Electronic Supplementary Information

Three Dimensional Nano-assemblies of Noble Metal Nanoparticles-Infinite Coordination Polymers as a Specific Oxidase Mimetic for Degradation of Methylene Blue without Adding Cosubstrate

Lihua Wang, Yi Zeng, Aiguo Shen,* Xiaodong Zhou, and Jiming Hu*

Key Laboratory of Analytical Chemistry for Biology and Medicine, Ministry of Education, College of Chemistry and Molecular Sciences, Wuhan University, 430072 Wuhan (P. R. China)

Experimental Section

Chemicals

Tetrachloroauric (III) acid and sodium citrate were purchased from Sigma (USA). Silver nitrate was obtained from Beijing Chemical Reagents Company (Beijing, China). Ascorbic acid was supplied by Sinopbarm Chemical Reagent Co., Ltd. 2,5dimercapto-1,3,4-thiadiazole (DMcT, ≥98%) was a product of Alfa Aesar. 3,5,3',5'tetramethylbenzidine (TMB) was obtained from Shanghai Kayon Biological CO., Methylene Technology D. blue (MB)was purchased from Sinopharm Chemical Reagent Co. Ltd. All other chemicals were of analytical grade or better quality, and used as received. Ultrapure water was obtained using a Milli-Q ultrapure (resistance > 18.2 M Ω cm) system.

Characterization

UV-*vis* studies were performed on a UV spectrometer (Shimadzu, UV-2550). Highresolution transmission electron microscopy (HRTEM) for a single 3D nanoassemblies NP and other TEM images were performed on a JEOL JEM-2100 microscope. The surface composition of 3D nano-assemblies were examined by X-ray photo electron spectroscopy (XPS) using a Model KRATOSXSAM-800 apparatus with Mg K_{α} X-ray source (1253.6 eV, 17 mA × 11.5 kV) and operated at a pressure better than 7 × 10⁻⁷ Pa. A CHI 660A electrochemical workstation (CHI Instrument Inc., USA) was used for the electrochemical experiments. A three-electrode system was employed, including glassy carbon electrodes (GCE, 3.0 mm in diameter), a carbon rod and a saturated calomel electrode (SCE), which served as the work electrode, the counter electrode and the reference electrode, respectively.

Preparation of hollow Au@Ag@infinite coordination polymers

core-shell nanoparticles (Au@Ag@void@ICPs NPs)

Au@Ag@void@ICPs NPs were prepared according to our previous report.¹ Typically, 200 μ L freshly prepared 0.5 mg mL⁻¹ DMcT aqueous solution (ultrasonically dispersed in phosphate buffer (PB) suspension (0.1 M, pH 7.4)) were added to the colloid solution of Au@Ag NPs (10 mL) with slow stirring, and the suspensions were then allowed to incubate for about three hours at room temperature. Finally, the obtained NPs were rinsed by centrifugation and resuspension with deionized water for three times.

Synthesis of three-dimensional nano-assemblies (3D nano-

assemblies)

In a typical synthesis, 20 μ L HAuCl₄ (1%, w/w) were introduced into 2 mL Au@Ag@void@ICPs NPs solution under vigorous stirring at room temperature for 15 min. Then, the mixture was stood for about 2 hours to make HAuCl₄ in the reaction system almost consumed.

Synthesis of Au NPs-ICPs Composites

In a typical synthesis, 2 mL AgNO₃ (1.69 mg/mL) solution were introduced into 1 mL freshly prepared 0.5 mg mL⁻¹ DMcT aqueous solution under vigorous stirring at room temperature for about 1 hour. Then, the obtained Ag-DMcT ICPs were rinsed by centrifugation and resuspension with deionized water for three times. Next, 20 μ L HAuCl₄ (1%, w/w) and 50 μ L 0.1 M H₂O₂ were sequentially introduced into 2 mL Ag-DMcT ICPs solution under vigorous stirring at room temperature for 30 min. Finally, the products (Au NPs-ICPs) were rinsed by centrifugation and resuspension with deionized water for three times.

Kinetic analysis

Kinetic measurements were carried out in time-drive mode by monitoring the absorbance change at 652 nm on a UV-*vis* spectrophotometer. Experiments were carried out using 20 μ L 3D nano-assemblies NPs as prepared in a reaction volume of 430 μ L BR buffer solution (pH 4.0) with 50 μ L 5.0 mM TMB as substrate, unless otherwise stated. The Michaelis-Menten constant was calculated using Lineweaver-Burk plots of the double reciprocal of the Michaelis-Menten equation, $1/v = (K_m/V_{max}) \cdot (1/[S] + 1/K_m)$.

