

Supporting information for

Quantitative determination of calcium ions by means of enhanced fluorescent of silver nanocluster complex

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Experimental Section

Materials and Agents Silver nitrate (AgNO_3 , 99.8%, Shanghai Chemical Reagent Co., Ltd.), sodium polyacrylate (PAAS, Sigma-Aldrich) were and calcium nitrate ($\text{Ca}(\text{NO}_3)_2$, AR, Sinopharm Chemical Reagent Co., Ltd.) used as received without further purification. Redistilled water (resistivity greater than 18 M cm) was produced by an artificial system. Hydrogen (99.5%) was purchased ECUST. (Hazard: The flammable and explosive limits of hydrogen gas mixed with air are 4-75% and 18-59% in volume percentage. Hydrogen gas must be handled in well-ventilated condition.)

Synthesis of AgNCs-AgNPs complexes AgNCs-AgNPs complexes were synthesized at a 50ml stainless steel reactor. A certain amount of freshly prepared AgNO_3 aqueous solution (0.5M) and sodium polyacrylate aqueous solution (0.5M) was added into the 50ml stainless steel reactor, after that it was diluted to 5ml with redistilled water. Next the stainless steel autoclave was filled with a certain pressure of H_2 . With stirred for tens' minutes at room temperature, fluorescent AgNCs-AgNPs complexes was prepared. According to the procedure, AgNCs-AgNPs complexes with different silver nitrate concentration (0.1mM, 0.25mM, 0.5mM, 0.75mM, 1.5mM, 2.0mM, 2.5mM, 4.0mM) and different the value of carboxyl group to silver ions (1:4, 1:2, 1:1, 2:1, 4:1, 6:1, 8:1, 10:1) under different the pressure of H_2 (0.4bar, 1.1bar, 1.6bar, 2.1bar, 2.6bar, 3.1bar) after stirred for 20 minutes. The prepared AgNCs-AgNPs complexes was saved at $4 \text{ }^\circ\text{C}$ for characterization and detection of calcium.

The interaction between Calcium ions and AgNCs-AgNPs complexes $\text{Ca}(\text{NO}_3)_2$ aqueous solution with 0.1M was prepared for using. 2ml of fresh prepared AgNCs-AgNPs complexes was placed in a brown glass flask volumetric. Then a series volume of $\text{Ca}(\text{NO}_3)_2$ aqueous solution were poured into the AgNCs-AgNPs complexes, and the mixed solution was stirred for 30 minutes at atmosphere.

Characterization. The UV-visible spectra of AgNCs-AgNPs complexes were obtained at the wavelength ranging from 300nm to 800nm at room temperature using a UV-2400 PC Uv-visible spectrophotometer. TEM image of AgNCs-AgNPs

complexes was performed on a JEOL JEM-2100 (HT) transmission electron microscope at 200kV, and the SEM images were operated on a S-4800 field emission scanning electron microscope. DLS was operated on a Malvern Nano-ZS with a detecting angle of 173° . Nano measurer software was used to analyze the size distribution and average diameter of AgNCs-AgNPs complexes by counting 300 particles to estimate.

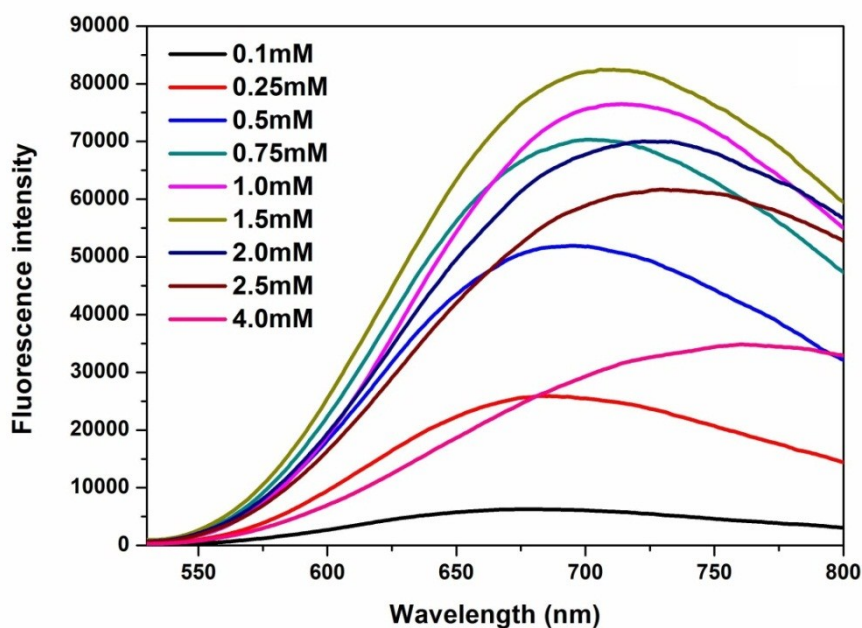


Figure S1. The emission spectra of the prepared AgNCs-AgNPs complexes with the various concentration of Ag⁺ at the H₂ pressure of 1.5bar and the [COO⁻]/[Ag⁺] value of 6 after 20min reaction time.

