
Polymer capped metal nanoparticles for sensor applications

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1. Abstract

Colloidal nanohybrids composed of a noble metal core coated by a protective shell of organic molecules are considered the first step towards the fabrication of devices to be applied in several areas, due to the large electromagnetic field generated in the vicinity of the metal surfaces when excited near the plasmon frequency. This contribution will give some results concerning preparation and spectroscopic investigation of polymer-coated silver and gold metal nanostructures. Two different classes of molecular adsorbates will be presented: polydiacetylenes and polyphenyleneethynylenes.

2. Introduction

One of the major challenge in materials chemistry is the preparation of nanostructures with properly designed properties. A recent advance in chemical synthesis enables preparation of colloidal nanohybrids composed of a noble metal core coated by a protective shell of organic molecules, with an excellent control of size and shape. Analogous systems can be obtained by physical methods, i.e. laser ablation of a metallic target in solution. In both cases, the preparation of polymer-decorated nanoassemblies can be exploited in the fabrication of optoelectronic and sensor devices. The choice of the fully chemical or the physico-chemical approach for the preparation of the nanohybrids depends on several parameters, and on the envisaged application, being the physical approach more reliable in terms of purity of the final products and the chemical one more versatile in terms of control of the dimension and dispersivity of the nanohybrids.

Here, two examples of polymer capped nanohybrids will be presented. The first one consisting of polydiacetylene-coated gold nanoparticles obtained by chemical reduction

methods. The second example concerns preparation of silver or gold nanoparticles obtained by laser ablation methods and subsequently capped with a fluorescent polymer.

3. Polydiacetylene-capped gold nanoparticles

Gold nanoparticles (NPs) having a diameter ranging from 1.5 to 8 nm and capped with the diacetylene monomer DS9 ((henicosa-10,12-diyn-1-yl)diacetylene) were prepared in organic solvents by following a modified version of Burst's method. The details of the synthesis protocol are reported elsewhere [1]. The monomer-capped NPs were exposed to 254 nm UV light from a mercury lamp in order to obtain topochemical polymerization of the DS9, according to the scheme illustrated in Figure 1. This compound, as all polydiacetylenes, can polymerize into different phases, corresponding to substantially different optical and spectroscopic properties, i.e. colour, nonlinear optical response, electrical conductivity. The possibility of controlling the polymer phase permits preparation of nanohybrids with tailored response to different external agents and opens the way to a wide range of applications in sensing systems.

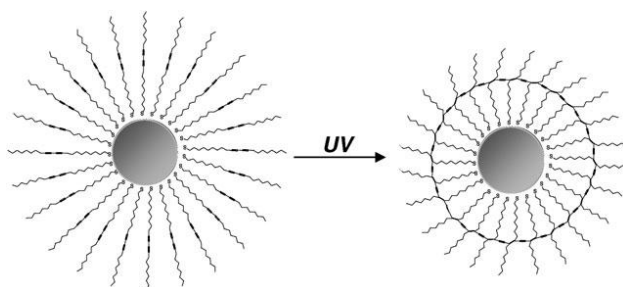


Figure 1. Scheme of the topochemical photopolymerization of DS9 chemisorbed on gold NP.

The polymerization process of our samples was monitored step by step by UV-Vis and by Raman spectroscopy. The details of the experimental equipments are again reported in ref. 1. Figure 2 a, b reports the data obtained after only 7 min of UV irradiation in the spectral regions where PDA signals occur for the particles of 1.6 and 4.1 nm mean diameter. The Raman spectrum of the sample consisting of smaller NPs (Figure 2 a) shows only very weak features at about 2100 and 1500 cm^{-1} , typical of the polymer in its red, low-conjugation form. A more enhanced Raman spectrum is observed for the sample containing bigger NPs (Figure 2 b), because of the resonance conditions of the surface plasmon band of gold NP with the

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exciting line. Indeed, the plasmon resonance, which is almost absent in the case of NPs having a diameter of 1-2 nm or less, is well pronounced for this sample and provides considerable field localization with consequent enhancement of the Raman response of the molecular adsorbate. In this case, indeed, two bands at about 2080 and 2100 cm^{-1} , associated with the blue and red polymeric phase respectively, are well evident in the triple bond region. In the broad solvent band around 1440 cm^{-1} a shoulder is observed at about 1460 cm^{-1} , that can be assigned to the double-bond stretching of the highly conjugated polymeric blue form. Despite the resonance conditions with the excitation line, the signals of the red form are less intense than those of the blue one, suggesting the predominance of the more extended chain conformation in this sample. From these data one can infer that the polymerization process is critically dependent on the core size and that the highly conjugated blue phase requires the more extended surfaces provided by larger nanoparticles.

