Preparation of Gold/Titania Core–Shell Nanocomposites with a Tunable Shell Thickness

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Abstract: Gold/titania nanocomposites with a core–shell structure were prepared by sol–gel reaction of titanium tetrabutoxide (TTBO) with gold nanoparticles, core-stabilized with cetyltrimethylammonium bromide (CTAB), using a ternary mixture of alcohol/acetonitrile/water as solvent. TEM characterization of the resulting constructs revealed spherical nanocomposites, each containing a single gold core. The mean diameter of the gold cores was 13 nm, while the thicknesses of titania shells were readily tuned in the range 4–30 nm by varying the alkyl chain length of the alcohol. In addition, the gold nanoparticles exhibited a deep red color, with an intense extinction peak at 527 nm, owing to their surface plasmon resonance (SPR) properties. When the Au nanoparticles were coated with a titania shell, their color changed to purple and the SPR peak shifted to a higher wavelength of 537 nm. Furthermore, the core–shell nanocomposites were found to display photocatalytic activity for the oxidation of 2-propanol under illumination by visible light (λ = 500–560 nm).

Key words: gold nanoparticle, gold/titania core–shell nanocomposite, photocatalytic activity, sol–gel reaction

1 INTRODUCTION

Gold/titania composite constructs have been extensively studied for their excellent catalytic properties toward the oxidation reaction of carbon monoxide[1,2]. Most studies have focused on small gold nanoparticles deposited on titania supports. Meanwhile, gold/titania nanocomposites with a core–shell structure have found various other potential applications, including photovoltaics and sensors through the combination of different properties of gold nanoparticles (e.g., light absorption by surface plasmon resonance) and titania shell (e.g., photocatalytic properties)[3].

Several reports have been published to date regarding the preparation of gold/titania core–shell nanocomposites. Caruso and co-workers[4,5] applied layer-by-layer adsorption of cationic poly(dimethylallylamine chloride) and anionic poly(sodium-4-styrenesulfonate) on gold nanoparticles followed by complexation with a water-soluble titania precursor, titanium bis(ammonium lactato) dihydroxide, and subsequent hydrolysis to synthesize titania shells. This method enables controlling the shell thickness up to ~10 nm. Yu and Mulvaney[6,7] have synthesized similar nanocomposites via sol–gel reaction of titanium acetylacetonate on the surface of gold nanoparticles pre-coated with mercaptoundecanoic acid. This method provides a very thin titania shell ~1 nm thick, which is likely to facilitate charge transfer between the metal core and the semiconductor shell. However, many core–shell particles are cross-linked by a network of titania particles, making it difficult to realize the intrinsic properties of the metal/semiconductor core–shell nanocomposites. Other research groups, including Li and Zeng[8], and Wu and co-workers[9], have synthesized gold/titania nanocomposites by using titanium tetrafluoride as a precursor. The use of this precursor leads to the formation of a petal-like structure of the titania shell around the gold core. Other researches, including the encapsulation of gold nanosheets within a titania shell, have also been reported[10]. However, tailoring the shell thickness over a wide range (from 4 to 30 nm) remains a challenge.

On the other hand, we recently reported the precise fabrication of highly dispersed silver/titania core–shell nanocomposites with a single silver core using CTAB–coated Ag nanoparticles as the core[11]. In that study, an ethanol/water mixture was used as the medium for the sol–gel reaction of titanium tetraisopropoxide (TTIP). Although, this method was suitable for silver, it could not be directly extended to
the synthesis of gold/titania core–shell nanocomposites, since sol–gel reaction of TTIP in ethanol/water occurs extremely rapidly to form any titania shell around the gold particles. To this end, we report on the development of the gold/titania nanocomposites with a core–shell structure using a ternary mixture of alcohol/acetonitrile/water containing titanium tetrabutoxide (TTBO). We found that the shell thickness can be readily tuned by selecting alcohols with different alkyl chain lengths. Furthermore, the dispersed core–shell nanocomposites were found to exhibit photocatalytic activity under irradiation of visible light (λ = 500–560 nm).

