Hybrid Gold Architectures for Sensing and Catalytic Applications

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ABSTRACT

Exquisite control of surface functionality is essential to tailor the chemical and physical properties of metal nanocrystals to the requirements of specific applications. Hybridization of gold nanoparticles with other components such as polymers and metal oxides can effectively introduce appropriate functionalities on the surface without changing their own properties, and thereby become a basic architecture for various applications such as sensors and catalysts. In the present work, we report two hybrid nanostructures comprising gold nanocrystals. PDMAEMA (poly(dimethylaminoethylmethacrylate))–gold hybrid nanocrystals were synthesized via a polyol process, which produced carboxylate functionality on the gold surface. This hybrid structure was employed for a sensitive pH-sensor in solution. On the other hand, porous silica-gold hybrid nanoreactors were produced by selective etching of gold cores from gold@silica core-shell particles. The nanoreactor framework exhibited high and controllable activity on the reduction of aromatic nitroxides. These two examples of hybrid gold architectures would be able to apply for other metal and metal oxide systems to develop biosensors and energy production catalysts.

INTRODUCTION

Morphology control of gold nanocrystals has been of major interest due to their intriguing structure-property relations in various diameter ranges [1]. Color changes are readily observed in gold nanoparticles with different size and shape in ~ 100 nm diameters. Tiny gold nanoparticles in several nanometer diameters are one of the best catalysts for low temperature oxidation of hydrocarbons. In order to employ the gold nanostructures for specific applications, appropriate functionality must be introduced on the nanocrystal surface to fit their physical and chemical properties to the requirements of applications [2]. Herein, we introduce two hybrid nanostructures including polymer-gold nanocrystals and silica-gold nanoreactors, and their uses for pH sensors and reaction catalysts. These hybrid architectures are expected to expand the utility of gold nanocrystals to a variety of applications, such as photonics, electronics, biosensing and imaging, and catalysis.

EXPERIMENT

Synthesis of PDMAEMA-gold hybrid nanocrystals

A PD (1,5-pentanediol, 96%, Aldrich) solution of PDMAEMA (0.10 mL, 0.15 M, M_w = 50,000, Polyscience) was added to boiling PD (5.0 mL). Immediately, a PD solution of $HAuCl_4$ (0.2 mL, 0.005 M, 99.9+%, Aldrich) was added, and the resulting mixture was refluxed for 5 h.

The hybrid particles were precipitated by centrifugation, and thoroughly washed with ethanol in a precipitation/dispersion cycle.

<u>Synthesis of porous silica-gold hybrid nanoreactors</u>

Colloidal gold nanoparticles and gold@silica core-shell particles were prepared by a modified polyol process and the Stöber method according to the literature [3]. A gold@silica core-shell particle dispersion in 2-propanol (1.0 mL, 1.6 mM with respect to the gold precursor concentration) was added to water (5.0 mL), and allowed to stir for 24 h at room temperature. A KCN (97%, Aldrich) aqueous solution (0.15 mL, 0.01 M) was added to the mixture and stirred for 10 min. The resulting particles were separated by centrifugation, and washed with 2-propanol several times to yield porous silica-gold (104 nm core diameter) hybrid nanoreactors. The additional amount (0.15 mL, 0.01 M) of KCN aqueous solution was added to the nanoreactor dispersion in 2-propanol yielding silica-gold (67 nm core diameter) nanoreactors. Further treatment of the KCN aqueous solution (0.10 mL, 0.01 M) led to generate silica-gold (43 nm core diameter) nanoreactors.

DISCUSSION

Synthesis of PDMAEMA-gold hybrid nanocrystals

In a polyol process, poly(vinyl pyrrolidone) (PVP) has commonly been utilized as a 'magic polymer' to control the shape and size of metal nanocrystals [4]. It is known that both carbonyl and tertiary amine groups of the pyrrolidone moiety in PVP strongly coordinate to the metal surface and stabilize the entire structure in solution. Therefore, it is very difficult to introduce specific functionality on the nanoparticle surface due to the strong surface adsorption of PVP, whereas ω-functionalized alkyl thiols are likely to be added on the particles stabilized by cationic surfactants [2].

