

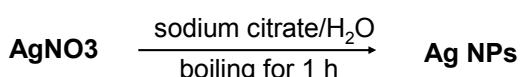
Supplementary Materials

Experimental Section:

Materials: Silver nitrate (AgNO_3) (99%, Aldrich), trisodium citrate dihydrate (99%, Fluka), ammonium hydroxide (28-30%, J. T. Baker,), tetraethoxysilane (TEOS) (98%, Fluka), 3-aminopropyl-trimethoxysilane (APS) (99%, Acros), and fluorescein isothiocyanate (FITC) (90%, Fluka) were used in preparing the nanocomposite samples. All chemical reagents were used as received without further purification. Water used in the preparation of all samples was purified with cartridges from Millipore (NANOPure, Barnstead, USA) to a resistivity of $18.0 \text{ M}\Omega\cdot\text{cm}$.

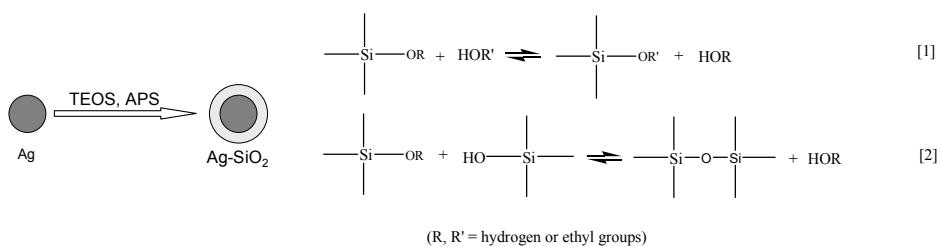
Methods:

1. Preparation of Ag nanoparticles



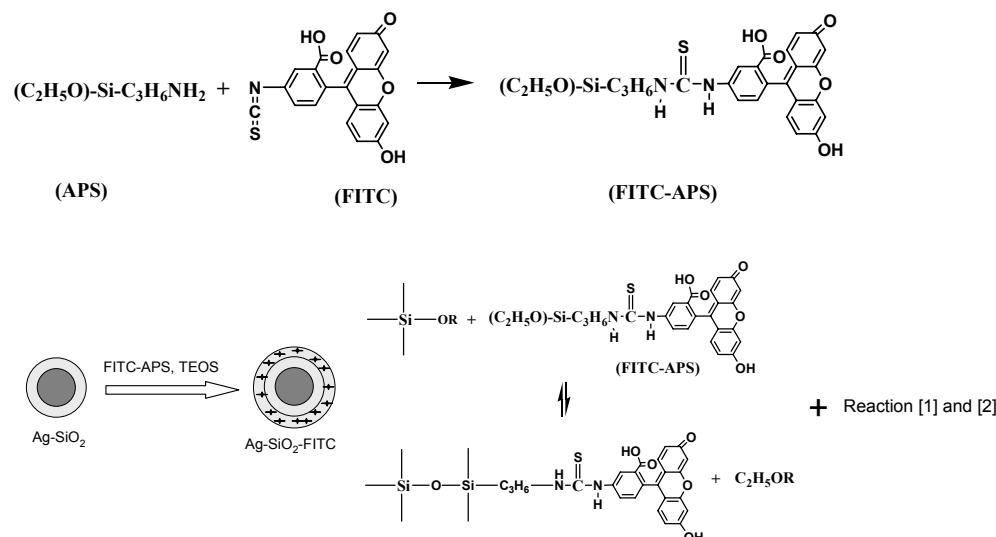
Ag nanoparticles (NPs) were prepared by a citrate reduction method [1]. 4.5 mg of AgNO_3 was dissolved in 100 mL of H_2O and brought to boiling. 2 mL of 1% sodium citrate solution was added. The solution was kept on boiling for ca. 1 h. The prepared Ag colloids have a plasmon absorption band peaked at 438 nm and a mean diameter of $75 \pm 5 \text{ nm}$. Ag NPs were purified by centrifugation at 10,000 rpm for 10 mins to remove the excess citrate ions.

2. Formation of the 1st SiO_2 shell on Ag NP



The preparation of Ag-SiO₂-fluorophore core-shell NPs involves deposition of two SiO₂ layers around Ag NPs. The deposition of the 1st SiO₂ shell followed the Stöber method [2]. 16 mL of the Ag colloids were first concentrated to 8 mL by centrifugation. 20 mL of ethanol and 1 mL of ammonium hydroxide (28-30 wt %) were then added, followed by addition of 0.2 µL of APS. The reaction medium kept stirring for 15 mins. APS was used to generate siloxy groups that are receptive to the deposition of SiO₂. Finally different amount of TEOS (0.3 µL, 0.6 µL, 0.8 µL, 1.0 µL, 1.2 µL, 1.5 µL) was added to initiate the formation of SiO₂. The reactions were maintained at 40 °C for 15 h. The thickness of the SiO₂ was controlled by the amount of TEOS used in the reaction. The formed Ag-SiO₂ core-shell NPs was used for deposition of the 2nd SiO₂ layer without any purification.

3. Formation of the 2nd SiO₂ shell (with FITC incorporated)



The synthesis the 2nd SiO₂ shell followed a modified Stöber method as described by A. Imhof *et al.* [3]. In this shell FITC was incorporated into the SiO₂ matrix. 8mg (0.021 mmol) of FITC was first dissolved in 3 mL of vacuum-distilled ethanol, followed by addition of 15 µL (0.064 mmol) of vacuum-distilled APS. The reactants were allowed

to react in dark for 24 hours under stirring. The amino group of the silane coupling agent APS reacts with the isothiocyanate group of FITC to form N-1-(3-triethoxysilylpropyl)-N'-fluoresceyl thiourea. The resulting solution is referred to as APS-FITC. To synthesize Ag-SiO₂-FITC core-shell NPs, 0.1 mL of ammonium hydroxide (28-30 wt %) was first added into 8 mL of the Ag-SiO₂ core-shell NPs. 3.5 μL of APS-FITC was then added into the above dispersion and stirred for 15 mins. After that 0.2 μL of TEOS was added to initiate the formation of the 2nd SiO₂ layer. The reaction was kept at 35 °C for 15h. The resulting Ag-SiO₂-FITC NPs were purified by centrifugation at 12,000 rpm for 5 min. The supernatant was removed and replaced with ethanol. This process was repeated for 3 times until no fluorescence of FITC was observed for the supernatant.

Characterizations: TEM images of the nanoparticle samples were recorded with a Philips CM10 electron microscope at an accelerating voltage of 100 kV. Samples were first dispersed in water. They were then dried down onto carbon-coated copper grids (150 meshes) for TEM observation. The average size of the NPs was determined from TEM image by counting 100 NPs. Fluorescence spectra of the samples were measured with a Perkin Elmer LS55 luminance spectrometer.

References

- [1] P. C. Lee, D. Meisel, *J. Phys. Chem.*, 1982, **86**, 3391.
- [2] W. Stöber, A. Fink, *J. Colloid Interface Sci.* 1968, **26**, 62.
- [3] A. Imhof, M. Megens, J. J. Engelberts, D. T. N. de Lang, R. Sprik and , W. L. Vos, *J. Phys. Chem. B* 1999, **103**, 1408.