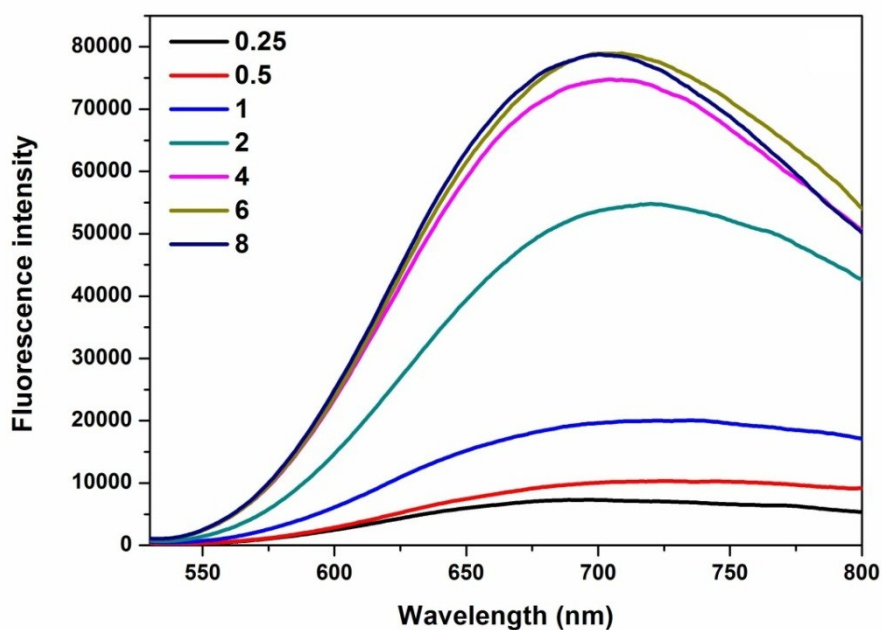


Figure S2. The emission spectra of the prepared AgNCs-AgNPs complexes with the various values of [COO⁻]/[Ag⁺] at the H₂ pressure of 1.5bar and the Ag⁺ concentration of 1.0mM after 20min reaction time.

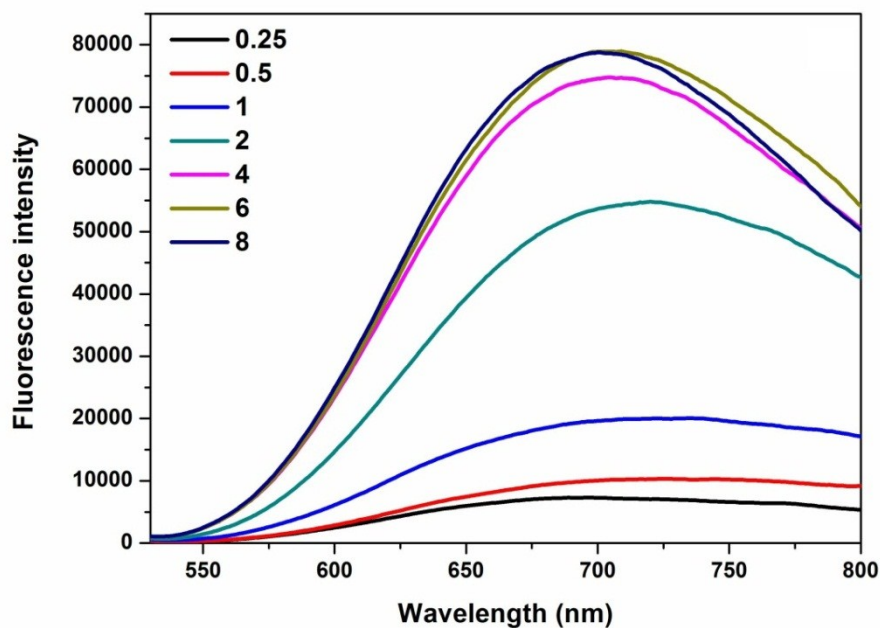


Figure S3. The emission spectra of the prepared AgNCs-AgNPs complexes with the various pressures of H₂ at the [COO⁻]/[Ag⁺] value of 4 and the Ag⁺ concentration of 1.0mM after 20min reaction time.