We have tried to incorporate a carboxylate functionality on the nanocrystal surface, because the carboxylate group generates a stable amide group with various amine-terminated biomolecules including amino acids and proteins. PDMAEMA has a structure containing both carbonyl and tertiary amine groups, and thereby is expected to show effective surface regulating behaviors as PVP does in the polyol process. The reduction of gold precursors in the presence of PDMAEMA under the conditions used for the synthesis of PVP-capped gold nanoparticles yielded gold octahedrons in more than 90% yield (Figure 1a). Figure 1b shows that the nanocrystals are very uniform with sharp edges, and the average edge size is estimated to be 64±7 nm. The addition of 1/200 equiv AgNO$_3$ with respect to the gold precursor concentration in the reaction mixture afforded cuboctahedrons as a majority (Figure 1c), and the use of 1/100 equiv AgNO$_3$ led to form gold nanocubes with rounded edges (Figure 1d). The average cube edge size is estimated to be 74±9 nm. The edge truncation from octahedrons by adding AgNO$_3$ is due to a selective underpotential deposition of silver species onto {100} gold surface, forming {100} facets on the final polyhedral morphology [5]. Such a versatile shape control indicates that PDMAEMA is a potential surface regulating polymer alternative to PVP. PDMAEMA is commercially available and biocompatible, which is excellent for bio-applications.

The infrared adsorption changes during the synthesis reveal the formation of carboxylic acid group in the final product. The adsorption band at 2770 cm^{-1} of pure PDMAEMA assigned
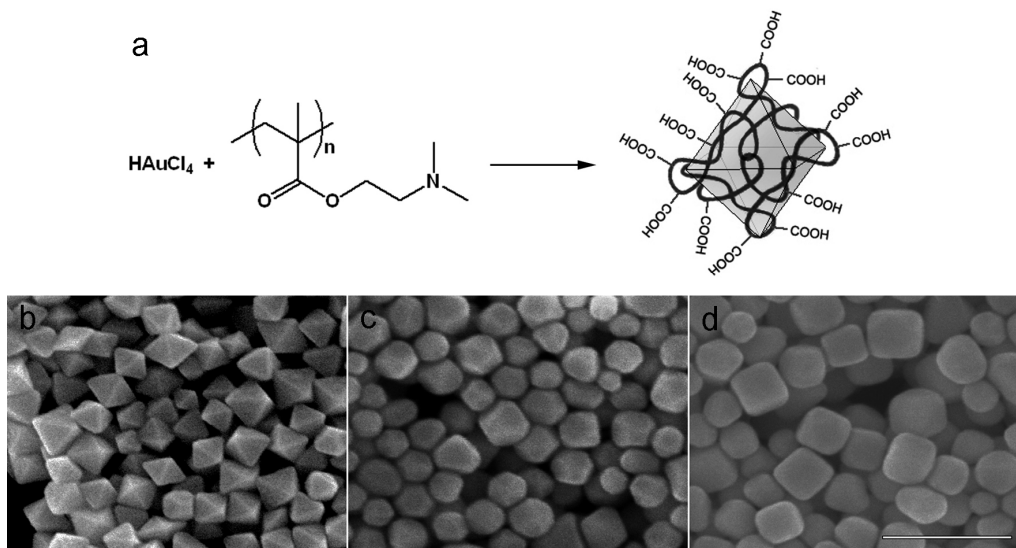
Figure 1. (a) Synthesis of PDMAEMA-gold hybrid nanocrystals. Hybrid nanocrystals with the shapes of (b) octahedral, (c) cuboctahedral, and (d) cubic. The bar represents 200 nm.