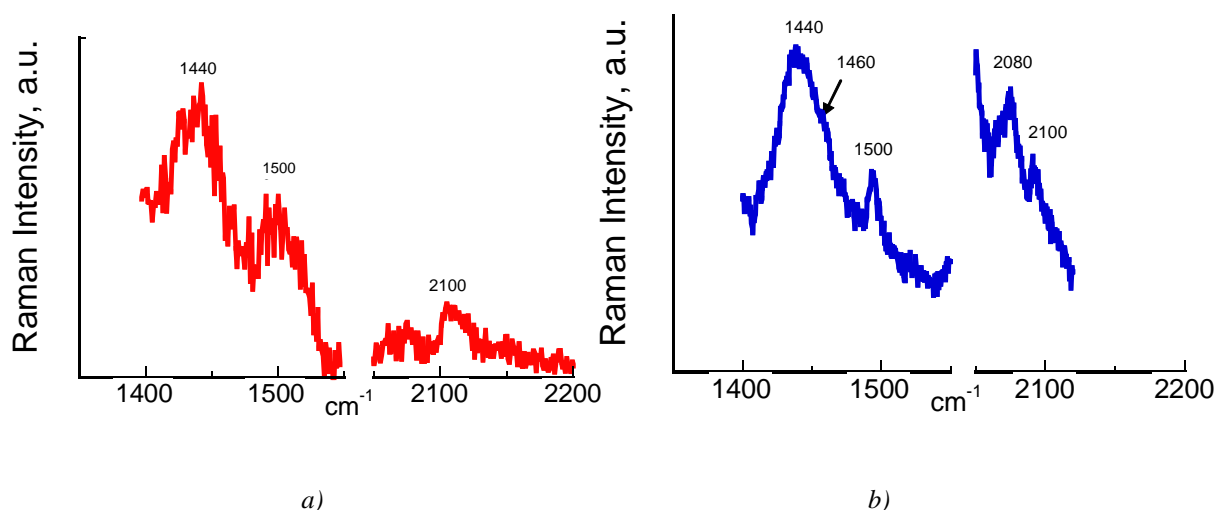


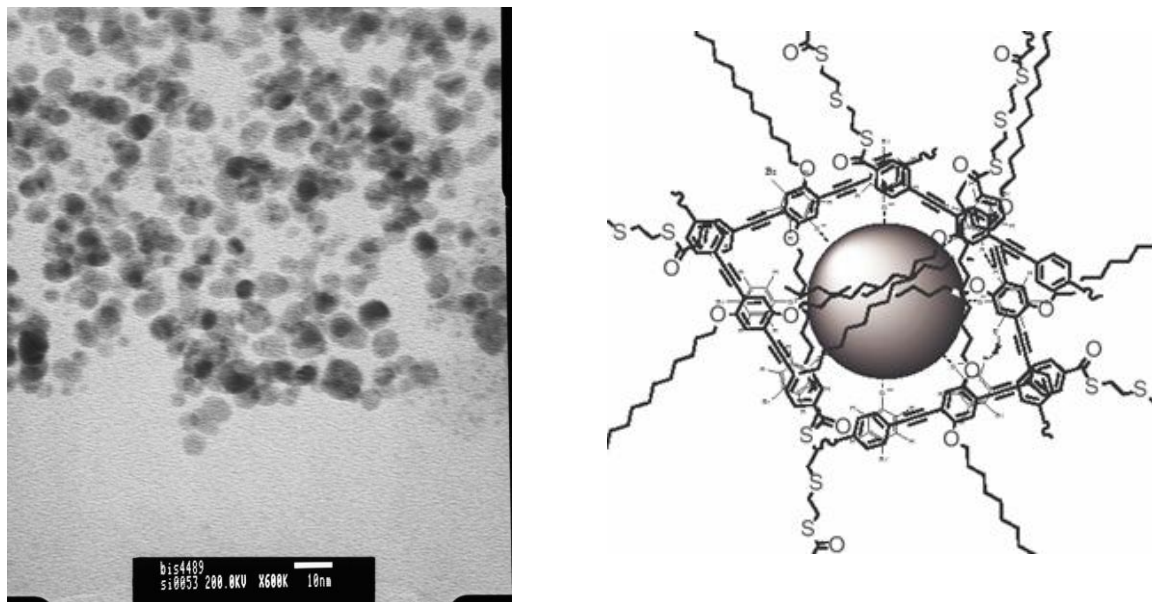
Figure 2. Raman spectra recorded in the double- and triple-bond regions of a toluene suspension of DS9-capped gold NPs having average diameter of 1.6 nm (a) or 4.1 nm (b), after 7 min UV exposure. Excitation: 514.5 nm.

4. Gold and silver nanoparticles capped with a fluorescent polymer

Laser ablation is a fast and versatile method to prepare suspensions of metal nanoparticles [2]. The use of different ablating wavelengths, time regimes and, eventually, post-irradiation permits fine tuning of the morphology of NPs. In particular, picosecond radiation has been demonstrated to be very efficient for preparation of gold nanoparticles in different environments. Proper choice of the ablating wavelength permits good control of

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particle dimensions and dispersivity [2]. We used laser ablation to prepare novel nanocomposites consisting of silver or gold nanoparticles capped by the polyphenyleneethynylenes PPEOC12 described in ref. 3. This compound, which is highly fluorescent in the blue region of the spectrum has been already inserted into organic light



a)

b)

Figure 3. a) TEM analysis of a gold-PPEOC12 suspensions in acetone:chloroform 1:1. b) Scheme of the coordination of PPEOC12 with gold. .

Figure 3 a reports a TEM image PPEOC12-capped gold NP. First, the NPs were prepared in acetone by laser ablation with the second harmonic of a ps Nd:YAG laser, according to the experimental details reported in ref. 2. The dimensions are almost mono-disperse around a diameter of 5 nm. Subsequently, the suspension in acetone was mixed and sonicated for 1 hour with a 1 g/l solution of PPEOC12 in chloroform. Fig. 3b shows the possible coordination of the polymer with the metal. Preliminary results shows that the introduction of gold NP in a PPEOC12 film can tune efficiently its electrical properties from semiconducting to conducting.

5. References

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