Size quantized formation and self-assembly of gold encased silver nanoparticles†

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Mixing aqueous dispersions of thiocyanate ion coated small (< 3.5 nm diameter) gold nanoparticles and EDTA covered larger (> 22 nm diameter) silver nanoparticles, results in the formation of robust gold encased silver nanoparticles; in contrast to using larger (> 11 nm diameter) gold nanoparticles which forms chained structures.[1]

Ligand shell coated metallic nanoparticles (often referred to as Monolayer Protected Clusters, MPCs) have been shown to behave like large molecules.[1–6] The present communication reports the first observation of a size quantized reactivity of MPCs resulting in the formation of gold encased silver nanoparticles which could be transferred from water to ethanol without any structural alteration and could be attached to a glass slide, *via* an aminobutyldimethylmethoxysilane linkage.

Five differently sized gold (2.8 ± 0.8, 3.5 ± 0.7, 11.6 ± 0.8, 17.9 ± 2.4 and 44.7 ± 7 nm) and two differently sized silver (22.8 ± 5.8 and 37.8 ± 9.0 nm) nanoparticles were prepared (details of the preparations and characterizations[7,8] are provided in the ESI†). The absorption spectra of the citrate ion coated 3.5 ± 0.7 nm diameter gold and the EDTA coated 22.8 ± 5.8 nm diameter silver nanoparticles in aqueous dispersions showed the characteristic surface plasmon absorption bands at 512 and 406 nm, respectively (Fig. 1). Mixing equal volumes of these gold and silver dispersions resulted in an absorption spectrum with two distinct maxima, but addition of aqueous NaSCN to this mixture, followed by incubation for 30 h produced a single surface plasmon band, centered at 506 nm (Fig. 1). An identical single 506 nm absorption band was also produced by mixing thiocyanate ion coated 3.5 ± 0.7 nm gold nanoparticles and EDTA coated 22.8 ± 5.8 nm silver nanoparticles and allowing them to stand for 30 h.
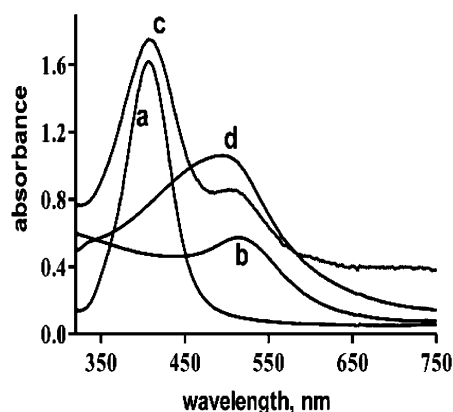
The absorption spectrum of the thiocyanate ion coated 2.8 ± 0.8 nm gold nanoparticles showed no surface plasmon absorption band (see ESI†) as expected for clusters containing fewer than 200 atoms.[9] Mixing of 1.0 mL 2.5 × 10⁻⁴ M of aqueous thiocyanate ion coated 2.8 ± 0.8 nm diameter gold and 1.0 mL aqueous 2.6 × 10⁻⁴ M nm diameter EDTA covered 22.8 ± 5.8 nm diameter silver nanoparticle dispersions resulted in a behavior similar to that shown in Fig. 1. The silver surface plasmon band (at 406 nm) gradually decreased and a new band appeared which shifted to longer wavelengths until it reached an equilibrium value at 620 nm (Fig. 2). The time dependence of this transformation was found to be relatively slow, equilibrium, typically, being reached 24 h subsequent to the mixing of the nanoparticle dispersions (Fig. 2). Decrease of the absorption intensity at 406 nm was much faster than the rate of appearance of the new band at 620 nm (insert in Fig. 2). This kinetic behavior indicates a complex transformation. An essentially identical behavior was observed on mixing aqueous thiocyanate ion coated 2.5 × 10⁻⁴ M, 2.8 ± 0.8 nm diameter gold and 1.3 × 10⁻⁴ M, 37.8 ± 9.0 nm diameter EDTA covered silver nanoparticle dispersions (see ESI†).

