**Supporting information**

# $SnO_2$ Nanocrystals Decorated-Mesoporous ZSM-5 Spheroidicity as Precious Metal-free Electrode Catalyst for Methanol Oxidations

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## Experimental

### 1. Chemicals and Reagents

Aluminium isopropoxide and TEOS (tetraethoxysilane) were obtained from Shanghai J&K, China. Tetrapropylammonium hydroxide (25%) and TPHAC (octadecyldimethyl (3-trimethoxysilyl propyl)ammonium chloride) with 60% methanol were obtained from SIGMA. Zeolite (ZSM-5) with Si/Al=50 was bought form Catalyst Factory of Nankai University.

### 2. Materials Synthesis

Firstly, ZSM-5 spheroidicity was prepared by hydrothermal method. Typically, 0.3066 g aluminium isopropoxide, 15.624 g TEOS, and 45 g $H_2O$ were added into to Duran bottle under stirring, and then the mixture was stirred continuously for 1 h at room temperature to form an evenly solution. After that, 10.98 g tetrapropylammonium hydroxid, 0.27 g NaOH and 45 g $H_2O$ were added into above solution , and was stirred for 4 h at 40 °C. Then the temperature was tuned to 100 °C, and continuously stirred for 48 h. After centrifugation and dried at 100 °C, the product was obtained. 0.5 g as synthesized material was added into a mixture solution of 100 g $H_2O$ and 60 g ethanol by ultrasonic dispersion, then 30 ml ethanol solution with 0.2 g TPHAC was added drop by drop at 10 °C under stirring, and continuously stirred for 5 h. After that, 10 mL (0.03 M) $SnCl_4.5H_2O$ solution was added and continuously stirred for 2h, then 10 ml (1.2 M) $NH_3$ $H_2O$ solution was dropped slowly under stirring. After centrifugation and dried, the product was calcined at 550 °C for 7 h in muffle furnace. Then the $SnO_2$ nanocrystals decorated homogeneously on ZSM-5 spheroidicity was obtained and named as $SnO_2$/ZSM-5.

For comparison, zeolite (ZSM-5) with the same Si/Al ratio (Si/Al=50), mesoporous silica, such as SBA-15 and KIT-6, and ɤ-$Al_2O_3$ were also used as support materials to load $SnO_2$ nanocrystal by the same method, and the obtained samples were named as $SnO_2$/ZSM-5, $SnO_2$/SBA-15, $SnO_2$/KIT-6, and $SnO_2$/ɤ-$Al_2O_3$, respectively. $SnO_2$ nanopowder was also prepared for comparison, which is synthesized by sol-gel method. Typically, 2.3 g $SnCl_4.5H_2O$ was dissolved in 100 ml $H_2O$ to form a solution of 0.066 M. Then 20 ml (1.2 M) $NH_3$ $H_2O$ solution was dropped slowly under stirring. After stirred continuously for 5 h at room temperature, the obtained sol was filtered and dried in freezer dryer. The formed gel was grinded in mortar and then calcined at 500 °C for 3 h in muffle furnace, then the $SnO_2$ nanopowder was obtained.

## 3. Structural Characterizations

The powder X-ray diffraction (XRD) patterns of prepared samples were recorded on a Rigaku D/Max-2550V X-ray diffractometer with a Cu-Ka radiation target (40 kV, 40 mA). The $N_2$ sorption measurements were performed using Micromeritics Tristar 3000 at 77 K, and the specific surface area and the pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Field emission scanning electron microscopic (FE-SEM) images were performed on a JEOL JSM-6700F field emission scanning electron microscopy. Transmission electron microscopy (TEM) images and Energy-dispersive X-ray spectra (EDX) were obtained on a JEOL 200CX electron microscope operating at 160 kV.

