Electronic Supplementary Information

Synthesis of silica-stabilized silver clusters aided by the designed mercaptosilane ligand

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1. Experimental section

1.1 Chemicals

All chemicals were purchased from commercial sources and were directly used as received. 1,2-dibromoethane \([\text{C}_2\text{H}_4\text{Br}_2, 99\%]\), o-sulfobenzimide [saccharine, 99%], chlorotrimethylsilane [TMSCI, 98%], 1,1,1,3,3,3-hexamethyldisilazane [HMDS, 96%] and 4-(trifluoromethyl)benzenethiol [HSPhCF\(_3\), 98%] were purchased from TCI, 4-bromothiophenol [HSPhBr, 98%] and cesium hydroxide solution [CsOH in water, 50 wt %] were purchased from Innochem, sodium borohydride [NaBH\(_4\), 98%] was purchased from Aladdin, tetrahydrofuran [THF, 99.5%], 4-mercaptobenzoic acid [HSPhCOOH, 90%] and polyoxyethylene(4)lauryl ether [Brij\(^{\text{\textregistered}}\)30, 99%] were purchased from Acros, magnesium turnings [Mg, 99.9%], tetraethyl orthosilicate [TEOS, A.R.], silver nitrate [AgNO\(_3\), 99.9%], triethylamine [TEA, 99%], tetraphenylphosphonium bromide [PPh\(_4\)Br, 99%] and all solvents in analytical purity were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai).

1.2 Apparatus

The UV-vis absorption spectra were recorded on a Lambda365 spectrometer of PerkinElmer. The transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) were conducted on a HT7700 transmission electron microscope of Hitachi with an acceleration voltage of 120 kV. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and Elemental mapping analysis were conducted on a Tecnai G2 F20 S-Twin transmission electron microscope of FEI with an acceleration voltage of 200 kV. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) were conducted on an iCAP7000 spectrometer of Thermo Fisher Scientific. The fourier transform infrared (FT-IR) spectra were recorded on a Nicolet iS10 of Thermo Fisher Scientific. The thermogravimetric analysis (TGA) were conducted on a SDT Q600 of TA Instruments. The proton nuclear magnetic resonance (\(^1\)H NMR) spectra were recorded on an AVANCE III HD of Bruker. The photoacoustic (PA) imaging were recorded on a Vevo LAZR of Fujifilm Visualsonics. The dynamic light scattering (DLS) were collected by Malvern Nanosizer. The photoluminescence (PL) spectra were recorded on a Cary Eclipse Fluorescence Spectrophotometer of Agilent. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on an Axis Ultra DLD XPS of Kratos.
1.3.1 Synthesis of ((4-bromophenyl)thio)trimethylsilane

The silicon-containing mercaptan ligand and its precursor were successfully prepared according to the reported method.[1] A mixture of 4-bromothiophenol (5.0 g), saccharine (35.0 mg) and chloroform (50.0 mL) was heated to the reflux temperature in an oil bath under \( \text{N}_2 \), HMDS (6.3 mL) was added subsequently. The reaction was then refluxed for 3 h and naturally cooled to room temperature. After removing the solvent by rotary evaporation under vacuum, 6.48 g (94% yield) of ((4-bromophenyl)thio)trimethylsilane (BrPhSSi(CH\textsubscript{3})\textsubscript{3}) as clear white crystals were obtained. \(^1\text{H}\) NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.36 (d, \( J = 8.5 \) Hz, 2H), 7.26 (d, \( J = 8.6 \) Hz, 2H), 0.27 (s, 9H) ppm. Known compound.[1]

1.3.2 Synthesis of 4-(triethoxysilyl)benzenethiol

\[ \text{Mg} \quad \text{TEOS} \quad \text{THF} \quad 15 \text{ min} \quad \rightarrow \quad \text{1,2-dibromoethane} \quad \text{TMSCl} \quad \text{EtOH} \quad 3 \text{ h} \quad \rightarrow \quad \text{HS} \quad \text{Si(OEt)}\textsubscript{3} \]

