

Spatially Resolved Scattering Correlation Spectroscopy

Using a Total Internal Reflection Configuration

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Supporting Information

Preparation and Characterization of Silver Nanoparticles

Silver nanoparticles were synthesized in aqueous solution according to the published procedures¹ with a minor modification. Briefly, gold seeds were firstly synthesized by dissolving 0.792 g beta-cyclodextrin (β -CD) in 98.6 mL water in a 250 mL three-necked flask with moderate stirring. After the β -CD dissolved adequately, 0.4 mL chloroauric acid (HAuCl_4 , 10 nM) was added to the flask. Then, the reaction flask was placed in a constant-temperature oil bath maintained at 130 °C with vigorous stirring. Two minutes later, 1 mL of sodium hydroxide (NaOH , 1.0M) was added to the flask in order to keep the pH of the solution to be 10-12. Heating continued for 20 minutes until the solution turned pink, indicating the formation of gold seeds. The next step was the preparation of a silver shell on the surface of gold nanoparticles. After passing through 0.2 μm filter membrane, the as-prepared gold nanoparticles (1 mL) was diluted with 97 mL water and then 1 mL silver nitrate (AgNO_3 , 20 nM) was added dropwise. This solution was incubated with vigorous stirring for 5 minutes and then 1 mL sodium citrate (40 mM) was added. The reaction mixture was heated on an oil bath of 130 °C with stirring for 30

minutes until the color of the solution turned reddish yellow, indicating the existence of Au(core)-Ag(shell) nanoparticles. All materials were commercially available and used as received unless otherwise noted. All water used in this study were ultra-pure water (18.2 MΩ) purified on Millipore Simplicity (Millipore). Transmission electron micrograph (TEM) images were taken with a JEM-2100 transmission electron microscope (JEOL, Japan). UV-vis absorption spectra of nanoparticles were obtained by using a UV-3501 spectrophotometer (Tianjin Gangdong Sci. & Tech. Development Co. Ltd., China). RLSCS measurements were performed on a home-built FCS system with a 488 nm laser (Ion Laser Technology Co. Ltd., China), whose details were similar to the experimental setup reported elsewhere.² Briefly, the expanded laser line was focused with a water immersion objective (UplanApo, 60×NA1.2, Olympus, Japan) to a small excitation volume within the solution of silver nanoparticles. The RLS intensity of nanoparticles in the excitation volume collected by the same objective successively passed through the dichroic mirror (505DRLP, Omega Optical) and a pinhole (about 35 μm), and finally monitored by a single-photon counting module (SPCM-AQR16, Perkin-Elmer EG&G, Canada). The RLS intensity fluctuations were correlated with a correlator card (Flex02-12D, correlator.com).

Imaging of Single Silver Nanoparticles by SRSCS

Figure S2 shows a typical image of silver nanoparticles in solution with 50% (in v/v) glycerol obtained by SRSCS system, and the exposure time was 50 ms. For convenient observation with the naked eye, the image was taken by an EMCCD camera (Cascade 650, Roper Scientific) that owned large imaging area (653 × 492 imaging array with the size of 4.9 × 3.7 mm²) with high spatial resolution (7.4 × 7.4 μm²/pixel). Herein, glycerol was used to only slow down the diffusion of silver nanoparticles. Furthermore, Brownian motion of single silver nanoparticles was clearly observed, and the corresponding video was illustrated in the supplementary data (Video S-1). The video was taken by Cascade 650 camera with exposure time of 9 ms per frame.

Single Molecule Tracking (SMT) of AgNPs

Tracking was conducted according to the published method.³⁻⁴ The diffusion process of nanoparticles was recorded by an EMCCD (Evolve 512, Roper Scientific) with the spatial resolution of 16 × 16

$\mu\text{m}^2/\text{pixel}$ and a stack of 100 frames with the exposure time of 30 ms per frame was collected successively. Then the trajectory of particles was tracked with the Image-Pro Plus software (Media Cybernetics, Silver Springs, MD) and the two-dimensional mean square displacement (*MSD*) was calculated using self-written programs in Matlab (MathWorks Inc.). The simple diffusion mode was employed to calculate the diffusion coefficient (*D*):

$$MSD(\Delta t) = 4D\Delta t$$

The diffusion coefficient was the average of 20 nanoparticles.