## 4. Electrochemical measurement

Electrochemical studies of prepared catalyst powders included cyclic voltammetry (CV), CO stripping voltammetry and methanol oxidation current-voltage. Electrochemical measurements were conducted at room temperature in a standard three-electrode configuration that utilized a saturated mercury/mercuric oxide reference electrode (MMO), a Pt mesh counter electrode and a thin-film layer of the catalyst (applied from an ink) as the working electrode. Electrodes were prepared using 1 mg $mL^{-1}$ solutions of catalyst inks made with 10 mg (7 mg catalyst +3 mg carbon black) of the catalyst powder, 7.95 mL of water, 2 mL of 2-propanol (IPA), and 50 μL of 5 wt% Nafion solution. These mixtures w5ere bath sonicated for 20 min and 10 μL of the ink was then applied to the glassy carbon tip. The electrodes were then dried at 40 °C for 30 min. Highly pure $N_2$ was used prior to the measurements to deaerate the electrolyte. Prior to performing CO stripping voltammetry, the working electrode was electrochemically cleaned in a solution of 0.5 M NaOH by cycling 5 times from -0.885

to 0.10 V. Then, pure CO gas was bubbled into 0.5 M NaOH for 10 min while the working electrode was held at -0.6 V. While the working electrode was still held at -0.6 V, pure $N_2$ was bubbled for 10 min to purge excess CO from the electrolyte. The potential was then swept to 0.1 V at 20 mV $s^{-1}$ to strip the adsorbed CO from the surface of the working electrode. Two subsequent sweeps from -0.885 to 0.10 V were then performed to ensure that all the bulk CO had indeed been removed from the electrode. For methanol oxidation test, alkaline solution with 0.5 M NaOH and different concentration (0.3, 0.5, 0.8 M) was used as electrolyte, and highly pure $N_2$ was used prior to the measurements to deaerate the electrolyte.

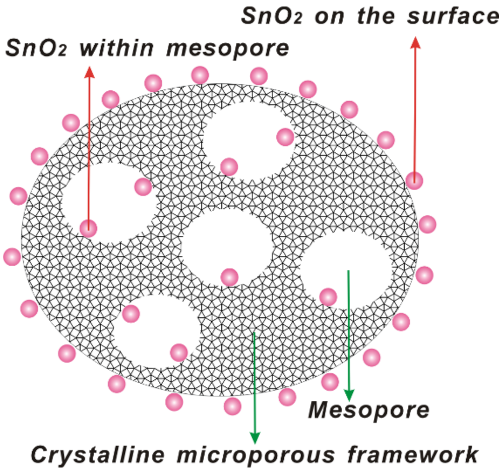
## Tables

**Table S1.** Pore structural parameters of prepared composite catalysts.

| Sample | $S_{BET}$[a]/m$^2$g$^{-1}$ | $D_{BJH}$[b]/nm | $V_{BJH}$[c]/cm$^3$g$^{-1}$ | $SnO_2$[d]/% |
|---|---|---|---|---|
| ZSM-5 | 394 | 7.2 | 0.13 | - |
| m-ZSM-5 | 402 | 6.5 | 0.23 | - |
| $SnO_2$/ZSM-5 | 362 | 6.2 | 0.1 | 4.2 |
| $SnO_2$/m-ZSM-5 | 371 | 6.4 | 0.2 | 3.8 |
| $SnO_2$ | 21 | - | - | - |
| XC-72R | 182 | - | - | - |
| $SnO_2$/SBA-15 | 730 | 7.2 | 1.3 | 3.9 |
| $SnO_2$/KIT-6 | 789 | 5.9 | 1.17 | 3.7 |
| $SnO_2$/γ-$Al_2O_3$ | 180 | - | - | 4.1 |

[a] BET surface area, [b] BJH desorption average pore diameter, [c] BJH desorption cumulative pore volume, [d] $SnO_2$ content (wt %) estimated by EDX spectra.

**Figures:**



**Scheme. S1** Structure schematic of a mesoporous ZSM-5 particle and the distribution of $SnO_2$ nanoparticles on the out/inner surfaces of it.

