Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Synthesis, Structure and Characterization of Fe_6 Molecular Cluster with Peripheral Sulfur Atoms-Capped Silver Nanoparticles

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Calculation of EF values for BSSC thin films

Surface enhancement factor (EF) of the silver nanoparticles can be calculated using the following equation:[1]

$$EF = \frac{N_{bulk} I_{surf}}{N_{surf} I_{bulk}} \qquad (1)$$

where I_{surf} and I_{bulk} denote the integrated intensities for the strongest band of the Fe_6 adsorbed on the surface silver nanoparticles and the solid Fe_6, respectively. N_{surf} and N_{bulk} represent the numbers of the corresponding surface and solid molecules effectively excited by the laser beam, respectively.

Calculation of N_{bulk}

The number of Fe_6 molecules excited in the bulk solid, N_{bulk}, can be calculated as following equation (2):

$$N_{\mathrm{bulk}} = \frac{\pi \left(\frac{d_{spot}}{2} \right)^2 D \rho_{Fe6} N_A}{M_{r,Fe6}} \qquad (2)$$

where $d$spot is the diameter of circular laser spot, D is the depth of the incident laser beneath the surface of Fe_6 solid, ρ_{Fe6} and $M_{r,\,Fe6}$ are the density and molecular weight of Fe_6, respectively, N_A represents the Avogadro constant. In this study, the laser spot was a circle with diameter of ~2 μm, and the depth the laser could reach was about 19 μm, the density (1.528g/cm^3) and molecular weight (2563.38 g/mol) of solid BT. The calculated value of N_{bulk} equals to 3.56×10^9.

Calculation of N_{surf}

For the Fe_6 molecules adsorbed on the surface of silver nanoparticles, assuming that the Fe_6 molecules are fully adsorbed and adopt a standing-up orientation on Ag surface, then the area occupied by one Fe_6molecule is considered to be equal to the cross-sectional area of the molecule. The numbers of the Fe_6 molecules effectively excited by the laser beam on the surface of the silver nanoparticles, $N_{surf,}$ could be calculated as following equation (3):

$$N_{\mathrm{surf}} = \frac{\pi\left(\frac{d_{spot}}{2}\right)^2}{A_{cs,Fe6}} \qquad (3)$$

where d_{spot} has the same definition as equation (2), $A_{CS,Fe6}$ is the of the Fe_6. The diameter of the Fe_6 is about 2 nm, so the cross-sectional area is ~3.14 nm^2. The calculated value of N_{bulk} equals to 1×10^6.

ASEF calculation

Raman intensity at 1076 cm^{-1} was used to calculate the EF. A baseline correction was conducted for EF value calculation at each spectrum. The I_{surf} and I_{bulk} at 1076 cm^{-1} were 5444 and 53. Thus, the EF was calculated to be 3.65×10^5.

Electrochemical properties of ferric nitrate

A gold disk was polished using alumina slurry (0.5 μm size), washed, degreased and sonicated in water before being used as the working electrode. A standard three-electrode arrangement was used with a platinum auxiliary electrode, an AgCl (10 MM $AgNO_3$ in acetonitrile)/Ag reference electrode, and 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) in acetonitrile as supporting electrolyte. Triple distilled water was used for preparing the ferric nitrate solution. Ferric nitrate coverage of the electrode was obtained by using 0.1 mol^{-1} ferric nitrate solution dropped in the cleaned Au electrode and then drying in air. Figure S1 is the CV of ferric nitrate on the gold disk electrode in 0.1 M TBAP (CH_3CN), and the $Fe(NO_3)_3$ has a significant irreversible reduction peak located at ca. -0.83 V.

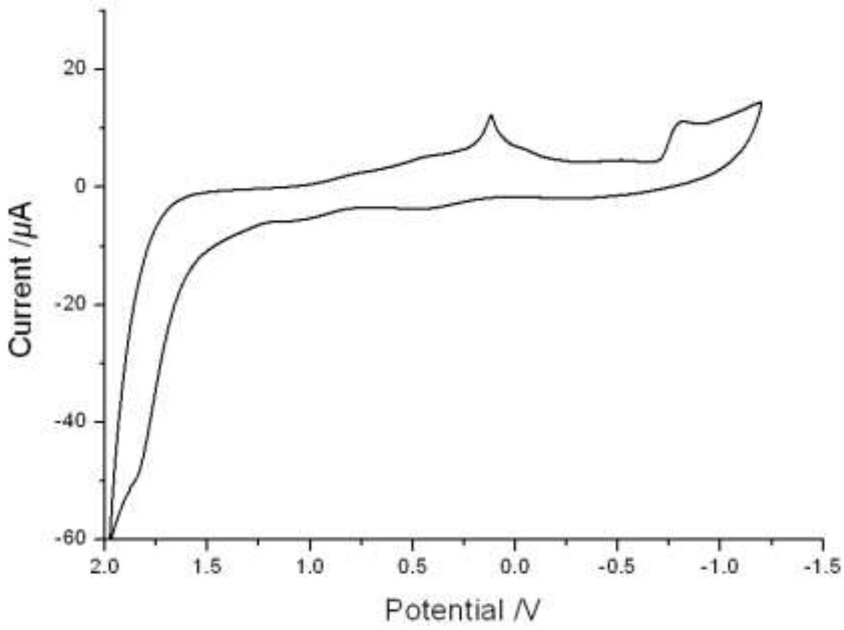

Figure S1. Cyclic voltammogram of ferric nitrate in acetonitrile, at room temperature with the scan rate of 100 mV s^{-1}.

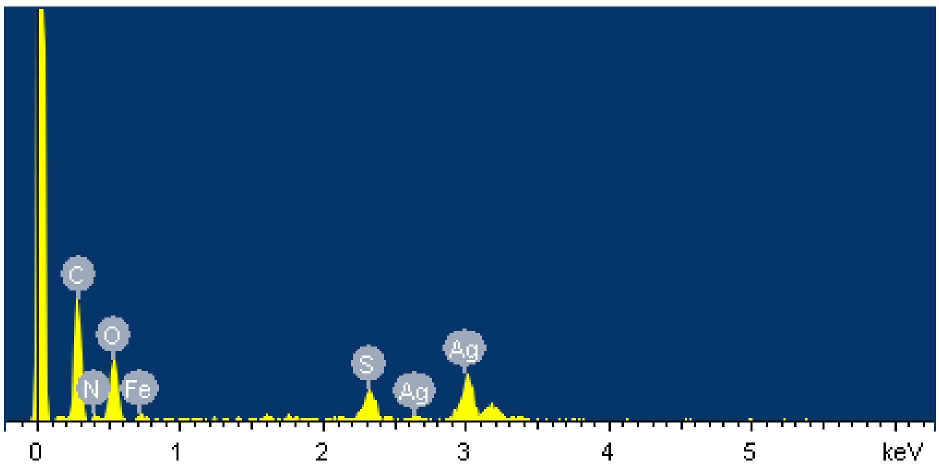

Fig. S2 X-Ray energy dispersive spectrum from the Ag@Fe_6.

S1 X.-M. Lin, Y. Cui, Y.-H. Xu, B. Ren, Z.-Q. Tian, Anal. Bioanal. Chemistry, 2009, 394, 1729.