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Coordination chemistry approach for the end-to-end assembly of gold nanorods

P.R. Selvakannan [a,d], Eddy Dumas [a], Frédéric Dumur [a], Christine Péchoux [b], Patricia Beaunier [c], Arnaud Etcheberry [a], Francis Sécheresse [a], Hynd Remita [d,*], Cédric R. Mayer [a,**]

[a] Institut Lavoisier de Versailles, CNRS-UMR 8180, PRES UniverSud, Université de Versailles Saint-Quentin-en-Yvelines, 45 Avenue des Etats-Unis, 78035 Versailles Cedex, France
[b] Génomique et Physiologie de la Lactation, INRA, UR 1196, Plateau de Microscopie Electronique à Transmission, 78352 Jouy-en-Josas, France
[c] Laboratoire de Réactivité de Surface, Université Paris VI, CNRS-UMR 7197, 4 Place Jussieu, 75252 Paris Cedex 05, France
[d] Laboratoire de Chimie Physique, Université Paris-Sud 11, CNRS-UMR 8000, Bât. 349, 91405 Orsay, France

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ABSTRACT

Gold nanorods synthesized by radiolysis were selectively end-functionalized by a fully conjugated thiol bearing a pendant terpyridine group; addition of ferrous ions led to the end-to-end 1D self-assembly of the nanorods. Similar results have been obtained when the preformed $[(HStpy)Fe(tpySH)]^{2+}$ dithiol complex was directly added to the gold nanorods.

1. Introduction

The assembly and the organization of noble metal nanoparticles of different shapes such as spheres, rods and triangles in a controlled and predetermined way is of crucial importance in the fabrication of nanoparticles based plasmonic devices [1]. Amongst the nanoparticles of various shapes, metal nanorods such as gold nanorods (Au-NRs) display fascinating optical properties. They exhibit two principal and distinct plasmon bands namely the transverse and the longitudinal plasmon bands when the plasmon oscillations take place along the width and along the length of the nanorods, respectively. Moreover, the position of the longitudinal plasmon band can be finely tuned from visible to near infrared by changing the aspect ratio of the NRs [2]. Along with their individual optical properties, the collective optical properties displayed by the 1D, 2D and 3D assemblies of NRs make them attractive optical materials for example as plasmonic waveguide superstructures in nanodevices. These collective optical properties and the sensitivity of the longitudinal plasmon band to the chemical environment have also been efficiently used to develop Au-NRs based chemical and biological sensors [3–5].

Synthesis of Au-NRs in solution mainly used the seed mediated approach [2,6–8], photochemical [9,10] or electrochemical methods [11]. HRTEM and mechanistic insights showed that these nanorods have {1 0 0} or {1 1 0} crystalline side faces stabilized by cationic surfactant cetyltrimethylammonium bromide (CTAB) and {1 1 1} crystalline end faces [12,13]. It is therefore possible to expect the selective functionalization of either the side faces or the end faces of the NRs depending on the affinity of the functionalizing agent for the different crystalline faces. This selective functionalization indeed opens up new perspectives and numerous wet chemical methods have been developed for the 1D assembly of NRs. Initial studies were realized by functionalization of NRs using biomolecules to induce 1D self-assembly of the NRs [14–16]. Au-NRs have been organized in one dimension using hydrogen bonding between end-functionalized NRs [17], electrostatic interactions [18,19] or bridging dithiols [20,21]. Other methods have been proposed by Liz-Marzàn et al. who used carbon nanotubes as templates to align NRs [22] and by Kumacheva et al. who described the formation of linear nanochains in selective solvents using thiol-terminated polystyrene attached to both ends of Au-NRs [23,24].

We recently described the functionalization of metal nanoparticles by metal complexes using direct synthesis, place exchange reaction or coordination chemistry on pre-functionalized metal nanoparticles [25–29]. Herein, the later approach has been efficiently used to align Au-NRs synthesized by γ-radiolysis [30]. Aliphatic and aromatic thiols are known to strongly interact with

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* Corresponding author. Fax: +33 1 69 15 61 88.
** Corresponding author. Fax: +33 1 39 25 44 52.
E-mail addresses: hynd.remita@lcp.u-psud.fr (H. Remita), cmayer@chimie.uvsq.fr (C.R. Mayer).

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the {1 1 1} faces of Au-NRs and this specific affinity has been used to selectively functionalized the {1 1 1} crystalline end faces of Au-NRs by the thiol-terminated terpyridine tpySH. The same method had been previously used by Rotello et al. for the assembly and aggregation of spherical gold nanoparticles bearing pendant terpyridine groups [31,32]. Herein, addition of ferrous ions to the selectively end-functionalized Au-NRs bearing terpyridine pendant chelating groups led to the 1D end-to-end assembly of the Au-NRs through the formation of *bis*-terpyridine iron(II) complexes.

2. Experimental

2.1. Materials and methods

All reagents and solvents were purchased from Aldrich and used as received. ESI-MS measurements were carried out with an API 3000 (ESI/MS/MS) PE-SCIEX triple quadrupole mass spectrometer. Instrument was operated in the positive ion mode. The experiments were performed either by direct infusion with a syringe pump with flow rate of 10 μL min^{-1} or by flow injection acquisition with flow rate of 200 μL min^{-1}. Standard experimental conditions were as follows: sample concentration 10^{-3}–10^{-5} M, nebulizing gas N_2: 7 units flow rate, ion spray voltage −5.00 kV, temperature: 200–400 °C, declustering potential: −20 V, focusing potential: −200 V, entrance potential: 10 V – UV–Visible–NIR spectral measurements were done using a VARIAN Cary 5000 spectrophotometer operated at the resolution of 1 nm. 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. Fluorescence spectral analyses were carried out with a VARIAN Cary Eclipse spectrofluorimeter and each sample was analyzed in a similar way (optical path length: 1 cm), from degassed solution under argon and upon excitation wavelength at 280 nm. Optical density was adjusted below 0.1 to avoid reabsorption artefacts. TEM observations were performed with a JEOL JEM 100 CXII transmission electron microscope (TEM) at an accelerating voltage of 100 kV, a Zeiss EM902 at 70 kV and for high resolution measurements with a JEOL JEM 2010 at 200 kV.

