



Regular Article

Preparation of concave magnetoplasmonic core-shell supraparticles of gold-coated iron oxide via ion-reducible layer-by-layer method for surface enhanced Raman scattering

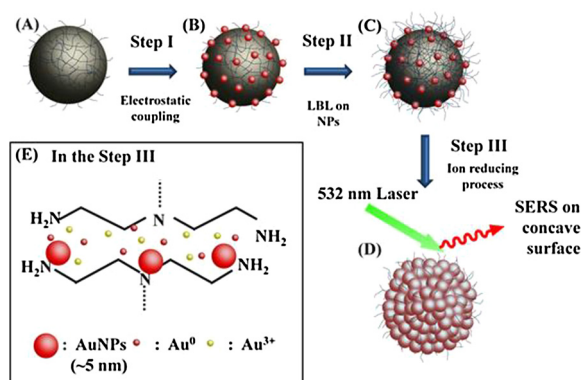


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GRAPHICAL ABSTRACT



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ABSTRACT

Preparation of suprastructure assemblies with unique colloidal and optical properties remains challenging. Non-uniform covering of magnetic nanoparticles (NPs) with an external inert Au shell has been attempted to protect the magnetic core against oxidation as well as to produce multifunctional supraparticles (SPs) possessing respective optical and magnetic properties. In this study, a concave Au NP coating was deposited on magnetic nanoparticles (MNPs) with precise control of the shell thickness and roughness through a layer-by-layer (LbL) assisted ionic reduction method termed ion-reducible LbL (IR-LbL) method. Surface enhanced Raman spectra were obtained using graphene quantum dots (GQDs) on the magnetically aligned structure of the prepared core-shell SPs. It is probable that this synthesis method and the generated SPs are essential for characterizing the merge of electronics and magnetism in the nano-regime and may be applicable for further electronics, magnetic storage, and biomedical applications.

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1. Introduction

Unique hybrid nanoscale suprastructures possessing dual magnetic and optical properties with colloidal nature are attractive owing to their potential applications, such as catalyst, surface

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enhanced Raman scattering, bio imaging and therapy [1–6]. In particular, concave metallic shell structures on a magnetic core are challenging to prepare with confinement of their unique optoelectromagnetic, catalytic, and biological properties originating from the abnormality of the electrical field in complicated surfaces [7–9]. These core-shell magnetoplasmonic supraparticles (SPs) can be functionalized with proteins, DNA, and other bio-molecules in combination with well-established gold-thiol surface chemistry for applications in bio-labeling, magnetic separation, and optical sensing [9]. Furthermore, these SPs have been extensively explored in pursuit of highly dense information storage devices and novel electronic components for spintronics [10,11]. For example, magnetic NPs with Au shell have been applied in external magnet-induced electronic circuits [12,13].

Many attempts have been made to manipulate the irregular morphology of the surface Au layer on the magnetic core to achieve non-uniformity. One representative method involves developing a limited passivation layer or epitaxial growth by reduction of Au ions on the surface of magnetic cores [14–18], in which, fine-tuning the size and shape of nano shells is crucial because of relationships between its topology and plasmonic property [19,20]. Recently, some groups presented novel approaches for achieving unique surface morphologies by anisotropic growth of Au layers [21,22]. Gold-coated iron core-shell and noble metal-coated magnetite NPs have also been synthesized using a reverse micelle method [23,24]. A polymer gap between the core and the shell was formulated to produce near infrared (NIR)-responsive Fe_3O_4 @Au nanocomposites [25]. While these prior studies have demonstrated the viability of synthesizing and assembling core-shell type NPs, precise control of the continuity of the metal coating, coating thickness, and size monodispersity, and thin film assembly of the NPs remain major challenges [26]. Furthermore, the high roughness obtained via irregular passivation of Au precursors on the magnetic core is another challenge. Preparing such particles with a uniform size/shape and core-shell morphology is hampered by significant obstacles, largely because of the lack of understanding of their formation mechanism and control of thermodynamic equivalence during the synthesis. In general, the concave structures are thermodynamically unstable and can potentially transform into spherical particles with time [27]. The formation of spiked or bristled particles is currently attributed to different tendencies of the stabilizers, as exemplified by thioglycolic acid [34], poly(vinylpyrrolidone) (PVP) [9], and cetyltrimethylammonium bromide (CTAB) [4], which are absorbed on diverse crystal faces [9,10]. In our previous paper, we reported a unique metallic core-shell nanocomplex formed by the self-assembly method, i.e., spiky gold-coated iron SPs (Fe_3O_4 @Au SPs) with diameters of 105–185 nm that exhibited strong magnetization [21]. These species exhibit unique physiochemical properties because of their well-defined shape and distinctive topological structure. However, the synthesis approach was still not attractive as a robust method for coating AuNPs in any core structure owing to the complex preparation process. We proposed gold-coated iron oxide core-shell supraparticles which has polyethylimine (PEI) as an anchoring group, since the PEI is effective connecting agent to make gold shells on the surface of inorganic nanostructures because it has rich amine groups which is adhesive to gold [28,29]. While the experimental process, a AuNPs coating was deposited on magnetic nanoparticles (MNPs) with precise control of the shell thickness and roughness through a PEI mediated layer-by-layer (LbL) assisted ionic reduction method, termed ion-reducible LbL (IR-LbL). LbL itself is an excellent technique for controlling the thickness of a coating layer by layer a sequentially repeated process [30]. However, when it is applied to the control of shell thickness growth, loss of most of the NPs is inevitable because of complicated aggregation due to various charge-charge interactions. Thus,