to the C-H stretching of the tertiary amine moiety disappears in the PDMAEMA-gold hybrid nanocrystals. The C=O stretching band at 1730 cm^{-1} of pure PDMAMA shifts to 1724 cm^{-1} for the gold nanocrystals. The addition of NaOH changes the C=O stretching to two characteristic bands at 1552 and 1427 cm^{-1}, corresponding to the asymmetric and symmetric carboxylate C=O stretchings. Because of the presence of carboxylic acid (or carboxylate) group, the PDMAEMA-gold hybrid nanocrystals exhibit a pH-induced assembly/disassembly process [6]. The plasmon peak of the gold nanocrystals is broaden and shifts to a longer wavelength by a decrease of pH from 11 to 2, (Figure 2a), indicating particle aggregation under an acidic environment. The region of pH 7 to 2 shows a linear relation between pH and the peak maximum shift (Figure 2b). The repetitive pH changes lead to uniform responses of the particle assembly and disassembly. These results indicate that the PDMAEMA-gold hybrid nanocrystals can be employed as a reliable pH sensor in solution. It is believed that this hybrid nanocrystal structure is also useful for selective chemical and biosensors, if appropriate probes are attached on the nanocrystal
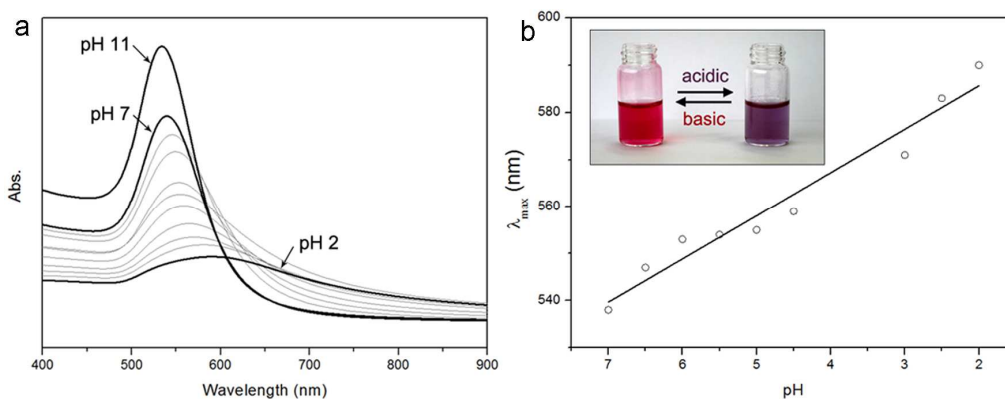

Figure 2. (a) UV-Vis spectral changes and (b) peak maximum changes of PDMAEMA-gold hybrid nanocrystals.

surface via ester or amide group formation.

Synthesis of porous silica-gold hybrid nanoreactors

In order to employ the catalytic property of metal nanocrystals, the particles are better to be adsorbed on metal oxide supports, because the supports can stabilize the particle surface, transfer reactants and products to active sites, and sometimes generate new active components on a particle-support interface [7]. Such bifunctional structures have widely been used for numerous gas and solution phase reactions. In bifunctional catalysts, uniform distribution of the metal nanoparticles on the spport is very important to preserve a large active surface area and to reduce surface inhomogeneity. If the active nanoparticles are covered with a porous metal oxide shell, each particle is completely isolated with a relatively homogeneous environment, and still has a large contact with the support [8]. The metal oxide shells can prevent severe aggregation of the active particles during the reaction progress.

Gold particles with an average diameter of 120±10 nm were coated with silica shells via the Stöber method. The resulting gold@silica core-shell particles were treated with a weak KCN aqueous solution. Cyanide ions selectively etched gold cores to yield silica-gold yolk-shell type hybrid nanoreactors (Figure 3a). Sequential addition of the KCN solution produced hybrid nanoparticles having smaller gold cores with the diameters from 104±9 nm (Figure 3b) to 67±8 nm (Figure 3c) and 43±7 nm (Figure 3d), respectively. Transmission electron microscopy images show that the silica layers were not destroyed by the KCN treatment.

