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Phase transfer of gold nanoparticles from aqueous to organic solution containing resorcinarene

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Abstract

Citrate-capped gold nanoparticles (NPs) in aqueous solution were transferred directly into the organic solution mesitylene containing C-undecylcalix[4]-resorcinarene (C11-resorcinarene). C11-resorcinarene, which has long hydrophobic tails and phenolic hydroxyl groups, acted as both a phase-transfer and a capping agent. The C11-resorcinarene-capped gold particles could be isolated and dispersed in different organic solvents. Optical absorption spectra corresponding to surface plasmon resonance provided a broad band centered at 534 nm for C11-resorcinarene-capped gold NPs in mesitylene. High-resolution transmission electron micrograph images revealed that the average particle diameter of C11-resorcinarene-capped gold NPs is ∼12 nm.

Keywords: Phase transfer; Organo-capped; Gold nanoparticles; Resorcinarene

1. Introduction

Metal nanoparticles (NPs) exhibit many chemical and physical properties and have been widely exploited for use in catalysis [1,2], photography [3], electronics [4], optics [5], and biotechnology [6,7]. Thus, numerous innovative techniques have been developed to synthesize metal NPs in polar [8–13] and nonpolar solvents [14–18] because size, stability, and properties depend strongly on the methodology. To obtain metal NPs in nonpolar solvents, Brust et al. [14,15] developed a biphasic methodology, involving transfer of metal ions into the organic layer using phase transfer reagents, followed by reduction with $NaBH_4$ in the presence of suitable single-chain monodentate capping agents. In a different approach, there have been some reports where metal nanoparticles formed in aqueous solution are transferred to the organic solution containing capping agents [19–24]. The advantages of the latter technique have been emphasized by Sastry and co-workers [24] in their recent report. It is noteworthy that this sort of phase transfer confers an extra advantage in metal particles catalyzing organic reactions in nonpolar solvents and in knowledge about media effects and the state of adsorption on the colloidal surface in contact with various environments. Besides, it is perhaps a most important pathway in directing nanoparticles into prescribed assemblies involving organic and inorganic constituents.

Gold NPs are of great interest because of their important applications in the areas of materials science and biomedicine. Wei and co-workers [25–31] have demonstrated that resorcinarene and its derivatives are good dispersants for stabilizing gold NPs in nonpolar solvents. There have been two different approaches: (i) aerosols of gold nanoclusters were bubbled directly into a 1 mM solution of resorcinarene in mesitylene; or (ii) an aqueous suspension of citrate-stabilized gold particles was treated with the solution of resorcinarene in THF followed by extraction with toluene in the presence of tetra-*n*-octylammonium salt. There are very few reports on phase transfer of aqueous colloidal gold particles into organic solution containing surfactant [19,20,23]. Here, we describe phase transfer of gold NPs from the aqueous phase into the organic phase containing resorcinarene without using any other additional phase transfer reagent.

Resorcinarene was selected over conventional single-chain monodentate dispersants for several reasons: (i) its adsorption

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onto the NP surface can be greatly stabilized by the cooperative multidentate nature of the interactions; (ii) it may reduce the entropy cost of dissolution because of its lower surfactant/particle ratio; and (iii) it may increase the solubility of NPs in nonpolar solvents because of the greater mobility of its pendant hydrocarbon tails.

2. Experimental

2.1. Materials and instruments

Hydrogen tetrachloroaurate(III) tetrahydrate (BDH, England), trisodiumcitrate (Wako, Osaka), dodecanal and mesitylene (Acros, Belgium), and resorcinol, hydrochloric acid, and ethanol absolute (Riedel-de Haën, Seelze) were purchased from the companies indicated in the parentheses. All chemicals were analytical reagent grade and were used as received without any further purification.

IR spectra were measured for samples as KBr pellets with a Perkin–Elmer 983 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz on a Bruker AC-400 spectrometer. UV–vis absorption spectra were recorded on a Hitachi U-3200 spectrophotometer. Samples for transmission electron micrograph (TEM) and high-resolution TEM (HRTEM) measurements were prepared by placing a drop of the aqueous or mesitylene (C11-resorcinarene-capped) solution of gold NPs onto a copper microgrid and drying at room temperature. TEM and HRTEM photographs were taken on Hitachi H-7100 and TECNAI-G2 transmission electron microscopes at acceleration voltages of 75 and 200 kV, respectively.

