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C_{60} Mediated Aggregation of Gold Nanoparticles

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Since their discovery in 1985 the fullerenes have been attracting tremendous research interest covering a wide range of fundamental and applied aspects.[1] From the point of view of nanostructure design they represent ideal construction units since they are monodisperse (C_{60}, C_{70}, C_{76}, etc.) and self-passivating, i.e., no protecting ligands or stabilizing agents are required to prevent particle fusion or irreversible aggregation. Metal and semiconductor nanoparticles do not generally fulfill these criteria. An increasing preparative repertoire is available to obtain fullerenes with adjacent functional groups, making them more amenable to subsequent supramolecular reactions.[2] The prominent role of fullerenes as building blocks has recently been challenged by thiol passivated gold nanocrystals[3] obtainable as monodisperse, practically pure compounds, which spontaneously form highly ordered superlattices.[3f] These particles exhibit a fascinating diversity of surface chemistry and their functionalization[3b] is from the preparative point of view considerably more straightforward than that of fullerenes, as demonstrated mainly by Murray and coworkers in a number of publications.[3g,i,n] First practical applications of these new materials in novel gas sensor devices are on the way.[3p] Stable solutions of gold nanoparticles in aromatic solvents can also be obtained in the absence of thiols yielding particles readily amenable to surface reactions without the need of functionalization.[4] In this communication we report the surprising finding that (C_{60})fullerene adsorbs to such particles of ∼5 nm diameter stabilized by the adsorption of bromide and quarternary ammonium ions[4f] in toluene solution. This leads to the precipitation of fullerene-linked gold particles. The experimental procedures are very simple and resemble those reported previously for dithiol-linked gold nanostructures.[4] A toluene solution of ∼5 nm gold particles stabilized with tetraoctylammonium bromide was prepared following a well-established procedure.[4a,e,h] A 200 mL sample of this freshly prepared solution (ca. 0.3 μM, based on 3500 Au atoms per particle) was mixed with 25 mL of a 0.5 mM solution of (C_{60})fullerene in toluene. Air was not excluded and the reaction mixture was stored in a stoppered flask in the dark. The intensely ruby colored solution changed color slowly to bluish violet within several hours, indicating the aggregation of gold particles,[4a,5] and after 2 days the formation of a black precipitate was observed. After 3 weeks most of the material had precipitated leaving a weakly violet supernatant solution. For examination by electron microscopy the precipitate was resuspended by sonication without filtering or washing,[6] and a droplet of this suspension was allowed to evaporate slowly on a 400 mesh Cu grid coated with an ultrathin (∼4 nm) amorphous carbon film (Ted Pella, USA). Specimens were examined on a JEOL 2000 EX transmission electron microscope operating at 200 kV. The strings of three-dimensional aggregates of 50−100 nm diameter observed (Figure 1a) are composed of discrete gold particles of 3−6 nm, and high-resolution images (Figure 1b) of the thinner border structures reveal clearly that the particles are not in direct contact with each other but are apparently *glued* together by a shell of fullerene molecules. The images are consistent with the assumption of a monolayer of fullerene covering each gold particle and hence leading to an interparticle spacing of ∼2 nm. Smaller spacings are also observed since the TEM images represent a two-dimensional projection of a three-dimensional structure. The fringe

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(6) Attempts were made to isolate the precipitate, but it was found that extensive washing with toluene removed the fullerene from the material, and the dried product had an elemental composition of 94% Au, 4.9% Br, 1% C, and 0.1% H. Inspection by TEM showed that the gold had sintered into relatively large (∼0.5 μm) polymorphous particles covered with a thin layer of a less dense material, probably AuBr. The presence of bromine at this stage indicates clearly that the nanostructures shown in Figure 1 still contain bromide ions adsorbed to the gold surface. The fullerene probably replaces the tetraoctylammonium ions which have been proposed to cap the adsorbed bromide ions on the particle surface in a tripod-type arrangement.[4f] Loss of an ammonium ion from the particle surface might be concurrent with an electron transfer step from the gold core probably to free fullerene in solution as suggested by ESR measurements. Both the elemental composition of the unwashed precipitate and the nature of the binding interaction are important open questions which are currently being addressed.

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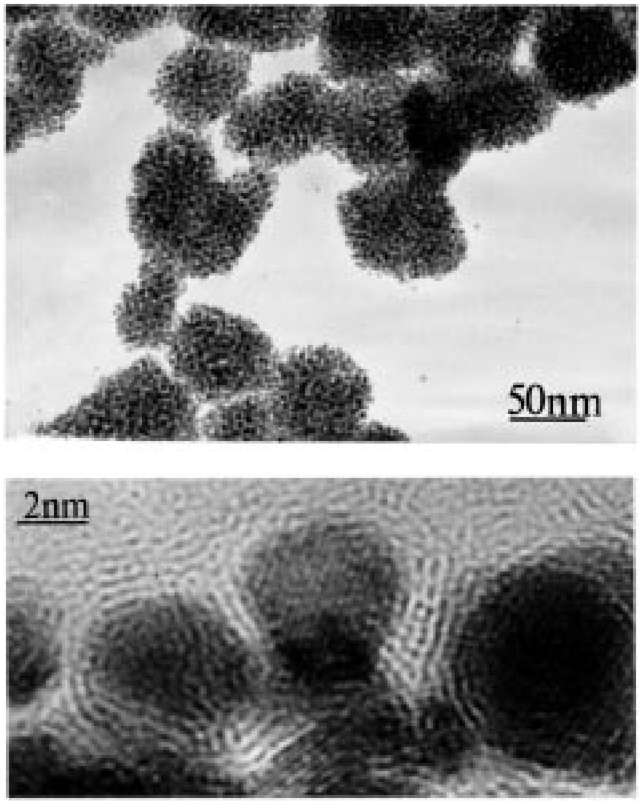

