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Silver nanoparticles modified by water-soluble leaning tower[6]arenes for

sensing and catalysis

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1. Materials and Methods

Materials: All the chemicals and solvents were purchased from commercial sources and used as received unless otherwise noted. Deionised water, purified by Experimental Water System (Lab-UV-20), was used in relevant experiments.

Methods: Fourier transform infrared (FT-IR) spectra were recorded on a Vertex 80 V spectrometer. Transmission electron microscopy (TEM) images were obtained on a Tecnai G2 S-Twin F20 instrument at an accelerating voltage of 200 kV. Ultraviolet–visible (UV-vis) spectra were collected on the Japan Shimadzu UV-2550 instrument. ¹H NMR spectra were recorded on Bruker AVANCE III-400 MHz instrument at 298 K. Chemical shifts were referred to tetramethylsilane (TMS). The zeta-potential value and hydrodynamic diameters of dynamic light scattering (DLS) were measured on ALV/CGS-3 compact goniometer system.

2. Synthetic Methods



Scheme S1. Synthetic route to WLT6 and control monomer M

2.1 Synthesis of WLT6:^[1] CLT6 (1.7 g 1.5 mmol) was added to a solution (15 mL) of sodium hydroxide (480 mg, 12 mmol). After stirring for 20min, WLT6 (1.92 g, 98%) was obtained as a white solid by removing water under reduced pressure. ¹H NMR (400 MHz, D₂O, 298K): δ 6.93 (s, 8H), 6.81 (s, 4H), 6.59 (s, 4H), 4.19 (s, 8H), 4.12 (s, 8H), 3.85 (s, 12H).

2.2 Synthesis of M:^[2] CMDM and sodium hydroxide were dissolved in ultrapure water.

After stirring for 20 min, M (1.3 g, 99%) was obtained as white solid by removing water under reduced pressure. ¹H NMR (400 MHz, D₂O, 298K) δ 7.16 (s, 4H), 6.87 – 6.56 (m, 6H), 4.32 (s, 4H), 4.27 (s, 4H), 3.90 (s, 4H).

2.3 Synthesis of WLT6-AgNPs: AgNO₃ (0.01 M, 207 μ L) was added to deionised water (10 mL), followed by the addition of WLT6 solution (0.01 M, 15 μ L) under continuous stirring. Then NaBH₄ (0.1 M, 0.01 mL) was added into the mixture solution. The reaction was further allowed for 0.5 h, and the WLT6-AgNPs colloidal solution colour turned yellow gradually. The obtained WLT6-AgNPs were centrifuged to remove the excessive WLT6.

2.4 Synthesis of M-AgNPs: AgNO₃ (0.01 M, 207 μ L) was added to deionised water (10 mL), followed by the addition of M solution (0.01 M, 30 μ L) under continuous stirring. The NaBH₄ (0.1 M, 0.01 mL) was added to the mixture solution. The reaction was further allowed for 0.5 h, and the M-AgNPs colloidal solution colour turned brownish yellow gradually. The obtained M-AgNPs were centrifuged to remove the excessive M.

3. Catalysis method

3.1 Catalytic Reduction of Nitrophenol Isomers by WLT6-AgNPs or M-AgNPs

Nitrophenol (110 μ L, 3.0 mM) and deionised water (2974 μ L) were added to a standard quartz cuvette with a 1 cm path length. When freshly prepared NaBH₄ (150 μ L, 0.1 M) was added, the colour of the mixture changed from light yellow to yellow-green immediately as a consequence of the formation of nitrophenolate ion. WLT6-AgNPs (66 μ L) and M-AgNPs (100 μ L) was added into the mixture, respectively, and the UV-

vis absorption spectra were recorded in the range of 200-700 nm at various time intervals (2 min, 2 min, and 1.5 min for p-, m-, and o-nitrophenol, respectively).

3.2 The Stability of WLT6-AgNPs for Repeated Catalytic Cycles

Nitrophenol (110 μ L, 3.0 mM) and fresh NaBH₄ (25 μ L, 0.01 M) were added into the above mixture. The timer was restarted at once, and the UV-vis absorption spectra were recorded in the same range at various time intervals. The procedure was repeated four times.

4. Detection method

4.1 Sensitive Detection of Cys by WLT6-AgNPs

Cys solution (200 μ L) was added to 1.8 mL WLT6-AgNPs colloid solution, thereby the mixture solutions with different concentrations of Cys (0, 0.1, 0.5, 1, 2, 4, 5, 6, 8, 10, 12, 14, 16, 1000 μ M) were obtained. The colour change was observed after standing for 30 min. The Cys-induced aggregation of WLT6-AgNPs was monitored by UV-vis spectroscopy during the addition of Cys to WLT6-AgNPs.

4.2 Sensitive Detection of Cys by M-AgNPs

Cys solution (200 μ L) was added to 1.8 mL of the M-AgNPs colloid solution leading to mixture solutions with different concentrations of Cys (0, 1, 2, 4, 5, 6, 8, 10, 20 μ M). The UV-vis absorption spectra of M-AgNPs containing different concentrations of Cys was monitored. The Cys-induced aggregation of M-AgNPs was monitored by UV-vis spectroscopy during the addition of Cys to M-AgNPs.