2 EXPERIMENTAL PROCEDURES

2.1 Materials

Chemicals including hydrogen tetrachloroaurate (III) tetrahydrate (HAuCl₄·4H₂O); hydrazine monohydrate; 1-butanol, acetonitrile; ethanol; 1-propanol; 1-pentanol; and 2-propanol were purchased from Wako Pure Chemical Industries. Cetyl-trimethylammonium bromide (CTAB) and titanium tetra-butoxide (TTBO) were purchased from Sigma-Aldrich. All the chemicals were used without further purification. Water was deionized to the resistivity of 18.2 MΩ cm using a Barnstead NanoPure system.

2.2 Preparation of Gold nanoparticles

The gold nanoparticles for cores were prepared by adding 0.5 mL of 10 mM aqueous hydrogen tetrachloroaurate (III) (HAuCl₄) to 20 mL of 2 mM cetyltrimethylammonium bromide (CTAB), under vigorous stirring. After 10 min, 0.5 mL of 1 M hydrazine was added with further stirring. The experiment was carried out at 27°C to ensure CTAB was above its Krafft point (25°C) (Scheme 1).

2.3 Preparation of titania coating on gold nanoparticles

A titania precursor solution was prepared separately by dissolving 0.025 mmol (8.5 μL) TTBO in a mixture of 25 mL of alcohol/acetonitrile (1/1, v/v). Subsequently, a 20 mL aliquot of dispersed aqueous gold solution was added to this precursor under vigorous stirring, which was continued for a further 2 hours. This step was carried out at ambient temperature (Scheme 2).

2.4 Characterization of nanocomposites

The gold/titania nanocomposites were characterized by transmission electron microscopy (TEM) (Hitachi H-7650, operating at 120 kV) and UV-Vis extinction spectroscopy (Agilent 8453A, optical path 1 cm).

2.5 Photocatalytic activity

Photocatalytic activities of gold/titania core–shell nanocomposites were investigated by oxidation of 2-propanol under visible light illumination. The photocatalytic reaction was performed using a 300 mL custom-built cylindrical glass vessel with a quartz ceiling, in which a porous sponge of polyvinyl alcohol impregnated with gold/titania core–shell nanocomposites was placed. Prior to the introduction of the substrate, the sample was irradiated with UV light (10 mW cm⁻²) from above for 1 h to activate the catalyst surface. Subsequently, the atmosphere was substituted with air with 50% of relative humidity. Following this, 0.4 μL of 2-propanol was injected into the vessel with a glass syringe and was left to stand in the dark for 2 h at 25°C, to attain an adsorption equilibrium. Finally, visible light (λ = 500–560 nm) was irradiated upon the sample with a 200 W Xe lamp equipped with a bandpass filter (Shott VG-9). The irradiance at the sample position was set to 500 mW cm⁻². At a fixed time interval, 20 μL of the gas phase was taken.
with a glass syringe and analyzed with a Shimadzu GC-8A gas chromatograph equipped with a TCD detector.

3 RESULTS and DISCUSSION

The core–shell nanocomposites prepared were characterized by transmission electron microscopy (TEM). Figure 1(a) shows a TEM image of spherical gold nanoparticles (mean diameter = 13 nm), employed as the cores of the fabricated gold/titania nanocomposites. The exceptional stability of the gold nanoparticle dispersion over the course of 1 year suggested an effective electrostatic stabilization by CTAB bilayers, which had formed on the metal surfaces. When this gold nanoparticle dispersion was added to a mixture of 1-butanol/acetone mixture (containing TTBO), thin titania shells formed around the metal surface, as shown in Figure 1(b). The mean diameter of the resulting core–shell particles was 37 nm. In this case, the final CTAB concentration (8.5 × 10⁻⁴ M) was set to below its critical micelle concentration (1.0 × 10⁻³ M) to ensure that no micelles were present in the bulk solution. This condition was important since micelles could have acted as nucleation sites for small titania particles.

