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Preparation of Highly Dispersed Core/Shell-type Titania Nanocapsules Containing a Single Ag Nanoparticle

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Noble metal nanoparticles are known to exhibit various colors arising from surface plasmon absorption[1−3] and size-dependent specific catalytic[4,5] and optical[6,7] properties. Although the nanoparticles have attracted attention in diverse fields of science and technology[8] because of their interesting properties, they are hardly usable by themselves since they are poor at dispersion stability and tend to aggregate in the medium. Then, many attempts have been made to improve their dispersion stability by coating the surface with polymers,[9−11] surfactants,[12] and silica.[13−15]

Meanwhile, recent articles have reported that the irradiation of monochromatic lights of various wavelengths on a thin titania film with deposited Ag nanoparticles causes repeated size-selective dissolution and deposition of the particles, thereby developing a multicolor photochromism, in which the color changes reversibly.[16,17] A paper has also reported a reversible charging−discharging effect in a Ag−titania composite, in which photoexcitation of titania produces an injection of electrons into Ag nanoparticles and the later discharge.[18] If individual core/shell-type titania capsules can be prepared by coating each of the Ag nanoparticles with titania, this method is hopeful as a way to improve the dispersion stability of noble metal nanoparticles, and the particles will find a wider scope of applications due to their optical characteristics, including photochromism and visible light responsive photocatalytic activity.[19−21] No report has so far dealt with the preparation of individual core/shell-type Ag/titania nanocapsules, though there have been reports concerning Ag−titania composite particles.[22−24] The present study aims to prepare highly dispersible core/shell-type titania capsules containing a single Ag nanoparticle using the sol−gel reaction of titania on the surface of the nanoparticle.

The chemicals used were silver nitrate ($AgNO_3$, 99.8%, Wako Pure Chem. Ind.) as Ag precursor, hydrazine monohydrate ($N_2H_4 \cdot H_2O$, 98.0%, Wako Pure Chem. Ind.) as reducing agent, cetyltrimethylammonium bromide (CTAB, Aldrich) as protective agent for particles, titanium tetraisopropoxide ($Ti[OCH(CH_3)_2]_4$ (TTIP), 95.0%, Wako Pure Chem. Ind.) as titania precursor, and ethanol (C_2H_5OH, 99.5%, Wako Pure Chem. Ind.) as solvent for TTIP.

Preparation of Ag nanoparticles was made in the following way.[25] An aqueous hydrazine solution (100 mM, 0.5 g) was added to an aqueous CTAB solution (1 mM, 20 g), and the mixture was stirred for 1 min at room temperature. To this mixed solution was added an aqueous $AgNO_3$ solution (50 mM, 0.5 g), and the mixture was stirred further for 10 min at room temperature to give a Ag nanoparticle dispersion. Core/shell-type titania capsules were prepared as follows. An ethanolic TTIP solution (1 mM, 25 g) was added to the Ag nanoparticle suspension, and the mixture was vigorously stirred for several minutes at room temperature to yield a suspension of Ag−titania composite particles.

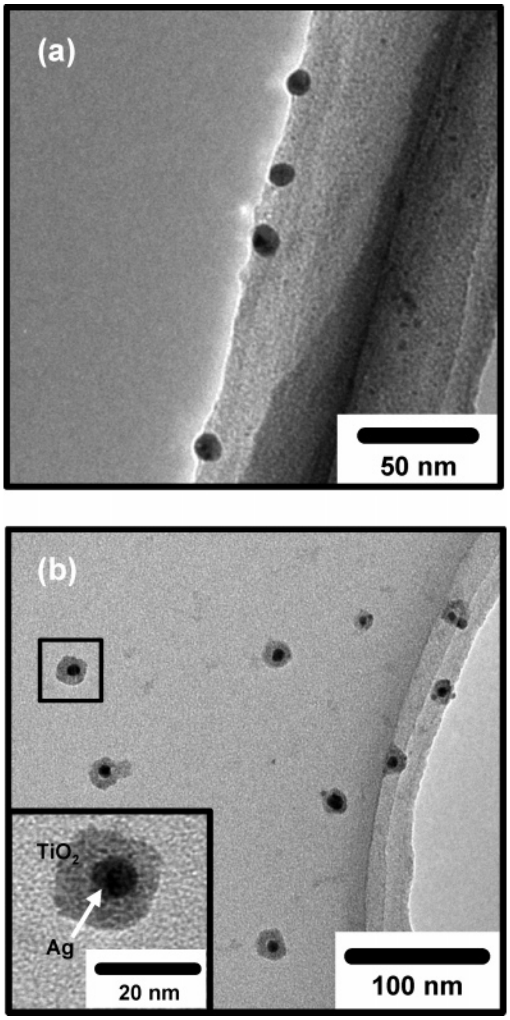

Figure 1. TEM images of (a) Ag nanoparticles and (b) TiO_2-coated Ag nanoparticles.