It should be noted that the position of the new absorption band, observed in the interaction of aqueous thiocyanate ion coated 2.8 ± 0.8 nm diameter gold nanoparticles and 37.8 ± 9.0 nm diameter EDTA covered silver nanoparticles (620 nm), is at a far longer wavelength than that previously reported for composite Ag/Au nanoparticles. In general, absorption bands of alloys fall between the maxima of their constituent silver and gold surface plasmon absorption bands and core–shell structures manifest themselves in two distinct bands.[10,11] Morphologies and absorption spectra of composite Ag/Au nanoparticles were, however, found to depend on the deposited metal atoms/surface ratio in a less than straight forward manner.[7] Indeed, Ag₉₃/Au₇ composite clusters had their surface plasmon band centered at 554 nm, compared to those observed for the

Fig. 1 Absorption spectra of aqueous dispersions of aqueous EDTA coated 22.8 ± 5.8 nm silver (a) and citrate ion coated 3.5 ± 0.7 nm diameter gold (b) nanoparticles. Curve (c) is the absorption spectrum of a 1:1 (v/v) mixture of (a) and (b). This spectrum does not change for days. The absorption spectrum shown in (d) was taken following the addition of 0.2 mL of 6.0 × 10⁻³ M aqueous NaSCN to (c) and incubation for 30 h.
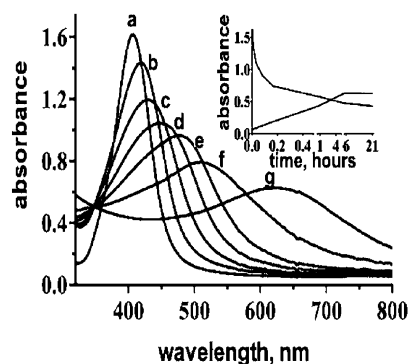

Fig. 2 Absorption spectra of a 1:1 mixture of 1.3 × 10⁻⁴ M, 22.8 ± 5.8 nm diameter EDTA protected silver nanoparticle and 2.6 × 10⁻⁴ M thiocyanate-ion protected 2.8 ± 0.8 nm diameter gold nanoparticle dispersions, taken at 0.5 (b), 2 (c), 5 (d), 10 (e), 30 (f) min and 21 h (g) subsequent to mixing; (a) = absorption spectrum of 1.3 × 10⁻⁴ M, 22.8 ± 5.8 nm diameter EDTA protected silver nanoparticle dispersions in water. The insert shows the time dependent changes of the absorbances at 406 and 620 nm. All concentrations are expressed in terms of the metal ions.
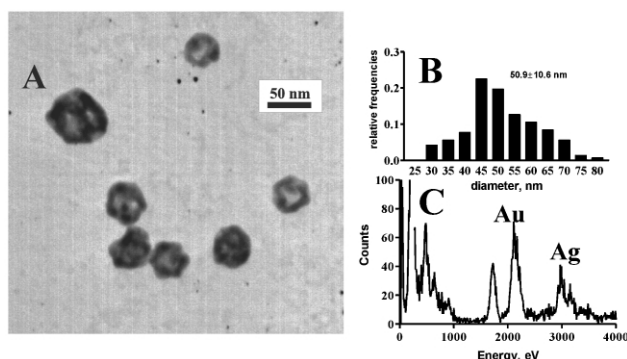
† Electronic supplementary information (ESI) available: experimental details; Figs. S1–S6 and Graphical Abstract. See: http://www.rsc.org/suppdata/cc/b1/b108163b/

Fig. 3 A typical transmission electron microscopic image (A), size distribution (B) and EDX analysis (C) of the gold decorated silver nanoparticles formed.

Fig. 4 Schematics illustrating the proposed interactions of thiocyanate ion coated 2.8 ± 0.8 and 11.9 ± 0.8 nm diameter gold nanoparticles with 37.8 ± 9.0 nm diameter EDTA covered silver nanoparticles.

constituting silver and gold nanoparticles at 420 and 520 nm, respectively.[12]

In contrast to the observed appearance of a new absorption band in the interactions of 2.8 ± 0.8 and 3.0 ± 0.6 nm diameter thiocyanate ion coated gold nanoparticles with larger EDTA covered silver particles (Figs. 1 and 2), mixing aqueous thiocyanate ion coated larger (11.6 ± 0.8, 17.9 ± 2.4 or 44.7 ± 7.0 nm) diameter gold nanoparticle dispersions with aqueous 22.8 ± 5.8 nm (or 37.8 ± 9.0 nm) diameter EDTA covered silver nanoparticle dispersions, in any proportion, lead to absorption spectra in which the individual surface plasmon absorption bands of the gold and silver nanoparticles had been retained (even weeks after their mixing), albeit with altered maxima (see ESI†).

