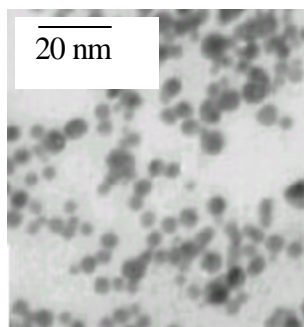


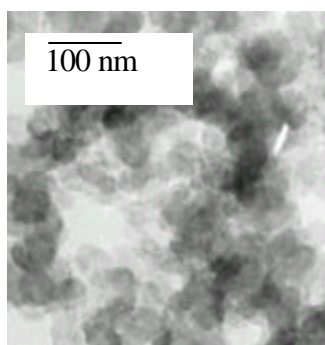
Electronic Supplementary Information



ESI 1: TEM image of photo-produced TX-100 stabilized Au(0)

ESI 2: Photoirradiation of H_{Au}Cl₄ in TX-100

Surfactant (TX-100) mediated UV-photoirradiation of H_{Au}Cl₄ produces Au nanoparticles under ambient temperature. Irradiation of H_{Au}Cl₄ solution for ~10 min is sufficient to reduce Au(III) ions under the prescribed concentration range and experimental condition. Longer irradiation (~30 min) evolved nanoparticles of Au with tight size distribution as a result of interparticle charge distribution (P. V. Kamat, M. Flumiani and G. V. Hartland, *J. Phys. Chem. B*, 1998, **102**, 3123).



ESI 3: TEM image of chemically prepared Se(0)

ESI 4: Preparation of solid phase AuSe nanoalloy

Solution phase gold-selenium nanoalloys was prepared irradiating the mixture of preformed TX-100 stabilized Au and Se nanoparticles. Upon prolong irradiation (with higher flux ~840 Lux, 1 Lux means 1 lumen flux of photon per sq. cm per sec)* the particles become agglomerated and settled down at the bottom of the cuvette. Then the surfactant mediated solid AuSe nanoalloy was washed several times with water to remove the surfactants. Finally the solid particles were washed with rectified spirit and dried under vacuum.

*The flux was monitored using a digital Lux meter (Model LX 101), Taiwan. The light intensity inside the photo-reactor was calibrated with an Ophir Power Meter (NOVA display and 30-A-SH sensor). Number of photons adsorbed by unit volume of the dye per second from the photoreactor of 100 Lux is 3.03×10^{15} .

ESI 5: Alloy formation

Alloying of nanoparticles sometimes can be best authenticated from the UV-visible spectra of the evolved alloys (while remain dispersed in a medium). If the constituting nanoparticles have maximum absorptions (λ_{\max}) in the UV-vis region then the evolved alloy particles generally shows λ_{\max} in between (K. Kim et al. *Chem. Commun.*, 2001, **1782** and T. Pal et al. *Nano Lett.*, 2001, **1**, 319). Confirmation of alloy formation from the spectra becomes difficult while one of the constituents does not show any peak in the UV-visible region. Under such circumstances (as it is the present case) the spectrum for the alloys are seen to trace a new spectral profile. The AuSe nanoalloys have a much smaller peak area than the physical mixture of the Au and Se nanoparticle dispersion at the same ratio (N. Toshima and T. Yonezawa, *New J. Chem.*, 1998, 1179). The full proof authentication of AuSe alloy formation comes from chemical reactivity differences and then again from TEM, SEM, XPS etc. studies.