Verification of the formation of core/shell-type titania capsules was performed with TEM observations (Hitachi Model H-7650). Formation of Ag nanoparticles was verified through UV−vis absorption spectrum measurements (Hitachi Model U-3310) and X-ray diffraction measurements (Rigaku, Model RINT2000, CuKα).

Figure 1 shows the typical TEM images of Ag nanoparticles and titania−Ag composite particles. Ag nanoparticles were spherical, and their size was about 10 nm (panel a). As shown in Figure 1b, well-dispersed core/shell-type Ag/TiO_2 nanoparticles were

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10.1021/ja058083c CCC: $33.50

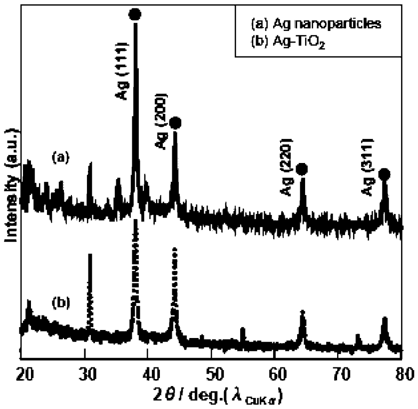

Figure 2. Wide-angle X-ray diffraction patterns of (a) Ag nanoparticles and (b) TiO_2-coated Ag nanoparticles.

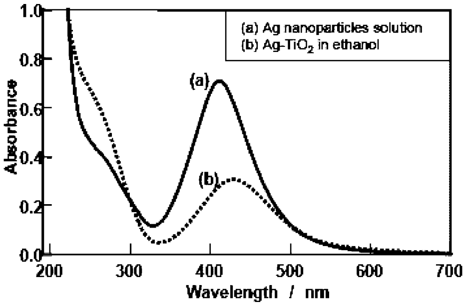

Figure 3. UV−vis spectra of (a) Ag nanoparticles and (b) TiO_2-coated Ag nanoparticles.

obtained after the sol−gel reaction of TTIP. In these composite particles, 10 nm Ag particle (core) is encapsulated within a 5−10 nm thick titania layer (shell). Dynamic light scattering measurements revealed that the size of titania−Ag composite particles is larger than that of Ag nanoparticles, thus supporting the TEM image obtained above.

Figure 2 shows the wide-angle XRD patterns of Ag nanoparticles (pattern a) and titania-coated Ag nanoparticles (pattern b). The pattern for Ag nanoparticles exhibited the diffraction peaks at $2\theta = 38.0$, 44.2, 64.4, and 77.3°, all of which coincided with those for Ag. Titania-coated Ag nanoparticles were found to keep the diffraction peaks characteristic of Ag crystal, whereas no peak assigned to titania crystal was detected, suggesting that the titania shell is amorphous.

Figure 3 shows the UV−vis absorption spectra of a Ag nanoparticle (curve a) and titania-coated Ag nanoparticle suspensions (curve b). The concentration of Ag nanoparticles in the suspension decreased 40% after coverage with TiO_2. The spectrum for the suspension of Ag nanoparticles had a surface plasmon absorption at 410 nm arising from the particles, and the color of the suspension was yellow, which is characteristic of Ag colloidal dispersions. A similar surface plasmon absorption due to Ag nanoparticles was observed for the suspension of titania-coated Ag nanoparticles at a wavelength longer than that for the suspension of Ag nanoparticles. This absorption shift is caused by a high refractive index of the titania shell[26,27] and strongly suggests a complete coverage of Ag nanoparticles with titania.

The experimental results obtained in this work demonstrate that titania capsules containing single Ag nanoparticles are successfully prepared using the sol−gel reaction of TTIP as titania precursor in a Ag nanoparticle suspension in the presence of CTAB as protective agent, and the thickness of the titania layer (shell) and the size of the Ag nanoparticle (core) are 5−10 nm and 10 nm, respectively. Almost all titania particles were found to have a core Ag nanoparticle in the TEM observations, suggesting that the sol−gel reaction of TTIP proceeds selectively on the surface of CTAB−Ag nanoparticles and CTAB catalyzes the sol−gel reaction.[28] Ethanol dissolves TTIP to form a stable solution and controls the rate of the sol−gel reaction when the solution is added to an aqueous Ag nanoparticle dispersion. Optimization of the experimental conditions would allow the sol−gel reaction to proceed site-selectively and at a moderate speed on the surface of Ag nanoparticles, thus yielding highly dispersed core/shell-type titania nanoparticles. Core/shell-type titania capsules containing Ag nanoparticles prepared in this work are expected to be usable as a photochromic material that changes its color reversibly and as a photocatalyst that has multifunctionality, including visible light responsivity, and these studies are currently under investigation. In addition, we have also succeeded in preparing titania-coated Au nanoparticles using the present method and will report in near future.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government. The authors thank Prof. Seong Geun Oh for his valuable suggestion.

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JA058083C