

Supporting Information

Fabrication of Continuous Highly-ordered Mesoporous Silica

Nanofibre with Core/Sheath Structure and Its Application as Catalyst

Carrier

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Experimental

Preparation of the mesoporous silica nanofibre via coaxial electrospinning.

Mesoporous silica nanofibres with core/sheath structure were prepared by applying the coaxial electrospinning device. Tetraethoxysilican (TEOS) (Aldrich) and Pluronic F-127 (sigma) were used as silica source and structure-directing agent respectively. The preparation was completed as follows: 0.5 g of Pluronic F-127 was dissolved in 1.0 g of ethanol followed by adding 0.26 g of 0.6 M nitric acid into the mixture, then 1.5 g of TEOS was added to the mixture with stirring, resulting in a clear solution. Keeping the solution stirred for 2 h at room temperature formed a sol, which was subsequently injected to the inner capillary of the mentioned coaxial electrospinning device. Driven by a syringe pump, another solution consisting of 0.63 g of PVP (Aldrich, Mw \approx 1,300,000) and 10 mL of ethanol was injected to the outer capillary. These two liquids were fed at rates of 0.3 mL/h, 1.0mL/h respectively. The spinneret that was made of

stainless steel, the inner capillary and the outer capillary were connected to a DC high-voltage supply. Usually, the output voltage was tuned in the range of 6.4 kV~8.5 kV to form steady electrospinning jets of starting materials. In the course of electrospinning, a piece of aluminum foil was well-grounded and placed 10 cm below the tip of the spinneret to collect the outcome nanofibres. After 10 min, the as-electrospun fibres were collected and then kept at 60 °C for 12 h to have the residual TEOS hydrolysis completely. Subsequently, the result nanofibre membrane was aged at 100 °C for 1 h to perfect liquid crystalline structure formed by the structure-directing agent. This proper aging process was essential to stabilize and to control the mesoporous structures before removal of the structure-directing agent. Thereafter, the nanofibre membrane was calcined at 550 °C for 6 h to remove the structure-directing agent and PVP completely. Then the high-quality ordered mesoporous silica nanofibre was obtained.

Preparation of mesoporous $\text{H}_2\text{N}(\text{CH}_2)_3\text{-SiO}_2$ nanofibre. 25.3 mg of mesoporous silica nanofibre was added into 5 mL of (3-Aminopropyl) trimethoxysilane (APTMS) solution (0.1 mol/L in acetonitrile) and functionalized with $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ groups.^[1] Followed by a centrifuging treatment to collect the solid product, the suspension was stirred for 12 hours at room temperature. After washed for several times and dried in *vacuum*, the mesoporous $\text{H}_2\text{N}(\text{CH}_2)_3\text{-SiO}_2$ nanofibre was obtained.

Preparation of catalysts (photosensitizers). The homogeneous catalysts **X1** was prepared according to the literature,^[2] the highly-ordered mesoporous—nanofibre-supported catalyst **X2** were prepared as follows: Dispersing 15 mg of

$\text{H}_2\text{N}(\text{CH}_2)_3\text{-SiO}_2$ nanofibre (or highly ordered mesoporous nanofibre) into 5 mL of $\text{Pt}(\text{L})\text{Cl}$ solution (7.0×10^{-5} mol/L in acetonitrile) and keeping the mixture stirred at room temperature for 3 hours, After separating by filtration and washing for ten times with acetonitrile, the pure supported catalyst was prepared. The loading amount of Pt (L) onto the mesoporous nanofibre was 5.6 mg/g obtained by calculating the decrease in UV-Vis absorption of $\text{Pt}(\text{L})\text{Cl}/\text{CH}_3\text{CN}$ at 440 nm (**Figure S2**).

Photosensitized oxidation. The sensitizers, 50 μL acetonitrile solution of **X1** (1.2×10^{-3} mol/L), and 5.8 mg of **X2** were respectively added to 5 mL of trans-stilbene solution (1.2×10^{-3} mol/L in acetonitrile, [cat]:[sub]=1:100), while 2 μL of n-tetradecane was also added as the internal standard for the following gas chromatography (GC). After bubbling with pure oxygen for 10 min, the suspension was irradiated by a 500 W high-voltage mercury lamp (applying a quartz jacket with water circulation to cool the lamp, a light filter to cut off light below 400 nm, and keeping oxygen bubbled in). In this study, the irradiation lasted for 1 hour and the reaction mixture was centrifuged under 15000 rpm for 3 min to separate the upper liquid for further GC examination. The GC results indicated that the conversion ratios of this reaction sensitized by the homogeneous catalyst **X1** and heterogeneous catalysts **X2** were 49.0%, and 80.3% respectively.

Recycling and Reuse of the supported catalyst X2. After the first run of photosensitized oxidation, the supported catalyst **X2** was separated from the reaction solution by filtration. Followed by washing with acetonitrile for 5 times, **X2** was reused

for the next run of photosensitized oxidation. The recycling and reuse of **X2** were repeated for 9 times.

