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Efficient approach to in-situ preparation of anisotropic and assemblable gold nanoparticles mediated by stimuli-responsive PDMAEMA

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ABSTRACT

Nowadays, stimuli-responsive materials have attracted much attention because of their potential applications in various fields, specifically when a plasmonic nanoparticle is chemically bonded to a polymeric chain. On the other hand, preparation of assemblable anisotropic gold nanoparticles is an interesting challenge and also, synthetic methods and tunability of the plasmonic properties are usually multi-step and complicated. Here, poly (*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) was used as a stimuli-responsive polymer substrate for in-situ reduction of chloroauric acid ($HAuCl_4$) and synthesis of smart Au-PDMAEMA nanocomposites with anisotropic shapes. pH- and temperature-sensitive PDMAEMA played its role as a reducing, stabilizing and shape controlling agent to produce triangular gold nanoparticles with tunable UV–Vis absorption domain. Effect of some structural parameters like molar ratio of reducing group to Au ions, addition type and seed-mediated growth methods were studied comprehensively. Responsivity of Au-PDMAEMA nanocomposites to some stimuli like temperature and pH and also their reversibility were examined. Optical investigations revealed reversible and reproducible shifts between UV–Vis (550 nm) and near-IR (700 nm) absorptions by triggering with pH and temperature. The introduced strategy may facilitate synthesis of smart plasmonic nanoparticles with multi-responsivity. Assembly and disassembly of triangular plate-like nanoparticles with several stimulants may open up new fields due to their orientation/packing toward self-assembly.

1. Introduction

Stimuli-responsive polymers display reversible or irreversible changes in their chemical structures and/or physical properties in response to specific triggers such as pH, temperature, ionic strength and light irradiation [1]. Homopolymers with the ability to respond to more than one of these triggers would be of great importance due to their simple composition. One of these well-known multi-responsive homopolymers is poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA). As a temperature-responsive polymer, it shows lower critical solution temperature (LCST) in water [2]. Besides, the existing tertiary amine groups can reversibly absorb and desorb proton in acid/base media (pH-sensitivity) [3], or under bubbling of CO_2/N_2 gases (CO_2-sensitivity) and heat [4,5]. These triggers will cause some variations in polarity and subsequent changes in solubility of the polymer chains.

In recent years, inorganic nanoparticles have attracted considerable attentions according to their potential applications in various fields. Gold nanoparticles (AuNPs) are excellent candidates because of their straightforward synthesis, high surface-to-volume ratio with reasonable biocompatibility, antimicrobial and antifungal properties which make them suitable in bio-related fields [6,7]. They also feature photo-responsivity due to the localized surface plasmon resonance (LSPR) phenomenon. LSPR is a result of collective oscillations of a nanoparticle conduction band electrons that interacts with light [8]. This characteristic could readily be tuned in visible to near-IR (NIR) regions, depending on the AuNPs size, shape and the surrounding chemical environment [9].

The involvement of polymers in the synthesis of AuNPs can provide interesting features in terms of colloidal stability, interaction of AuNPs with the media and controlled growth of the nanoparticles during reduction process [10]. It has been shown in few recent studies that some polar polymers, bearing amine or PEGylated functional groups, could act as both reducing agent and stabilizer for the synthesis of AuNPs [11,12]. The exploitation of amphiphilic block copolymers as simultaneous stabilizer and reducing agent has been studied too [13–15]. In 2006, Armes and his group utilized a diblock copolymer comprising of poly (2-(methacryloyloxy)ethyl phosphorylcholine) (PMPC) and PDMAEMA for the synthesis of sterically-stabilized gold nanoparticles in the aqueous solution [13]. They showed that PDMAEMA blocks become partially protonated upon addition of $HAuCl_4$ and the remaining

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non-protonated tertiary amines are responsible to reduce $AuCl_4^-$ counter ions to zerovalent gold, simultaneously. This results in the adsorption of PDMAEMA blocks onto the AuNPs surface, while PMPC blocks serve as stabilizing groups. In another study, the effect of temperature on the one-pot synthesis of AuNPs in the presence of PDMAEMA was reported in the aqueous solution at low pH and without any other extra reagent [14]. Although few reports exist on the employment of PDMAEMA in the in-situ synthesis of AuNPs [13–15], the obtained gold nanoparticles are only spherical and the effect of structural parameters has not been studied comprehensively yet. Importantly, the study on the induced stimuli-responsive behavior of the prepared AuNPs has been ignored, and we have recently reported the phase switchability behavior of gold nanostructures prepared in the presence of PDMAEMA [16]. Moreover, most of the reports dealing with the preparation of smart/responsive inorganic nanoparticles are based on the prior synthesis of nanoparticles, e.g. through the reduction of a precursor followed by hybridization or ligand exchange with an as-prepared polymer [17] or modification and subsequent surface-initiated polymerization [18,19]. On the other hand, anisotropic plate-like nanoparticles show edge enhanced fields and it has recently been found that the geometrical aspects in anisotropic nanoparticles like triangular nanoparticles can be exploited as an important tool to control directional interactions for nonconventional ordered assemblies, *i.e.* in producing novel properties [20,21]. Therefore, triangular plate-like AuNPs, with switchable assembly/disassembly will be quite fascinating.

