3 E. Best, I. Hinz and H. Wendt, in *Gmelin Handbook of Inorganic Chemistry (Gmelin Handbuch der Anorganischen Chemie)*, ed. H. Karl Kugler, Springer-Verlag, Berlin, 1979, **Vol. 10**, pp 168–180.
- 4 M. Yamada, A. Kuzume, M. Kurihara, K. Kubo and H. Nishihara, *Chem. Commun.*, 2001, **23**, 2476.
- 5 X. Gao, T. Gao and L. Zhang, *J. Mater. Chem.*, 2003, **13**, 6.
- 6 A. Watillon and J. Dauchot, *J. Colloid Interface Sci.*, 1967, **27**, 507.
- 7 M. Quinn and G. Mills, *J. Phys. Chem.*, 1994, **98**, 9840.
- 8 A. Pal, *Talanta*, 1998, **46**, 583.
- 9 R. J. Puddephatt, *The Chemistry of Gold*, Elsevier Scientific Publishing Company, New York, 1978, p. 37.
- 10 R. A. Zingaro and W. Charles. Cooper, *Selenium*, Van Nostrand Reinhold Company, New York, 1974, p. 342.
- 11 (a) M. Treguer, C. de Cointet, H. Remita, J. Khatouri, M. Mostfavi, J. Amblard, J. Belloni and R. de Keyser, *J. Phys. Chem. B*, 1998, **102**, 4310; (b) S. Link, Z. L. Wang and M. A. El-Sayed, *J. Phys. Chem. B*, 1999, **103**, 3529.