



Controlled assembly of plasmonic nanoparticles using neutral-charged diblock copolymers



Quanyi Yin^a, Xia Han^a, Virginie Ponsinet^{a,b,c,*}, Honglai Liu^a

^a State Key Laboratory of Chemical Engineering, Department of Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China

^b CNRS, Centre de Recherche Paul Pascal, UPR 8641, 115 Avenue Schweitzer, 33600 Pessac, France

^c Univ. Bordeaux, Centre de Recherche Paul Pascal, UPR 8641, 115 Avenue Schweitzer, 33600 Pessac, France

ARTICLE INFO

Article history:

Received 24 March 2014

Accepted 22 May 2014

Available online 16 June 2014

Keywords:

Electrostatic complexation

Block copolymers

Gold nanoparticles

Polyelectrolytes

Localized surface plasmon resonance

ABSTRACT

In this study, our aim was to control the assembly of plasmonic nanoparticles by using the electrostatic assembly of oppositely charged colloidal species. Gold nanoparticles (Au NPs) were modified with a carboxyl-terminated polymeric ligand, O-(2-carboxyethyl)-O'-(2-mercaptoethyl) heptaethylene glycol (SH-PEG₇-COOH), so that they are negatively charged on the pH range 5–10 and they stand elevated ionic strength (up to 1 M NaCl) without loss of colloidal stability. Block copolymers poly[(ethylene glycol) methyl ether-block-(N,N-dimethylamino-2-ethyl methacrylate)] (mPEG-PDMAEMA), with a neutral mPEG block and a pH-sensitive positively charged PDMAEMA block were synthesized by atom transfer radical polymerization (ATRP). The formation of complexes, driven by the electrostatic attraction between opposite charges and by the release of the condensed counter ions, was investigated using dynamic light scattering and spectrophotometry. The relative quantities of polymer chains and nanoparticles in the suspension were shown to affect the size of the formed complexes. In this report, it is also shown that the complex formation is reversible. Stable complexes of typical size 400 nm were formed, which could be used as building blocks for new optical materials.

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1. Introduction

The interest for nanostructures has exploded in the recent years, with many applications in view [1], from bio-medical sensing [2,3] to optical circuitry [4]. The need for ever higher degrees of diversity in structures and functions has led to the search for new and versatile fabrication methodologies, among which self-assembly has become an unavoidable and highly promising route [5,6]. Self-assembly induces spontaneous organization in soft condensed matter. Based on intermolecular interactions of energy close to kT , it produces very resilient structures, easily distorted by external fields but easily healed and recovered. Some of these structures present characteristic sizes at the nanoscale and variable degrees of order, among which liquid crystals, surfactants (or more generally amphiphiles) and block copolymers. They have been used to organize solid nanoparticles, therefore combining structural control, soft matter versatility and solid state properties. Versatile

properties in self-assembled composites of solid nanoparticles and supramolecular materials were indeed demonstrated for magnetism [7], magneto-optics [8], optical sensing [9], catalysis [10], as well as photocatalysis [11] to cite a few. Among the exciting emerging functional nanomaterials, metamaterials are artificial composites presenting unusual properties of light propagation thanks to a specific structure at a length scale smaller than the operational wavelength. The search for meta-properties in the visible domain, which could open the way to technical breakthrough in optics such as hyperlenses [12] and cloaking [13], is mostly focused on nanostructured plasmonic systems. The powerful but costly techniques of nanolithography have been successfully used to manufacture nanostructured surfaces and demonstrate the validity of the concepts of meta-materials at the frontiers of the visible domain [14]. However, large-scale, 3D and tunable metamaterials still present huge fabrication challenges, which could be met by the use of chemistry and self-assembly of metallic nanoparticles, acting as plasmonic resonators, into dense ordered structures [15]. Metallic nanoparticles, specifically gold and silver nanoparticles, indeed present absorption bands in the visible or near infrared regions, due to localized surface plasmon resonances (LSPR) [16], which depend on their size, morphology (spheres, rods, etc.) and environment. These resonances provide large

* Corresponding author. Address: Univ. Bordeaux – CNRS, Centre de Recherche Paul Pascal, UPR 8641, 115 Avenue Schweitzer, 33600 Pessac, France. Fax: +33 556845600.

E-mail addresses: xhan@ecust.edu.cn (X. Han), ponsinet@crpp-bordeaux.cnrs.fr (V. Ponsinet), hlliu@ecust.edu.cn (H. Liu).

amplitude variations in the nanoparticle optical responses. Wet chemistry produced silver and gold nanoparticles, or their colloidal derivatives, have been increasingly used as building blocks for the fabrication of metamaterials [17–20]. As a matter of fact, assemblies as structurally simple as dense spherical aggregates of plasmonic nanoparticles have been proposed as useful building blocks for materials presenting novel meta-properties [21], in particular because they are likely to present a magnetic dipolar resonance, which could be used to produce metamaterials with artificial optical magnetism [22] and possible components for hyperlenses [12] and cloaking [13]. A requirement is that the global spherical object presents a Mie magnetic resonance at a wavelength, at which the inside assembly of metal nanoparticles presents a strong permittivity, and it is predicted that this can be achieved with submicronic assemblies of gold nanoparticles, at red or near-infrared wavelengths. Similar properties can in principle be obtained with silver NPs and our studies focus on gold for mere experimental reasons (chemical stability of the NPs, spectral range of our optical setups). The controlled assembly of gold nanoparticles has been proposed by several routes, using block copolymer self-assembly [23,24], emulsion-templating [25], hydrophobic interactions [26], smart polymer brush coverage [27] or specific ligand association [28], for example. However, in order to have a good control of the plasmonic response of the assembled objects, several constraints need to be fulfilled altogether, which is not commonly verified. First the nanoparticles need to be large enough (>10 nm) so that their localized surface plasmon resonance is not significantly damped by finite-size effects [29]; then the assemblies should include all plasmonic nanoparticles in the system, so that the optical response is not the combination of the responses of assembled and non-assembled nanoparticles. Then, the assemblies should be appropriate for being organized in a dense material without loss of structural control. Finally, tunability and reversibility of the assembly process would be a very interesting feature for the versatility of the material formulation and study.