a novel process is suggested wherein a minimal LbL process is conducted by changing the concentration or binding time of the polymer, leading to remarkable control of the shell thickness in the range of 2–3 nm in one round of the LbL process. After the process to forming the shell on MNPs unique morphology of Au shell which is composed of self-assembled AuNPs' suprastructure anchored with PEI was observed by electron microscope, called supraparticle (SP). Highly enhanced Raman scattering signal of rhodamine-B and QDs were measured on SPs' surface and additional enhancement was obtained on magnetically aligned structure of SPs. It is probable that this synthesis method and the generated SPs are essential for characterizing the merging of electronics and magnetism in the nano-regime and may be applicable for further electronics, magnetic storage, and biomedical applications.

2. Experimental method

2.1. Materials

Polyethyleneimine (PEI, branched, M_w : ~25,000 g mol⁻¹), chloroauric acid (HAuCl_4), hydroxylamine hydrochloride ($\text{NH}_2\text{-OH}\cdot\text{HCl}$), Iron(III) chloride hexahydrate ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$), sodium acetate anhydrous (NaAc), 8-mercaptooctanoic acid (8-MOA), ethylene glycol, poly(diallyldimethyl ammonium chloride) (PDDA), and poly (acrylic acid) (PAA) were all obtained from Sigma-Aldrich Inc. (Milwaukee, WI). Sodium hydroxide was obtained from Yakuri Pure Chemicals Co., Ltd. (Kyoto, Japan). Sodium borohydride (NaBH_4) was obtained from Junsei Chemical Co., Ltd. (Chuo-ku, Japan). Trisodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7\cdot 3\text{H}_2\text{O}$) and cysteamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{SH}$) were obtained from Fluka (Buchs, Switzerland). Ethanol was obtained from SK Chemicals (Seongnam, South Korea). Deionized water (>18.2 m cm⁻¹) was used in most experiments (Human Corporation, Seoul, South Korea). All chemicals were used as received with no further purification.

2.2. Step I: synthesis of PEI-coated MNPs (MNP@PEI)

Firstly, magnetic NPs were synthesized by solvothermal synthesis [31]. The surface of the prepared NPs was modified with PEI (denoted as MNP@PEI). In detail, 0.68 g of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ was dissolved in 20 ml of ethylene glycol to form a transparent solution. Subsequently, 1.2 g of sodium acetate anhydrous (NaAc) and 0.5 g of PEI were added to the solution. The mixture was stirred vigorously for 20 min at 60 °C and transferred to a home-made autoclave and reacted at 220 °C for 2 h. The resultant black precipitates were rinsed three times with deionized water and ethanol to separate the supernatant with the assistance of a permanent magnet. The precipitates were then dried in a vacuum oven at 60 °C under 0.05 atm of pressure for 12 h and redispersed in deionized water (2 mg mL⁻¹).

2.3. Step II: AuNP decorated MNPs (MNP@PEI@Au SPs) by LbL method

The electrostatic interaction between positively charged PEI and the negatively charged AuNPs was exploited to synthesize the MNP@PEI@Au SPs via the facile LbL method. First, colloidal AuNPs (~3 nm) were produced in separate glassware by reducing HAuCl_4 (1 w/v%) using NaBH_4 (0.075 w/v%) in sodium citrate (38.8 mmol L⁻¹) [32]. The aqueous solution of the prepared MNP@PEI (1 mg mL⁻¹) was then added to 5 mL of the prepared AuNP solution, where the electrostatic surface charge of each NP was +34.2 mV and -22.4 mV, respectively. The mixed solution was sonicated for 1 min and this solution was gently shaken for 2 h until the color changed from brown to reddish brown. Finally, the MNP@PEI@AuNP composite was separated from the solution

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