Figure 2 shows the dispersion color comparison between the gold nanoparticles and gold/titania core–shell nanocomposites, and their corresponding UV-Vis extinction spectra. As can be seen in the figure, the gold nanoparticles exhibit a deep red color, with an intense absorption peak at 527 nm, owing to surface plasmon resonance (SPR).
property. When the gold nanoparticles were coated with titania shell, their color gradually changed to purple and their SPR peak shifted to a higher wavelength, 537 nm. This red-shift can be attributed to an increase in the optical dielectric constant of the dispersion media containing the gold nanoparticles ($\varepsilon_{H_2O} = 1.77$, $\varepsilon_{acetonitrile} = 1.81$, $\varepsilon_{butanol} = 1.96$, $\varepsilon_{TiO_2(rutile)} = 6.84$). According to the Mie theory\(^{14,15}\), the SPR wavelength ($\lambda_{sp}$) is defined on the basis of the dielectric constant when the condition $\varepsilon_1(\lambda_{sp}) = -2 \varepsilon_m$ is fulfilled. Here $\varepsilon_1$ represents the real part of wavelength-dependent complex dielectric function for the metal and $\varepsilon_m$ is the dielectric constant of the dispersion medium, which is independent of the wavelength. Since $\varepsilon_1$ of gold is a decreasing function of the wavelength in the visible region\(^{17}\), an increase in $\varepsilon_m$ due to the surface coating with titania shell should cause a redshift, which is consistent with our experimental results. On the other hand, we observed that the molar extinction coefficient of gold increased slightly from $4.44 \times 10^3$ to $5.63 \times 10^3$ M$^{-1}$ cm$^{-1}$, owing to the encapsulation with titania, at all the peak wavelengths. This implies an increased contribution to scattering of light by the titania shell\(^{14,15}\). The solution maintained its transparency, however; this can reasonably account for the absence of bulk titania particles as large as visible wavelengths.

Subsequently, we attempted to tune the shell thickness by using alcohols with different alkyl chain lengths (C$_2$–C$_5$) as a component of ternary solvents for the sol–gel reaction of titanium alkoxide. As shown in Fig. 3, ethanol provides the thinnest shell ($\sim 4$ nm), while 1-pentanol provides the thickest shell ($\sim 30$ nm). This suggests that the shell thickness can be tailored by controlling the rate of the sol–gel reaction of TTBO; alcohols with longer alkyl chain suppress the sol–gel reaction more effectively, leading to thicker titania shells\(^{18}\).

In this method, it is essential to select a titanium alkoxide of moderate reactivity. We observed that TTIP hydrolyzed too rapidly and did not yield core–shell nanocomposites in any of the solvents investigated. Whereas, when TTBO was employed, the sol–gel reaction occurred at a slower rate, allowing for the formation of stable shells.

![Fig. 3 TEM images of Au/TiO$_2$ core–shell nanocomposites prepared in the mixed alcohol/acetonitrile/water solvents containing alcohols with different alkyl chain lengths. [Au] = 1.06 × 10$^{-4}$ M, [CTAB] = 1.06 × 10$^{-3}$ M, [TTBO] = 5.56 × 10$^{-4}$ M. Solvent: alcohol/acetonitrile/water = 28/28/44 in volume fraction.](image-url)
within a suitable condition.

The composition of the mixed solvent was another important factor for the formation of the core–shell constructs. Figure 4 shows TEM images of gold/titania nanocomposites prepared at different 1-butanol/acetonitrile compositions. In the absence of acetonitrile (a), titania formed independently, forming a developed network structure, while the gold particles displayed no coating of titania shell. In the presence of 14% acetonitrile (1-butanol/acetonitrile = 3/1; v/v) (b), majority of the gold nanoparticles were coated with titania shell. However, they were linked together by a titania network, though the network was less developed than in (a). At 28% acetonitrile (1-butanol/acetonitrile = 1/1) (c), all the gold particles were covered with titania shells along with a small fraction of titania particles without a metal core, while the networked structure of titania was absent. However, higher volume fractions of acetonitrile (d, e) brought about a remarkable aggregation of nanocomposite particles.

