

Novel nanostructures of gold–polypyrrole composites

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Different novel nanostructures of gold–polypyrrole composites are observed by the transmission electron microscopy, for the first time, with the advent of block copolymer micelles.

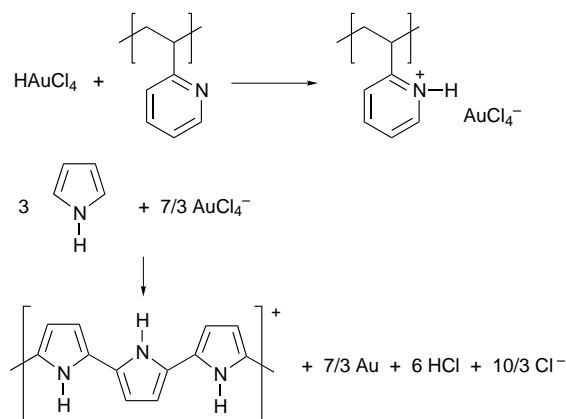
Nanoparticles of gold and other noble metals and semiconductor particles, in a more general sense, exhibit a variety of useful optical, electrical and catalytic properties. All these properties strongly depend on the careful choice of preparative strategies, which could provide long term stability and ease in processability.^{1–4} Polymer nanocomposites is one such approach and one of the important objectives in recent research is to prepare monodisperse particles, regularly dispersed in a polymer matrix. The synthesis of noble metal sols in a polymerising non-conducting system such as poly(methyl methacrylate) has recently been documented in the literature.⁵ The first prerequisite for the formation of kinetically controlled monodisperse colloids is the availability of well defined dispersions. Block copolymer micelles provide an excellent means for such dispersions,⁶ by which the particles of a definite size can be formed and stabilized within the core, yielding monodisperse colloids.

With the advent of block copolymer micelles, we have demonstrated very recently, a facile and versatile route to the fabrication of monodisperse, single gold (Au) nanocluster, *ca.* 7 nm, in diameter (core) surrounded by a shell of polypyrrole (PPY), both within the spherical microdomains.^{7–9} In this report, the first observation of different, novel nanostructures of Au–PPY, is described.

In the first method, a micellar solution of polystyrene-block-poly(2-vinylpyridine) (0.5 mass%) in toluene was treated with tetrachloroauric acid (0.5 and 0.7 equiv. to 2VP units) which got selectively bound within the P2VP cores of the micelles. When this solution was treated with pyrrole (PY), polymerization occurred, yielding polypyrrole under concurrent formation of Au nanoparticles, as supported by FTIR and UV–VIS measurements. The bipolaron bands at 1210 and 925 cm^{-1} indicated the formation of PPY in its doped state.⁷ The chemical conversion is depicted in Scheme 1.

TEM images were acquired with a Philips 400 microscope operating at 80 kV. The samples were prepared by placing a

drop of the colloidal polymer solution onto a carbon-coated Cu grid on an underlying tissue paper, leaving behind a thin colloidal film. In a typical concentration, *i.e.* $[\text{PY}]/[\text{HAuCl}_4] = 4.0$, uniform, monodisperse Au particles with a mean diameter of 7 and 9 nm, are vividly seen with a shell of PPY, respectively in Fig. 1(a) and (b), upon annealing the thin film at 130 °C for 1 h. When the above procedure is repeated, but with



Scheme 1

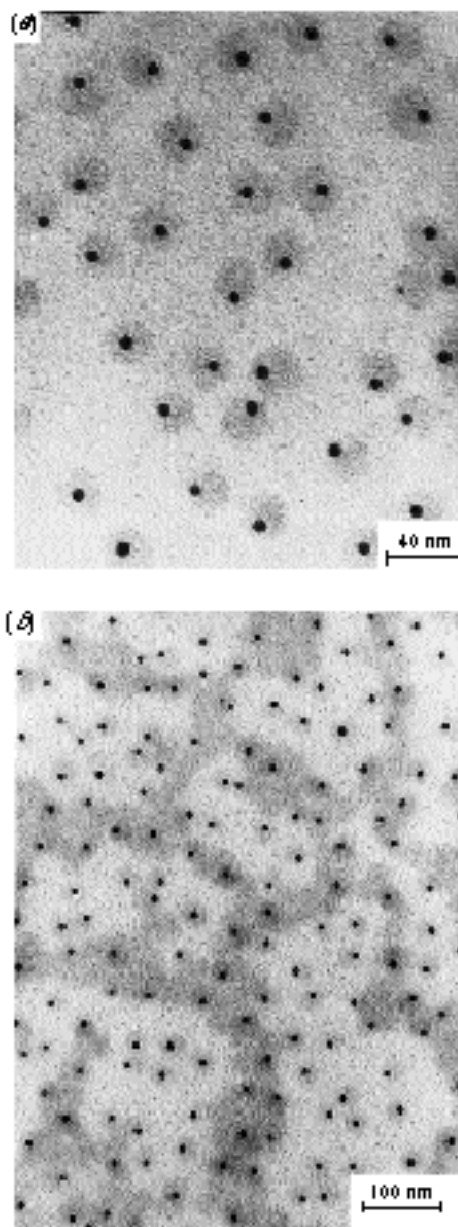


Fig. 1 Transmission electron micrographs of thin colloidal polymer films ($[\text{PY}]/[\text{HAuCl}_4] = 4.0$) after annealing at 130 °C for 1 h. (a) 7 nm Au ($[\text{HAuCl}_4]/[\text{2VP}] = 0.5$); (b) 9 nm Au ($[\text{HAuCl}_4]/[\text{2VP}] = 0.7$) in each micelle. The grayish area represents PPY.