Characterization

The prepared nanofibres were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and N₂ adsorption-desorption measurements. Transmission electron microscopy was conducted on a JEOL JEM-2100F microscope operating at an acceleration voltage of 120 kV. The scanning electron microscopy images were captured using a HITACHI S-4300 scanning electron microscopy operating at an acceleration voltage of 10kV. FT-IR spectra were recorded on a Varian 3100 spectrometer. XRD tests were carried out on Rigaku D/max-2000 wide angle goniometer (Cu-K α radiation, $\lambda = 0.15418$ nm). Surface areas were determined by analyzing the N₂ adsorption isotherm according to the BET method using QUADRASORB SI. Gas chromatography (GC) was recorded on Techcomp GC7890F.

The FT-IR spectra of the prepared mesoporous silica nanofibres (MSNF) (**a**), APTMS functionalized mesoporous silica nanofibres (**b**) and the Pt(II) complex anchored sample (**c**) were shown in **Figure S1**. The peaks at 1085 cm⁻¹, 810 cm⁻¹ and 461 cm⁻¹ were assigned to the symmetric stretching of Si-O-Si, asymmetric stretching of Si-O-Si, and bending of Si-O respectively. The peak at 960 cm⁻¹ was assigned to symmetric stretching of Si-OH. The peak at 960 cm⁻¹ decreased when MSNF was treated with APTMS (**a**) and Pt(II)L complex consequently to form **b** and **c** indicating Si-OH was reacted with APTMS, while peaks appeared at 1564 cm⁻¹ and 700 cm⁻¹ indicating the

existence of -NH_2 group ($\text{NH}_2 \delta$). The loading ratio of the Pt(II)L complex was relatively low, and the corresponding signals were hardly observed.

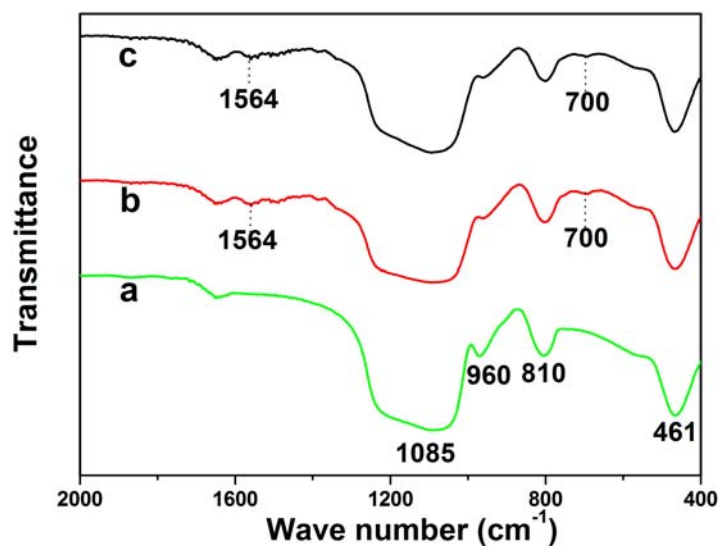


Figure S1. FTIR spectra of the mesostructured silica nanofibres (a), APTMS functionalized the mesostructured silica nanofibres (b) and Pt(II) complex anchored sample (c).

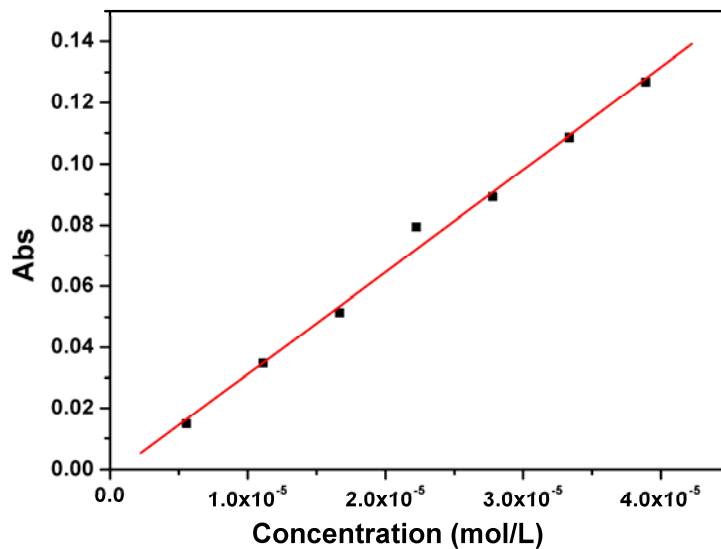


Figure S2. The UV-Vis absorption at 440 nm of the Pt(L)Cl complex in CH₃CN as a function of its concentration. The relative coefficient is 0.998.

- [1] C. J. Liu, S. G. Li, W. Q. Pang, C. M. Che, *Chem Commun* **1997**, 65-66.
- [2] S. W. Lai, M. C. W. Chan, T. C. Cheung, S. M. Peng, C. M. Che, *Inorg. Chem.* **1999**, *38*, 4046-4055.