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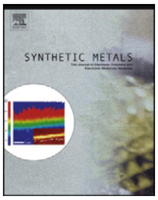

Core–shell nanoparticle of silver coated with light-emitting rubrene: Surface plasmon enhanced photoluminescence

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ABSTRACT

Silver (Ag) nanoparticles (NPs) with a diameter of 50–100 nm were fabricated by using a reduction process of silver nitrate with sodium citrate. Using the Ag NPs, hybrid core (Ag)–shell (organic light-emitting rubrene) NPs were prepared through a hydrothermal process. The formation of hybrid core–shell NP of Ag-rubrene was confirmed through transmission electron microscope images. From ultraviolet and visible absorption spectra, the Ag and rubrene characteristic peaks were simultaneously observed for the core–shell NPs. Using a high-resolution laser confocal microscope (LCM), the photoluminescence (PL) intensity of the Ag–rubrene core–shell single NP was about 300 times higher than that of the rubrene single NP. This remarkable enhancement of PL efficiency in the core–shell single NP is due to the energy transfer effect in the surface plasmon resonance coupling between Ag and rubrene materials.

1. Introduction

Surface plasmon in nanoscale metals and their hybrid nanostructures has been intensively studied in the field of plasmonics, bio-sensing, and optoelectronics [1–3]. For metal–semiconductor hybrid nanostructures, when the absorption energy of the surface plasmon for nanoscale metals matches with the emitted photon energy of luminescence semiconductors, the surface plasmon resonance (SPR) coupling can occur, resulting in the enhancement of the photoluminescence (PL) efficiency [4–10]. Therefore, the SPR coupling in various hybrid nanostructures has been applied to increase the efficiency of optoelectronic devices [2], biosensors [1,11], light-emitting devices [12], and light-harvesting cells [13].

Core–shell nanoparticles (NPs) of metal–semiconductor are attractive nanostructures to study the SPR, because of geometrical isotropy to an incident electromagnetic wave [14]. The photoresponsive semiconducting shell in the core–shell NPs protects against oxidation of core–metal NP [15], which can be applied to optoelectronics with the increased efficiency based on the SPR coupling [16]. π-Conjugated organic rubrene and tris (8-hydroxyquinolinato) aluminium (Alq_3) are promising systems for the core–shell NPs, because of the excellent light-emission and charge transport properties [17,18]. The organic light-emitting molecules can be physically attatched or chemically bonded to the core–metal NPs through an external pressure or chemical modification, respectively.

Herein, the hybrid NPs consisted of Ag as a core and light-emitting rubrene as a shell, which were fabricated through a hydrothermal process, in which the external high pressure can assist to attach distinct materials homogeneously. The core–shell nanostructure of the Ag–rubrene was confirmed by HR-TEM images. The PL intensity of the Ag–rubrene core–shell single NP measured by a high-resolution laser confocal microscope (LCM) was dramatically enhanced about 300 times, compared to that of the rubrene single NP. This is explained in terms of the energy transfer effect in SPR coupling.

2. Experimental

The Ag NPs were prepared by using a reduction process of silver nitrate ($AgNO_3$) with sodium citrate ($C_6H_5Na_3O_7$) [19]. The $AgNO_3$ (0.01 M) aqueous solution in the deionized (D.I.) water (450 mL) was mixed with $C_6H_5Na_3O_7$ solution at 100 °C. When the color of the mixed solution was changed to gray, the solution was naturally cooled down to room temperature (RT). Then, the Ag NPs were obtained by centrifuge of the solution. Organic rubrene NPs were prepared through a reprecipitation method [20]. The

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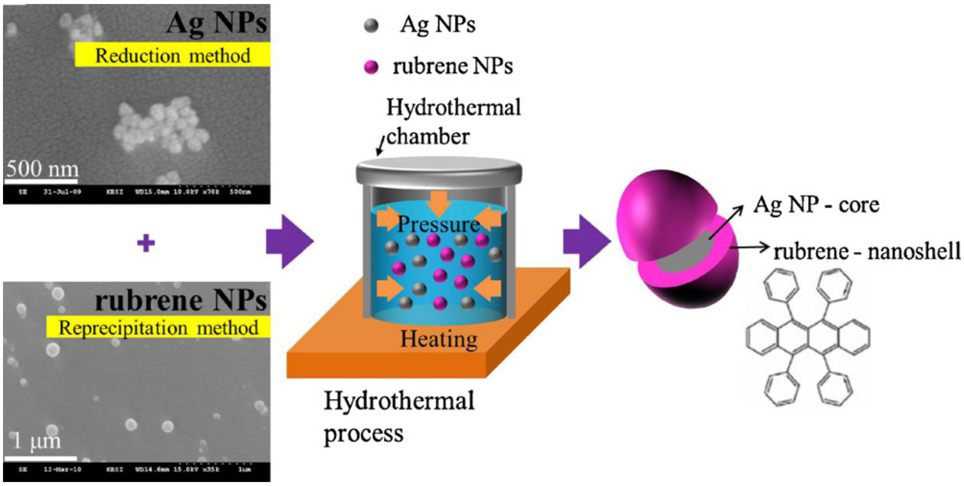