Diblock copolymers are preeminent assembling materials [30], as they present diverse self-assembly phenomena, produce organized structures with length scales of tens of nanometers and therefore offer great promises for the formulation of multifunctional materials. These macromolecules, made of two molecular chains of distinct chemical nature covalently linked together, can self-assemble in the solid state due to a microphase separation between the two incompatible moieties [31,32], or in a solvent due to a contrast of the two blocks in their solvent affinity [33,34]. Other types of assembly processes exist, including that of the electrostatic complexation of neutral-charged diblock copolymers with oppositely charged colloidal species. It has been studied in the cases of homopolymers [35], low-molecular weight surfactants [36,37], biomolecules [38], multivalent ions [39], or nanoparticles [40]. The driving force for this complexation mechanism includes an enthalpic gain related to the pairing of the oppositely charged species; and an entropic gain, arising mostly from the release of the counter ions initially condensed both on the nanoparticle surface and along the polymer backbone [41]. The presence of free electrolytes was shown to have a strong impact on this mechanism, as high ionic strength hinders the complexation altogether. Moreover, a so-called desalting transition was shown to allow the control of the complex sizes, as in the study published in Ref. [42]. While mixing negatively charged nanoceria with cationic-neutral poly(trimethylammonium ethylacrylate)-*b*-poly(acrylamide) block copolymers, these authors found that, with decreasing ionic strength, the system underwent an abrupt transition, at a threshold ionic strength (around 0.4 M), between an unassociated and a cluster state. To the best of our knowledge, this assembly methodology was not applied before to the control of the plasmon resonances of metallic nanoparticle

assemblies, although there is a strong interest in such a control [17,43,44].

Here we report on the formulation of controlled dense assemblies of negatively charged gold nanoparticles using their electrostatic complexation with neutral-positively charged hydrosoluble mPEG₆₃-PDMAEMA₉₇ diblock copolymers. We first present the materials and methods, then in a “Results and discussion” section, we present the synthesis and characterization of the individual entities, their assembly via the electrostatic complexation and the resulting optical properties.

2. Experimental section

2.1. Materials

Water was distilled and subsequently purified to Millipore Milli-Q quality. All glassware was cleaned in a bath of freshly prepared aqua regia solution (HCl/HNO₃, 3:1), then rinsed thoroughly with H₂O before use. Auric acid aqueous HAuCl₄, sodium citrate aqueous C₆H₅O₇Na₃, and O-(2-carboxyethyl)-O'-(2-mercaptoethyl) heptaethylene glycol C₁₉H₃₈O₁₀S (or HS-PEG₇-COOH) were used as received. Poly(ethylene glycol) methyl ether (mPEG, Alfa Aesar), and 2-Bromoisobutyryl bromide (98%, Aladdin), were used as received. N,N-Dimethylamino-2-ethylmethacrylate (DMAEMA, 97%, AlfaAesar) was purified with a column filled with activated Al₂O₃ (200–300 mesh) to remove the inhibitor, stored over CaH₂ at –26 °C, and then distilled under reduced pressure before polymerization. Triethylamine (TEA, Aldrich, 99.5%) was refluxed with *p*-toluenesulfonyl chloride, distilled, and stored over CaH₂. CuBr was washed with pure acetic acid, absolute ethyl alcohol, and anhydrous ethyl ether, and then dried in vacuum at room temperature. Other reagents were purified following standard procedures prior to use. Tetrahydrofuran (THF) and toluene were stirred over sodium and benzophenone, distilled before used. Pentamethyldiethylenetriamine (PMDETA) and other reagents were of chemical analysis grade.

2.2. Sample preparation

2.2.1. Functionalization of macroinitiator mPEG-Br

The mPEG (10.0 g) was dissolved at room temperature in 100 mL of toluene in a 250 mL flask, which was then set in an ice-water bath, thus cooling the solution to 0 °C. Triethylamine (1 mL) was added directly to the solution. 2-bromoisobutyryl bromide (0.8 mL) was added dropwise over 1 h under vigorous stirring and this solution was stirred in the ice-water bath for 1 h. Then, the reaction mixture was transferred to room temperature and stirred overnight. The solution was treated with charcoal, which was subsequently removed by filtration, and most of the toluene was removed by rotary evaporation prior to precipitation into an excess of cold (–5 °C) ether. The crude polymer was dried under vacuum, dissolved in water at pH 8–9, and then extracted with CH₂Cl₂. The organic layer was collected and dried over MgSO₄, and removal of the solvent under vacuum at 30 °C led to isolation of the purified macroinitiator (mPEG-Br).

2.2.2. Synthesis of neutral-charged diblock copolymers

mPEG-*b*-PDMAEMA diblock copolymers were synthesized following the route shown in Scheme 1, via atom transfer radical polymerization (ATRP), using mPEG-Br as the macroinitiator in a tightly sealed Schlenk flask under nitrogen atmosphere. The reactions were controlled by fixing the feed ratio of mPEG-Br/CuBr/PMDETA/DMAEMA to 1/1/1.1/100 in molar ratio and that of M(DMAEMA)/V(THF) to 50% in weight ratio. In a typical experiment, mPEG-Br was

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