Transmission electron microscopic images of mixtures of thiocyanate ion coated *small* gold nanoparticles and EDTA coated larger silver nanoparticles (24 h subsequent to mixing) showed the presence of gold encased silver nanoparticles and some unattached small gold nanoparticles. Centrifugation (10 000 rpm, 1 h), careful decantation of the supernatant and subsequent redispersion of the residue in water (or in ethanol) resulted in TEM images in which there were essentially no small unattached gold nanoparticles. A typical TEM image (Fig. 3A) of this redispersed gold encased silver nanoparticles showed the presence of only composite aggregated particles each of which had distinct darker outer and lighter inner regions. The lighter inner and the darker outer regions in the TEM images are due to silver and gold since the latter scatters the electrons more efficiently than silver. From image analysis the diameter of the gold encased silver nanoparticles was calculated to be 50.9 ± 10.6 nm (Fig. 3B). This value is some 13 nm bigger than that determined for the parent silver nanoparticles (37.8 ± 9.0 nm diameter) indicating a substantial, and possibly occasional multilayer, coverage by the gold nanoparticles. The presence of both gold and silver in a given cluster is also substantiated by EDX (Fig. 3C). In typical samples we observed 46 and 54% silver and gold atoms (with 2.6% standard deviation). Assuming a perfect core–shell structure of 37.8 nm diameter silver core and 13.1 nm diameter gold shell we calculate the volumes of the core and the shell to be 41.4 and 58.6%, respectively. The *ca.* 5% discrepancy between the EDX values and the volume calculations is not unreasonable considering the imperfections of the gold shell as evidenced by the TEM.

In contrast, TEM images obtained from mixtures of thiocyanate ion coated gold nanoparticles with diameters larger than 11 nm and EDTA coated silver nanoparticles showed the presence of chain structures (see ESI†).

Significantly, the gold encased silver nanoparticle dispersions had long term stabilities (unchanged absorption spectrum and TEM images for months if stored in the dark), could be isolated as solids and redispersed in water or in ethanol without any structural alterations. Gold encased silver nanoparticles could also be self-assembled onto aminobutyldimethylmethox-
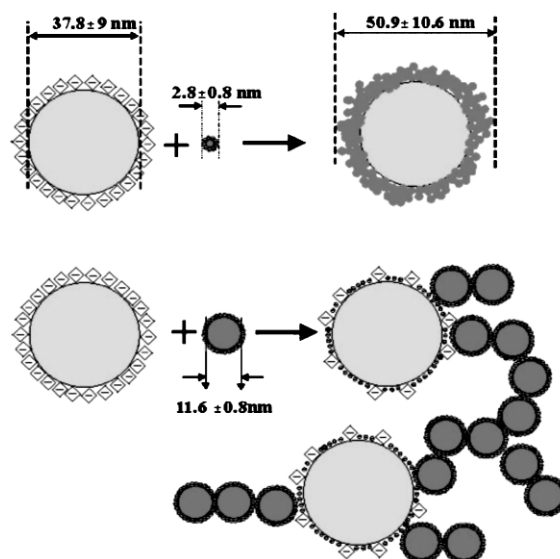
ysilane coated glass slides (see ESI† for details). Absorption spectrum of the self-assembled gold decorated silver nano-particles resembled closely to their counterparts in aqueous dispersions and to that obtained for sequential self-assembly (*i.e.*, EDTA coated silver nanoparticles were self-assembled and then thiocyanate ion coated gold nanoparticles were self-assembled onto the silver nanoparticles, see ESI† for details).

Size quantized interactions of gold nanoparticles with silver nanoparticles is the most significant finding of the present report. Being a stronger nucleophile, the thiocyanate ion replaces EDTA from the surface of metallic nanoparticles. Extremely small gold nanoparticles attract thiocyanate ions so strongly that they are being carried with their protective shells to replace EDTA from the silver nanoparticles. This results in the formation of robust gold encased silver nanoparticles (Fig. 4). In contrast, the larger gold nanoparticles release some (if not all) of their thiocyanate ion shells which replaces EDTA on the silver nanoparticles and leave the two metallic nanoparticles distinct which undergo chain formation (Fig. 4 and ESI†).

Notes and references

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