Surface plasmon modes of gold nanospheres, nanorods, and nanoplates in an organic solvent: Phase-transfer from aqueous to organic media

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ABSTRACT

We present a process for the phase-transfer of gold nanoparticles from an aqueous to an organic medium with normal alkanethiols. This method can be applied not only to large nanospheres ($d \sim 100$ nm) but also to anisotropic nanoparticles like nanorods and nanoplates. It allows the comparison of the nanoparticle optical properties when they are dispersed in both aqueous and organic media.

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1. Introduction

Metal nanoparticles have been of significant interest in fields such as photonics, electronics, biosensors, and catalysis, because these materials show size- and shape-dependent physicochemical and optoelectronic properties that are quite different from the bulk species [1–6]. Especially, gold nanoparticles have been on the center of such applications because there are many well-established colloidal synthetic routes, giving rise to a homogeneous size- and shape-distribution, which consequently leads to fine-tuning of their corresponding physicochemical properties. For example, when gold nanospheres are approximately 5–100 nm in diameter, the hue of colloidal dispersion is red or pink. Such nanospheres have a localized surface plasmon resonance (LSPR) in the range of 500–600 nm [7,8]. In order to push the wavelength of Au LSPR to near-infrared spectral window, the shape of the nanoparticles needs to be changed to other shapes such as nanoshells, nanorods and nanoplates [9–11]. The synthetic methods for these nanoparticles are developed in an aqueous medium because of water's ability to dissolve a variety of ions and surfactants. In contrast, their synthesis in organic media is limited by the poor solubility of the

metal ion precursors [12]. For example, various sizes ($d < 10$ nm) gold nanospheres of relatively high monodispersity could be obtained by following the synthetic approach developed by Brust et al., which involves the phase-transfer of Au^{3+} from water to toluene with an aid of phase-transfer agent [13]. These nanospheres are alkanethiol-capped nanoparticles (known as monolayer protected clusters, MPCs) and are readily dispersed in a variety of organic media [14]. However, with this method, either large nanospheres ($d > 10$ nm) or anisotropic nanoparticles with other shapes cannot be synthesized with good monodispersity. Thus, the phase-transfer of nanoparticles from aqueous to organic medium with complicated capping agents has been suggested as an alternative approach [15]. Nanoparticles prepared in an organic medium is interesting for applications to catalytic processes and for surface modification with other organic functional groups to fine-tune their properties [12]. Also, it will be fundamentally interesting to investigate the shift of LSPR of various shapes (and sizes) of nanoparticles depending on the change of dispersion media in order to develop color filters or surface plasmon sensors. Herein, we present a process for the phase-transfer of gold nanoparticles from an aqueous to an organic medium with normal alkanethiols. This method can be applied not only to large nanospheres ($d \sim 100$ nm) but also to anisotropic nanoparticles like nanorods and nanoplates. It allows the comparison of the nanoparticle optical properties when they are dispersed in both aqueous and organic media.

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2. Materials and methods

2.1. Synthesis of Au nanospheres

The Au colloid solution (d = 13 ± 1 nm) was prepared using a conventional methodology [16]. Briefly, 100 mL of a 1.0 mM aqueous $HAuCl_4·3H_2O$ solution was added to 100 mL of triply deionized water (Millipore), which was then boiled. Ten milliliters of a 38.8 mM aqueous solution of sodium citrate was added and boiled for 30 min.

A seed-mediated growth approach was used for large Au colloid solution.

A volume of 4 mL of a 20 mM aqueous $HAuCl_4·3H_2O$ solution and 0.4 mL volume of a 10 mM aqueous $AgNO_3$ solution were added to 170 mL of triply deionized water. Fifteen milliliters of the aforementioned 13 nm Au NP sol was added to the solution. Thirty milliliters of 5.3 mM ascorbic acid was then added slowly (0.6 mL/min) with constant stirring. The resulting NP diameter was determined to be 33 (±3) nm. When the seed amount was changed to 3 mL under the same experimental conditions, the resulting NP size was 49 (±4) nm. For a 72 (±4) nm colloid sol, 1.8 mL of the seed solution was added.

2.2. Synthesis of Au nanorods [17,18]

2.2.1. Seed solution preparation

Ten microliter of 0.1 M aqueous CTAB solution was mixed with 0.125 mL of 0.02 M aqueous $HAuCl_4·3H_2O$. Six-hundred microliter of ice-cold aqueous $NaBH_4$ solution was then added, which resulted in a color change to brownish yellow. Two different concentrations of $NaBH_4$ solution were used; 6 and 10 mM. Seeds prepared from 6 mM $NaBH_4$ were labeled as seed 1, and seeds from 10 mM $NaBH_4$ were seed 2.

2.2.2. Preparation of NRs with an aspect ratio ~2.6 ($d ≈ 20 ± 3$ nm, $L ≈ 51±4$ nm)

A mixture of 2.5 mL of 20 mM aqueous $HAuCl_4·3H_2O$ solution, 550 μL of 0.1 M ascorbic acid, and 400 μL of 0.01 M aqueous $AgNO_3$ solution was added to 95 mL of 0.1 M aqueous CTAB solution. One-hundred and twenty microliter of the seed 2 solution was added to the prepared growth solution and incubated for 5 h at room temperature without agitation.