2.2. Preparation of C-undecylcalix[4]resorcinarene [32]

Resorcinol (12.8 g, 0.12 M) and dodecanal (22.08 g, 0.12 M) were dissolved in ethanol (120 ml). The mixture was cooled down to 0 °C. Hydrochloric acid (12 M, 18.5 ml) was instilled slowly into the reaction mixture with stirring. After complete addition of hydrochloric acid, the temperature was raised to 70 °C, and stirring was continued an additional 10 h under nitrogen. Upon cooling to room temperature, a precipitate was formed, which was separated by filtration and washed thoroughly with hot water. The product was dried in a vacuum and recrystallized from MeOH and then hexane–acetone. IR (KBr disk): 3496, 3363, 2919, 2846, 1619, 1507, 1427, 1308, 1169, 1082, 904, 831, 718, 619, and 526; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.62–9.29 (ArOH, m, 8 H), 7.19 (ArH, s, 4 H), 6.09 (ArH, s, 4 H), 4.29 (ArCRHAr, t, 4 H, $J = 15.2$ Hz), 2.21, 1.38 and 1.26 ($–CH_2–$ 80 H), and 0.87 ($–CH_3$, t, 12 H, $J = 13.2$); ^{13}C NMR (400 MHz, $CDCl_3$): δ_C 150.08, 149.80, 124.47, 123.49, 102.58, 102.40, 33.61, 33.43, 32.27, 30.15, 30.06, 30.00, 29.75, 28.43, 23.09, and 14.57.

2.3. Preparation of aqueous gold NPs by citrate reduction method

Gold NPs (particle diameter ∼12 nm) were prepared by following the citrate reduction method [33]. Two milliliters of trisodium citrate (0.2 M) was added to a 50-ml aqueous solution of $HAuCl_4$ (1 mM) under boiling conditions. The solution initially developed a grey color, which finally changed to red within a few minutes with continued boiling. The average particle size was ∼12 nm. The solution was stored and used for further experiments.

2.4. Phase transfer of gold NPs

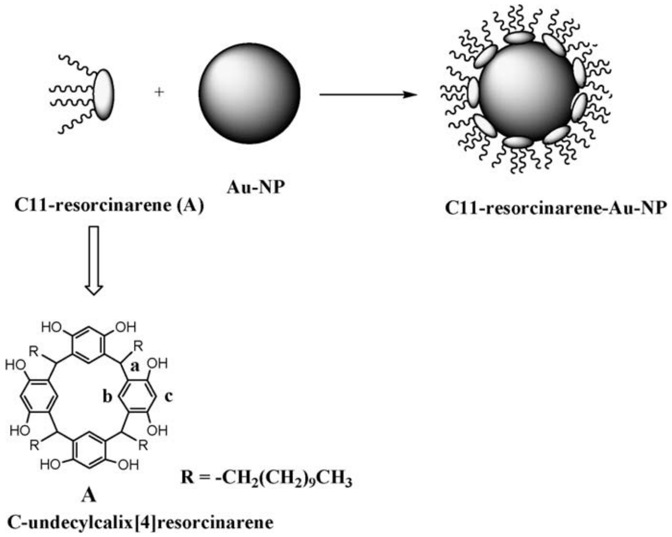
The experiment was accomplished by the addition of an aqueous solution of gold NPs (14.85 nM) to a solution of C11-resorcinarene (1 mM) in mesitylene, leading to a biphasic mixture that was then stirred vigorously at room temperature overnight. A few more sets of such sort of biphasic mixture were made and stirred. Each set contained 5 ml of C11-resorcinarene solution (1 mM) in mesitylene, but the added microliter volume of aqueous solution of gold NPs (14.85 nM) was varied from set to set. Two immiscible layers resulted from this addition: a colorless organic solution on top of the red-wine-colored gold NP solution. During stirring, the colorless C11-resorcinarene in mesitylene solution became purple, indicating phase transfer of gold NPs from the aqueous to the organic phase. The solution was allowed to settle for 2 h and the organic layers separated. Similar performance was done for each set. The color of the mesitylene solutions became deep purple and stabilized for several months. UV–vis spectra of the organic phases were recorded.

