

Supplementary Information

A Ternary Hybrid Nanoreactor with Thermoswitchable Catalytic Performance

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Abbreviations

LCST: Lower critical solubility temperature

ARGET ATRP: Electron transfer activation and regeneration of atom transfer radical polymerization

NPs: Nanoparticles

MSNP: Mesoporous silica nanoparticle

PNIPAm: Poly(N-isopropyl acrylamide)

MB: Methylene blue

TEOS: Tetraethylorthosilicate

CTAB: Etyltrimethylammonium bromide

APTES: 3-aminopropyl triethoxysilane

VC: ascorbic acid

XRD: X-ray diffraction

TEM: Transmission electron microscopy

FT-IR: Fourier Transform Infrared spectroscopy

Materials

Tetraethylorthosilicate (TEOS, 98%), etyltrimethylammonium bromide (CTAB, 95%), sodium hydroxide (NaOH), silver nitrate (AgNO_3), toluene (analytically purity), 3-aminopropyl triethoxysilane (APTES, 99.0%), Triethylamine, 2-bromoisobutyryl bromide (98%), N,N-dimethylformamide (DMF), N-methylpyrrolidone (NMP, analytically purity), Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, >99%), triphenylphosphine (PPh_3 , >99%), N-isopropyl acrylamide (NIPAM, analytically purity), ascorbic acid (VC, >99.7%), Methylene blue (MB, >99%). Unless otherwise noted, chemicals were obtained from Sinopharm Chemical Reagent Co. Ltd. (China) and used as received without further purification.

As shown in Scheme 1, this hybrid nanoreactor was prepared as follows:

Synthesis of silver NPs contained MSNP (Ag@MSNP)

First, for the synthesis of unmodified MSNP, 100 mg CTAB was dissolved in 50 mL water. After adding 0.35 mL sodium hydroxide aqueous solution (2 M), the mixture was heated to 72 °C. 0.5 mL TEOS was added dropwisely to the aqueous

solution, and the mixture was vigorously stirred for 2 h. Then 50 mL of 0.05 M silver nitrate solution was added dropwisely in the dark. The solution was continuous stirred for 12 h. The solid was filtered and washed several times with distilled water and ethanol. After dried at 60 °C for 12 h, the resulting powders were calcined at about 550 °C for 6 h under N₂ gas to obtain Ag@MSNP.

Synthesis of amino-functional Ag@MSNP.

Typically, 1 g Ag@MSNP, 30 mL distilled toluene, and 2.5mL of APTES (0.011mol) were added in a 100 ml flask with fully dispersing. After evacuating air with N₂ for 20 min, the flask was immersed in an oil bath at 95 °C. The mixture was stirred for 16 h, then cooled and exposed to air. The solid was filtered and washed with DMF three times. Finally, the product was dried at 60°C for 12 h to gain amino-functional Ag@MSNP.

Synthesis of ATRP Initiator-Immobilized Ag@MSNP

Typically, 1 g of amino-functionalized Ag@MSNP, 30 mL of toluene, and 2 mL triethylamine (0.014mol) were added in a dried 100mL flask immersed in an ice water bath. The solution was stirred and the mixture of 1.5 mL of 2-bromoisobutyryl bromide (0.012mol) and 10 mL toluene was dripped slowly into the solution. After evacuating air with N₂ for 20 min, the solution was stirred for 16 h. After filtered, the solid powders was washed with DMF three times and dried at 60°C for 12 h to get ATRP Initiator-Immobilized Ag@MSNP.

Synthesis of Ag@MSNP with PINPAm grafted on the surface (Ag@MSNP-PNIPAm) through an AGET ATRP polymerization

A typically polymerization procedure was as follows: 0.0108 g of FeCl₃•6H₂O, 0.104 g of PPh₃, 0.08 g of ATRP Initiator-Immobilized Ag@MSNP, 0.3 g of NIPAM and 5 mL NMP were added to a dried ampoule to get a well-dispersed solution under stirring. After treated in ultrasonic for 5 min, 0.09 g VC was quickly added into the solution, and the ampoule was flame sealed and immersed in a thermostatic water bath at 65 °C for 24 h to polymerize. Then the ampoule was exposed to air and gradually cooled. The solid was filtered and washed with distilled water to obtain the final product, namely Ag@MSNP-PNIPAm. For a comparative

study, three controls named "MSNP", "Ag@MSNP" and "MSNP-PNIPAm" were also prepared under comparable conditions. MSNP was the pure mesoporous silica nanoparticles, no silver NPs contained and no PNIPAm grafted on surface. Ag@MSNP and MSNP-PNIPAm were prepared in a similar condition with that of Ag@MSNP-PNIPAm, except for no PNIPAm chains grafted or no Ag NPs contained, respectively.