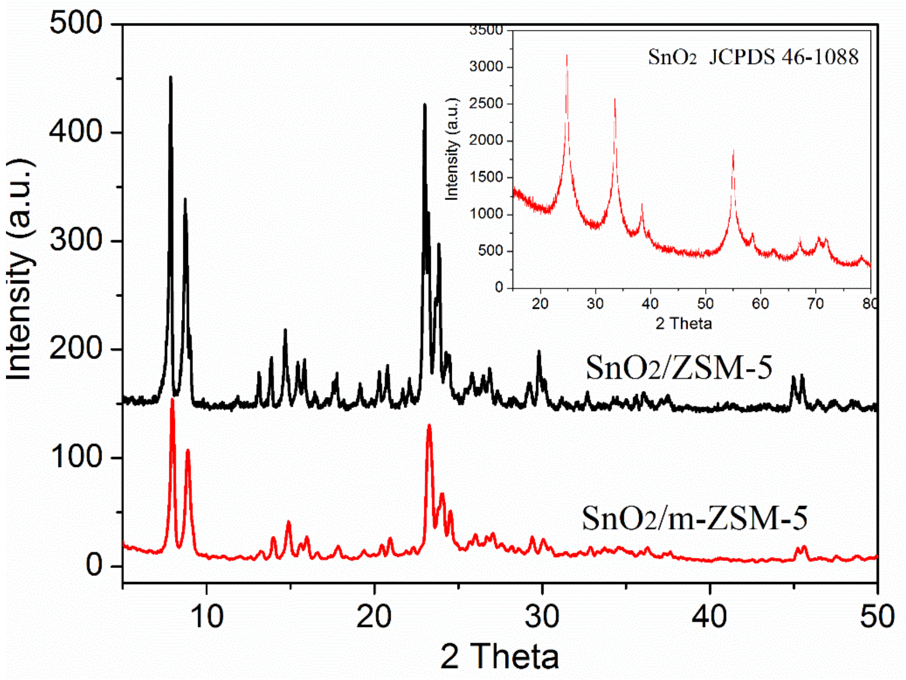


**Figure. S1** XRD patterns of the samples $SnO_2$/m-ZSM-5 and $SnO_2$/ZSM-5 nanocomposites, and the reference sample $SnO_2$ in the inset.