2.5. Preparation of C11-resorcinarene–Au NPs

A biphasic mixture of C11-resorcinarene in mesitylene (100 ml, 1 mM) and gold NPs in water (20 ml, 14.85 nM) was stirred overnight. The organic phase was separated using a separating funnel, and HRTEM images of the organic phase were taken. Evaporation of the solvent gave a purple-colored solid. Excess C11-resorcinarene was separated out by recrystallization from hot MeOH. The methanolic solution was then evaporated and gave a purple color solid which was dried in vacuum. UV–vis spectra were recorded by dispersing C11-resorcinarene-capped gold NPs in different organic solvents.

3. Results and discussion

C-undecylcalix[4]-resorcinarene (A) (Scheme 1) was prepared following reported method [32]. C-alkylcalix[4]-resorcinarenes exhibit four conformers [34,35]. Among these, the crown conformer is the most thermodynamically stable isomer. It has a cylindrical structural conformation; all four substituents at the methylene bridges linking the resorcinol moieties are tethered downward from the upper rim, while hydroxyl groups point upward, above its cavity. ^{1}H NMR spectrum of this conformer has a single resonance for protons H_a, H_b, and H_c (Scheme 1), whereas the chair conformer has two signals for H_b and H_c protons [34]. The ^{1}H NMR spectrum of our prepared C-undecylcalix[4]-resorcinarene shows a single resonance for H_a, H_b, and H_c protons at 4.28, 7.19, and 6.09 ppm, respectively;



Scheme 1.

these are in accord with a C_{4v}-symmetric crown conformation [34,35].

The phase transfer of gold NPs from the aqueous to the organic phase was accomplished by using C11-resorcinarene in mesitylene with simple stirring of two immiscible phases. Stirring left an emulsified of water–mesitylene mixture that led to the spontaneous transfer of gold particles from the aqueous phase to organic phase, where gold particles were capped by C11-resorcinarene (Scheme 1). In this regard, C11-resorcinarene played two roles: (i) it brought the gold particles into contact with the immiscible solvent phase by emulsification; and (ii) it enveloped the particles, allowing them to transfer. Because of the dual role, this approach involved the use of large excess of C11-resorcinarene. This process, however, is the simplest compared to other reported methods [19,20] because it neither requires acid [20] nor vigorous shaking [23] to facilitate the transfer process. Sastry et al. [23] have mentioned that they were unable to phase transfer of gold particles by simply stirring two-phase solutions with a magnetic stirrer. The key to our success might be the use of multidentate resorcinarene as a phase-transfer reagent as well as a capping agent. Resorcinarene has eight binding sites (eight phenolic OH groups) and its multidentate nature appears to have guided the interaction on the gold particle surface in a cooperative fashion. Wei and co-workers [25–31] have established concrete evidence of resorcinarene-encapsulated gold NPs in organic solvents.