A mixture of Mg (1.0 g), TEOS (6.5 mL) and solvent THF (10.0 mL) were refluxed for 15 min under \( \text{N}_2 \) protection. Then, 1,2-dibromoethane (0.5 mL) and BrPhSSi(CH\textsubscript{3})\textsubscript{3} (3.5 g) which was freshly prepared were added into the mixture in sequence. After reacting 3 h and being cooled down to the room temperature, TMSCl (2.5 mL) were added. The solvent was removed under vacuum. Finally, about 10 mL ethanol (EtOH) was added and the mixture was filtered to remove residue under \( \text{N}_2 \). After removing the EtOH under vacuum, 2.9 g (79% yield) of light yellow crystalline 4-(triethoxysilyl)benzenethiol (HSPhSi(OEt)\textsubscript{3}) were obtained. The impurities would be removed in the process of subsequent silver cluster synthesis. \(^1\text{H}\) NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.43 (d, \( J = 8.7 \) Hz, 1H), 7.14 (d, \( J = 8.4 \) Hz, 1H), 3.77 (m, 6H), 1.28 (t, \( J = 7.0 \) Hz, 9H) ppm. Known compound.[1]

1.3.3 Synthesis of \( \text{Ag}_{44}\)-Si(OEt)\textsubscript{3} nanoclusters

\[ \text{AgNO}_3 \quad + \quad \text{Si(OEt)}\textsubscript{3} \quad + \quad \text{PPh}_4\text{Br} \quad + \quad \text{NaBH}_4 \quad \xrightarrow{\text{TEA} \quad \text{DCM} / \text{MeOH} / \text{H}_2\text{O}, 0 \text{ \degree C}, 2 \text{ h}} \quad [\text{Ag}_{44}(\text{SPhSi(OEt)}\textsubscript{3})_{30}]\text{[PPh}_4\text{]}_4 \]

The oil-soluble \([\text{Ag}_{44}(\text{SPhSi(OEt)}\textsubscript{3})_{30}]\text{[PPh}_4\text{]}_4\) (in short, \( \text{Ag}_{44}\text{-Si(OEt)}\textsubscript{3} \)) was prepared according to the reported method with minor alteration.[2] Briefly, \( \text{AgNO}_3 \) (20.0 mg) was ultrasonic dissolved in
methanol (MeOH, 1.0 mL). The newly compounded PPh₄Br dichloromethane (DCM) solution (1.0 mL, 12.0 mg·mL⁻¹) and the synthesized mercaptosilane ligand HSPhSi(OEt)₃ (200.0 mg) were added to the above solution in order. After stirring 20 min at 0 °C, TEA (50.0 μL) and NaBH₄ aqueous solution (1.0 mL, 45.0 mg·mL⁻¹) were added quickly. The reaction mixture was aging for 2 h at 0 °C and the color gradually changed from light yellow to purplish-red or even deeper. Then, the aqueous phase was removed and the organic phase was washed with water several times. Black powder was precipitated from DCM/hexane (about 1:20 by volume) and stored below -15 °C.

1.3.4 Synthesis of Ag₄₄CF₃ nanoclusters

\[
\text{AgNO}_3 + \text{PPh}_4\text{Br} + \text{NaBH}_4 \xrightarrow{\text{TEA}} \text{DCM} / \text{MeOH} / \text{H}_2\text{O}, 0 ^\circ\text{C}, 12 \text{h} \rightarrow [\text{Ag}_{44}(\text{SPhCF}_3)_{30}]\left(\text{PPh}_4\right)_4
\]

We successfully synthesized [Ag₄₄(SPhCF₃)₃₀](PPh₄)₄ (in short, Ag₄₄-CF₃), under the same conditions as 1.3.3 except that 10.0 μL 4-(trifluoromethyl)benzenethiol (HSPhCF₃) was used as the thiol ligand instead of 4-(triethoxysilyl)benzenethiol and the aging time extended to 14 h.

1.3.5 Synthesis of Ag₄₄-COOH nanoclusters

\[
\text{AgNO}_3 + \text{SPhCOOH} + \text{NaBH}_4 \xrightarrow{\text{CsOH}} \text{EtOH} / \text{H}_2\text{O}, \text{rt.}, 2 \text{h} \rightarrow [\text{Ag}_{44}(\text{SPhCOOH})_{30}]\text{Na}_4
\]

The water-soluble [Ag₄₄(SPhCOOH)₃₀]Na₄ (in short, Ag₄₄-COOH), was prepared according to the reported method.[3] Firstly, HSPhCOOH (154.0 mg) was dissolved into 12.0 mL ethanol and AgNO₃ aqueous solution (21.0 mL, 2.0 mg·mL⁻¹) was added subsequently. The pH of the solution was then raised to 12 by adding aqueous CsOH (50 wt %). After slowly dropwise adding NaBH₄ aqueous solution (9.0 mL, 1.1 mg·mL⁻¹), the reaction was incubated under room temperature (rt.) for 2 h. The raw product was firstly separated from the solution by centrifuging at 8000 rpm for 5 min and then precipitated with dimethyl formamide (DMF) to remove remaining soluble impurities from the reaction. The collected clusters were dissolved into DMF solution (containing 1 vol % acetic acid) for further use.
1.3.6 Synthesis of Ag$_{44}$-Si(OEt)$_3$@SiO$_2$

