

Electronic Supplementary Information

Enhanced Electrochemiluminescence Sensor from Tris (2, 2'-bipyridyl) ruthenium (II)

Incorporated into MCM-41 and Ionic Liquid Based Carbon Paste Electrode

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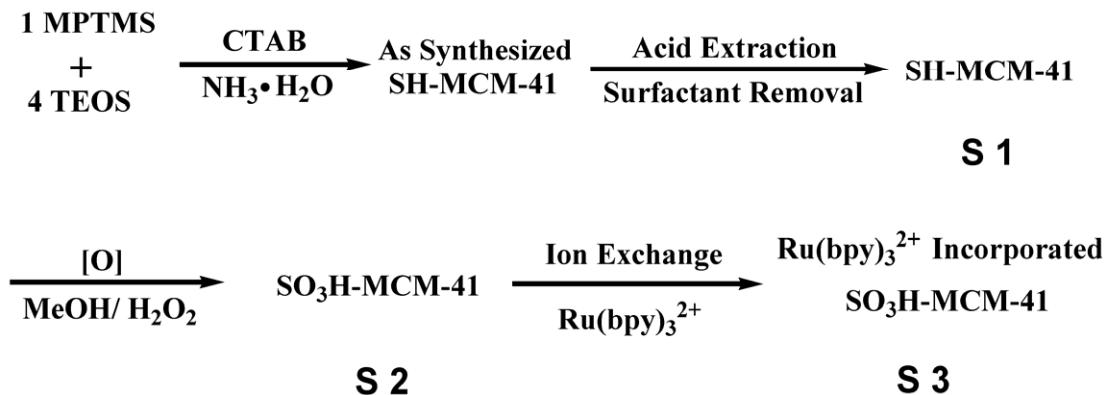
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Sample Synthesis.

The samples were prepared according to the synthetic routes given in Scheme S1.

Scheme S1



Preparation of SH-MCM-41 (S1). S1 were prepared according a previously published procedure.¹ Briefly, 2.4 g cetyltrimethylammonium bromide (CTAB) dispersed in a solution

containing 50 mL of deionized water, 45 mL of ethanol and 13 mL of 28% ammonia. Total 18.3 mmol of MPTMS and TEOS (in 5 mL of ethanol) with molar ratio of 1:4 was then added to the surfactant solution. When a white precipitate was observed, the solid products were filtered off, washed with ethanol, and dried under vacuum for 24 h. The acidic extraction technique was used to remove surfactant from the hybrid materials. After extracting surfactant, the solids were filtered again, washed, and dried as mentioned above.

Preparation of $\text{SO}_3\text{H-MCM-41}$ (S2). The S1 was oxidized using H_2O_2 in a methanol-water mixture according to a previously reported method.¹

Preparation of $\text{Ru}(\text{bpy})_3^{2+}$ Incorporated $\text{SO}_3\text{H-MCM-41}$ (S3). The S2 incorporated $\text{Ru}(\text{bpy})_3^{2+}$ were prepared by stirring a suspension of 232 mg S2 in 10 mL solution containing the $\text{Ru}(\text{bpy})_3^{2+}$ at a concentration of about 25 mM for 24 h. Then the solid particles were filtered, washed extensively with water, and dried in a vacuum for 24 h to produce S3.

Sample Characterization.

The formation of S1 and removal of surfactant was characterized by FTIR using a Perkin-Elmer model 580B IR spectrophotometer (USA) with the KBr pellet technique. In panels a and b of the Figure S1, the formation of the Si-O-Si framework was evidenced by the bands located at 1072 cm^{-1} (ν_{as} , Si-O), 796 cm^{-1} (ν_s , Si-O), and 461 cm^{-1} (δ , Si-O-Si). In addition, the surfactant-extracted MCM-41 only exhibited weak template (ν , C-H) vibrations at $2700\text{-}3000 \text{ cm}^{-1}$ and δ (C-H) vibrations at 1375 cm^{-1} disappeared, which confirmed that most of the surfactant had been removed.

The resulting samples were also characterized by Small-angle X-ray diffraction patterns (XRD) recorded with Rigaku-Dmax 2500 diffractometer (Japan) using Cu $\text{K}\alpha$ radiation (40 kV and 200

mA) at a step width of 0.02° . As illustrated in Figure S2, the XRD patterns were characterized by lower intensity of the d_{100} reflection due to relatively low degree of cross-linking of the silica network.

