Synthesis of polyaniline–gold nanocomposites using ''grafting from'' approach†

Sunil K. Pillalamarri,[ab] Frank D. Blum[ab] and Massimo F. Bertino*[bc]

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Polyaniline–gold nanocomposites containing polyaniline nanostructures attached to well-dispersed uniform-size gold nanoparticles were obtained using a surface initiation approach.

Polyaniline nanostructures have recently been the focus of intense study due to their potential applications in sensing and catalysis.[1] Different groups have shown that sensors based on polyaniline nanofibers have a faster response time compared to bulk polyaniline.[2] This advantage is primarily due to their high surface areas.

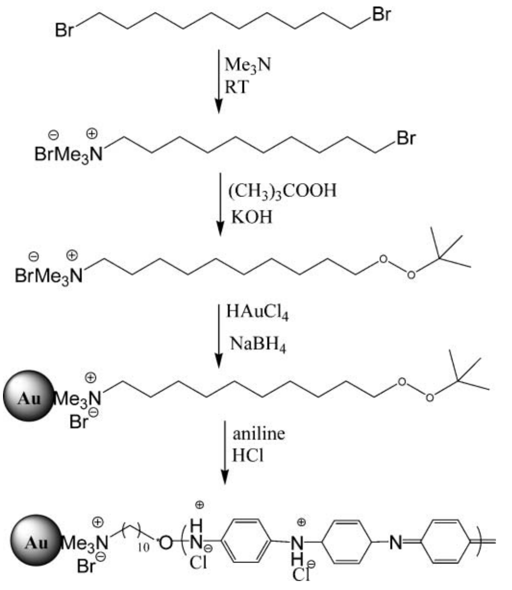
Hybrid systems consisting of inorganic nanoparticles with *p*-conjugated polymers as supporting matrices have interesting properties, particularly for dielectrics, energy storage, catalytic activity, and magnetic susceptibility.[3] A few groups have reported the synthesis of polyaniline–metal nanocomposites using different chemical and electrochemical approaches.[4] Many of the composites will have low surface areas, especially if the metal nanoparticles were dispersed in bulk polyaniline matrices.

In most of the previous studies, no strong attachment between polymer and metal matrices was reported. The attachment between organic and inorganic counterparts in these hybrid systems may play a crucial role in electronic devices, since charge transfer at the contact between a metal nanoparticle and an organic semiconductor plays an important role in many areas of technology.[5] The ''grafting from'' approach is an effective means of enhancing the attachment between polymers and filler matrices. For example, polymer brushes may be fabricated with surface initiation.[6] In this paper, we report the synthesis of polyaniline–gold nanocomposites where both components have large surface areas and are strongly attached to each other.

In our procedure, we synthesized polyaniline nanofibers by initiating the polymer chain at the surface of gold nanoparticles. A peroxide-modified surfactant was used for initiation and to control the polyaniline morphology. This procedure has multiple advantages, such as (i) synthesis of gold nanoparticles and nanorods, (ii) synthesis of polyaniline nanofibers, and (iii) increased compatibility between gold nanoparticles and the polyaniline matrix. In addition, our synthesis used emulsion polymerization to generate stable emulsions and to ease processing of rigid polymers like polyaniline.[7]

The procedure for the synthesis of polyaniline–gold nanocomposites, using a ''grafting from'' approach, is shown in Scheme 1. Gold nanoparticles were synthesized with standard techniques,[8] and stabilized by surfactants that carry a peroxide group. The peroxides initiate polymerization when the nanoparticles are added to an aniline solution.

10-Bromodecylperoxide was synthesized following the procedure of Velten *et al.*[9] Spherical gold nanoparticles with a narrow-size distribution and the gold nanorods were synthesized following procedures outlined by the Murphy group,[8] except, we used 10-bromodecylperoxide instead of cetyltrimethylammonium bromide (CTAB) to stabilize the gold nanoparticles. Polyaniline nanofibers, end grafted to gold nanoparticles, are shown in Fig. 1(a–c). Fig. 1(a) and 1(b) shows micrographs taken as a function of polymerization time. In the initial stages of polymerization (30 min), micelles (made up by surfactants adsorbed on gold nanoparticles) formed as shown in Fig. 1(a). As polymerization proceeded, networks of filament-like polyaniline attached to gold nanoparticles were formed, as shown in Fig. 1(b). The size of the gold nanoparticles, measured with TEM, was around 5 nm and in close agreement with the size estimated from peak-width analysis of XRD spectra.