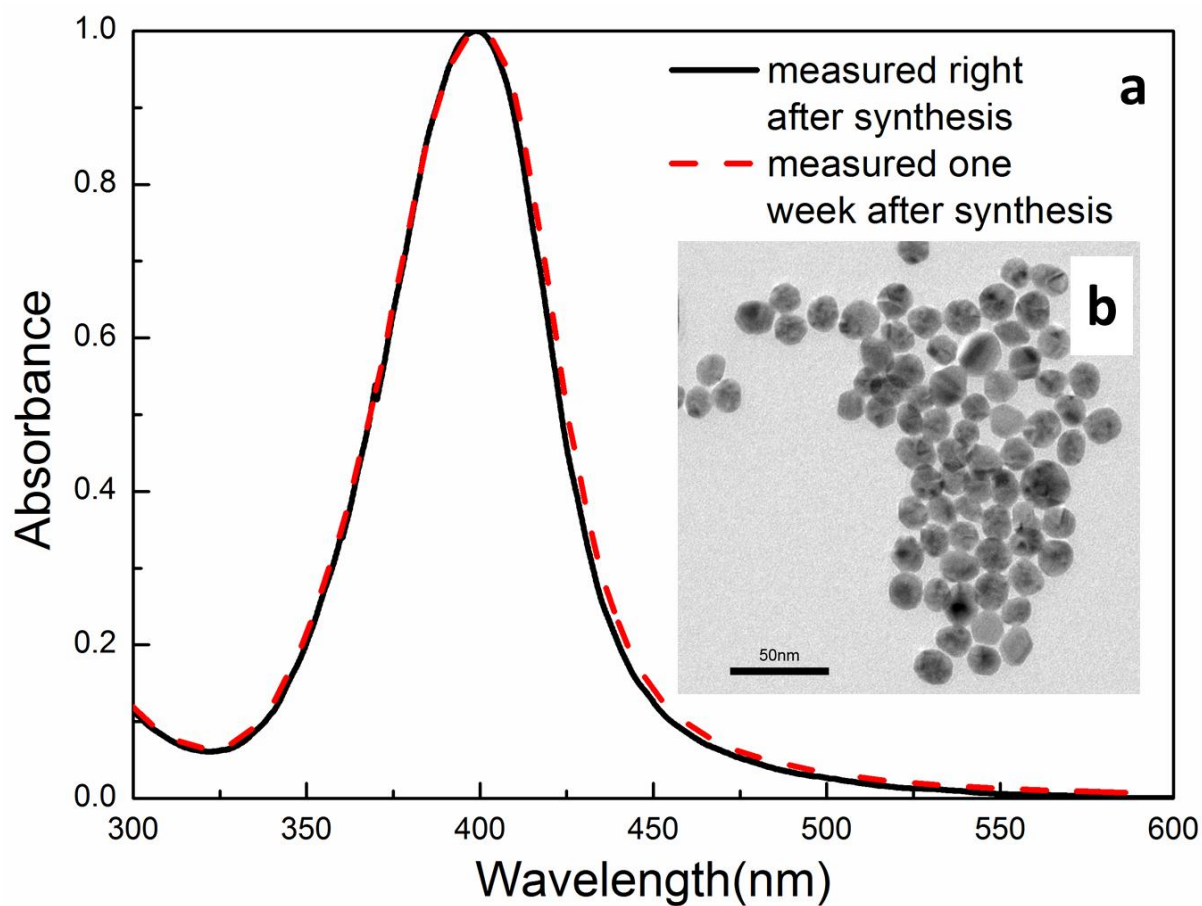


Figure S1. (a) UV-vis absorption spectra of silver nanoparticles solution. (b) TEM image of silver nanoparticles. Scale bar, 50 nm.

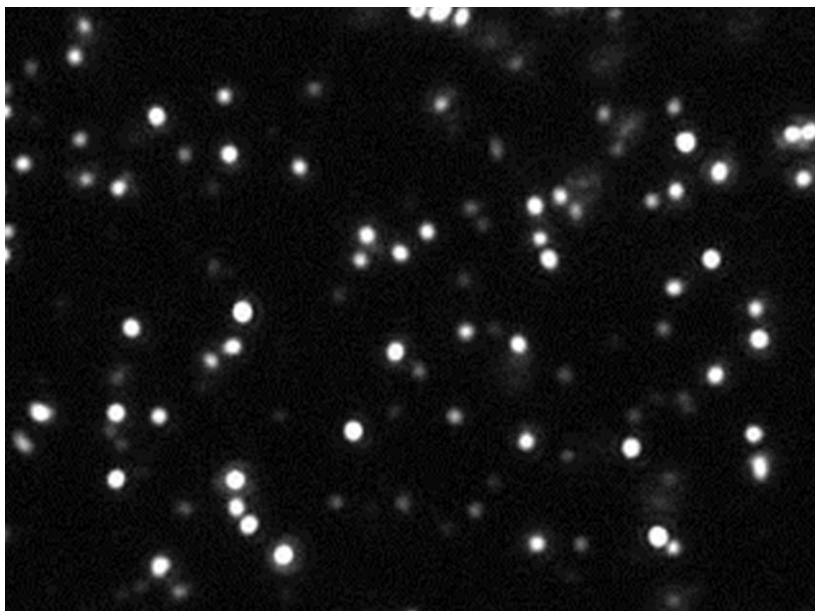


Figure S2. A typical image of silver nanoparticles in 50% (in v/v) glycerol solution. The concentration of silver nanoparticles was about 1.0×10^{-10} M.