The permeability of the silica layers was measured by adding a small amount of quinoline into the silica-gold hybrid nanoreactors in 2-propanol, and checking the extinction maximum change. A gradual shift of the plasmon peak estimated the diffusion coefficient to be ~4.74×10^{-19} m^2s^{-1}, which is comparable to the value of PBzMA (poly(benzylmethacrylate)-gold hybrid nanoparticles [9]. The diffusion may be ascribed to occur through defects or unpolymerized sites of the silica layers. These porous silica-gold hybrid nanoreactors were employed for the
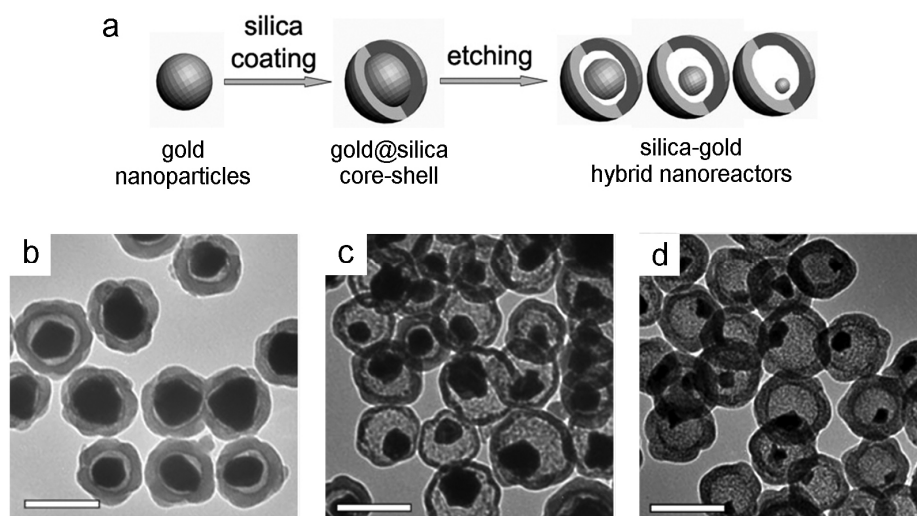

Figure 3. (a) Synthesis of porous silica-gold hybrid nanoreactors. Transmission electron microscopy images of porous silica-gold nanoreactors with gold core diameters of (b) 104 nm, (c) 67 nm, and (d) 43 nm. The bars represent 200 nm.

reduction of p-nitrophenol with $NaBH_4$. Without the catalysts, the reaction did not proceed at all. Since excess $NaBH_4$ was used, the effect of BH_4^- concentration was negligible, and the reaction followed a pseudo-first order kinetics. The reaction progress was checked by the peak intensity decrease of p-nitrophenol at 400 nm. The rate constant of the reaction varied from 1.4×10^{-2} to 3.9×10^{-3} s^{-1} as the gold core diameter diminished from 104 to 43 nm. However, the turnover frequency (TOF) of the catalyst surface atoms increased five folds from 6.6 to 36 s^{-1}, indicating that the small gold cores have a high surface roughness as shown in Figure 3d, and the edges and kinks on their rough surface exhibit higher reactivity than the smooth surface sites did.

The nanoreactor framework has another advantage of easy separation and dispersion in the reaction mixture. It is anticipated that the nanoreactor design can be a versatile platform for various reactions by using different metals and metal oxide systems.

CONCLUSION

We have shown that hybridization of gold nanocrystals with PDMAEMA and porous silica shells is very useful for sensing and catalytic applications. The PDMAEMA-gold hybrid nanocrystals had carboxylate functionality on their surface, and exhibited a pH-sensitive assembly/disassembly behavior. The carboxylate group is also good to link with biomolecules via amide or ester formation. The porous silica-gold hybrid nanoreactors could catalyze the reduction of p-nitrophenol with $NaBH_4$. The choice of appropriate metal-metal oxide pairs would be able to apply the nanoreactor framework for numerous solution and gas phase reactions. In order to expand the utility of gold nanocrystals, hybridization with various components such as metals, semiconductors, and molecular units is in progress.

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