Fig. 1. Schematic illustration of fabrication procedure of Ag–rubrene core–shell NPs. SEM images (on the left) are for Ag NPs (top) and rubrene NPs (bottom). Schematic chemical structure of rubrene molecule is shown in the bottom of right.

rubrene powder (98% purity) was purchased from Sigma–Aldrich Co. and used without further purification. The rubrene solution dissolved in tetrahydrofuran (THF) was rapidly added into the D.I. water, and then the hydrophobic rubrene materials formed as NPs with a diameter of 161 (±53) nm in water solution. To fabricate the Ag–rubrene core–shell NPs, the hydrothermal process was employed [21]. The prepared Ag NPs and rubrene NPs were mixed with D.I. water in the hydrothermal closed chamber (Parr Instrument Acid Digestion Bombs, 4744 general purpose bomb). The hydrothermal chamber with the samples was heated at 110 °C in the vacuum oven for 5 h. Because of the closed space of the chamber, the NPs were influenced by the high external pressure during the hydrothermal treatment. After the hydrothermal treatment, the chamber was cooled down to RT for 6 h. Fig. 1 shows a schematic illustration of the fabrication procedure of the Ag–rubrene core–shell NPs, and it shows scanning electron microscope (SEM, Hitachi 4300) images of the Ag and rubrene NPs.

The PL images and spectra of the core–shell and rubrene single NPs were measured by using a homemade laser confocal microscope (LCM). For LCM PL excitation, an Ar-ion laser (λ_{ex} = 488 nm) was used. During the measurement, laser power and exposure time was fixed at 30 μW and 1 s for identical experimental conditions. The ultraviolet and visible (UV/vis) absorption spectra were measured by Agilent 8453 UV/vis spectrophotometer.

3. Results and discussion

The formation of the Ag–rubrene core–shell NPs was visualized using a high-resolution transmission electron microscope (HR-TEM Tecnai 20) images. Fig. 2(a and b) shows HR-TEM images of the Ag single NP and the Ag–rubrene core–shell single NP, respectively. The polyhedron shape with a mean diameter of 72 (±16) nm for Ag NPs was observed in the HR-TEM image. From the HR-TEM image and its magnification as shown in Fig. 2(b and c), respectively, the thin rubrene material with a thickness of ∼5 nm was coated on the surface of the Ag NP, indicating the core–shell NP. The mean diameter of the Ag–rubrene core–shell NPs was 77 (±17) nm.

To confirm the Ag–rubrene hybrid nanostructure, UV/vis absorption spectra of the rubrene NPs and the Ag–rubrene core–shell NPs were compared, as shown in Fig. 3. The inset of Fig. 3 shows the UV/vis absorption spectrum of the Ag NPs, in which, because of the localized SPR [22] and different physical shapes and sizes [23] such as polyhedron of Ag NPs, the broad optical absorption peak was observed at 410–490 nm (2.53–3.02 eV). The UV/vis absorption characteristic peaks of rubrene NPs were observed at 463, 497, and 533 nm due to vibronic band transitions [18]. From the UV/vis absorption spectrum of the Ag–rubrene core–shell NPs, all absorption characteristic peaks of both Ag and rubrene materials were simultaneously observed at 438, 463, 497, and 533 nm (Fig. 3). Therefore, the coexistence of the Ag and rubrene materials in the core–shell NPs was confirmed.

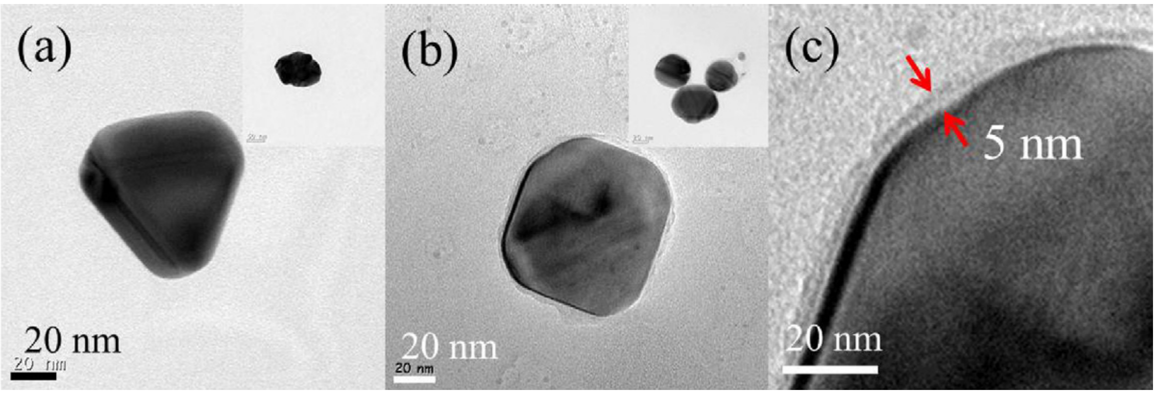

Fig. 2. (a) HR-TEM image of Ag single NP. Inset: HR-TEM image of other Ag NP. (b) HR-TEM image of Ag–rubrene core–shell single NP. Inset: HR-TEM image of other core–shell NPs. (c) Magnification of HR-TEM image of the Ag–rubrene core–shell single NP.