

Light-induced flocculation of gold nanoparticles†

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Gold particles have been formed in water-in-oil microemulsions doped with a photodestructible surfactant. UV light-induced nanoparticle flocculation has been achieved after photolysis of the photosurfactant, leading to a reduction in the steric stabilization provided by the surfactant layer.

Here it is shown that UV light can be used to destabilize gold nanoparticles, eventually leading to colloidal instability and phase separation. The Au nanoparticles have been synthesized in an organic solvent, and stabilized by a mixed adsorbed layer comprising an inert non-ionic hexaethylene glycol monododecyl ether (C₁₂E₆) and a photolyzable anionic surfactant hexylphenyl-azosulfonate (C6PAS). Incident UV irradiation induces a selective breakdown of the photoactive C6PAS, leading to a reduction in the colloid stability and flocculation of the Au nanoparticles. UV-Vis spectroscopy has been used to characterize the formation of gold particles and photochemical breakdown of C6PAS; additionally, transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDXA) have been used to characterize size, shape and composition of Au particles before and after exposure to UV light.

Reverse micelles present flexible and robust reaction media for synthesis of inorganic nanoparticles^{e.g.} ¹. In the general case recovery of nanoparticles from the liquor, and separation from any un-reacted reagents and/or background micelles still presents a significant challenge. Typical approaches employed are energy intensive ultracentrifugation,² solvent evaporation³ and temperature induced phase separation as well as addition of anti-solvents.⁴ Recent work⁵ has demonstrated recovery of silver nanoparticles in reverse micelles of AOT/C₁₂E₄ by addition of anti-solvent CO₂. An advantage of this method is that surfactant remains in the continuous phase. The use of polymer-modified reverse micelles⁶ has been shown to be beneficial for recovery of nanoparticles as it prevents any change in particle dimensions upon extraction. Temperature induced nanoparticle recovery has also been achieved.⁷ There are numerous scientific and commercial applications of surfactant-stabilized inorganic nanoparticles,^{e.g.} ^{7,8} hence it is of interest to explore novel approaches to separation and recovery of these products.

Photodestructible surfactants like C6PAS were first introduced by Sherrington *et al.*,⁹ and properties and applications of photo-surfactants in colloidal systems have recently been reviewed.¹⁰ The photolabile surfactant C6PAS has been previously used to recover hydrophobic additives from aqueous micelle solutions,¹¹ and the

concept of photo-destabilized microemulsions has been also employed to induced phase separation.¹² These changes in dispersion stability occur owing to UV-induced breakdown of the hydrophilic C6PAS into insoluble hydrophobic photoproducts (hexylbenzene and 4-hexylphenol). The final composition depends on various factors, including solvent environment and C6PAS concentration; this photochemistry is detailed in Supporting Information.

Surfactant-stabilized gold particles were prepared by reduction of auric potassium tetrachloride (KAuCl₄) with sodium borohydride (NaBH₄), in mixed reversed micelles formed with photo-sensitive C6PAS and inert nonionic C₁₂E₆ in isooctane solvent. Microemulsions were prepared by adding aliquots of aqueous phases to the surfactant–solvent mixture to give the desired water content ($w = [\text{water}]/[\text{surfactant}]$). Separate microemulsions containing aqueous KAuCl₄ solutions, and NaBH₄ were made up. To form Au nanoparticles the reductant-containing microemulsion was added drop-wise to a system containing KAuCl₄; these samples were stable over a period of months in the dark.

Different microemulsions at various Au concentrations and water contents (w) were investigated (Supporting Information†). The C6PAS mole ratio, defined by $X_{\text{C6PAS}}(\%) = 100\{[\text{C6PAS}]/([\text{C}_{12}\text{E}_6] + [\text{C6PAS}])\}$ was varied to achieve an optimized flocculation. Stable gold microemulsions were formed with $w = 8$, total surfactant concentration = 0.3 M and $X_{\text{C6PAS}}(\%) = 10$. This system resulted in a strong Au particle flocculation after UV irradiation in quartz cells with a 100 W high-pressure unfiltered white source at 25 °C for 130 minutes. (Supporting Information†). Before irradiation samples appeared as a uniform green-colored microemulsion. After UV irradiation a catastrophic phase separation was observed, leading to a dense population of black flocculate clusters (Fig. 1). If these post-irradiated samples were shaken, the particles appeared to re-disperse, but eventually separated again after standing for 3 h.

UV-Vis spectra (Fig. 2) showed the disappearance of the C6PAS peak at $\lambda_{\text{max}} = 420$ nm, and the Au band $\lambda \sim 525$ nm after UV irradiation. The transparent supernatant post-irradiated solution phase did not show any characteristic C6PAS absorption due to complete photolysis of C6PAS and flocculation of gold nanoparticles

TEM was carried out (JEOL 1200EX operating at 120 kV) to image the nanoparticles and characterize particle size and shape. EDXA was employed to obtain a semi-quantitative elemental analysis of TEM images (Supporting Information†). Fig. 3 (a) shows that before irradiation the gold particle size was in the range 30–130 nm. The systems imaged after irradiation were the phase separated Au flocculate taken from the bottom of the cuvettes: sizing analyses were very difficult to carry out due to the multi-component nature of the system. The insoluble photoproducts of