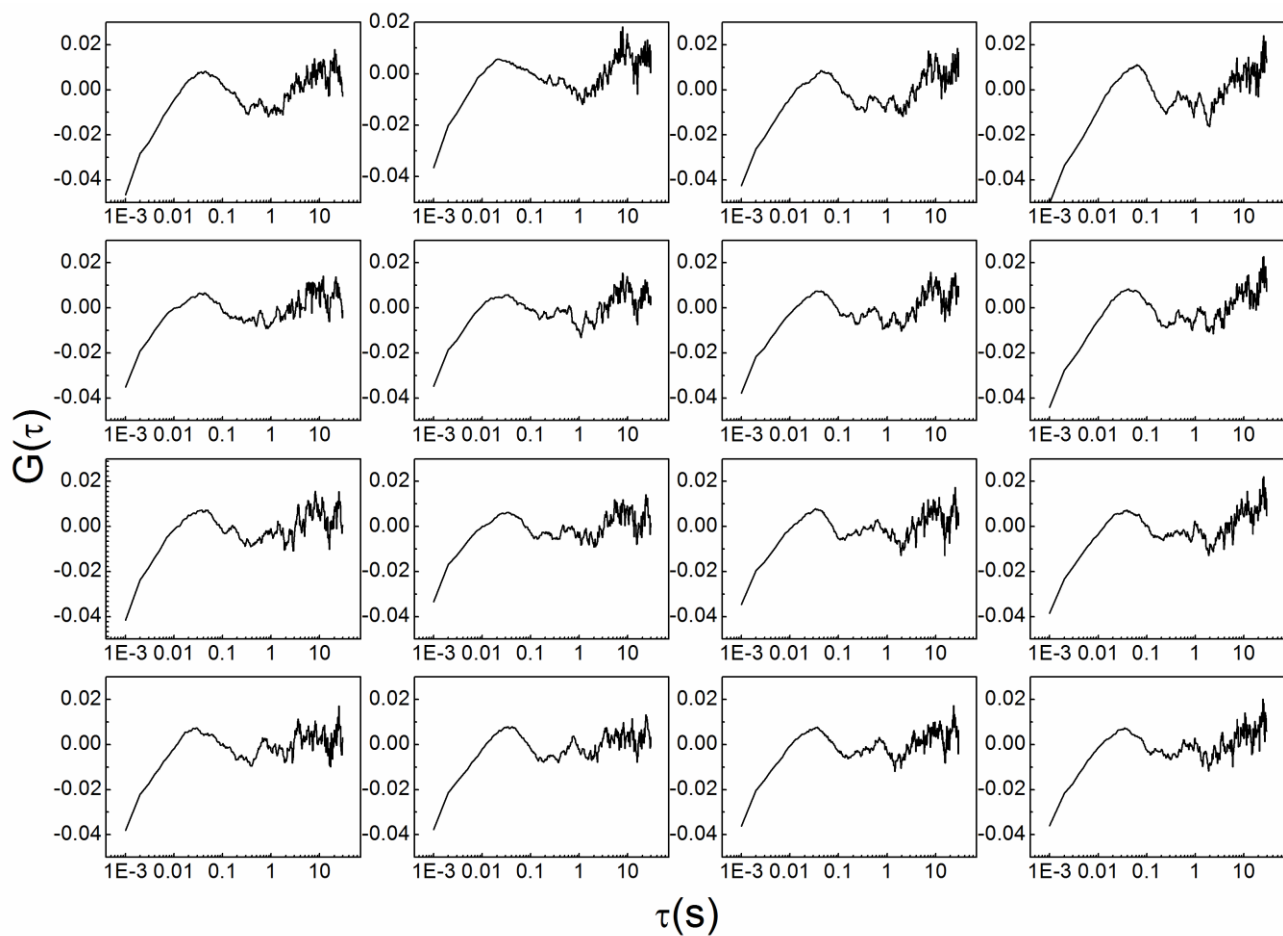


Figure S3. The fit residuals of all 16 autocorrelation curves in Figure 1.