2.2.3. Preparation of NRs with an aspect ratio ~3.8 ($d ≈ 13 ± 1$ nm, $L ≈ 49 ± 4$ nm)

A mixture of 2.5 mL of 20 mM $HAuCl_4·3H_2O$, 550 μL of 0.1 M ascorbic acid, and 600 μL of 0.01 M $AgNO_3$ was added to 95 mL of 0.1 M CTAB solution. One-hundred and twenty microliter of the seed 1 solution was added to the prepared growth solution.

2.3. Synthesis of Au nanoprisms [19]

2.3.1. Seed solution preparation

0.5 mL of 20 mM aqueous $HAuCl_4·3H_2O$ solution was added to 36.5 mL of deionized water (Millipore). And then one milliliter of a 10 mM aqueous solution of sodium citrate and 1 mL of 100 mM aqueous $NaBH_4$ (ice-cold) solution were added with vigorous stirring.

2.3.2. Preparation of nanoprisms (edge L = 161 (±13) nm and thickness = 12 (±1) nm)

A mixture of 108 mL of 0.05 M aqueous CTAB (from Fluka) solution and 54 μL of 0.1 M aqueous NaI solution was divided into three containers labeled with 1, 2, and 3. Container 1 and 2 hold 9 mL of the mixture and container 3 holds the rest solution of 90 mL. Then, a mixture of 125 μL of 20 mM aqueous $HAuCl_4·3H_2O$ solution, 50 μL of 100 mM NaOH, and 50 μL of 100 mM ascorbic acid were added to each container 1 and 2. A mixture of 1.25 mL of 20 mM $HAuCl_4·3H_2O$, 0.5 mL of 100 mM NaOH, and 0.5 mL of 100 mM ascorbic acid were added to container 3.

One mL of the seed solution was added to the container 1 with mild shaking. Then, 1 mL of container 1 solution was added container 2. After 5 s shaking, the whole solution of container 2 was added to container 2. After 30 min, the color of container 3 shows magenta-purple.

2.4. Synthesis of Au nanodisks [20]

1.5 mL of a mixture of 10 mL of 0.05 M CTAB and 250 μL of 20 mM of $HAuCl_4·3H_2O$ was added to 10 mL of Au nanoprism solution. After 1 h, the reaction completes.

2.5. Phase-transfer of Au nanoparticles

A total of 20 mL of Au nanoparticle colloid was transferred to a Teflon cell to the top of which was added 10 mL of hexane to form an immiscible water/hexane interface. One mL of normal alkanethiols ($4.17 × 10^{-7}$ M in hexane) were added to the hexane layer. Then, 6 mL of ethanol was added drop-wise to the surface of the water/hexane layer, leading to trapping of the nanoparticles at the interface. The hexane layer evaporates spontaneously leaving the nanoparticle films on the water surface. A glass slide whose surface was pretreated by immersing into 0.1 M octadecyltrimethoxysilane solution in hexane for 30 min was brought in contact with the top of Au nanoparticle film, leading to the nanoparticle transfer to the surface of glass slide. Then, the glass slide was immersed into normal alkanethiol solution ($4.17 × 10^{-7}$ M in toluene) for 30 min. The glass slide was taken out of the alkanethiol solution and then was re-immersed in pure toluene with ultrasonic agitation, resulting in nanoparticle dispersion in toluene.

2.6. Synthesis of 16-mercapto-N-octadecylhexadecanamide ($CH_3(CH_2)_{17}NOC(CH_2)_{10}SH$)

A mixture of ocatadecylamine (50 mM in toluene), 16-Mercaptohexadecanoic acid (50 mM in toluene), and N,N′-Dicyclohexylcarbodiimide (50 mM in toluene) was heated for 8 h at 110 °C with stirring under reflux condition. Supernatant solution was separated from white urea precipitate. The supernatant was evaporated, leading to the powder form of 16-mercapto-N-octadecylhexadecanamide.

3. Results and discussion

3.1. Phase-transfer of gold nanoparticles from water into toluene

Fig. 1 shows the preparation of alkanethiol-capped nanoparticles. Gold nanoparticle colloids are prepared in an aqueous medium. A total of 20 mL of such colloid was transferred to a Teflon cell to the top of which was added 10 mL of hexane to form an immiscible water/hexane interface. A certain amount (~$4.17 × 10^{-7}$ M) of alkanethiol was added to the hexane layer. Then 6 mL of ethanol was added drop-wise to the surface of the water/hexane layer. Nanoparticles became destabilized (i.e., their surface charge gradually decreased) when the dielectric constant of the water was decreased by the addition of ethanol with a lower dielectric constant [21,22]. The water/hexane interface entraps the destabilized nanoparticles in order to decrease the interfacial energy between water and hexane. The nanoparticles at the interface are partially coated with alkanethiols due to the strong interaction