Supplementary material (ESI) for Chemical Communications

Supplemental Information

Silver-Enhanced Fluorescence Emission of Single Quantum Dot Nanocomposites

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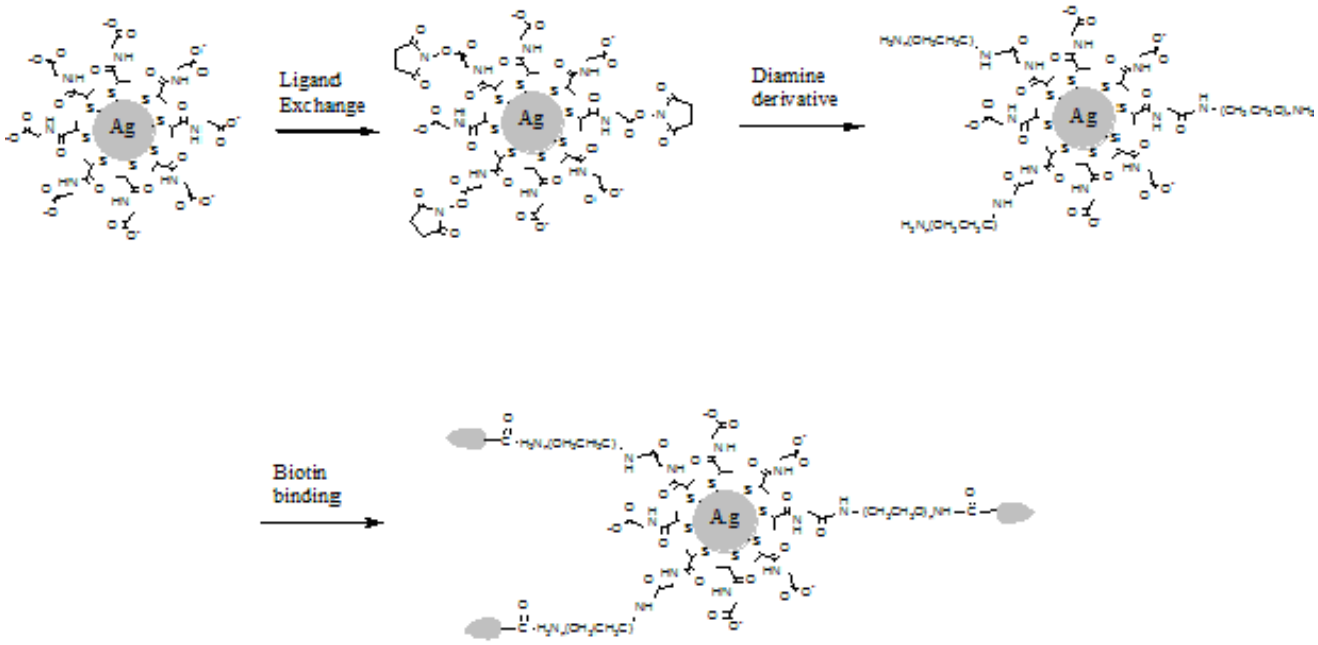


Synthesis and Characterization of Biotin-coated Silver Nanoparticles

All reagents and spectroscopic grade solvents were used as received from Sigma-Aldrich. Cy5-labeled avidin was commercially from Molecule Probe. RC dialysis membrane (MWCO 50,000) was purchased from Spectrum Laboratories, Inc. Nanopure water (>18.0 $M\Omega cm^{-1}$) purified using Millipore Milli-Q gradient system, was used in all experiments. (2-mercapto-propionylamino) acetic acid 2,5-dioxo-pyrrolidin-1-ylester was synthesized as our previous report [1].

Preparation and terminal succinimidylation of tiopronin-coated silver nanoparticle.

Tiopronin-coated silver nanoparticles were prepared using a modified Brust reaction with a mole ratio of tiopronin / silver nitrate = 1 / 6 in methanol using excess amount of sodium borohydride as reducing agent [2]. These silver particles were succinimidylated via ligand exchange [2,3]. (2-mercapto-propionylamino) acetic acid 2,5-dioxo-pyrrolidin-1-ylester (2 x 10^{-6} M) and silver particle (2 x 10^{-7} M) were co-dissolved in a mixing solvent of water / ethanol (v/v = 1/1) and stirred for 72 h at room temperature. The ligands displacements were expected to occur on the metal cores in a mole ratio of 1:1 [4,5]. Unbound compounds were removed by centrifuging at 6,000 rpm for 30 min. The residuals were dispersed in water and then further purified by dialysis against water (MWCO 50,000).