Synthesis of irresponsive triangular AuNPs has already been reported in the presence of different reducing agents and surfactants in the seeded growth process by employing e.g. the extract from lemongrass plant [22], aegle marmelos gum [23], ascorbic acid and CTAB [24,25], and also ascorbic acid together with potassium bromide on a carbon nanotube sheet [26]. Single-step process has also been applied in the presence of tryptophan and CTAB [27]. Also, polymeric reducing agents like PVA at high temperature [28] and polyvinylpyrrolidone [29] have already been used. Recently, some reports have been published on assembly and disassembly of responsive spherical AuNPs for applications like simultaneous targeting and phototherapy or multimodal imaging [30–32]. However and to the best of our knowledge, the preparation of smart/switchable triangular gold nanoparticles/nanocomposites has not been reported until now. Here, a facile, high yield and one-pot synthetic method is introduced for producing smart triangular AuNPs in the aqueous phase. The prepared PDMAEMA acts as a substrate, reducing agent and stabilizer, while attached chemically to AuNPs. In order to investigate the feasibility of tuning LSPR properties, some parameters like molar ratio of nitrogen-containing groups to Au^{3+} (N/Au), addition type of $HAuCl_4$, the presence of surfactant and seeding on the morphology and optical properties of the obtained nanocomposites have been studied in details. The simplicity in the use of this homopolymer could justify the formation of these responsive nanoparticles in such systems. Assembly of the obtained anisotropic AuNPs was examined by applying some stimulants such as pH and temperature and their responses were verified. These promising multi-responsive Au-PDMAEMA materials have potentiality to be exploited in non-linear optics, thin film optoelectronic devices, drug delivery systems, nanosensors and therapeutic applications.

2. Experimental section

2.1. Materials

N,N-dimethylaminoethyl methacrylate) (DMAEMA), azobisisobutyronitrile (AIBN), 2,2-azobis [2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044), 1,4-dioxane, n-hexane and methylene chloride were purchased from Merck Chemical Co. $HAuCl_4$ (chloroauric acid) and CTAB (cetyltrimethyl ammonium bromide) were supplied from Sigma-Aldrich. Deionized (DI) water was used in all recipes.

Table 1
Recipe for preparation of Au-PDMAEMA nanoparticles.

Sample	N/Au[a] (molar ratio)	$HAuCl_4$ Conc.[a] (M)	CTAB Conc. (M)	Seed amount[b] (μL)	Addition type
NCA-1	100	6.33×10^{-6}	–	–	Batch
NCA-2	50	3.16×10^{-6}	–	–	Batch
NCA-3	10	6.33×10^{-5}	–	–	Batch
NCA-4	100	6.33×10^{-6}	–	–	in 5 portions
NCA-5	50	3.16×10^{-6}	–	–	in 5 portions
NCA-6	10	6.33×10^{-5}	–	–	in 5 portions
NCA-S1	–	5×10^{-4}	0.008	2000	Batch
NCA-S2	–	5×10^{-4}	0.008	30	Batch
NCA-S3	–	5×10^{-4}	0.04	30	Batch
NCA-S4	–	2×10^{-3}	0.008	30	Batch

[a] The amount of Au in NCA series is based on N/Au molar ratio and in NCA-S series depends on $HAuCl_4$ concentration. Also, the amount of PDMAEMA in all recipes is 0.01 g mL^{-1}.

[b] NCA-2 sample was utilized as the seed in preparation of NCA-S series samples.

2.2. Preparation of Au-PDMAEMA nanoparticles

DMAEMA was polymerized through a conventional solution radical polymerization in 1,4-dioxane (concentration of 30 g L^{-1}) and in presence of AIBN (1 wt% relative to DMAEMA) as the initiator under N_2 atmosphere at 80 °C for 3 h. The obtained polymer was precipitated in cold n-hexane and under reduced pressure at room temperature (Molecular weight of the obtained PDMAEMA was measured and will be discussed in Section 3.2.1). Next, an aqueous solution of the prepared PDMAEMA (10 mL, 0.01 g mL^{-1}) and various amounts of $HAuCl_4$ solution in water (from a 0.001 M stock solution) were mixed batch-wise or portion-wise, depending on the recipe. Each portion of $HAuCl_4$ was added within 10 min intervals in the portion-wise recipe. Typically for preparation of NCA-1, 0.1 g of the synthesized PDMAEMA was dissolved in 10 mL deionized water. Then, 64 μL stock solution of $HAuCl_4$ was added and the mixture was magnetically stirred at 35 °C for 1 h.

The effects of molar ratio of nitrogen containing groups to Au^{3+} ions (N/Au), addition type, presence of the previously prepared Au-PDMAEMA (as the seed) and CTAB as the surfactant on the size and morphology of the obtained nanoparticles were investigated (Table 1). NCA and NCA-S sample codes represent nanoparticles in the absence and presence of CTAB, respectively. In NCA-S series, certain amount of $HAuCl_4$ (in 5 mL solution) was stirred with the added CTAB (based on the recipe) during 10 min primarily. Then, different amounts of NCA-2 (as the seed) were introduced and after 20 min, 5 mL of PDMAEMA aqueous solution (1 wt%) was added and the mixing process was continued for 30 min. Typically for NCA-S1, 0.014 g CTAB was dissolved in 2.5 mL deionized water and subsequently added to 2.5 mL stock solution of $HAuCl_4$ to form a 5 mL solution. The solution was stirred magnetically for 10 min. Next, 2000 μL of the final NCA-2 solution was introduced and then, 5 mL PDMAEMA aqueous solution (1 wt%), as reductant, was added and the mixing process continued for 30 min at 35 °C. Finally, Au-free PDMAEMA was removed by centrifugation at 9000 rpm for 10 min.

2.3. Characterization

Molecular weight and its distribution were determined using a GPC Agilent 1100 (CA, USA). GPC was equipped with a differential refractive index (RI) detector (Waters 2960), quaternary pump, PL gel 10 μm column, and calibrated with polystyrene standards. THF was used as the eluent with a flow rate of 0.3 mL min^{-1}. Powder X-ray diffraction (XRD) pattern was obtained using a Philips X'Pert MPD X-ray diffractometer with Cu Kα radiation (1.5406 Å; 40 kV, 40 mA) at a