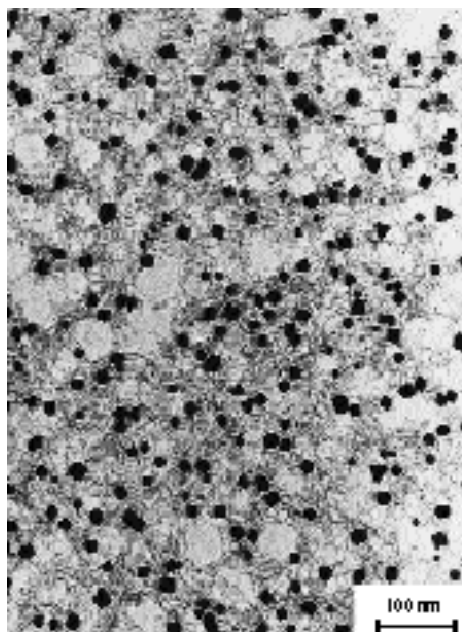


Fig. 2 Transmission electron micrograph of a thin film cast from a colloidal polymer solution (stirred heavily, but without annealing), exhibiting spherical, cubic, tetrahedral and octahedral Au particles

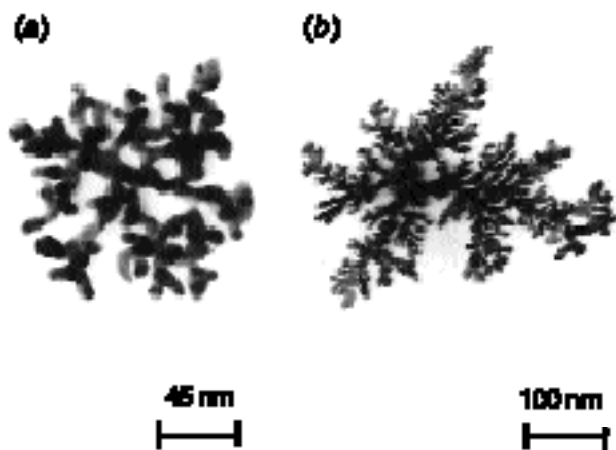


Fig. 3 TEM pictures depicting dendritic nanostructures of thin films cast from block copolymer ionomers, after vapour phase polymerization (VPP) of PY. (a) after 2 h of VPP; (b) after overnight VPP.

heavy stirring of the micellar solution and without heating, different shapes of Au particles, *viz.*, spherical, cubic, tetrahedral and octahedral, are observed (Fig. 2). Here, the spherical domains cannot be seen owing to the fact that the spherical micelles coagulate with each other, yielding different shapes of Au, dispersed in a PPY matrix, marked by a grayish area. Most importantly, the nanoparticles of Au with different shapes resemble the shape-controlled synthesis of Pd nanoclusters.¹⁰ It is obvious that an ordered aggregation produces uniform particles (Fig. 1), since a disordered aggregation would result in polydisperse particles of variable morphology (Fig. 2).

Interestingly, we have observed elegant 'dendritic' nanostructures (Au-PPY fractals?), in another different approach, by employing vapour phase polymerization of PY onto solution cast films of block copolymer ionomers (Fig. 3). Dendritic growth occurs even at a lesser polymerization time (≤ 30 min). Thick branches radiated after 2 h of polymerisation. This large random supramolecular structure, known in short as DLA (diffusion-limited aggregate),¹¹ represents a very wide variety of growth (here, polymerization and coagulation), allowing building of one particle after the other and letting the particle diffuse and stick to the growing structure. The pioneering work of Kaufman *et al.* delineated PPY fractals obtained by the diffusion-limited electrochemical polymerization of PY.¹²

In conclusion, we have observed different elegant nanostructures of composites of Au, with a little nudge in the preparative strategies. Different (spheroids, cuboids) Au nanoparticles may have important implications in the field of catalysis. Importantly, the block copolymer architecture is useful for commercial applications of a processable form of PPY by providing colloidal stability to the suspension of PPY.¹³ Furthermore, the new observation of 'dendritic' nanostructures, could open up new vistas in supramolecular structures. Over and above, conducting and semiconducting polymer/metal junctions could provide intriguing perspectives to develop novel electronic devices.¹⁴

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Notes and References

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