Biotinylation of silver particles.

The succinimidylated ligand on the metal particle was lengthened and aminated by two step surface reactions. The succinimidylated metal particles (1 x 10^{-7} M) were co-dispersed in water with an excess amount of poly bis(ethylene glycol) (3-aminopropyl) (MW 1,500, 5 x 10^{-6} M) [3]. The solution was stirred for 2 h, and then a drop ammonium was added dropwise to block non-reacted terminal succinimidyl esters. The solution was removed by centrifugation at 6,000 rpm. The residue was washed with water, and then dispersed in the same volume of water / methanol mixture in v/v =1/1. The metal particles (1 x 10^{-7} M) were biotinylated by co-dissolving an excess amount of biotin N-succinimidyl ester (2 x 10^{-6} M). The solution was stirred for 4 h. The suspension was removed by centrifugation at 6,000 rpm. The residue was washed by methanol and water respectively and then dispersed in 10mM PBS buffer solution at pH = 7.2. The metal particles were purified by dialysis against 10mM.

Conjugation of biotinylated metal particles and Streptavidin functionized QDs.

Streptavidin QD was dissolved in 10 mM PBS buffer solutions (pH = 7.2) and the concentration was controlled to be 1 x 10^{-7} M. The biotin-metal particles and QDs were mixed at a fixed molar ratio (1:5) to incubate in buffer solution under stirring and the conjugation occurred at room temperature for at least 8 h [6]. The product was collected after centrifuging. Excess QDs were removed by ethanol precipitation.

TEM measurements. The size distribution of metal core was analyzed with Scion Image Beta Release 2 counting at least 50 particles.

Reference.

1. Zhang, J.; Roll, D.; Geddes, C. D.; Lakowicz, J. R. *J. Phys. Chem. B.* **2004**, *108*, 12210.

2. Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801.

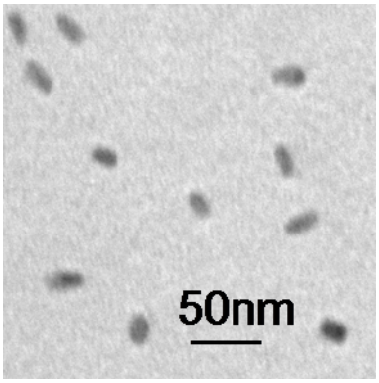
3. Zhang, J.; Fu, Y.; Lakowicz, J. R. . J. Phys. Chem. C 2007, 111, 50.

4. Zhang, J.; Fu, Y.; Chowdhury, M. H.; Lakowicz, J. R. . J. Phys. Chem. C 2007, 111, 11784.

5. Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. Acc. Chem. Res. 2000, 33, 27.

6. Ingram, R. S.; Hostetler, M. J.; Murray, R. W. J. Am. Chem. Soc. 1997, 119, 9175.

A TEM image of individual Ag nanoparticles



Single molecule experiment

Single-molecule measurements were performed using a confocal microscopy system (MicroTime 200, Picoquant, Germany) with an excitation line at 470 nm. Images were recorded by raster scanning (in a bidirectional fashion) the sample over the focused spot of the incident laser with a pixel integration of 0.6 ms. The excitation power into the microscope was maintained less than 0.1 μW. Time-dependent fluorescence data were collected with a dwell time of 50 ms. The fluorescence lifetimes of single molecules were measured by time-correlated single photon counting (TCSPC) with the TimeHarp 200 PCI-board (PicoQuant). The data was stored in the time-tagged-time-resolved (TTTR) mode, which allows recording every detected photon with its individual timing information. In combination with a pulsed diode laser, Instrument Response Function (IRF) widths of about 300 ps FWHM can be obtained, which permits the recording of sub-nanosecond fluorescence lifetimes, extendable to less than 100ps with reconvolution. Lifetimes were estimated by fitting to a χ^2 value of less than 1.2 and with a residuals trace that was fully symmetrical about the zero axis.

Single-molecule lifetime fitting for intensity decays curves shown in Figure 3

$$\tau_{av} = \frac{\sum_i Ampl_i \cdot Lifet_i^2}{\sum_i Ampl_i Lifet_i}$$

The average lifetime τ_{av} shown in the experiment is the amplitude-weighted averaged lifetime calculated from the fit result (Equation 1). In this expression, the values $Ampl_i$ represent amplitudes of the components, the values $Lifet_i$ are the decay times.