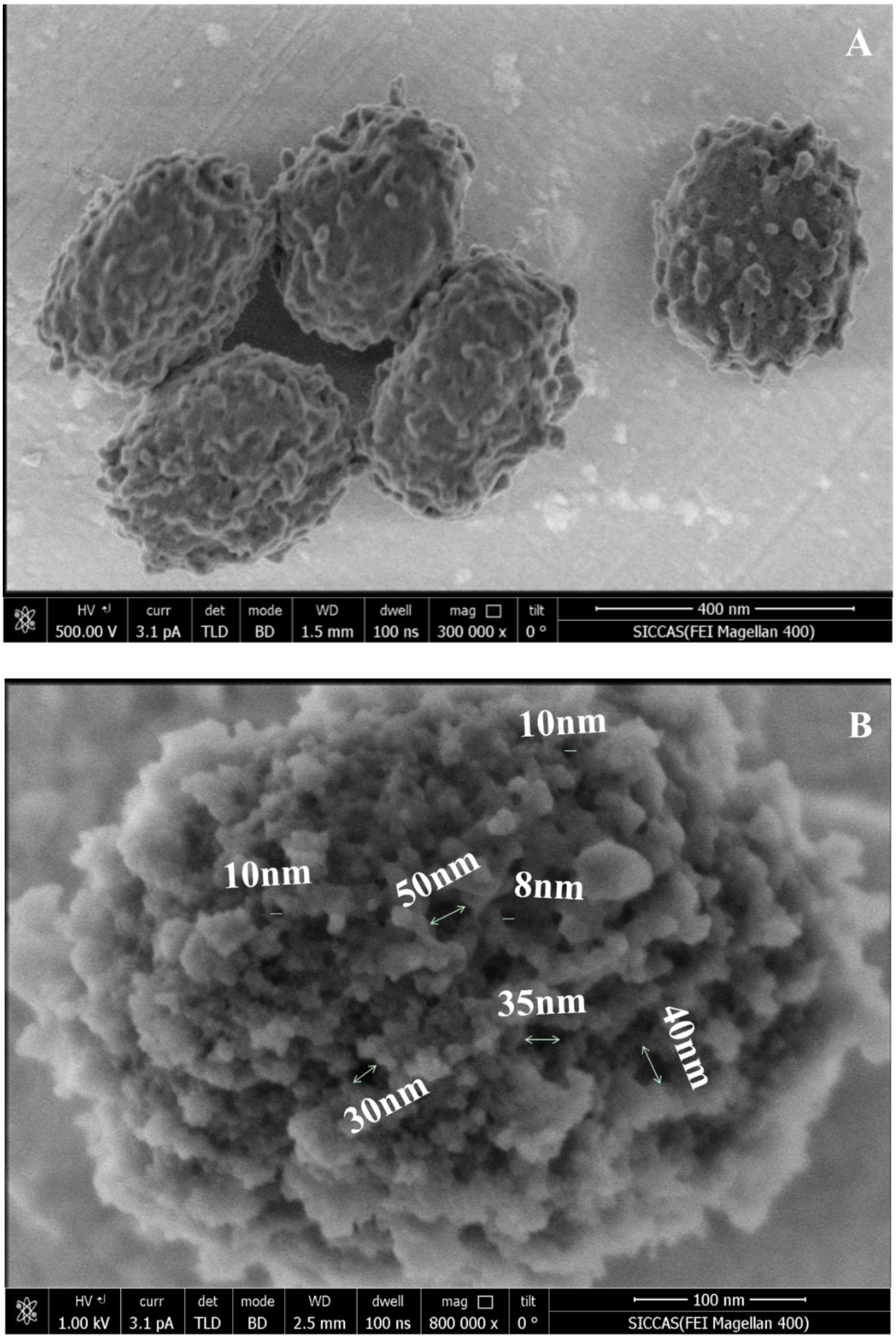


**Figure. S2** SEM images with different magnifications of prepared $SnO_2$/m-ZSM-5 nanocomposite.

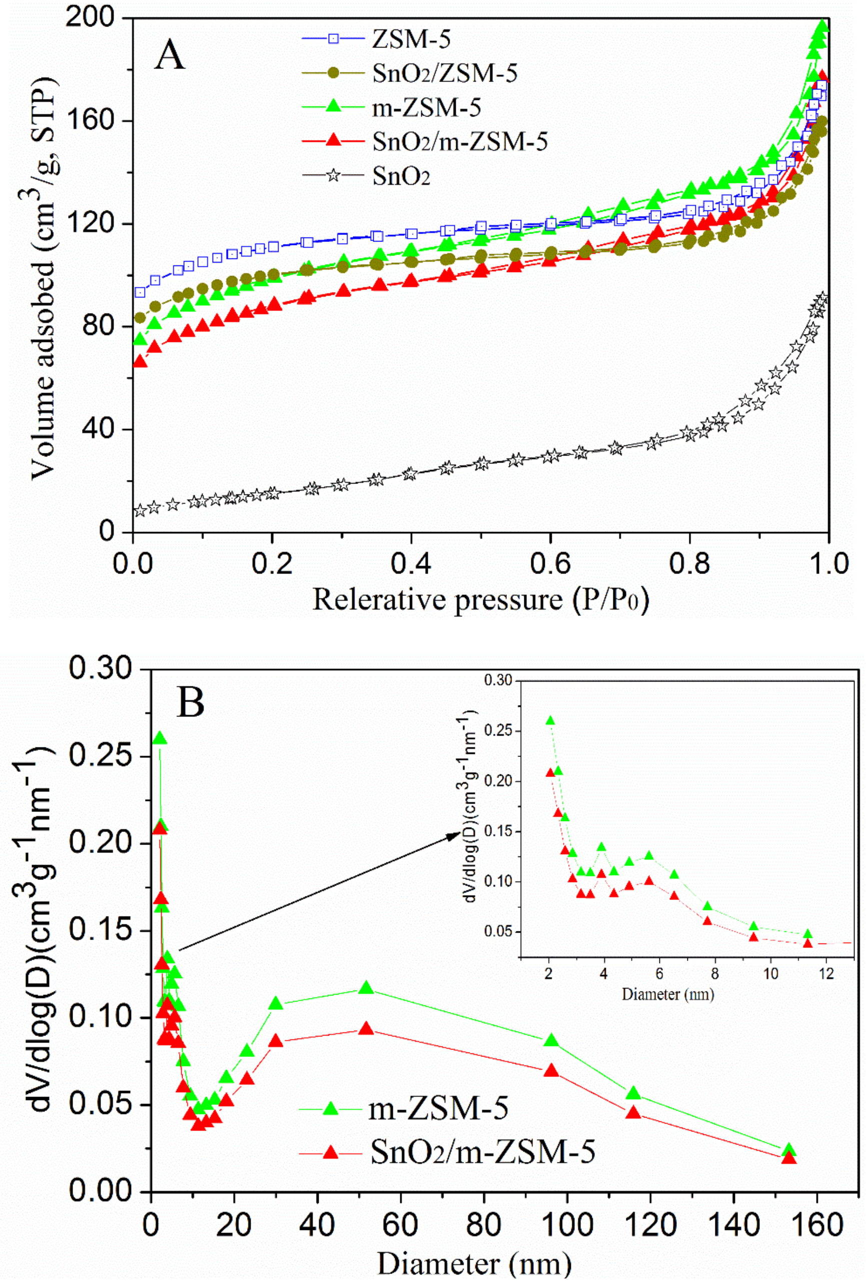


**Figure. S3** Nitrogen-sorption isotherms of synthesized samples (A), and the corresponding pore-size