



Polyhedral gold nanocrystals/polyelectrolyte composite film: One-pot synthesis via interfacial liquid plasma polymerization



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ABSTRACT

In contrast with the conventional *in situ* and *ex situ* methods for the preparation of polymer-based nanocomposites in which the polymer matrix (for both methods) and metal nanoparticles (for the *ex situ* method only) are prepared separately prior to being combined to form the composite, polyhedral gold nanocrystal/polymer composite film was successfully synthesized through combining the *in situ* formation of gold nanocrystals (AuNCs) and simultaneous polymerization of the polyelectrolytes from ionic liquids and surfactants under atmospheric pressure plasma. The composite film contained a large number of well-shaped polyhedral AuNCs. The AuNCs are stereoscopically distributed in the polyelectrolyte matrix without agglomeration. The size of the AuNCs prepared in a 3 mm deep reactor decreased along the cross section of the composite film from top to bottom, while they were uniform in size when they were prepared in a 5 mm deep reactor. In the presence of the Au precursors, the polymer film thickness increases to 7.03 μm , which is two-fold thicker than that of the polymer film prepared without adding Au precursors. Through the density functional theory (DFT) calculations, the critical role of Triton X100 was clearly demonstrated in the formation of the well-shaped AuNCs. The composite film exhibited the reduction of ~66% in Young's modulus and the reduction of ~44% in hardness compared to the neat polymer film. Finally, an appropriate mechanism is proposed for the formation of the polyhedral AuNC/polyelectrolyte composite film.

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1. Introduction

Metal nanocrystal-polymer composite films have received significant attention for a wide range of applications over the past few decades [1–4]. This is due to combining the properties of two fundamentally different materials in the composite, which leads to improved physical and chemical properties. Until now, there have been two prominent approaches to preparing polymer nanocomposite films. The first approach is an *ex situ* process, where pre-synthesized nanocrystals are mixed with a polymer. In this process, the polymer matrix only functions as the dispersion medium. However, this approach results in the agglomeration of

nanocrystals due to the high polymer viscosity [5]. Moreover, the nanoparticle agglomeration is difficult to separate, even using external shear forces. The second approach is an *in situ* process, where an appropriate metal precursor is dispersed in the polymer solution and then the metal ions are reduced to metal nanocrystals using chemical reagents or physical process [6–8]. For the *in situ* approach, the metal nanocrystals are intricate components of polymer chains. Therefore, they can be well dispersed in a polymer matrix. However, a potential disadvantage in both approaches is that the polymer is first prepared in an external synthesis step. Thus, complicated steps are required in order to synthesize the polymer, which might result in a low purity level of the products.

Gold nanocrystals (AuNCs) represent an ideal platform for surface plasmon resonances, catalysts, nanomedicines, bio-sensors, etc. [9–12]. When AuNCs are incorporated on the surface of a polymer or embedded into the polymer matrix, the resulting

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nanocomposites exhibit enhanced activity in Raman scattering [13] and nanomedicine [14] compared with using only AuNCs. *In situ* methods are candidates for fabricating these nanocomposites due to their advantage as described above. However, AuNCs prepared using this approach are spherical or irregular, and are not well-faceted shapes. The important role of well-faceted shapes of AuNCs in chemical and biological sensing and nanomedicine has been clearly demonstrated [15,16]; thus, in order to control the shape of AuNCs, various process factors have been adjusted and investigated, such as the temperature, reducing agent, and shape-directing additive. However, this approach results in numerous synthesis steps or in the formation of unexpected intermediate products that must be removed. Thus, the development of highly faceted and well-shaped AuNCs embedded in the matrix remains a challenge.

In order to prepare AuNC/polymer composites, two *in situ* methods can be used: the chemical *in situ* method and the physical *in situ* method [14,17–21]. In the chemical *in situ* method, a gold salt precursor such as HAuCl_4 is mixed with a polymer solution in order to form a homogeneous system. Then, a reducing agent such as NaBH_4 is added to the system in order to reduce the number of gold ions forming gold nanoparticles [14,17]. As a consequence, the excess solvents, reducing agents, and subsequent isolation must be removed. However, these cannot be completely removed, which results in a low purity composite. In contrast, physical *in situ* methods such as UV irradiation, microwave, and plasma have significant potential as alternative candidate methods that do not use chemical reducing agents, which is due to the high quality of the obtained AuNCs such as high dispersity and high purity [18–20]. However, for all physical *in situ* methods, the polymer must be prepared separately before mixing with the metal salt precursors, which leads to the need for more steps in order to fabricate a well-designed composite. Recently, a new method was developed for the preparation of a polymer electrolyte film via interfacial liquid plasma polymerization using one atmospheric pressure plasma in contact with ionic liquid; this method is named the ionic liquid plasma system [22]. The polymer electrolyte film was polymerized from ionic liquid, which is a green solvent, and Triton X100. Due to the well-controlled plasma parameters, the obtained polymer films exhibit uniform thickness. Moreover, using the same ionic liquid plasma system, metal nanocrystals have been successfully synthesized [23,24]. This method produced high purity metal nanocrystals because it did not use the vacuum operation, reducing agents, and capping agents. Thus, the ionic liquid plasma system clearly demonstrated the ability to create polymer films and metal nanoparticles, which enable the process of synthesizing polymer nanocomposites.