The significant variation in the composite structure owes to the different properties of 1-butanol and acetonitrile used for the titania precursor\(^{19}\). Both these components contribute to the retardation of TTBO sol–gel reaction of in water; 1-butanol suppresses the nucleation of titania by stabilizing the precursor, while acetonitrile inhibits the crystal growth of titania, owing to its poor hydrogen bonding property. The solubilities of TTBO in the ternary mixtures containing these two solvents are also different: 1-butanol is a good solvent for the precursor, while acetonitrile is not. Accordingly, a moderate volume fraction of acetonitrile efficiently suppresses the network formation of titania particles and promotes an isotropic growth toward spherical titania shells, while excessive amounts of acetonitrile leads to the reduction in the solubility of TTBO and causes a remarkable aggregation of titania.

Another important factor for the formation of core–shell nanocomposites may be the hydration of CTAB bilayers around the gold nanoparticles. Since the metal core is located at the center of each particle, it is reasonable to assume that the CTAB surface acts as a nucleation site for the titania shell. In this regard, the hydration of the CTAB head group (trimethylammonium cation) plays a crucial role in the formation of the titania shells. Determination of the hydration shell thickness for the CTAB adsorption layer on gold nanoparticles is currently under way.

Finally, the photocatalytic activity of the gold/titania core–shell nanocomposites prepared in 28% acetonitrile (1-butanol/acetonitrile = 1/1; Fig. 4 (c)) was investigated by using the oxidation of 2-propanol as a model reaction. Titania nanoparticles without cores were used as control. Figure 5 shows the evolution of the 2-propanol concentration in the gas phase. Note that the initial decrease in the

![TEM images of Au/TiO_2 nanocomposites prepared in the mixed 1-butanol/acetonitrile/water solvents with different compositions: (a) 56/0/44, (b) 42/14/44, (c) 28/28/44, (d) 14/42/44, (e) 0/56/44 in volume fraction. [Au] = 1.06 × 10^{-4} M, [CTAB] = 8.47 × 10^{-5} M, [TTBO] = 5.56 × 10^{-4} M.](image-url)

**Fig. 4** TEM images of Au/TiO_2 nanocomposites prepared in the mixed 1-butanol/acetonitrile/water solvents with different compositions: (a) 56/0/44, (b) 42/14/44, (c) 28/28/44, (d) 14/42/44, (e) 0/56/44 in volume fraction. [Au] = 1.06 × 10^{-4} M, [CTAB] = 8.47 × 10^{-5} M, [TTBO] = 5.56 × 10^{-4} M.
dark is associated with the absorption onto the catalyst surface. Once the adsorption of 2-propanol reached an equilibrium (2 h), visible light ($\lambda = 500–560$ nm) was irradiated. Under the irradiation, the concentration of 2-propanol decreased further, and as a result, acetone was produced. On the other hand, no oxidation of 2-propanol was observed for pure titania nanoparticles.

The mechanism of this photocatalytic activity is yet to be ascertained. However, it is proposed that a temporal charge separation, generated by the surface plasmon resonance of gold nanoparticles, can be transferred to titania to promote the photocatalytic activity\(^{20}\). Hence, fine-tuning the thickness of titania shell is desirable for studying charge transfer mechanisms.

**4 CONCLUSIONS**

Dispersed gold/titania core–shell nanocomposites were successfully prepared by sol–gel reaction of TTBO dissolved in an alcohol/acetonitrile/water ternary solvent. The thickness of the titania shells could be finely tuned between 4 and 30 nm by varying the chain length of the alcohol component. Furthermore, the core–shell nanocomposites were found to exhibit photocatalytic activity under the irradiation of visible light ($\lambda = 500–560$ nm). These core–shell nanoparticles can be excellent candidates for studying the mechanism of SPR-assisted photocatalysis under visible light.

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**References**


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