Electronic Supplementary Information

A self-switchable Ag nanoreactor exhibiting outstanding catalytic properties

Shunsheng Cao, a,b* Juanrong Chen, b Yi Ge, b Long Fang, a Ying Zhang, a Anthony P. F. Turner c*

a School of Materials Science and Engineering, Jiangsu University, Xuefu Road 301, Zhenjiang, 212013, P. R. China.

b Cranfield Health, Vincent Building, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK, E-mail:

c Biosensors & Bioelectronics Centre, IFM, Linköping University, SE-58183, Linköping, Sweden.

Corresponding to: E-mail address: sscaochem@hotmail.com; Anthony.turner@liu.se
Materials

Unless otherwise noted, chemicals were obtained from Aldrich (Sigma-Aldrich Company Ltd, Dorset, UK) and Fisher (Fisher Scientific UK Ltd, Loughborough, UK) and used as received without further purification. Styrene, K$_2$S$_2$O$_8$, absolute ethanol, and aqueous ammonia (28 wt.%) are the products of the Sinopharm Chemical Reagent Co., LtdS (China) and were used as received except styrene (St), which was purified with 5 wt.% NaOH solution prior to use. Tetraethyl orthosilicate (TEOS) was obtained from Nanjing Yudeheng Silane coupling agent Co., Ltd (China) and used as received. Water for the reaction and analysis was collected from the Direct-Q UV System (Millipore).

Abbreviations

NIPA: N-isopropyl-acrylamide

AMPS: 2-acrylamide-2-methylpropane sulfonic acid

MBA: N,N'-methylenebisacrylamide

4-NP: 4-nitrophenol

TEM: transmission electron microscopy

SEM: scanning electron microscopy

STEM: scanning transmission electron microscopy

BET: Brunauer-Emmett-Teller

ICP-AES: inductively coupled plasma atomic emission spectroscopy

DLS: dynamic light scattering

CPS: cationic polystyrene spheres

HS: hollow silica particles

Ag-HS: Ag loaded hollow silica nanoreactor

Ag-N: Ag-hollow silica-PNIPA nanoreactor

Ag-N-A: Ag-hollow silica-PNIPA/PAMPS nanoreactor
LCST: lowest critical solution temperature: 32°C

**Cationic polystyrene templates**

The monodisperse cationic polystyrene (CPS) beads were prepared via emulsifier-free polymerization as follows: All of the initiators including K$_2$S$_2$O$_8$, H$_2$O, and styrene were placed into a 100 mL four-necked flask equipped with a mechanical stirrer, an N$_2$ inlet, a Graham condenser, and a heating mantle. After flushing the system with nitrogen gas for 20 min, the polymerization was conducted at 70°C for 4 h with a stirring rate of 400 rpm, followed by the continuous addition of DMC (2-(methacryloyloxy) ethyltrimethylammoniumchloride) according to our previous works. The resulting solid was filtered and washed repeatedly with warm deionised water.

![Fig S1. TEM image of cationic polystyrene particles](image)

**Synthesis of functional hollow silica microspheres (HS)**

The hollow silica microspheres were prepared using allyltrimethoxysilane (ATS) as functional monomer. In the first step, the cationic polystyrene particles (CPS), as the template, were suspended into ethanol medium, and then, tetraethyl orthosilicate (TEOS) and ammonia were added quickly and the mixture was reacted at 50°C for around 6 h with constant stirring in the presence of ATS, generating the core/shell type of CPS/SiO$_2$ particles. A small amount of CH$_2$Cl$_2$ was added into this reactive medium for 12 h. Finally, the spheres obtained were separated from the reaction medium using a millipore filter and washed several times with the mixture of ethanol and CH$_2$Cl$_2$ according to our previous work. 

---

1. [Link to reference 1]
2. [Link to reference 2]
3. [Link to reference 3]
Silver treatment of HS spheres

The synthesized hollow silica spheres (0.2 g) were added to 40 mL of aqueous solution of silver nitrate (0.8 g) and ammonium hydroxide (0.01 wt%), and the mixture was stirred for 6 h. The silver-coated hollow silica nanocomposite was collected and washed with deionised water.
Fig. S3A. TEM and SEM images of Ag nanoparticles loaded onto hollow silica spheres

Fig. S3B. Particle distribution of Ag nanoparticles loaded onto hollow silica spheres

Fig S3C. STEM image (a) and corresponding EDX mapping (b) of Ag nanoparticles loaded onto hollow silica spheres

Preparation of Ag-N-A Nanoreactor

After silver treatment of HS spheres, N-isopropylacrylamide (NIPA: 0.6g) was polymerized in the presence of N,N’-methylenebis-acrylamide (MBA) (0.5 wt% of the weight of NIPA), a cross-linker, onto the surface of the Ag-HS particles. Subsequently, 2-acrylamide-2-methylpropanesulfonic acid (AMPS: 0.91g) swelled the particles and was polymerisation in the presence of MBA (0.5 wt% of the weight of AMPS) to form an interpenetrating polymer network (PNIPA/PAMPS). Finally, the synthesized hybrid spheres were reduced to Ag with an excess amount of
sodium borohydride at 40°C to produce on/off-switchable and positively thermo-sensitive nanoreactors (Ag-N-A).

Two comparative samples, as above-mentioned, namely Ag-HS and Ag-N, were also prepared under comparable conditions. During the preparation of Ag-N, AMPS was replaced with the same amount (in moles) of NIPA. Ag-HS and Ag-N to have the same hollow structure as Ag-N-A, but no PNIPA/PAMPS and PAMPS were included in their shell networks, respectively.

Fig. S4A. TEM images (a, b), DLS curve (c) and BET isotherms (d) of the on/off switchable Ag-N-A nanoreactor
Characterization

The internal and external morphology of the hollow silica spheres, Ag-HS, Ag-N and Ag-N-A nanoreactors were characterized using transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy dispersive X-ray analysis (EDX) mapping, scanning electron microscopy (SEM), and BET (Brunauer-Emmett-Teller). The content of Ag loaded in hollow silica spheres was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The particle size distributions of the hollow silica spheres and Ag-N-A were determined by means of dynamic light scattering (DLS) performed at 25°C at a scattering angle of 90° using a goniometer equipped with a self-rotation unit and a He-Ne laser (Mastersizer-X) (Malvern, UK).
Catalysis measurement

In triplicate, 4-nitrophenol (4 mg/ml) was added into an excess amount of NaBH4 contained in a glass vessel. A given amount of the composite particles (about 0.1 mg mL⁻¹) was then added, after which the UV-vis spectra of the samples were immediately taken every 20 minutes in the range of 300-550 nm. The conversion of substrate was determined by measuring the change in intensity of the peak at 400 nm, which is attributed to the 4-nitrophenate ions. The reported values were the mean of three measurements.

Fig. S5A. Catalytic activity of the Ag-HS nanoreactors for the reduction of 4-nitrophenol
Fig. S5b. Catalytic activities of the prepared Ag-N-A nanoreactors with the different initial loading content of AgNO₃, a) 0.2g; b) 0.4g; c) 0.8g and d) 1.0g.

Fig. S5c. Role of MBA on the on/off switchable Ag-N-A nanoreactor.
Fig. S5D. TEM image of Ag nanoparticles loaded onto hollow silica spheres

Reference


7. Z. Chen, Z. Cui, C. Cao, W. He, L. Jiang, W. Song. Langmuir 2012, 28, 13452