distribution curves (B) with the magnified region in the inset.

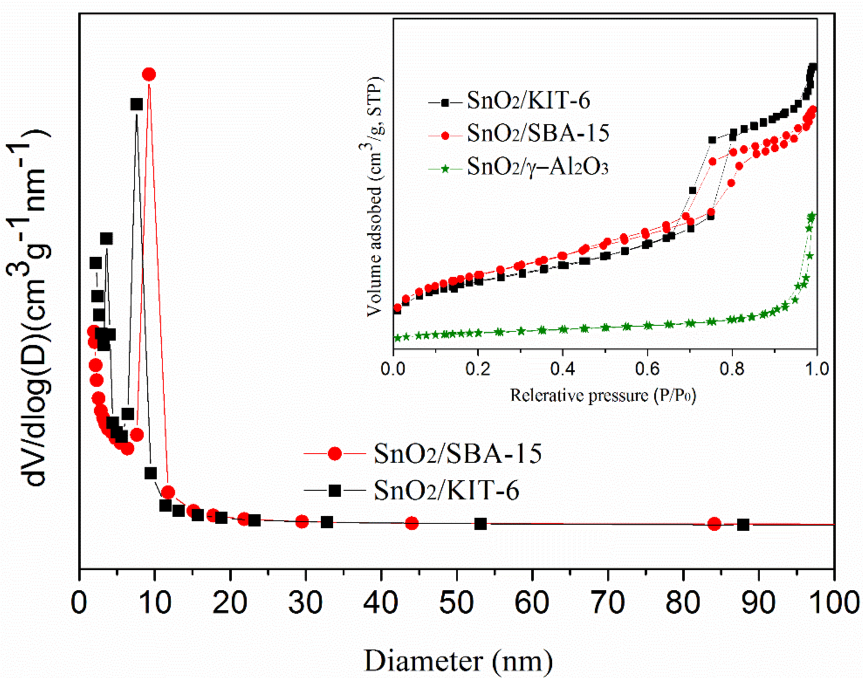


**Figure. S4** Nitrogen-sorption isotherms (inset) of reference samples $SnO_2$/SBA-15, $SnO_2$/KIT-6 and $SnO_2/\gamma\text{-}Al_2O_3$, and the corresponding pore-size distribution curves.