The N_2 adsorption/desorption isotherms of samples were obtained using a Nova 1000 analyzer (USA) with nitrogen. The samples were outgassed for 4 h at 120°C before the measurements. The textural data of the materials are given in Table 1. All these samples displayed type I isotherm curves² due to the large portion of MPTMS (Figure S3). From the Table 1, the Brunauer-Emmett-Teller (BET) surface area (S_{BET}), the pore volume (V) and the pore diameter (D) were all decreased after oxidation as expected due to the bigger size of SO_3H groups relative to SH moieties, which indicated the functional group was grafted into the inside of the pore and the pore size was ca 1.38 nm calculated by the Barrett-Joyner-Halenda (BJH) methods. To our knowledge, the diameter of the $\text{Ru}(\text{bpy})_3^{2+}$ ion is ca 1.3 nm,² therefore it can incorporate into the pore effectively. In addition, $\text{Ru}(\text{bpy})_3^{2+}$ cannot leach out from the silica matrix because of the strong electrostatic interaction between $\text{Ru}(\text{bpy})_3^{2+}$ and sulfonic acid groups.

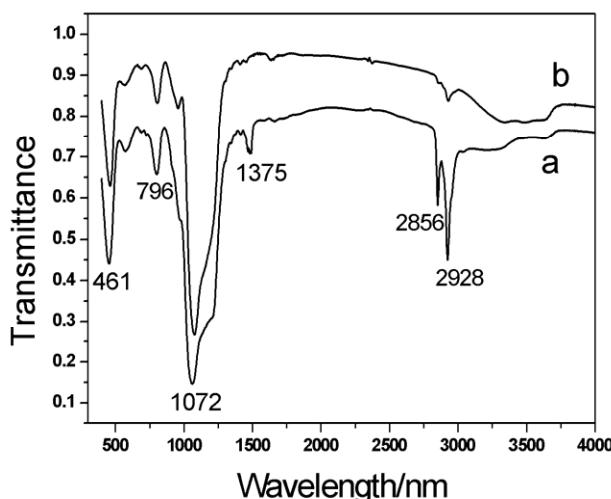


Figure S1. FTIR spectra of samples before (a) and (b) after extracting surfactant (S1).

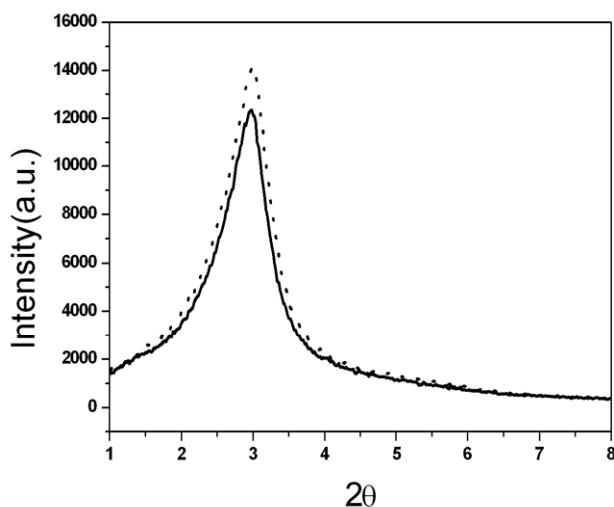


Figure S2. Powder X-ray diffraction patterns of S1 (dotted line) and sample S2 (solid line).

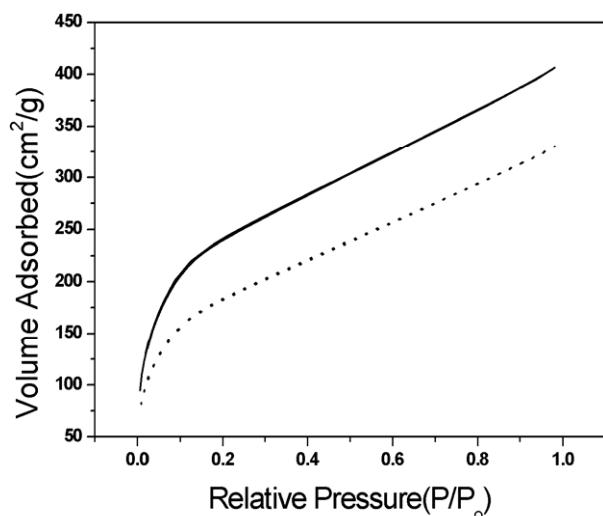


Figure S3. N_2 adsorption and desorption isotherms of S1 and S2 (dotted line).

Table 1. Textural data of the MCM-41

Sample	S_{BET} ^[a] (m^2/g)	V ^[b] (cm^3/g)	$D^{[c]}$ (nm)
S1	842	0.63	1.41
S2	645	0.51	1.38

[a] BET surface area (S_{BET})

[b] Pore Volume (V)

[c] Pore Diameter (D)

Reference

1 V.Ganesan and A.Walcarius, *Langmuir*, 2004, **20**, 3632.

2 T. Huang and R. W. Murray, *Langmuir*, 2002, **18**, 7077.