Scheme 1 Scheme for synthesis of surface-initiated polyaniline–gold nanocomposites.

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[a] *Department of Chemistry, University of Missouri-Rolla, Rolla, MO 65409, USA*
[b] *Materials Research Center, University of Missouri-Rolla, Rolla, MO 65409, USA*
[c] *Department of Physics, University of Missouri-Rolla, Rolla, MO 65409, USA. E-mail: massimo@umr.edu; Fax: (573) 364-4715*

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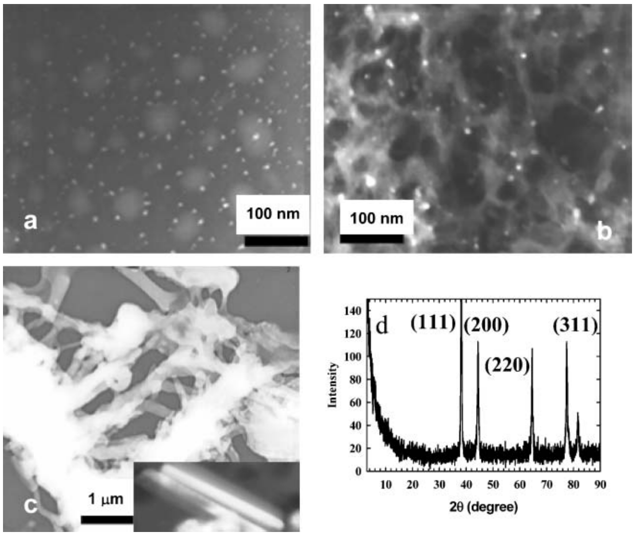

Fig. 1 (a) Micelles formed by 10-bromodecylperoxide attached to Au nanoparticles during initial stages of polymerization, (b) polyaniline nanofibers attached to Au nanoparticles after polymerization, (c) polyaniline nanofibers attached to Au nanorods (inset shows Au nanorods before polymerization), and (d) XRD spectrum of polyaniline–gold nanocomposites.

When gold nanorods were employed instead of spherical gold nanoparticles, the rods became covered with the polymer, and fibers joined neighbouring rods, as shown in Fig. 1(c). The diameter of the rods was 25 nm before polymerization (see ESI†), and increased to around 1 μm after polymerization. Our results show that 10-bromodecylperoxide is similar to CTAB in controlling gold particle morphology, and that it can also initiate polymerization. Fig. 1(d) reports a XRD spectrum obtained for the sample in Fig. 1(c). The intense peaks are due to the reflections from gold lattice planes.

The presence of gold nanoparticles capped with 10-bromodecyl peroxide was necessary to obtain high-aspect ratio polyaniline. Polymerization of aniline, in the absence of gold nanoparticles using *tert*-butyl hydroperoxide as an initiator, resulted in bulk-polyaniline. We also carried out emulsion polymerization in the presence of CTAB-capped gold nanoparticles, under identical reaction conditions, and no well-defined polymer nanostructures were found.

Based on the chemistry of our system, the oligomers must initially form in the proximity of the Au surfaces since the peroxide initiator is attached to the gold nanoparticles. There may also be catalytic activity at the surfaces[10] and the presence of the oligmers themselves[11] may also play a role in fiber formation. The oligomers probably remain close to the surface because of their interaction with the initiator and of the interaction between the gold surface and the imino groups.[11] Fibers formed in the initial stages of polymerization might act as seeds for additional fiber growth.[1]

In summary, we report a procedure to synthesize polyaniline–gold nanocomposites by surface-initiated polymerization of aniline from gold nanoparticle surfaces. The procedure allows control over the morphology of polyaniline and gold, and results in the attachment of gold particles to the polyaniline. These composites are expected to be advantageous, compared to bulk polyaniline metal composites, due to improved attachment between polyaniline and gold and also due to the nanoscopic dimensions of both polyaniline and gold.

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