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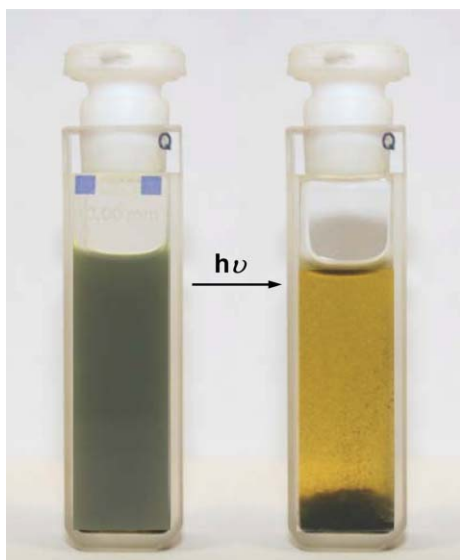


Fig. 1 Gold microemulsion with $X_{\text{C6PAS}}(\%) = 10$, [surfactants] = 0.3 M, $w = 8$ and [Au] = 0.08 M. Before (left) and after irradiation (right).

C6PAS decomposition formed large needle-like structures in the background of the TEM images, as seen before¹³ (Supporting Information, Fig. S8 (b)†). In the photo-induced flocculate gold particle shapes were irregular, suggesting changes in form compared to the initial systems, and the individual sizes were in the range 15–120 nm (Fig. 3 (b)). EDXA analyses (Supporting Information†) confirmed the formation of Au nanoparticles, and that no significant changes in elemental composition had occurred after UV irradiation.

A significant population of Au nanoparticles can be recovered by this novel photo-flocculation approach. However, full flocculation of Au nanoparticles is difficult to achieve, owing to the presence of inert C_{12}E_6 co-surfactant needed to stabilize the microemulsions. A limitation of this process is that after photolysis of C6PAS the Au particles can potentially be re-stabilized by the remaining C_{12}E_6 . Therefore, to effect photo-flocculation it is

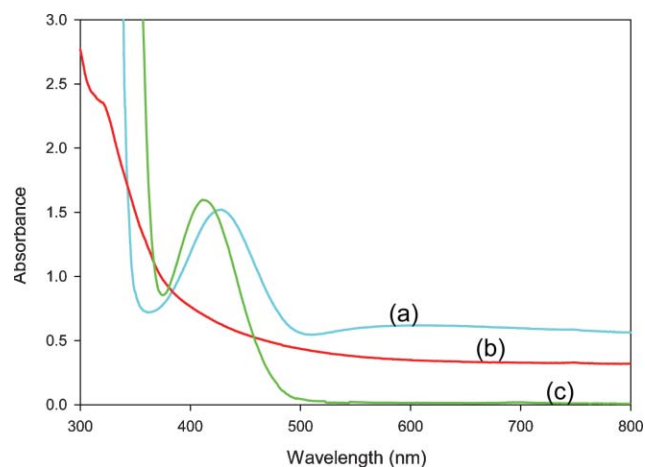


Fig. 2 UV-Vis spectra of [Au] = 0.08 M microemulsion, $X_{\text{C6PAS}}(\%) = 10$, [surfactants] = 0.3 M and $w = 8$ before (a, cyan) and after irradiation (b, red). Gold-free microemulsion containing the photosurfactant C6PAS before irradiation (c, green).

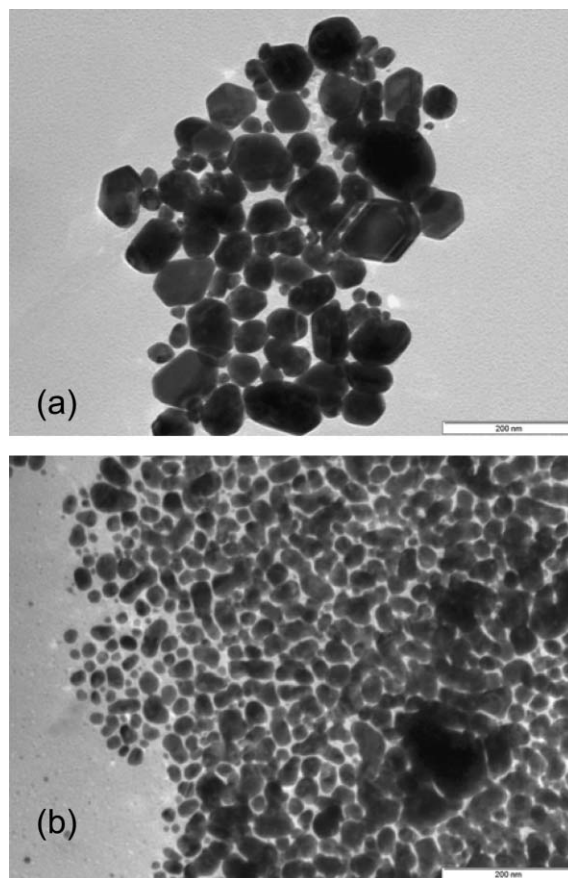


Fig. 3 TEM images for Au nanoparticles before (a) and after irradiation (b).

necessary to find the optimum ratio of photodestructible to inert surfactants to achieve sufficient reduction in the surface stabilization.

Stable Au nanoparticles have been synthesized in mixed reversed micelles of C6PAS/ C_{12}E_6 in isooctane. The use of UV light to induce destabilization of the microemulsion and flocculation of the particles provides an interesting, and potentially useful particle separation method. This approach may find future applications in solid-state chemistry, catalysis and biotechnology.

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