2.2. Synthesis of proligand and coordination complex

2.2.1. 4′-(4-Mercaptophenyl)-2,2′:6′,2″-terpyridine (tpySH)

tpySH was synthesized following previously published procedure, without modification and with similar yield [33].

2.2.2. $[Fe(tpySH)_2]Cl_2$

tpySH (68.3 mg, 0.20 mmol) and $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ (39.2 mg, 0.10 mmol) were refluxed for 2 h in a mixture of EtOH/H_2O (20/20 mL). The hexafluorophosphate salt of $[Fe(tpySH)_2]^{2+}$ was precipitated by addition of a concentrated aqueous solution of $NaPF_6$ to the previous solution. $[Fe(tpySH)_2](PF_6)_2$ was recovered by filtration, washed with ethanol and dried with diethylether. The chloride salt of $[Fe(tpySH)_2]^{2+}$ was prepared by addition of an excess of tetrabutylammonium chloride to an acetone solution of $[Fe(tpySH)_2](PF_6)_2$. $[Fe(tpySH)_2]Cl_2$ was recovered by filtration, dried with diethyl ether and used without further purification. MS (ESI): 369.2 ($[Fe(tpySH)_2]^{2+}$ requires 369.4).

2.3. Synthesis of gold nanorods and 1D assemblies

2.3.1. Synthesis of gold nanorods (Au-NRs) using γ-radiolysis

Cetyltrimethylammonium bromide (CTAB) (600 mg) were dissolved in 20 mL of hot water under stirring. Tetraoctylammonium bromide (TOAB) (8.2 mg) and 20 μL of an aqueous solution of $HAuCl_4$ (0.1 M) were then added simultaneously and the solution was stirred for 2 h. To this mixture, 45 μL of acetone, 35 μL of cyclohexane and 0.18 mL of an aqueous solution of $AgNO_3$ (0.01 M) were successively added under stirring. After 30 min of stirring, the solution was deaerated by a flow of nitrogen prior to radiolysis. Immediately after this, the solution was subjected to γ-radiolysis (^{60}Co source) for 14 h. The color of the solution changed from orange yellow to brown, indicating the formation of Au-NRs [30]. This solution was centrifuged at 5000 rpm and the resulting precipitate was re-dispersed in 10 mL of water. This procedure was repeated few times to remove the free CTAB molecules.

Various methods based on seed mediated growth have been reported for controlled synthesis of Au-NRs [2,6,7,34]. The factors affecting the nucleation and growth of Au-NRs synthesized by seed mediated method have been widely investigated, and in particular, the importance of the surfactant CTAB, including surfactant concentration, counterion, alkane chain length on the yield and morphology of the resulting nanoparticles has been studied [8]. Cyclohexane is known to promote elongation and it has been added, in our synthesis, to swell the aliphatic part of the CTAB micelles [35]. TOAB acts as a cosurfactant and also promotes elongation. Acetone scavenges the solvated electrons induced by the solvent radiolysis leading to the formation of the reducing alcohol radical $(CH_3)_2C{\cdot}OH$. This radical will slowly reduce gold ions. The reduction and growth mechanisms have been studied in details [30].

The presence of silver ions is crucial for the synthesis of NRs: without silver ions, irradiation induces the reduction of gold ions into spherical nanoparticles. In the seed mediated synthesis, it has been also shown that the control of the NRs anisotropy is enhanced in the presence of Ag(I) during the formation of the NRs [2]. To explain the anisotropic growth of seeded Au-NRs, a mechanism of underpotential deposition (UPD) of Ag^+ ions has been proposed [36,37]. It has also been demonstrated that the $AgBr_2^-$, CTA^+ complex adsorbs strongly on Au-NRs [38].

2.3.2. End-to-end assembly of Au-NRs through sequential addition of tpySH and Fe^{II}

Hundred microliter of a 1 mM methanolic solution of tpySH were added to 10 mL of the purified aqueous solution of Au-NRs (see above) and the resulting mixture was stirred overnight. The solution was then centrifuged at 5000 rpm to remove the non-grafted tpySH ligands. The functionalized Au-NRs were then re-dispersed in 10 mL of water and 100 μL of a 1 mM aqueous solution of $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ were added. The resulting solution was stirred overnight to induce the assembly of the Au-NRs.

2.3.3. End-to-end assembly of Au-NRs using the preformed $[Fe(tpySH)_2]^{2+}$ complex

Hundred microliter of a 1 mM aqueous solution of $[Fe(tpySH)_2]Cl_2$ were added to 10 mL of the purified aqueous solution of Au-NRs (see above). The resulting solution was stirred overnight to induce the assembly of the Au-NRs.

3. Results and discussion

Au-NRs used in the present work were synthesized by γ-radiolysis [39,40]. We have developed a novel one-pot method to prepare gold nanorods of different aspect ratios using radiolysis [30]. This synthesis leads to monodisperse nanorods. Briefly, $HAuCl_4$ and TOAB were added to a stirred aqueous CTAB solution (above the CMC). Acetone, cyclohexane and silver nitrate were then successively added to the previous solution. Cyclohexane was added to swell the bilayers of CTAB. The final solution was flushed with nitrogen and irradiated by the ^{60}Co gamma source (dose rate = 2.2 kGy h^{-1} for 14 h). The