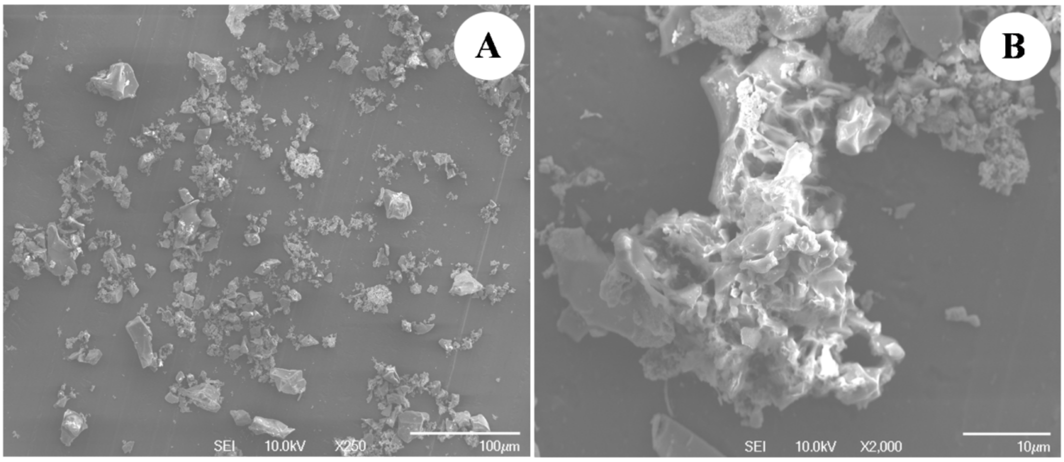


**Figure. S5** SEM images of referene sample $SnO_2$ prepared by sol-gel method.

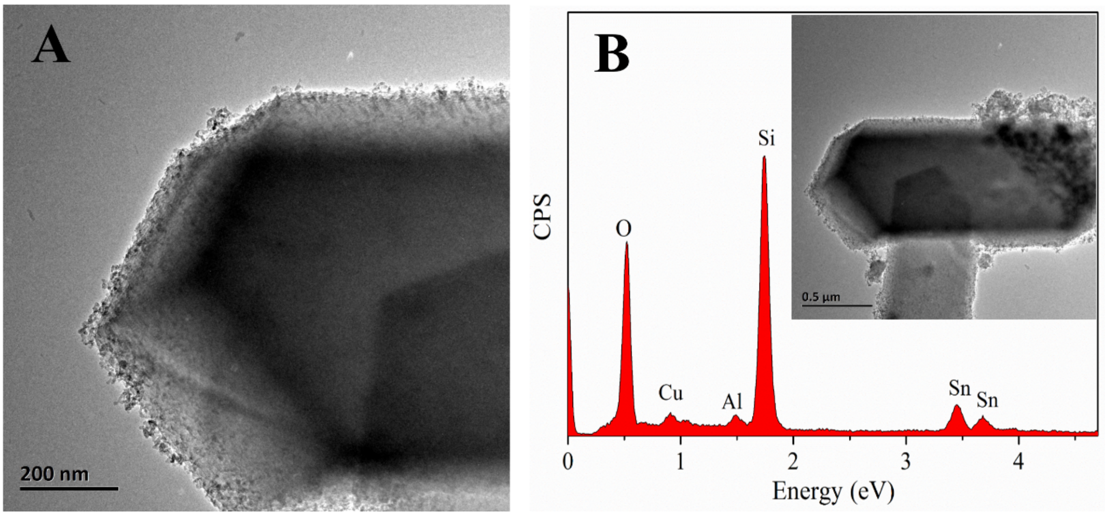


**Figure. S6** TEM image of reference sample $SnO_2$/ZSM-5 (A) and the EDX spectrum (B) of the image in the inset.

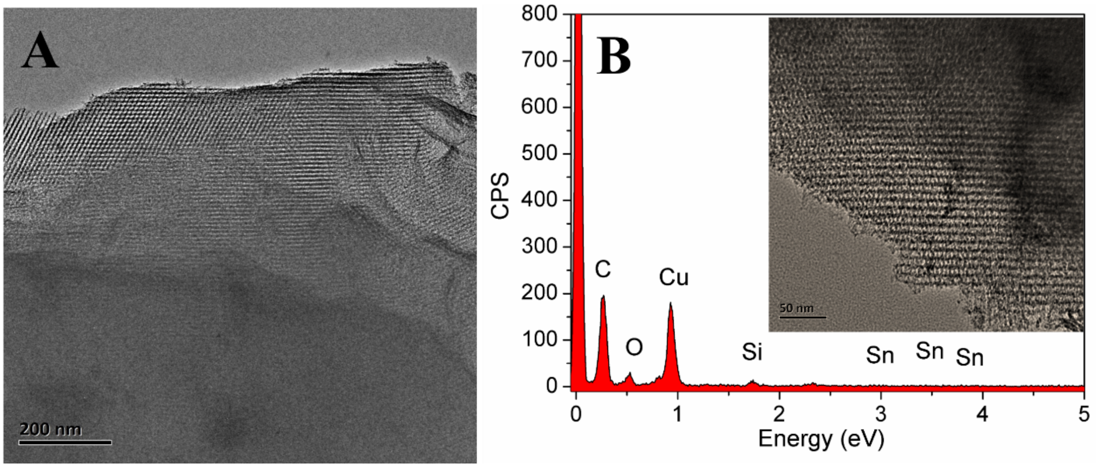