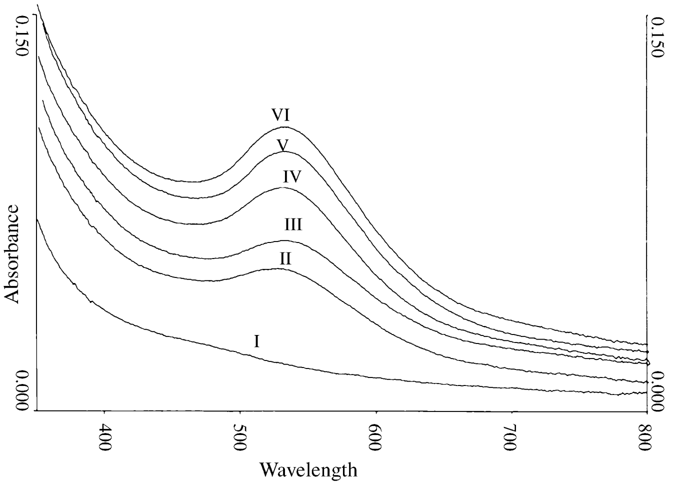


Fig. 1. UV–vis spectra of resorcinarene-capped gold nanoparticles in mesitylene. Different volumes of Au-NP (14.85 nM): (I) 0, (II) 100, (III) 150, (IV) 200, (V) 250, and (VI) 300 µl were added to the 5-ml mesitylene solution of resorcinarene (1 mM).

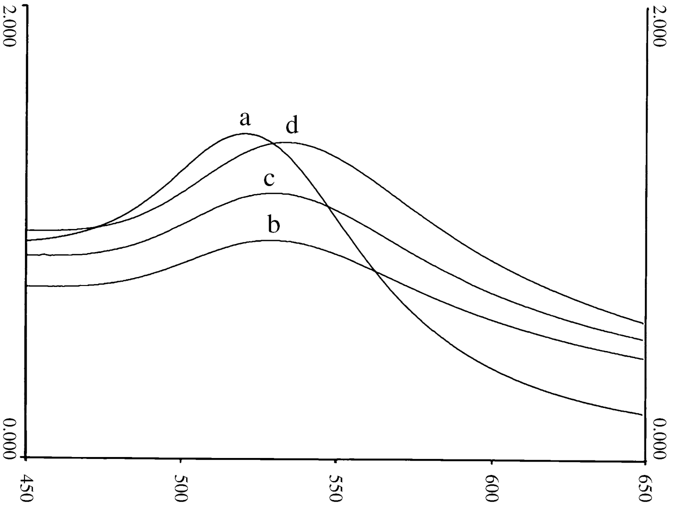


Fig. 2. UV–vis spectra of gold nanoparticles in different solvents: (a) water ($n = 1.333$); (b) n-heptane ($n = 1.387$); (c) dichloromethane ($n = 1.424$); and (d) mesitylene ($n = 1.499$).

Fig. 1 shows the UV–vis spectra of C11-resorcinarene-capped gold NPs in mesitylene. The absorption maxima at 534 nm is attributed to the surface plasmon (SP) resonance of gold nanoparticles. The origin of the SP band for gold NPs of less than 20-nm core sizes is the coherent excitation of free conduction electrons; this excitation results from polarization of the electrons induced by the electrical field of incident light [10], which is largely isotropic for well-isolated spherical NPs. Fig. 1 also reveals that the intensity of the absorbance maxima increases with the increase of C11-resorcinarene-capped gold NPs in the organic phase. The number of gold particles in the organic phase increases the number of C11-resorcinarene-capped Au-NPs depending on the microliter volume of aqueous phase added. The isolated product of C11-resorcinarene-capped gold NPs was dispersed in different solvents and their UV–vis spectra were recorded. Fig. 2 represents the UV–vis spectra of gold NPs in different solvents, producing a red wine color in water and purple in n-heptane, dichloromethane and mesitylene. The SP bands of C11-resorcinarene-capped gold NPs in organic solvents [n-heptane ($\lambda_{\max} = 530$; refractive index (n) $= 1.387$), dichloromethane ($\lambda_{\max} = 532$; $n = 1.424$), and mesitylene ($\lambda_{\max} = 534$; $n = 1.499$)] show slight broadening and red-shift in comparison with the citrate-capped gold NPs in aqueous solution ($\lambda_{\max} = 520$; $n = 1.333$). Changes in the optical properties of C11-resorcinarene-capped gold NPs in organic solutions may result from the effects of the solvent refractive index [19,29] and adsorption of resorcinarenes onto the gold surface. Nevertheless, no time-dependent changes in the UV–vis spectra or precipitation were observed even a month after the

