1,10-Phenanthroline and 1,10-phenanthroline-terminated ruthenium(II) complex as efficient capping agents to stabilize gold nanoparticles: Application for reversible aqueous–organic phase transfer processes

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ABSTRACT

1,10-Phenanthroline (*phen*) and 1,10-phenanthroline-terminated ruthenium(II) complex [Ru-L*phen*]$^{2+}$ have been used to stabilize and functionalize gold nanoparticles (Au-NPs). The strong interaction between the nitrogen atoms of *phen* and the surface of Au-NPs allowed for the phase transfer of Au-NPs from toluene to aqueous phase containing [Ru-L*phen*]$^{2+}$. Reverse phase transfer of these Au-NPs from water to acetonitrile by substituting the Cl$^-$ counter anion by PF$_6^-$ has also been demonstrated. Such facile post-functionalization, phase transfer and solvent transfer processes using metallic complexes bearing a terminal phenanthroline pendant group constitute a prerequisite for further studies of the electronic and optical properties of these NCs in various media.

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1. Introduction

Noble metal particles on nanometer scale represent a large emerging field of great fundamental and practical interest and are receiving worldwide attention [1]. These nanoscale metal particles are attractive due to the unique catalytic, optical, and electronic properties arising from their size [2]. Among them, gold and silver nanoparticles (NPs) have attracted most attention because of their chemical stability, their "easy" functionalization and their large variety of size and shape [3,4]. The development of synthesis protocols for nanomaterials, based on gold or silver NPs, with tunable physicochemical properties is an important goal in nanotechnology. Research in this field has undergone a rapid expansion following the effective method proposed by Brust et al. [5]. Depending on the target application, several key parameters must be considered such as the size and shape of the nanocomposites (NCs), the reaction medium, the nature of the functionalizing agent and its interaction with the metallic surface. This interaction can be ensured by a variety of functions such as thiols [3,5], amines [6,7], carboxylates [8] or phosphines [9]. Numerous procedures have been described to generate stable colloidal solutions of functionalized NCs but two methods are commonly used. In the first one, the direct functionalization, the functionalizing agent also plays the role of stabilizing agent [10]. In the second one, the post-functionalization, the metallic NPs are initially stabilized by a lig-

and easily replaceable which is then substituted by the appropriate functionalizing agent. Several easily substitutable stabilizing agents have already been used such as tetraoctylammonium [5,11,12], citrate [13,14], or phosphine [15]. Such controlled ligand exchanges around the metallic NPs have already been used successfully to allow phase transfers from aqueous medium to organic solvents, and vice versa, and therefore to produce NCs with solvent-adaptable properties [16–18].

Many of the functionalized NCs described to date contain complex organic ligands such as DNA [19] and dendrimers [20]. A new class of nanocomposites recently emerged in which the functionalization of metallic NPs has been done by inorganic systems [21–23]. This new class of materials remains much less developed and usually involves long alkyl thiol chains between the metallic complex and the surface of the nanoparticle [3,24]. In the past four years, we have studied the direct synthesis of gold NPs coated by metallic complexes [25–27]. The interaction between the metallic complexes and the surface was not ensured by the conventional thiol function but by the nitrogen atom(s) of pyridine, 1,10-phenanthroline (*phen*) and more recently thiocyanate pendant groups [28]. Moreover, the usual long alkyl chain was replaced by a fully conjugated system between the metallic NPs and the metallic center in the complex. This type of connection is potentially interesting to favor electronic transfers between the two components of the NCs. All our previous results used a direct functionalization of the Au-NPs by metallic complexes. However, it is difficult to control the size and shape of the NCs in aqueous medium during direct functionalization. We therefore decided to develop the
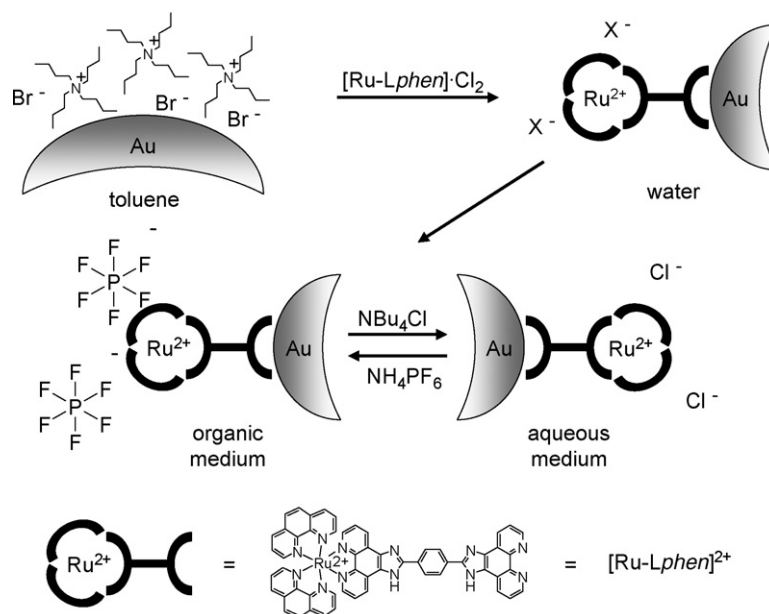
Scheme 1. Post-functionalization pathway leading to Au-NPs stabilized by the ruthenium complex [Ru-L*phen*]$^{2+}$ (upper part) and aqueous/organic medium transfers by anionic exchange around the NCs (lower part).

post-functionalization approach to enhance the homogeneity of the final size and shape of the NCs in aqueous solution.