4.3 Selective Detection of Cys by WLT6-AgNPs

For comparison, 200 µL of different amino solutions (Gly, Val, Leu, Ile, Pro, Phe, Tyr,

Trp, Ser, Thr, Met, Asn, Gln, Asp, Glu, Lys, Arg, His) were added to the 1.8 mL of WLT6-AgNPs colloid solution, and the UV-vis spectrums were recorded after standing for 30min. To study whether other amino acids interfere with Cys detection, six amino acids (200 μ L, 10 mM) were added into 1.8 mL of WLT6-AgNPs solution, respectively, and the UV-vis spectrums were recorded, followed by adding Cys (100 μ L, 10 mM) into the mixture and the UV-vis spectrums were recorded.



5. Characterization of M-AgNPs

Fig. S1 (a) UV-vis absorption spectrum of M-AgNPs. (b) Transmission electron microscopy (TEM) image of M-AgNPs.

6. Zeta-potential values of WLT6-AgNPs and M-AgNPs, and the



stability of WLT6-AgNPs

Fig. S2 (a) Zeta-potential values of WLT6-AgNPs and M-AgNPs. (b) Time-dependent UV-vis absorption spectrum changes of WLT6-AgNPs.

7. Catalytic reduction of *o*-nitrophenols and *m*-nitrophenol by



WLT6-AgNPs

Fig. S3 Catalysis of nitrophenol by WLT6-AgNPs with NaBH₄: time-dependent UV-vis absorption spectrum changes for (a) *o*-nitrophenol and (c) *m*-nitrophenol. The $ln(A_t/A_0)$ versus time for the catalytic reduction of (b) *o*-nitrophenol and (d) *m*-nitrophenol.

8. Catalytic reduction of nitrophenols with different steric hindrance by M-AgNPs



Fig. S4 Catalysis of nitrophenol by M-AgNPs with NaBH₄: Time-dependent UV-vis absorption spectrum changes for (a) *p*-nitrophenol, (c) *o*-nitrophenol and (e) *m*-nitrophenol. The $\ln(A_t/A_0)$ versus time for the catalytic reduction of (b) *p*-nitrophenol, (d) *o*-nitrophenol and (f) *m*-nitrophenol.

9. Catalytic reduction of nitrophenols with different steric hindrance by WLT6-AgNPs



Fig. S5 Catalytic reduction of nitrophenols with different steric hindrances by WLT6-AgNPs.

Catalyst	C _p -nitrophenol (mM)	k _{app} (min ⁻¹)	K (mg min ⁻¹)	Ref.
AWLT6-AuNPs	0.1	0.156	-	[S1]
AgNPs@SCOF	0.107	1.06	0.0424	[S3]
Ag ⁰ @CMP	10	0.0815	0.011	[S4]
Fe ₃ O ₄ @PPy-MAA/Ag	40	0.17	-	[S5]
AgNPs/RGO-LS	0.05	1.893	0.0249	[S6]
GO-EDA-AgNPs	0.1	0.02	0.02	[S7]
Pd-GA/RGO	5	0.12	-	[S8]
Pt1Au1-PDA/RGO	0.1	0.34	5.6	[S9]
Ag@CNC	0.4	0.24	0.004	[S10]
Pd@CHI	0.15	0.139	-	[S11]
WLT6-AgNPs	0.1	0.28	28	This work
M-AgNPs	0.1	0.02	-	This work

Table S1. Comparison of catalytic efficiencies of various Ag catalysts and other noble metal catalysts for *p*-nitrophenol reduction

10. The host-guest interaction between macrocyclic WLT6 and Cys





Fig. S6 ¹H NMR spectra (400 MHz, 298 K, D₂O) of (a) WLT6, (b) WLT6 + Cys (1:1 molar ratio) and (c) Cys at 5.0 mM at pD 7.8.



Fig. S7 ¹H NMR spectra (400 MHz, 298 K, D₂O) of (a) WLT6, (b) WLT6 + Gly (1:1 molar ratio), and (c) Gly at 5.0 mM at pD 7.8.



11. Hydrodynamic diameters distribution of WLT6-AgNPs and WLT6-AgNPs-Cys

Fig. S8 The hydrodynamic diameter distribution of WLT6-AgNPs and WLT6-AgNPs-Cys.

Sensors	LOD	Ref.
	(µM)	
AgNPs-HAP	2.03	[S12]
GSH-Ag NCs	0.51	[S13]
Dex/AgNPs	12	[S14]
citrate-capped AgNPs	1.5	[S15]
water-dispersible DIC-decorated AuNPs	2.2	[S16]
DPC-AgNPs	0.25	[S17]
β -cyclodextrin-AgNPs	0.0046	[S18]
WLT6-AgNPs	0.493	This work

Table S2. Comparison of the lowest limit of detection (LOD) of various Ag/Au basednano-sensors for L-cysteine

12. NMR Spectra



Fig. S9 ¹H NMR spectrum (400 MHz, 298 K, D₂O) of WLT6.



Fig. S10 1 H NMR spectrum (400 MHz, 298 K, D₂O) of M.

13. References

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