A reverse microemulsion method of coating silicon was used to synthesize the Ag$_{44}$-Si(OEt)$_3$@SiO$_2$ composite structure,$^4$ the specific operation is as follows. The mixture of oil phase n-heptane (9.4 mL) and surfactant Brij®30 (3.0 mL) was stirred rapidly for 15 min. Then H$_2$O (600.0 μL) and Ag$_{44}$-Si(OEt)$_3$ DMF solution (900.0 μL, 0.3 μmol·mL$^{-1}$) were dropwise added in order. After stirring for another 15 min, ammonia solution (150.0 μL) was added slowly and the mixture was stirred for 40 min. Finally, the silica precursor TEOS (20.0 μL) was added. After 24 h stirring, about 10 mL ethanol was used to destabilize the solution. The precipitation collected by centrifuging at 11000 rpm for 10 min was washed several times with ethanol and n-heptane alternately.

1.3.7 Synthesis of Ag$_{44}$-CF$_3$/SiO$_2$ or Ag$_{44}$-COOH/SiO$_2$

The Ag$_{44}$-CF$_3$ or Ag$_{44}$-COOH was used as a control and the preparation of Ag$_{44}$-CF$_3$/SiO$_2$ or Ag$_{44}$-COOH/SiO$_2$ followed the same procedures depicted above, except that Ag$_{44}$-Si(OEt)$_3$ DMF solution was replaced by Ag$_{44}$-CF$_3$ DMF solution (900.0 μL, 0.3 μmol·mL$^{-1}$) or Ag$_{44}$-COOH aqueous solution (900.0 μL, 0.3 μmol·mL$^{-1}$).

2. Characterizations

2.1 4-(triethoxysilyl)benzenethiol ligand

![Fig. S1] $^1$H-NMR spectrum of ((4-bromophenyl)thio)trimethylsilane in CDCl$_3$.  

2.2 Ag₄₄ nanoclusters

Table S1 The Ag/Si in Ag₄₄:S(OEt)₃ NCs based on ICP-AES⁹ and theoretical value.

<table>
<thead>
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<th>ICP-AES</th>
<th>theoretical</th>
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<tr>
<td>Ag/Si</td>
<td>3.9</td>
<td>5.6</td>
</tr>
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</table>

⁹For the ICP-AES analysis, about 1 mg of Ag₄₄:S(OEt)₃ was dissolved with 100 μL hydrofluoric acid (HF) plus 900 μL nitric acid (HNO₃) mixed solution and transferred to a 10 mL volumetric flask.

Fig. S2 ¹H-NMR spectrum of 4-(triethoxysilyl)benzenethiol in CDCl₃.

Fig. S3 TGA of Ag₄₄:S(OEt)₃.
Fig. S4 DLS of (a) Ag$_{44}$-Si(OEt)$_3$ DMF solution, (b) Ag$_{44}$-CF$_3$ DMF solutions and (c) Ag$_{44}$-COOH DMF solution (containing 1 vol % acetic acid).

Fig. S5 UV-vis absorption spectra of Ag$_{44}$-CF$_3$ in DMF heated in air at 60 °C for different time.

Fig. S6 UV-vis absorption spectra of Ag$_{44}$-Si(OEt)$_3$ dispersed in silica coating reaction solution (black line) and after 7 days (red line).
2.3 Ag$^{44}$-Si(OEt)$_3$@SiO$_2$ composite structure

![UV-vis absorption spectra](image)

**Fig. S7** UV-vis absorption spectra of reaction liquid centrifugal supernatant of the (a) Ag$^{44}$-COOH/SiO$_2$, (b) Ag$^{44}$-CF$_3$/SiO$_2$ and (c) Ag$^{44}$-Si(OEt)$_3$@SiO$_2$.

![TEM image](image)

**Fig. S8** TEM image of SiO$_2$.

**Table S2** The Si/Ag in Ag$^{44}$-Si(OEt)$_3$@SiO$_2$ based on ICP-AES$^a$ and XPS analysis.

<table>
<thead>
<tr>
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<th>ICP-AES</th>
<th>XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Ag</td>
<td>13.9</td>
<td>15.9</td>
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</table>

$^a$For the ICP-AES analysis, about 1 mg of Ag$^{44}$-Si(OEt)$_3$@SiO$_2$ was dissolved with 100 μL hydrofluoric acid (HF) plus 900 μL nitric acid (HNO$_3$) mixed solution and transferred to a 10 mL volumetric flask.