Based on our earlier studies regarding the strong interaction between 1,10-phenanthroline derivatives and metallic NPs, we describe here our results on the stabilization of Au-NPs using 1,10-phenanthroline. We then used the ruthenium complex [(*phen*)$_2$Ru(2,2'-*p*-phenylene-*bis*-(imidazo[4,5-*f*][1,10]phenanthroline))]·Cl$_2$ ([Ru-L*phen*]$^{2+}$) bearing a phenanthroline pendant group for the post-functionalization, by phase transfer of preformed Au-NPs from toluene to aqueous solution. We finally took advantage of the strong affinity of *phen* with metallic surface to develop a facile and reversible water ↔ organic solvent transfer by controlled anionic exchange (PF$_6^-$ ↔ Cl$^-$) around the NCs (Scheme 1).

2. Experimental

2.1. Materials and methods

All reagents and solvents were purchased from Aldrich or Acros and used as received. All aqueous solutions were prepared using ultrapure water purified with a Millipore-Q$^+$ system. [(*Phen*)$_2$Ru(2,2'-*p*-phenylene-*bis*-(imidazo[4,5-*f*][1,10]phenanthroline))]·(PF$_6$)$_2$ ([Ru-L*phen*]·(PF$_6$)$_2$) was synthesized by following the procedure previously reported, without modification and with similar yields [26]. The chloride salt of [Ru-L*phen*]$^{2+}$ was precipitated by addition of an excess of tetrabutylammonium chloride to an acetone solution of the hexafluorophosphate salt. Visualization of gold nanoparticles was performed with a transmission electron microscope (TEM) (microscope JEOL 2010 UHR) in the "Centre Régional de Mesures Physiques" Paris 6: a drop of diluted solution was deposited and dried on a grid. UV/vis spectra were recorded using a Perkin Elmer UV/vis/NIR lambda 19 PC scanning spectrophotometer. Each sample was analyzed in a similar way (optical path length: 1 cm): 0.1 mL of colloidal solution was diluted in 2.9 mL of similar solvent.

2.2. Synthesis of Au-NPs coated by 1,10-phenanthroline

All syntheses were carried out with 29.5 μmol (11.6 mg) of chloroauric acid trihydrate in 20 mL of solvent (deionized water or mixed methanol/water (1/1) solution). R is defined as the molar concentration ratio $R = [phen]/[Au^{III}]$.

2.2.1. Synthesis of Au-phen (R = 0.5, 2 and 6) in water

HAuCl$_4$·3H$_2$O and *phen* (2.7 mg, $R = 0.5$; 10.6 mg, $R = 2$ and 31.9 mg, $R = 6$) were dissolved in 20 mL of water. An aqueous solution of NaBH$_4$ (0.4 M, 120 μL) was then added at once. The mixture was stirred during one hour leading to a change of the color of the solution from orange to dark purple.

2.2.2. Synthesis of Au-phen (R = 0.5, 2, 4 and 6) in H$_2$O/MeOH (1/1)

The same procedure was repeated except that a mixture of 10 mL of water and 10 mL of methanol was used as solvent instead of pure water. The amounts of *phen* were: 2.7 mg, $R = 0.5$; 10.6 mg, $R = 2$; 21.2 mg, $R = 4$; 31.9 mg, $R = 6$.

2.3. Ligand exchange and extraction of gold nanoparticles from toluene to aqueous solution using the chloride salt of [Ru-Lphen]$^{2+}$ as phase transfer agent

The ligand exchange and phase transfer were realized by a modification of the Brust two-phase synthesis [5]. HAuCl$_4$·3H$_2$O (11.6 mg, 29.5 μmol) was first solubilized in water (1 mL) and was then transferred in toluene (4 mL) using tetraoctylammonium bromide (27.1 mg, 49.6 μmol) as the phase-transfer agent. NaBH$_4$ (0.928 mL, 0.4 mol L^{-1}) was then added at once to the previous toluene solution and the resulting mixture was stirred during one hour. [Ru-L*phen*]·Cl$_2$ (15.5 mg, 14.8 μmol) in water (20 mL) was finally added and the resulting mixture was stirred during one hour. The initial orange aqueous solution turned to dark brown confirming the phase transfer of the Au-NCs from toluene to aqueous solution. This Au-NCs hydrosol was denoted *sample A-Cl*.

2.4. Reversible transfers, aqueous medium ↔ organic medium, of Au-NPs coated by ruthenium complexes using anionic exchange around the NCs

2.4.1. Transfer from mixed water/methanol medium to acetonitrile

A saturated aqueous solution of NH$_4$PF$_6$ was added to the freshly prepared *sample A-Cl*. The resulting solution was stirred