Measurements

FT-IR spectra were recorded using a Thermo Nicolet (Madison, WI, USA) Nexus 470 FT-IR spectrometer, using KBr as the sample holder.

XRD data was measured on a Philips 1730 powder X-ray diffractometer.

TEM experiments were carried out on a JEM-2100 transmission electron microscope. Elemental mapping images were obtained on an American FEI Tecnai G2 transmission electron microscopy (operated at 300 kV).

Nitrogen adsorption-desorption isotherms were measured on a micromeritics instrument (ASAP2020).

The electrochemical tests were employed on a CHI 760E electrochemical workstation equipped with a three-electrode configuration (Au-plate working electrode, Pt-wire counter electrode and Ag/AgCl ref. electrode). Nanoreactors (10 mg) that pre-absorbed with 1mmol MB were placed into a cuvette encircled by a diffusion-eliminated sonication apparatus (supporting electrolyte: 0.01 M KCl; 5 mL). The substrate transiently desorbed was cyclic-voltammetrically scanned by the workstation until a stable desorption/reduction profile was achieved (scanning range, +0.6 to - 0.4 V; scanning rate, 1 mV s⁻¹).

The catalytic property of the prepared smart catalyst was evaluated using the model reaction of methylene blue (MB) with NaBH₄ catalyzed by silver NPs. 10 mg catalysts, 45 mL MB aqueous solution (20 mg/L) and 10 mg NaBH₄ were mixed to fulfil the reaction at a given temperature. The reduction of MB was monitored by a UV-2550 spectrophotometer at 664 nm.

To determine the ability to repeat the switchable catalytic activity of Ag@MSNP-PNIPAm, 10 mg Ag@MSNP-PNIPAm, 45 mL MB aqueous solution

(20 mg/L) and 10 mg NaBH₄ were mixed to carried out the catalytic reaction at 25°C. After 10 min, Ag@MSNP-PNIPAm was separated from the mixture by centrifugation and the conversion of MB was determined by a UV-2550 spectrophotometer. Then, the Ag@MSNP-PNIPAm separated from the last experiment, 45 mL MB aqueous solution (20 mg/L) and 10 mg NaBH₄ were mixed again to react at 45°C, instead of 25°C. After 10 min, Ag@MSNP-PNIPAm was separated once again from the mixture and the conversion of MB was determined. After that, the Ag@MSNP-PNIPAm separated from the last experiment was used to carry out the next reaction again at 25°C, and so on.

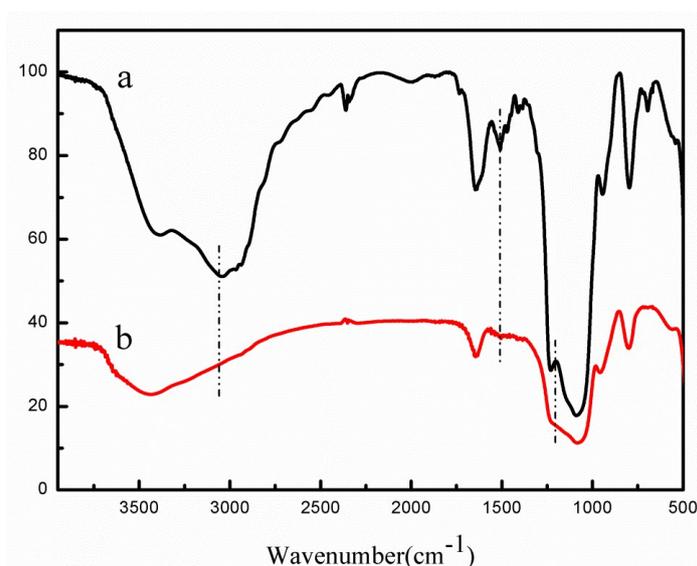


Fig. S1 FT-IR spectra of Ag@MSNP-PNIPAm (a), and MSNP (b)