Because the size of Ag$^{44}$-Si(OEt)$_3$ was relatively small and the proportion of Si mass was only 6%, the number of Ag$^{44}$-Si(OEt)$_3$ nanoclusters in the Ag$^{44}$-Si(OEt)$_3$@SiO$_2$ composite structure (about 22.4 nm radius) was calculated as follows:

$r_{\text{Si/Ag}}$: the mass ratio of Si to Ag tested by ICP-AES;

$R$: the radius of Ag$^{44}$-Si(OEt)$_3$@SiO$_2$;
$N_A$: the Avogadro constant;

$m$: the mass, $n$: the molar mass, $M$: the relative atom or molecular mass (the corner mark stands for the corresponding atoms or molecules).

$$m_{\text{Ag}} = \frac{n_{\text{Si}}}{r_{\text{Si}/\text{Ag}}} = \frac{n_{\text{SiO}_2} \cdot M_{\text{SiO}_2}}{r_{\text{Si}/\text{Ag}}} = \frac{\rho_{\text{SiO}_2} \cdot \frac{4}{3} \pi R^3}{M_{\text{SiO}_2} \cdot \frac{\pi}{13.9}} = \frac{2.31 \cdot \frac{\text{g}}{\text{cm}^3} \cdot \frac{\frac{3}{2} \pi}{60.08 \cdot \text{g/mol}^3} \times 22.4 \cdot \text{nm}^3}{13.9} = 3.658 \times 10^{-18} \text{g}$$

$$N_{\text{Ag}_{44} - \text{Si}(OEt)_3} = n_{\text{Ag}_{44} - \text{Si}(OEt)_3} \cdot N_A = \frac{m_{\text{Ag}}}{M_{\text{Ag}}} \cdot \frac{44}{44} \cdot N_A = \frac{3.658 \times 10^{-18} \text{g}}{107.87 \cdot \text{g/mol}^{-1} \cdot 44} \times 6.02 \times 10^{23} \text{mol} = 464$$

2.4 The contrast experiments

![Fig. S9 UV-vis absorption spectra of Ag$_{44}$-Si(OEt)$_3$@SiO$_2$ ultrasonically dispersed in DCM (inset: the photos of the solution).](image)

![Fig. S10 TEM image of Ag$_{44}$-CF$_3$/SiO$_2$.](image)
2.5 The application exploration

**Fig. S11** TEM image of Ag\textsubscript{44}-COOH/SiO\textsubscript{2}.

**Fig. S12** PL spectra of Ag\textsubscript{44}-Si(OEt)\textsubscript{3} (black line) and Ag\textsubscript{44}-CF\textsubscript{3} (blue line) excited by 480 nm emission in air.

**Fig. S13** PL spectra of Ag\textsubscript{44}-Si(OEt)\textsubscript{3} (black line) and Ag\textsubscript{44}-CF\textsubscript{3} (blue line) excited by 480 nm emission in N\textsubscript{2}.
Fig. S14 PT heating curve of SiO$_2$ solid under laser irradiation (0.25 W·cm$^{-2}$, 655 nm) with images before and after irradiation (inset).

Fig. S15 UV-vis absorption spectra of Ag$_{44}$Si(OEt)$_6$@SiO$_2$ solid after laser irradiation.

Fig. S16 PT heating curve of Ag$_{44}$Si(OEt)$_6$@SiO$_2$ solid with different power densities (0.05, 0.10, 0.25 W·cm$^{-2}$, 655 nm).
Fig. S17 Fitting curve of PT heating final temperature of 2 mg·mL$^{-1}$ Ag$_{44}$-Si(OEt)$_3$@SiO$_2$ in 1 vol % DMF aqueous solution with different power densities (0.25, 0.50, 0.75, 1.00 W·cm$^{-2}$, 655 nm).

Fig. S18 Fitting curve of PT heating final temperature of Ag$_{44}$-Si(OEt)$_3$@SiO$_2$ solid with different power densities (0.05, 0.10, 0.25 W·cm$^{-2}$, 655 nm).

Fig. S19 UV-vis absorption spectra of 2 mg·mL$^{-1}$ Ag$_{44}$-Si(OEt)$_3$@SiO$_2$ in 1 vol % DMF aqueous solution before (black line) and after (red line) the ON/OFF irradiation (1.00 W·cm$^{-2}$, 655 nm) cycles repeated four times.
3. References