Figure 1. (a) Transmission electron micrograph showing agglomerates of fullerene linked discrete gold particles of relatively uniform size. (b) High-resolution image of a typical border region of a three-dimensional network of (C_{60})fullerene-linked gold particles.

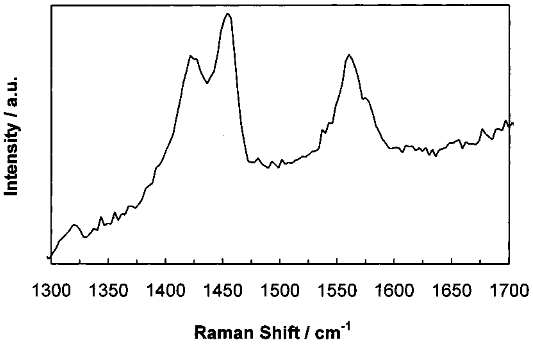

Figure 2. SERS spectrum (He/Ne laser, 632.8 nm) of (C_{60})fullerene adsorbed to a self-assembled monolayer of gold particles on a mercaptosilane functionalized glass surface.

structure corresponding to the fullerene molecules shows a periodicity of 0.42 nm that could be consistent with the {113} plane spacing in fcc fullerene crystals.[1d] Other packing arrangements in this novel system are, however, more likely and could also lead to a similar fringe periodicity. Further work is required to elucidate the precise structure of the fullerene containing shell. Control samples prepared in the absence of fullerene show neither fringe structures between the gold particles nor particle aggregation. The origin of the binding interaction between gold particles and fullerene molecules is unclear, but the observation of an ESR spectrum similar to that observed on electrochemical reduction of C_{60}[7] suggests the involvement of an electron-transfer process. This is currently being studied in more detail. Fullerenes have been reported to adsorb on several metal surfaces,[8] and the preparation of self-assembled monolayers of functionalized fullerenes has been achieved.[9] Their interaction with nanoscopic metals in solution presented here has not been reported previously, probably due to the difficulties of finding a common solvent for fullerenes and unprotected metal colloids, which are generally available as hydrosols. The interaction of (C_{60})fullerene with silver islands of approximately 10−20 nm has been studied previously by Hou and co-workers after co-deposition of silver and fullerene vapors under high-vacuum conditions.[10] TEM images of these silver islands showed fringe structures of fullerene molecules closely associated with the surface of the metal islands similar to those observed in the present system, although the fringe periodicities observed were somewhat different. Apart from the C_{60}/Au particle aggregation in solution described here, fullerene also adsorbs to immobilized gold nanoparticles of the same type. A self-assembled monolayer of gold particles on a mercaptosilane functionalized glass slide was prepared as described previously,[4b,c,g] immersed for 1 h in a 0.5 mM toluene solution of (C_{60})fullerene, and rinsed thoroughly with toluene. Since the gold particles employed are known to be excellent Raman enhancers[4d] the resulting *hetero*-bilayer structure lends itself to examination by surface enhanced Raman spectroscopy (SERS). Figure 2 shows the peaks in the SERS spectrum corresponding to the ω_2(Ag) ("pentagonal pinch"), ω_7(Hg), and ω_8(Hg) modes at 1455, 1425, and 1560 cm^{-1}, giving clear evidence for the presence of the fullerene, which, contrasting the behavior of the material precipitated from solution, is not removed by rinsing with toluene. The shifts of the ω_2(Ag) and ω_8(Hg) peaks, by 15 and 10 cm^{-1}, respectively, to lower wavenumbers in comparison with literature data[1d] may be indicative of electron transfer from the gold particles to the adsorbed fullerene molecules.[1d] This has also been observed in Hou's work on co-deposited silver/fullerene films,[10] but a more detailed investigation is required to quantify the extent of charge transfer in these systems.

In conclusion, it has been shown that (C_{60})fullerene mediates the aggregation of tetraoctylammonium bromide stabilized gold particles in toluene solution to form a novel type of nanocomposite with the fullerene relatively weakly bound to the surface of the gold particles. Likewise, the formation of self-assembled monolayers of fullerene on immobilized gold particles has been observed and examined by SERS also, giving some indication of negative charge donation to the adsorbed layer of fullerene molecules. While the systems reported here do not exhibit any long-range order, given the rapid progress in the state of the art in this field, highly ordered gold particle superlattices, whose interstices and interparticle gaps are filled with fullerene molecules, can be envisaged as a not too distant possibility. The preparation of such ordered materials is currently being explored. Besides their fundamental interest, gold-fullerene structures are promising candidates for novel sensor materials, catalysis, and *bottom-up* fabrication of single-electron transistors.[11]

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