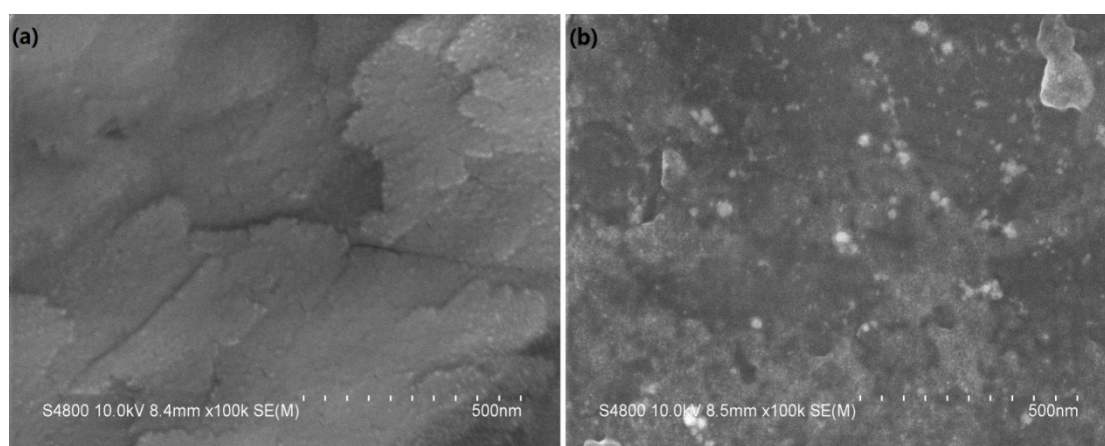


Figure S4. SEM images of as-prepared AgNCs-AgNPs complexes from different lengths of stirring: (a) 20min, (b) 60min.

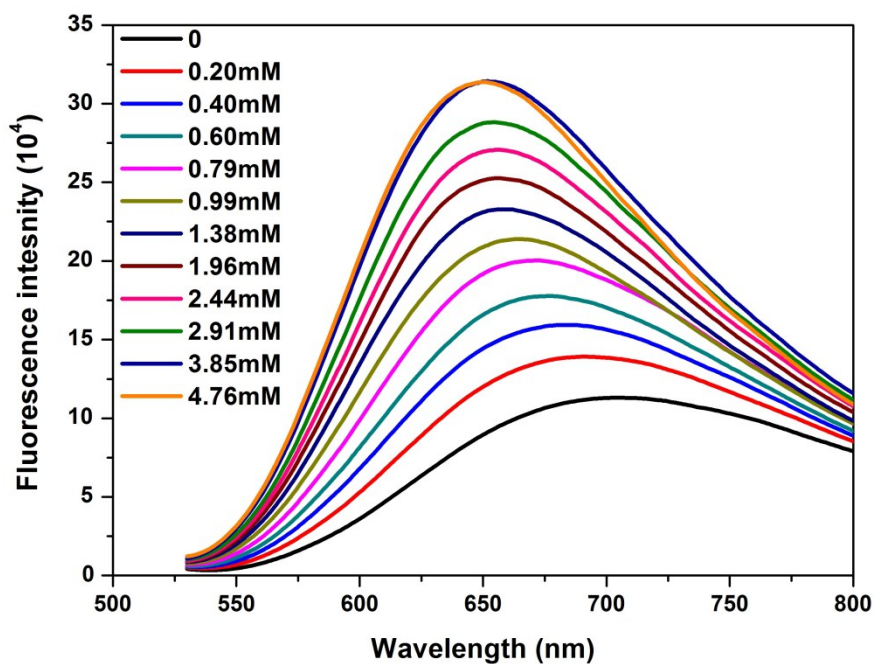


Figure S5. The emission spectra of the prepared AgNCs-AgNPs complexes with the various concentrations of Ca^{2+} ions at excitation wavelength of 520nm.

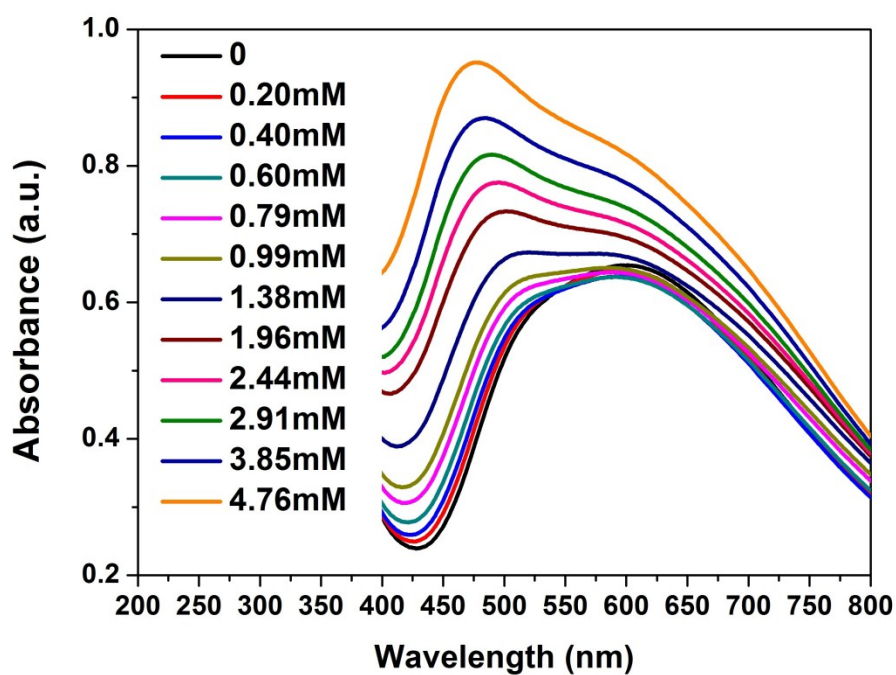


Figure S6. The absorption spectra of the prepared AgNCs-AgNPs complexes with the various concentrations of Ca^{2+} ions.