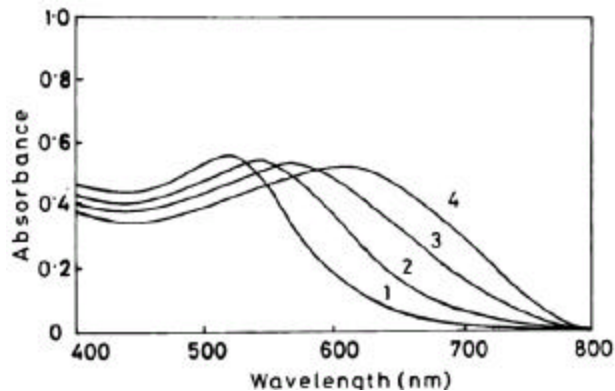
The red shift in the plasmon absorbance band of gold in the alloy is not due to the agglomeration of gold particle in presence of selenium. This can be explained by the

difference in the spectral profile of the physical mixture with respect to the alloy at same experimental time.

The confusion of alloy or core-shell structure was clarified by cyanide effect. If the particles would have core-shell structure instead of alloy then cyanide will cause the dissolution of shell component at first and consequently the peak due to core component will appear. But the persistence of color as well as peak position in cyanide environment clearly evidences the formation of extremely stable nanoalloys.

ESI 6: Fluorescence study

A direct evidence of AuSe nanoalloy formation emerged out from the alloy induced change in the emission profile of a probe molecule, eosin ($\lambda_{em} \sim 551$ nm). The nanoalloy of varying composition shifted the emission peak of eosin to the red (λ_{em} 553-560 nm) region. In contrary a blue shift (λ_{em} 543-548 nm) for the probe was observed for the Au and Se mixture (unexposed) having the same composition as was employed for the alloy.

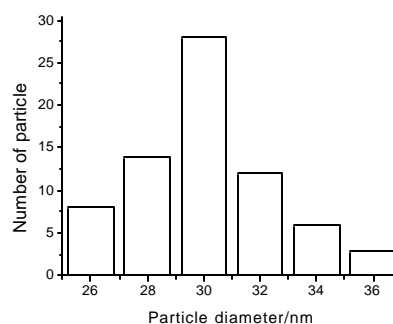
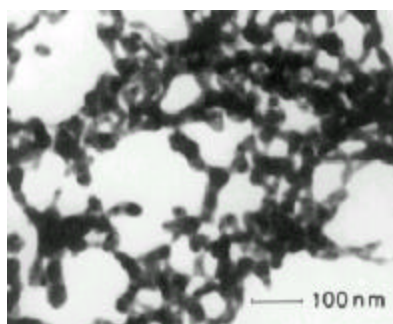


ESI 7: UV-visible spectra of AuSe alloy

Condition: Au:Se= (1)100:0, (2) 60:40, (3) 70:30, (4) 80:20.

ESI 8: Atomic Force Microscopy

The tapping mode technique (M. Quinta, E. Haro-Poniatowski, J. Orales and N. Batina, *Appl. Surf. Sci.*, 2002, **195**, 175) was employed to image the particles under ordinary laboratory condition. In this mode, the AFM tip is oscillating near its resonance frequency and only touches the sample periodically. This enables minimum sample damaging and provides better images for the sensitive ‘soft’ samples as in case of AuSe alloy. All images were recorded at a very slow scan rate to avoid sample damaging. Due to this precaution, no impact on the image was observed. Images were recorded in light, amplitude and phase modes simultaneously.



ESI 9: TEM image and diameter histogram of the AuSe nanoalloys

The TEM images of the nanoparticles (Au, Se, AuSe) was done in a Hitachi H-9000 NAR Instrument at a magnification of 100k. The sample was prepared by placing a drop of solution on a carbon coated copper grid.

ESI 10: Elemental ratio of AuSe nanoalloys from EDX analysis

Feeding mixture Au/Se (v/v)	Elemental ratio (Au/Se) of each particle				
	1	2	3	4	average
80:20	81.4:18.6	77.6:22.4	86.3:13.7	79.8:20.2	81.3:18.7
70:30	75.6:24.4	71.3:28.7	69.4:30.6	73.2:26.8	72.4:27.6
60:40	59.6:40.4	57.9:42.1	63.2:36.8	56.2:43.8	59.2:40.8