Supporting Information

Length Control of Ag Nanorods in Mesoporous SiO₂-TiO₂ by Light Irradiation

Go Kawamura,*a Mai Murakami,b Teruhisa Okuno,b Hiroyuki Mutoa,b and Atsunori Matsudaa,b

*a Department of Electrical and Electronic Information Engineering
b Department of Environmental and Life Sciences, Toyohashi University of Technology,
1-1 Hibarigaoka, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan.
*E-mail: gokawamura@ee.tut.ac.jp, Tel: +81-532-44-6791, Fax: +81-532-48-5833
Detailed experimental procedures

A mixture of the surfactant Pluronic P123 (Sigma-Aldrich), 2 M HCl (Wako, Japan), and ion-exchanged water (IEW) was added to tetraethoxysilane (TEOS, Shin-Etsu, Japan), and then stirred at 40 °C for 20 h. Titanium tetra-n-butoxide (TTB, Wako, Japan) was added, and the solution was stirred for a further 6 h. The molar ratio of [TEOS+TTB]:P123:IEW in 2 M HCl:IEW was 1:0.017:5:194. For the preparation of (100-x)SiO$_2$-xTiO$_2$ templates, only the ratio of TEOS to TTB was varied. The stirred solution was transferred into an autoclave vessel and kept at 80 °C for 24 h. The resulting precipitate was collected by suction filtration, washed with IEW and ethanol (EtOH, Wako, Japan), and then dried in an ambient environment. The obtained powder was suspended in a mixture of toluene (Wako, Japan) and hexamethyldisilazane (HMDS, Nacalai Tesque, Japan) at 30 °C for 18 h to allow silylation of the outer surface of the powder. The powder was filtered, washed with EtOH, and then added to a mixture of diethyl ether (Wako, Japan) and EtOH and stirred at 60 °C for 5 h to remove the surfactant from the mesopores. Prior to the deposition of Ag, the inner surface of the mesopores in the powder was functionalized with hemiaminal groups (-NH-CH$_2$-OH) using 3-aminopropyltriethoxysilane (APTES, Shin-Etsu, Japan) and formaldehyde (Wako, Japan) to effectively adsorb and reduce Ag ions in the mesopores. To do this, the powder was immersed in a solution of APTES (1 wt% in toluene) and stirred at 80 °C for 6 h. The powder was filtered and then washed with EtOH. The solid was dispersed in a solution of formaldehyde (37 wt% in EtOH) at 40 °C for 1 h to functionalize the inner wall of the mesopores with hemiaminal groups. After washing and drying, a powder with a silylated outer surface and hemiaminal-functionalized inner
wall was obtained. For the deposition of Ag, the mesoporous powder was added to a solution of AgNO₃ (Wako, Japan, 10 mM in H₂O:EtOH = 1:4 (vol%)) and stirred at 40 °C for 0.5 h. During or after this process, the sample was irradiated with light using a 300 W Xe lamp with bandpass filters (490−550, 570–690, or 650–810 nm, ~5 mW/cm²). This induced excitation of SPR on Ag NRs of specific length, allowing the aspect ratios of the Ag NRs in the mesoporous templates to be precisely controlled.

Low and high magnification transmission electron microscope (TEM) images were taken with Hitachi H-800 (Japan) and JEOL JEM-2100F (Japan) TEMs operating at 200 kV, respectively. X-ray diffraction (XRD) measurements were performed using a Rigaku RINT UltimaIV diffractometer (Japan) with CuKα radiation (λ = 1.5406 Å). Ultraviolet-visible-near infrared (UV-Vis-NIR) diffuse reflectance (DR) spectra were measured with a JASCO V-670 UV-Vis-NIR spectrometer (Japan).