

Gold nanosheets *via* reduction of aqueous chloroaurate ions by anthracene anions bound to a liquid–liquid interface†

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Anthracene anions bound to a liquid–liquid interface and charged by photochemically reduced Keggin ions when exposed to aqueous chloroaurate ions result in the formation of high concentration of thin, gold nanosheets at the interface.

Gold nanoparticles find application in a variety of fields ranging from catalysis,¹ to electron microscopy markers² to DNA detection.³ It is of little surprise that a large number of experimental methods exist in the literature for the synthesis of spherical gold nanoparticles in water⁴ and in non-polar organic solvents.^{5,6} There is growing interest in the development of methodologies for the synthesis of gold nanoparticles of varying shapes such as nanorods^{7,8} and prisms⁹ motivated to a large extent by the unusual optical properties expected from nanoparticles with morphology anisotropy.¹⁰ An interesting possibility for introducing shape anisotropy in gold nanoparticles is to synthesize them in constrained environments such as those provided by Langmuir–Blodgett films¹¹ or at well-defined two dimensional interfaces. We have investigated the latter approach recently and have shown that gold nanosheets and nanoribbons can be grown at the air–water interface by the spontaneous reduction of subphase chloroaurate ions by 4-hexadecylaniline Langmuir monolayers.¹²

In this communication, we demonstrate the synthesis of gold nanoparticles of predominantly sheet-like morphology by the reduction of aqueous chloroaurate ions at the interface between aqueous chloroauric acid and chloroform containing anthracene anions as illustrated in Fig. 1. Anthracene is the smallest unsubstituted aromatic hydrocarbon with a positive electron affinity (0.53 eV)¹³ and can exist in a stable valence anion

state.¹⁴ We have accomplished electron transfer to anthracene molecules present in chloroform by exposure to photochemically reduced aqueous phosphotungstate [PTA, Keggin ions, (PW₁₂O₄₀)³⁻] ions (step 3, Fig. 1).¹⁵

Thereafter, the anthracene anions are exposed to aqueous chloroaurate ions (steps 4 and 5, Fig. 1) and lead to the reduction of the metal ions and formation of gold nanosheets at the liquid–liquid interface. To the best of our knowledge, the use of anthracene anions in the synthesis of gold nanostructures has not been demonstrated so far.

In a typical experiment, 1 ml of propan-2-ol was added to 15 ml of deaerated 10⁻³M aqueous solution of phosphotungstic acid (H₃PW₁₂O₄₀, from Aldrich Chemicals and used as-received) and this solution was irradiated by UV light (pyrex filter, > 280 nm, 450 W Hanovia medium pressure lamp) for 4 h. The UV-vis spectra recorded after and before UV-irradiation are shown as curves 1 and 3 respectively in Fig. 2A (step 1, Fig. 1). After irradiation, the solution turned blue and exhibited two absorption bands at ca. 480 and 760 nm that are characteristic of reduced phosphotungstate ions (Troupis *et al.*, Ref. 15).

To the UV-irradiated PTA solution, 15 ml of 10⁻³M anthracene in chloroform was added and the solution vigorously stirred (steps 2 and 3, Fig. 1). During this stage, it was observed that the intensity of blue colour in the aqueous Keggin ion solution gradually reduced, suggesting oxidation of the Keggin ions. This is clearly reflected in the UV-vis spectrum recorded from the aqueous phosphotungstic acid solution after anthracene addition as a complete loss of the bands at 480 and 760 nm (Fig. 2A, curve 2).

As mentioned earlier, anthracene molecules possess a positive and fairly large electron affinity^{13,14} and it is possible that oxidation of UV-irradiated Keggin ions in steps 2 and 3 of our procedure (Fig. 1) occurs *via* electron transfer to anthracene molecules present at the water–chloroform interface. Following

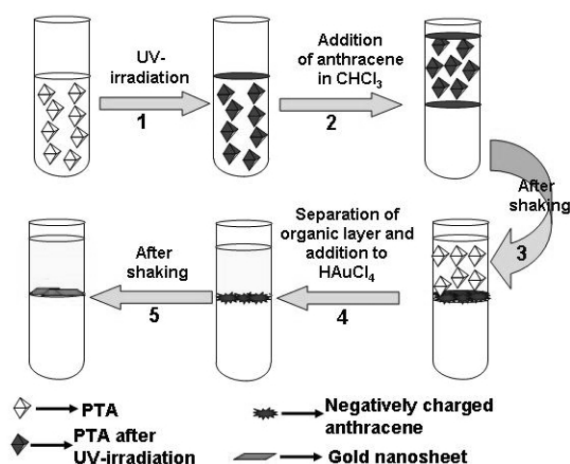


Fig. 1 Scheme showing the various steps in the synthesis of gold nanosheets at the interface between anthracene-containing chloroform and aqueous chloroauric acid solution (see text for details).

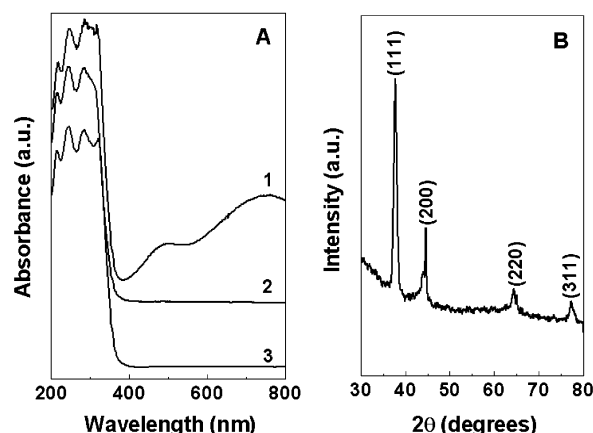


Fig. 2 A) UV-vis spectra recorded from 1: 10⁻³ M aqueous PTA solution after UV irradiation; 2: UV-irradiated aqueous PTA solution after stirring with 10⁻³ M anthracene in chloroform; 3: 10⁻³ M aqueous solution of PTA before UV-irradiation. B) XRD pattern recorded from gold nanoparticles/nanosheets grown at the liquid–liquid interface using anthracene anions (see text for details).