**Figure. S7** TEM image of referene sample $SnO_2$/KIT-6 (A) and the EDX spectrum (B) of the image in the inset.

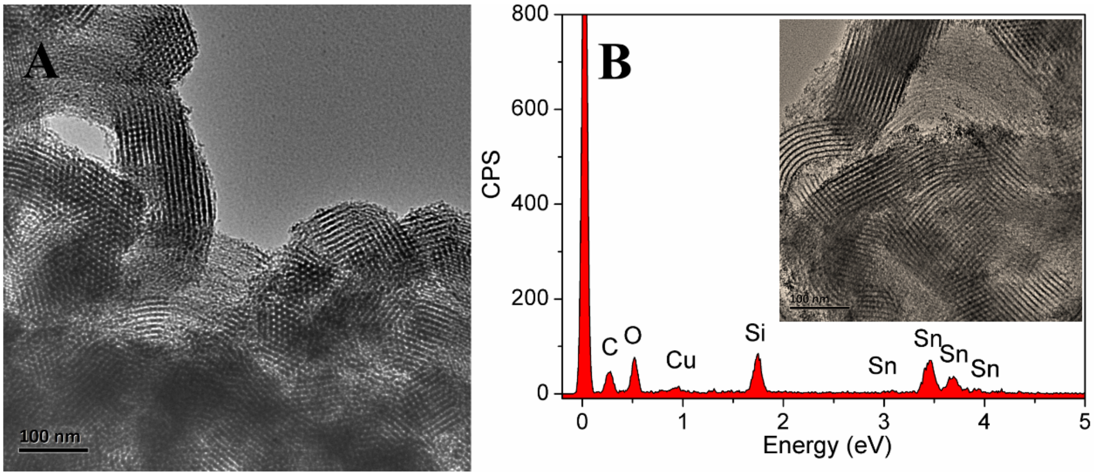


**Figure. S8** TEM image of referene sample $SnO_2$/SBA-15 (A) and the EDX spectrum (B) of the image in the inset.

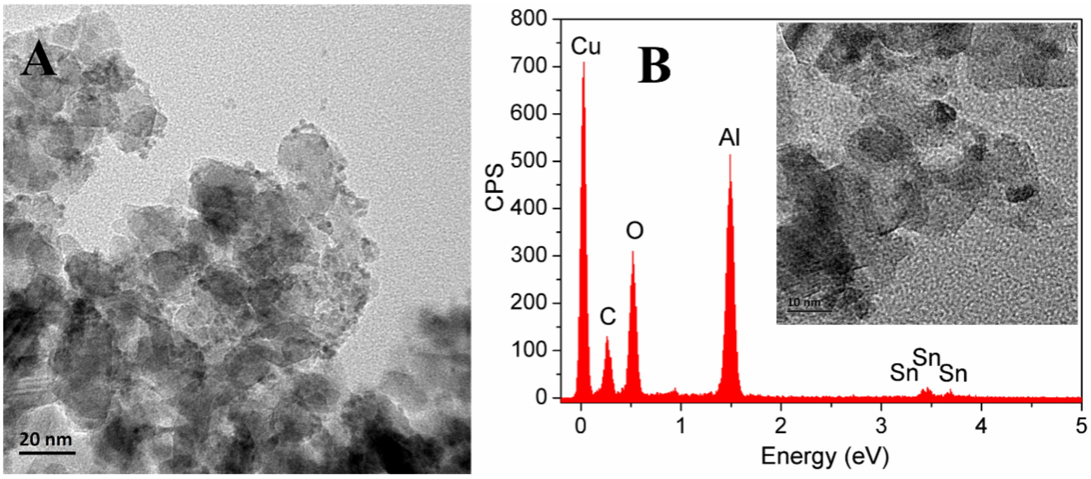


