

Synthesis of *p*-sulfonatocalix[4]arene modified silver nanoparticles as colorimetric histidine probes

Dejun Xiong, Mingliang Chen and Haibing Li*

Key Laboratory of Pesticide and Chemical Biology (CCNU), Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, PR China

E-mail: lhbing@mail.ccnu.edu.cn

Experimental details

Synthesis of *p*-sulfonatocalix[4]arene: The procedure according to Shinkai's method¹⁻³ was slightly modified as follows. Calix[4]arene (1g) was mixed with 10 mL of concentrated H₂SO₄. Then the solution was heated at 70 °C for 3h. An aliquot was withdrawn from the solution and poured into water to determine the progress of the reaction. The reaction was completed when water-insoluble material was not detected. After cooling, the precipitate was recovered by filtration. The precipitate was dissolved in 4 mL water before addition of 20 mL brine. Finally, 1.3 g *p*-sulfonatocalix[4]arene was obtained after evaporation of water in yield of 66.3%; Single spot on paper chromatography (water-2-propanol 1:1 v/v); IR (KBr) ν_{OH} 3431, 3188 cm⁻¹, ν_{SO_3} 1187, 1049 cm⁻¹; ¹H NMR (D₂O) δ (ppm): 3.45, 4.25 (d, 8H, ArCH₂Ar), 7.93 (Ar H, s, 8H).

Synthesis of *p*-sulfonatocalix[4]arene modified silver nanoparticles

2 mL of 10⁻² M AgNO₃ solution was added to 96 mL of triply distilled water. To this solution, 2 mL of 10⁻² M *p*-sulfonatocalix[4]arene aqueous solution was added as stabilizer with stirring for 20 min. And then, 8.8 mg of NaBH₄ was added to the

solution. The mixture was continually stirred for 5 min at room temperature. The silver colloids were finally obtained.

Synthesis of mercaptoacetic acid modified silver nanoparticles

To the solution of 2 mL of 10^{-2} M AgNO_3 solution and 96 mL of triply distilled water, 8.8 mg of NaBH_4 was added. And then, 2 mL of 10^{-2} M mercaptoacetic acid aqueous solution was added as stabilizer with stirring for 7 hours at room temperature.

The stability of $p\text{SC}_4\text{-Ag}$ NPs and MA-Ag NPs

Fig. S1 shows the adsorption spectra of $p\text{SC}_4\text{-Ag}$ NPs and MA-Ag NPs recorded on different times. For $p\text{SC}_4\text{-Ag}$ NPs, there was no obvious change in the shape, position and symmetry of the absorption peak during the initial one month, except for a little decrease of the absorbance intensity. However, for MA-Ag NPs, it is shown that the obvious change in the shape, position and symmetry of the absorption peak and the dramatical decrease of the absorbance intensity. The results indicate $p\text{SC}_4\text{-Ag}$ NPs are more stable than MA-Ag NPs.

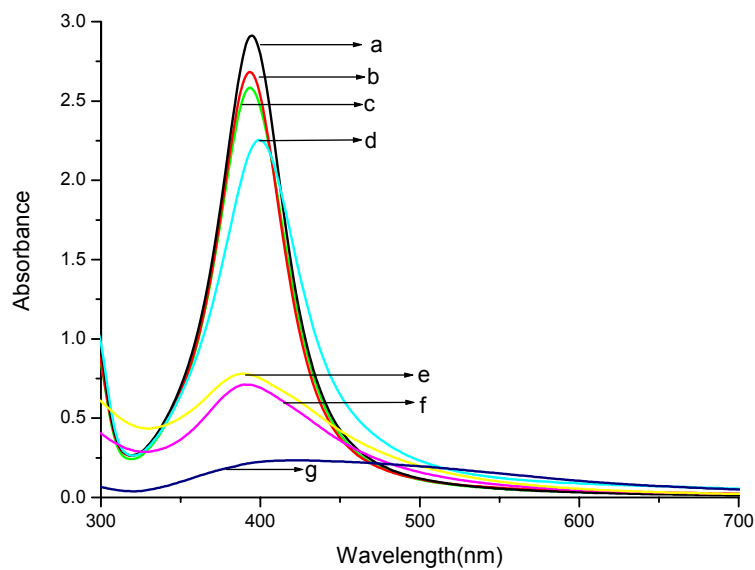


Fig.S1 The absorption spectra of pSC_4 -AgNPs recorded at: (a) 0, (b) 48 h, (c) 120 h, (d) 720 h (one month) and MA-Ag NPs recorded at: (e) 0 (f) 24 h (g) 240 h

References

- 1 S. Shinkai, S. Mori, H. Koreishi, T. Tsubaki and O. Manabe, *J. Am. Chem. Soc.*, 1986, **108**, 2409
- 2 S. Shinkai, K. Araki, T. Tsubaki, T. Arimura and O. Manabe, *J. Chem. Soc. Perkin Trans. I*, 1987, 2297.