steps 2 and 3, the chloroform layer was carefully separated from the biphasic mixture and to this, 15 ml of 10^{-3} M aqueous solution of HAuCl_4 was added (step 5, Fig. 1). After vigorous stirring of this biphasic solution for 15 minutes, a bluish-black film was observed to form at the water–chloroform interface (step 5, Fig. 1). The aqueous layer was carefully removed and the film present on the surface of chloroform was carefully lifted onto carbon-coated transmission electron microscopy (TEM) grids, quartz slides and Si (111) wafers for further analysis.

Fig. 2B shows the X-ray diffraction pattern¹⁶ recorded from the anthracene anion layer after reaction with aqueous AuCl_4^- ions (step 5, Fig. 1). A number of sharp Bragg reflections can be seen which can be indexed based on the fcc structure of gold. It is clear that the blue-black film formed at the interface between chloroform and water consists of particles of crystalline gold. This can only occur by reduction of the aqueous AuCl_4^- ions by anthracene anions thus clearly establishing that electron transfer had occurred from UV-irradiated Keggin ions and anthracene (steps 2 and 3, Fig. 1). Keggin ions are known to exhibit strong and characteristic Bragg reflections in the 2θ region scanned in Fig. 2B.¹⁷ The absence of Bragg reflections other than those of gold indicates that the aqueous Keggin ions are not bound to the anthracene membrane. This discounts the possibility of interfacially bound Keggin ions as reducing agents in the formation of gold nanoparticles. The UV-vis absorption spectrum of a gold nanoparticle–anthracene film lifted onto a quartz substrate (supporting information, S1†) showed an unusual absorption band at 450 nm. This is considerably blue-shifted relative to the normally observed surface plasmon absorption band of ~ 520 nm for gold nanoparticles and may be a consequence of severe shape anisotropy in the particles (see below).

Fig. 3 shows representative TEM pictures recorded from different regions of the Au–anthracene film.¹⁸ In addition to a small number of fairly spherical particles, the TEM images clearly show that the film surface is covered with a large concentration of thin sheets of gold. The morphology of the individual gold particles range from spherical to ellipsoidal to triangular while their size was measured to be in the regime 10 to 80 nm. The characteristic feature of the TEM pictures is the presence of sheets of gold, one of which is indicated by an arrow in Fig. 3A. A large sheet spans almost the entire expanse of Fig. 3B.

From the contrast exhibited by the sheets relative to the individual particles (Fig. 3A) and the presence of clear strain features due to buckling of the sheets (Fig. 3B, identified by arrows), it is inferred that they are often extremely thin. An estimate of the thickness of the nanosheets was done by atomic force microscopy (AFM) of films deposited on Si (111) wafers (supporting information, S2†). The thickness of the sheets

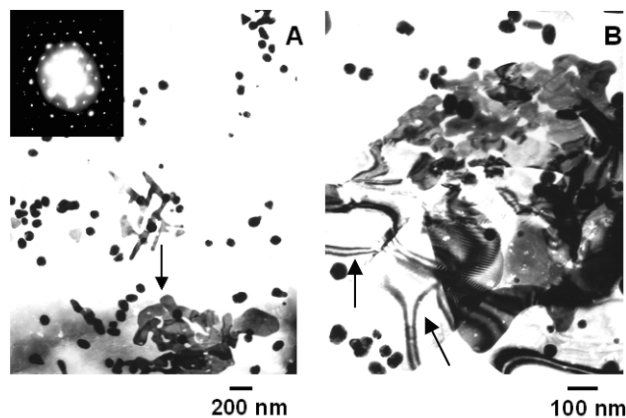


Fig. 3 A and B) Representative TEM images recorded from the gold nanoparticles/nanosheets grown at the liquid–liquid interface (see text for details). The inset in Fig. 3A shows the SAED pattern recorded from the gold nanosheet indicated by an arrow in this figure.

ranged from 30–300 nm and a relatively thick sheet of *ca.* 280 nm is shown in S2. The large anisotropy in the morphology of the gold nanostructures is clearly a consequence of the localised reduction of the gold ions by anthracene anions occurring at the liquid–liquid interface (step 5, Fig. 1). The thickness of the gold nanostructure would be limited by the fact that the reducing surface is truly two-dimensional as argued for similar structures obtained by us during the spontaneous reduction of gold ions near hexadecylaniline langmuir monolayers.¹² The selected area electron diffraction (SAED) pattern recorded from the gold nanosheet identified by the arrow in Fig. 3A is shown as the inset of Fig. 3A. The pattern is characteristic of single crystalline gold. A control experiment was performed wherein aqueous chloroauric acid solution was vigorously stirred with a chloroform solution of anthracene by bypassing steps 1–3 in our protocol (Fig. 1). No reduction of the AuCl_4^- ions was observed clearly indicating that electron transfer from UV-irradiated Keggin ions to anthracene is the crucial step in obtaining a two-dimensional reducing interface.

In summary, it has been demonstrated that thin nanosheets of gold may be formed by the reduction of aqueous chloroaurate ions at a liquid–liquid interface bearing anthracene anions. The anthracene anions have been created by electron transfer from Keggin ions that were reduced by irradiation with UV light. This strategy opens up the exciting possibility of using anthracene anions in the synthesis of nanomaterials of variable morphology.

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