This study establishes a new strategy for the preparation of well-shaped, well-dispersed polyhedral AuNCs embedded simultaneously in the polymer matrix. In order to achieve this, for the first time, a combination of plasma polymerization with the *in situ* formation of nanocrystals was conducted. The plasma polymerization is based on the surfactant-assisted polymerization at the plasma-liquid interface using 1-butyl-3-methylimidazolium tetrafluoroborate and Triton X100 as the starting materials. In order to demonstrate the effect of the polymer film on the *in situ* formation of the well-shaped AuNCs, the preparation of the AuNCs was performed without adding Triton X100 to the reaction mixture. In order to understand the mechanism of the growth in size and the formation of various shapes of polyhedral AuNCs, the formation of the AuNC/polyelectrolyte composite film was undertaken at different plasma exposure times. Next, the effect of the Au precursors on the thickness of the obtained polymer films was investigated. We also investigate surface-enhanced Raman scattering (SERS) of the AuNC/polyelectrolyte composite film treated with

benzenethiol (BT) solutions. Finally, the mechanism of the *in situ* formation of the polyhedral AuNC/polymer composite film using the interfacial liquid plasma polymerization method is proposed.

2. Experimental section

2.1. Materials

$\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ (99.999% trace metals basis), Triton-X100, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄), benzenethiol, acetone, and ethanol were purchased from Sigma-Aldrich (USA). Argon gas was obtained from Yonhap LPG (Korea).

2.2. Synthesis of polyhedral AuNC/polyelectrolyte composite film

A [BMIM]BF₄ solution of 1.5 mol% Triton X100 was first prepared using a Vortex Mixer-KMC-1300V for 15 min. Then, 10 mg of $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ was added to 2 ml of the mixture followed by sonicating in a bath sonicator for 15 min. Next, 0.5 ml of the final mixture was dropped into a Teflon reactor (15 × 30 mm, 3 mm deep). The liquid film was exposed under an atmospheric pressure plasma flame with conditions of 150 W power, 5 lpm Ar gas flow rate, and 10 min treatment time [22]. The gap between the power electrode and the liquid film was 2 mm. After the plasma polymerization, the synthesized composite film was immersed into ethanol in order to separate the film from the reactor. Next, the composite film was washed with acetone followed by washing with distilled water several times. Then, it was dried in oven at 60 °C for 1 h.

2.3. Synthesis of AuNCs without using Triton X100

For the synthesis of AuNCs, all synthetic procedures were the same as the polyhedral AuNC/polyelectrolyte composite film synthesis, except the absence of Triton X100 in the mixture of the Au precursor and [BMIM]BF₄. After the plasma reduction, the precipitates were collected after centrifugation at 10,000 rpm for 10 min. They were washed with acetone and ethanol several times.

2.4. Characterization of polyhedral AuNC/polyelectrolyte composite film

The ultrastructure of the synthetic composite film was carefully observed through measuring the film thickness using a scanning electron microscope (SEM; JSM-7000F, JEOL, Japan). The characterization of the composite was also conducted via transmission electron microscope (TEM; JEM-2100F, JEOL, Japan). The remaining solutions were characterized using ultraviolet-visible (UV-Vis) spectroscopy (Agilent Cary 60 UV-Vis, USA). X-ray photoelectron spectroscopy (XPS) spectra were collected using a Sigma Probe Thermo Fisher VG Scientific spectrometer (MULTILAB 2000, Thermo Scientific, USA) equipped with a monochromatic Al K α X-ray source. The thermal stability of the polymer was determined using a thermal gravimetric analysis (TGA) (Mettler-Toledo Inc., USA) in air condition. Mechanical strength of the composite films was tested by using nanoindentation system (Nano Indenter XP, M.T.S, USA).

2.5. Density functional theory (DFT) calculations

In order to clarify the chemical steering effect of [BMIM]BF₄ and Triton X100 on the growth of AuNCs, a set of models were designed for the DFT calculations of the chemical affinity of BMIM-derived C₅N₂H₈, Triton X100-derived C₂OH₄, and C₂H₃ motifs to Au. It was hypothesized that the short structural motifs of [BMIM]BF₄ and

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