Table S1 BET pore volume and pore size of MSNP and Ag@MSNP-PNIPAm

| Specimens | V _{Total} (cm ³ /g) ^a | D(nm) ^b |
|--------------------|--|--------------------|
| MSNP | 0.87 | 12.29 |
| Ag@MSNP- PNIPAm | 0.77 | 9.72 |

^a V_{Total}: total pore volume is estimated at a relative pressure P/P₀=0.99.

^c D: adsorption average pore width determined from BET method.

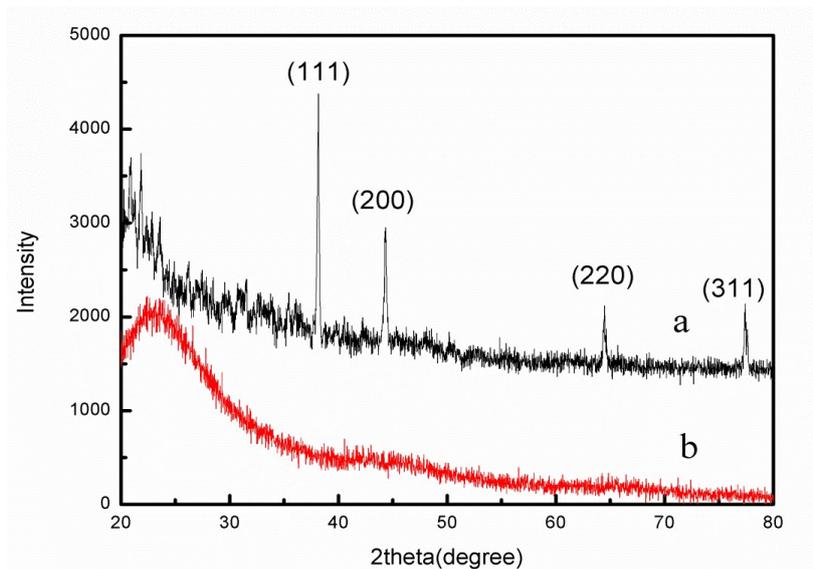


Fig. S2 XRD patterns of Ag@MSN-PNIPAm (a), and MSNP (b)

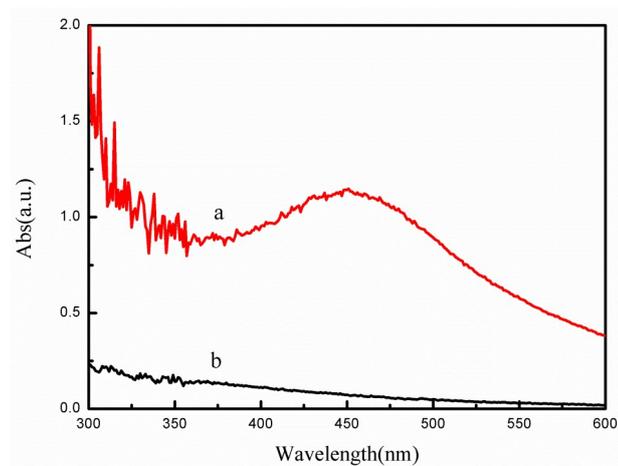


Fig. S3 UV-Vis absorption spectra of Ag@MSN-PNIPAm (a) and MSNP (b)