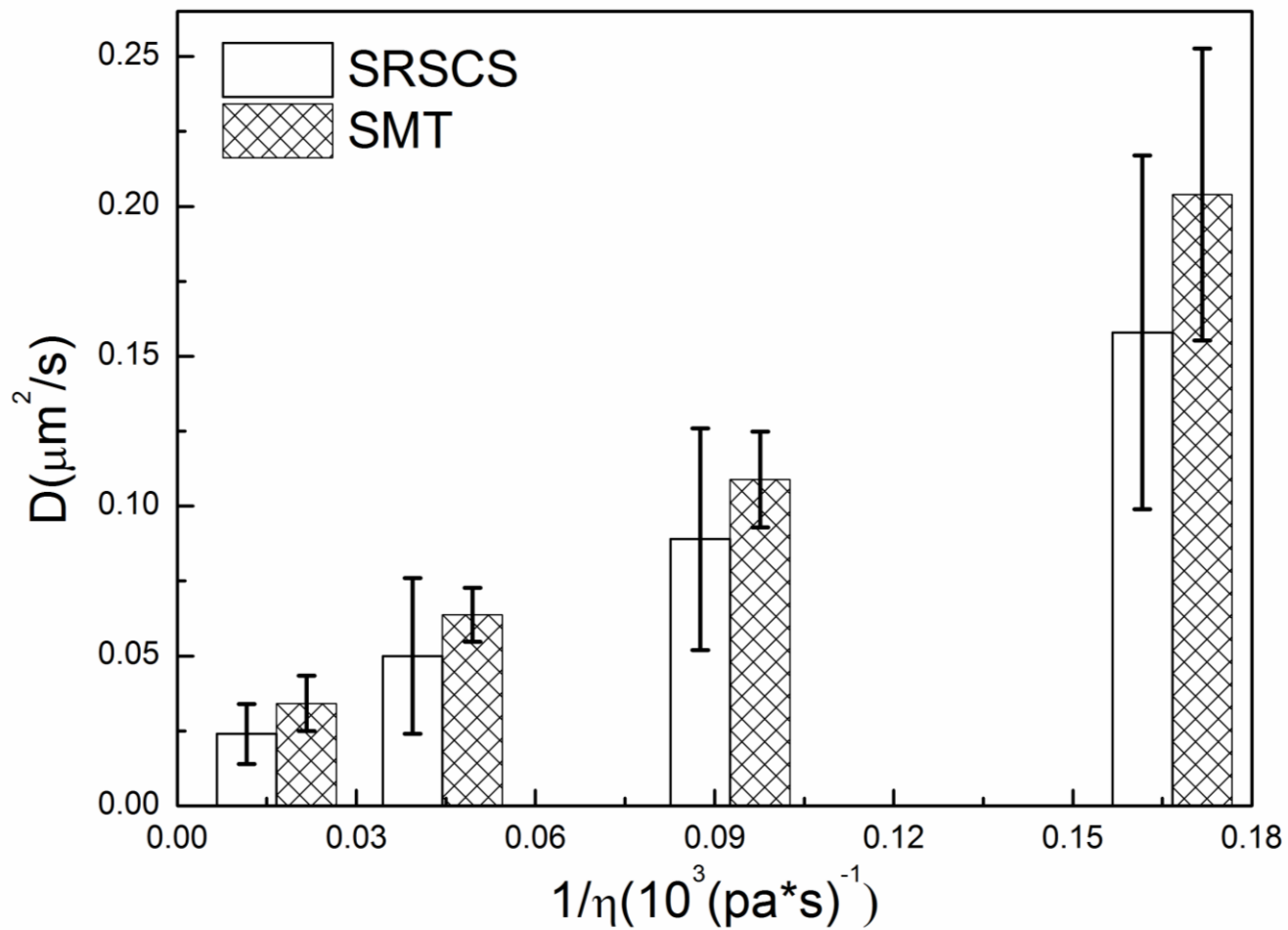


Figure S4. A comparison of diffusion coefficient D of silver nanoparticles in the solutions of different viscosity measured by using the SRSCS and single molecule tracking (SMT).

Table 1. A comparison of particle number N of silver nanoparticles in the solutions using hardware binning and software binning modes.

| Binning mode | Particle number (N) | |
|-----------------|---------------------|------------------|
| | Hardware binning | Software binning |
| no binning | 3.89 ± 1.05 | 3.89 ± 1.05 |
| 2×2 | 5.07 ± 0.66 | 4.51 ± 1.13 |
| 3×3 | — | 5.24 ± 1.14 |
| 4×4 | 5.69 ± 0.44 | 6.02 ± 1.09 |
| 5×5 | — | 6.76 ± 0.95 |

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