Catalytic oxidation of MB

In a typical reaction, 500 μ L 3D nano-assemblies NPs solution was added to 50 μ L MB aqueous solution (50 mg/L). The mixture was then heated to 80 °C. At various time intervals, parts of the mixture was taken and separated quickly by centrifugation. Finally, the supernatants were analyzed with a UV-*vis* spectrophotometer to evaluate the catalytic degradation of MB.



Fig. S1 Extinction spectra of 30 nm Au NPs (a), Au@Ag NPs (b), Au@Ag@void@ICPs (c) and 3D nano-assemblies (d).



Fig. S2 The statistical distribution of small gold NPs sizes in the 3D nano-assemblies.



Fig. S3 XPS spectra of the as freshly synthesized 3D nano-assemblies: (A) survey spectrum and (B) high resolution of O spectrum.

Table S1. Element concentration of the 3D nano-assemblies by XPS analysis.

Element	Au	Ag	С	S	Ν	Cl	0
Concentration (%)	17.15	10.1	32.08	13.8	14	6.59	6.27



Fig. S4 Influence of the composition of Au@Ag NPs changed with different volume of AgNO₃: (A) 50, (B) 100, (C) 300 and (D) 500 μ L on the nanostructures of 3D nano-assemblies.



Fig. S5 Influence of the volume of HAuCl₄ (1%): (A) 5, (B) 10, and (C) 20 μ L on the nanostructures of 3D nano-assemblies.



Fig. S6 SEM images of (A) Ag-DMcT ICPs and (B) Au-ICPs composite.



Fig. S7 UV-*vis* spectra of the reaction solution containing TMB in the presence of the Au-ICPs hybrid materials.



Fig. S8 The influence of H_2O_2 on the catalytic oxidation of TMB by 3D nanoassemblies: (A) in the absence of H_2O_2 and (B) in the presence of H_2O_2 .



Fig. S9 The absorbance evolution at 652 nm of TMB catalyzed by 3D nano-assemblies over time at different pH values.



Fig. S10 Photographic image of vials containing TMB in BR buffer (pH 8.0) showing absence of any color change upon addition of 3D nano-assemblies.



Fig. S11 Effect of dissolved oxygen (red line) on TMB oxidation at pH 4.0. The reaction rate after bubbling with high purity nitrogen for 30 minutes hardly reduced (black line).



Fig. S12 Cyclic voltammograms of bare GCE in a 5 mL BR buffer (pH 4.0) without (black line) and with (red line) 200 μ L 5 mM TMB solution; the 3D nano-assemblies-modified GCE in a 5 mL BR buffer (pH 4.0) with 200 μ L (blue line) and 600 μ L (purple line) 5 mM TMB.



Fig. S13 Steady state kinetic assays at different pH values. Double reciprocal plots of oxidase activity of 3D nano-assemblies, while keeping constant the concentration of 3D nano-assemblies. TMB was used as substrate.

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pН	$K_{\rm m}$ (μ M)	V _{max} (10 ⁻⁸ M s ⁻¹)
4.0	4.31	12.7
5.0	6.75	9.7
6.0	13.0	8.8
7.0	35.5	8.1

Table S2. 3D nano-assemblies' oxidase-like kinetic parameters at different pH values. $K_{\rm m}$ is the michaelisconstant; $V_{\rm max}$ is the maximal reaction rate.

	$K_{\rm m}({\rm mM})$	V _{max} (10 ⁻⁸ M s ⁻¹)
3D nano-assemblies NPs	4.31×10^{-3}	12.7
HRP ²	0.434	10.0
Fe ₃ O ₄ MNPs ²	0.098	3.44
CeO ₂ ³	3.8	70.0

Table S3. Comparison of the kinetic parameters for different nanomaterials.



Fig. S14 Time-dependent UV-*vis* spectra of MB solution catalyzed by (A) pure Au NPs, (B) Au@Ag NPs, (C) Au@Ag@void@ICPs NPs, or (D) no adding any catalysts.



Fig. S15 Time-dependent UV-vis spectra of MB solution catalyzed by 3D nano-assemblies at room temperature.



Fig. S16 The absorption spectra of TMB oxidation with 3D nano-assemblies as the catalyst at different temperature: room temperature (black line) and 80 °C (red line).

References

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