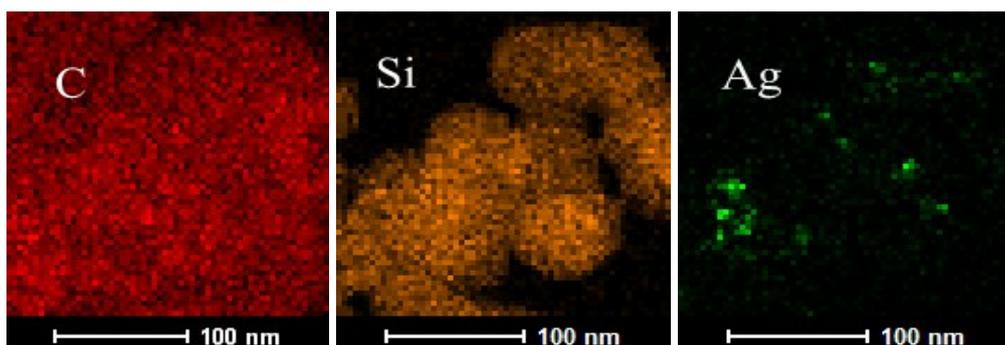


Fig. S4 Elemental mapping images of Ag@MSN-PNIPAm

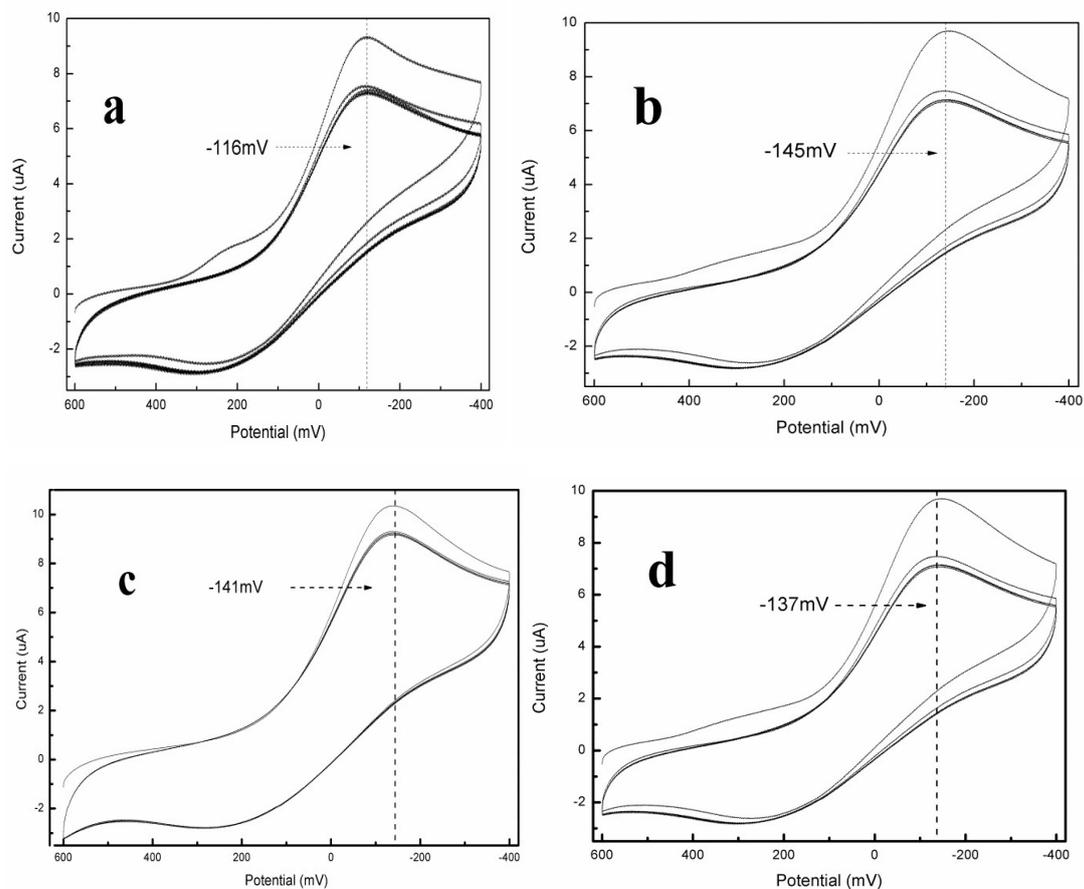


Fig. S5 DCV profiles with MB desorbing from control nanoreactors at different temperatures. a: MSNP-PNIPAm at 25°C; b: MSNP-PNIPAm at 45°C; c: MSNP at 25°C; d: MSNP at 45°C