*Electronic Supplementary Information*

# A novel green process for the synthesis of glutaraldehyde by $WS_2$@HMS material with aqueous $H_2O_2$

**Quanjing Zhu, Xiaofeng Chu, Zhaoyan Zhang, Wei-Lin Dai,* and Kangnian Fan**

*Department of chemistry & Shanghai key laboratory of molecular catalysis and innovative material, Fudan University, Shanghai 200433, P. R. China.*

## 1. Materials.

Tetraethyl orthosilicate (TEOS), dodecylamine (DDA), ethanol, tungsten disulfide ($WS_2$), cyclopentene oxide (CPO), 76 wt.% aqueous $H_2O_2$, tributyl phosphate (TBP), and acetone were of analytical grade and were used as received.

## 2. Catalyst preparation.

### 2.1. HMS

Mesoporous siliceous HMS was prepared according to a well-established procedure delineated by Tanev and Pinnavaia[1] using TEOS as silica source and DDA as template agent. Typically, the HMS materials were prepared by dissolving 5.04 g of DDA in 53.33 g of deionized $H_2O$ and 39.42 g of ethanol under vigorous stirring before adding 21.39 g of TEOS dropwise. The solution mixture was then stirred at ambient temperature for 4 h. The resulting gel was aged for 18 h at ambient temperature to afford the crystalline templated product. After that, the resulting solid was recovered by

filtration, washed with deionized water, and dried at 393 K, followed by calcinations at 873 K for 5 h.

2.2. $WS_2$@HMS

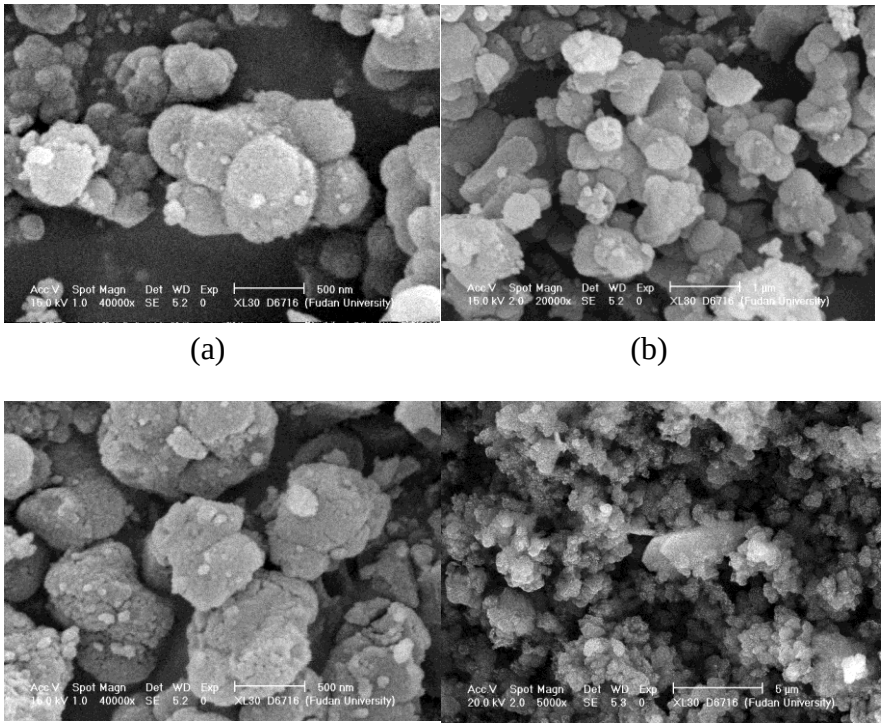
The $WS_2$/HMS catalysts with different $WS_2$ loadings were prepared by sonochemical method. In a typical procedure, firstly, the pre-specified amount of freshly calcined HMS were introduced into 100 mL of water and stirred for 20 min at room temperature and then the mixture was subjected to sonication until HMS was highly dispersed in the water. After that, the required amount of $WS_2$ was added into the mixture. After sonication for another 2 min, the mixture was stirred for 30 min at room temperature. The excessive water was finally evaporated at 353 K with stirring and the catalysts was obtained after dried at 373 K (denoted as $WS_2$@HMS).

## 3. Catalyst characterization

Nitrogen adsorption-desorption isotherms at 77 K were measured with a Micromeritics Tristar 3000 instrument and the samples were outgassed at 523 K before each measurement. The specific surface areas were calculated following the BET method. The wide-angle XRD scanning studies were conducted on a Bruker D8 Advance X-ray diffractrometer operated at 40 mA and 40 kV with Cu Kα radiation. Transmission electron microscopy (TEM) were obtained using a JEOL 2011 microscrope operating at accelerating voltage of 200 kV. Scanning electron microscopy (SEM) were obtained using a PHILIPS XL 30 microscope operating at accelerating voltage of 20 kV. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a

Perkin-Elmer PHI 5000C ESCA system equipped with a hemispherical electron energy analyzer. The Mg Kα (*hv* =1253.6 eV) anode was operated at 14 kV and 20 mA. The carbonaceous C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BEs).

## 4. SEM results of HMS and 20%$WS_2$@HMS.




(a) (b)

(c) (d)

**Figure S1. SEM images of (a, b) HMS and (c, d) 20%$WS_2$@HMS.**

## 5. Procedure for the selective oxidation of CPO with aqueous $H_2O_2$.

In a typical experiment, 0.696 g of the $WS_2$@HMS material (20%), 7.5 mL of TBP and 0.52 mL of 76 wt.% aqueous $H_2O_2$ (14.6 mmol) were introduced into the regular glass reactor at 308 K with vigorous stirring. The reaction was started by adding 1.00 mL of CPO (11.2 mmol) into the above mixture and was kept for 1 h. The catalyst was

easily recovered with filtration. The quantitative analysis of the reaction products in the filtrate was performed by the GC method and the different products in the reaction mixture were identified by means of GC-MS on HP 6890GC/5973 MS.

The reusability of the catalysts was carried out as follows: after each recycle, the catalyst was simply separated by filtration, washed with TBP for 2 times and acetone for 2 times, and reused in the next run.

**Reference**

1 P. T. Tanev and T. J. Pinnavaia, A neutral templating route to mesoporous molecular sieves, *Science*, 1995, **267**, 865.

.