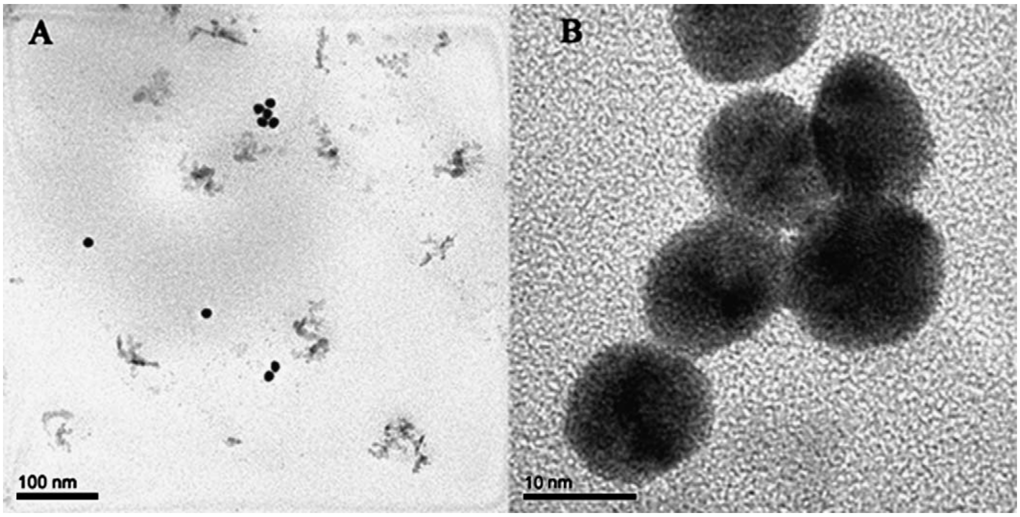


Fig. 3. High-resolution transmission electron micrograph images of resorcinarene-capped Au-NPs: (A) C11-resorcinarene-capped Au-NPs; (B) C11-resorcinarene-capped Au-NPs at high magnification.

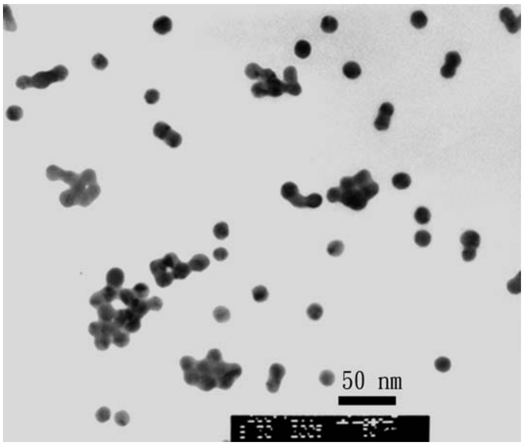


Fig. 4. Transmission electron micrograph of gold nanoparticles in aqueous phase.

phase transfer, clearly indicating that the C11-resorcinarene-capped gold NPs are extremely stable in the organic phase.

HRTEM images of C11-resorcinarene-capped Au-NPs in mesitylene and TEM image of citrate-capped Au-NPs in water are shown in Fig. 3 and Fig. 4, respectively. These were obtained by placing a drop of the corresponding solutions on the carbon-coated copper grid and allowing drying at ambient temperature. The average particle diameter of C11-resorcinarene-capped Au-NPs in mesitylene and citrate-capped Au-NPs in water are found to be the same, ~12 nm, indicating that phase transfer and surface binding with C11-resorcinarene do not affect the particle size and also ruling out the possibility of aggregation. Nevertheless, the particles were better dispersed in the organic solution than in the aqueous phase.

4. Conclusions

The phase transfer of gold NPs from aqueous to organic phase has been accomplished using C11-resorcinarene in mesitylene without any other additional reagent. C11-resorcinarene-capped gold nanoparticles could be isolated by vacuum evaporation of the solution and redispersed in different organic solvents. Because of its simplicity, this new approach could be a significant contribution to preparing resorcinarene-capped gold NPs. HRTEM images revealed no increase in particle diameter after transfer from aqueous to organic phase. We hope that the multidentate resorcinarene can be used both as the phase transfer and the capping agent for other metal NPs in the phase transfer process.

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Supporting information

The online version of this article contains additional supporting information.

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