**Figure. S9** TEM image of referene sample $SnO_2/\gamma\text{-}Al_2O_3$ (A) and the EDX spectrum (B) of the image in the inset.

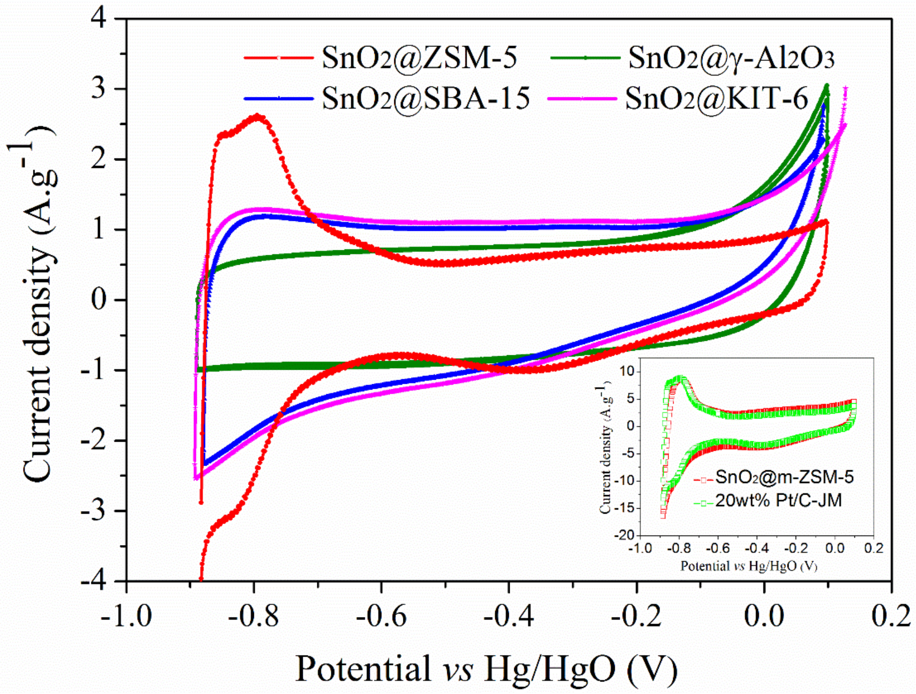


**Figure. S10** CV curves of different reference samples in 0.5 M NaOH solution at a scan rate of 0.05 V $s^{-1}$ under 20 ℃, and the CV curves of $SnO_2$@m-ZSM-5 and commercial 20wt% Pt/C-JM in the inset.

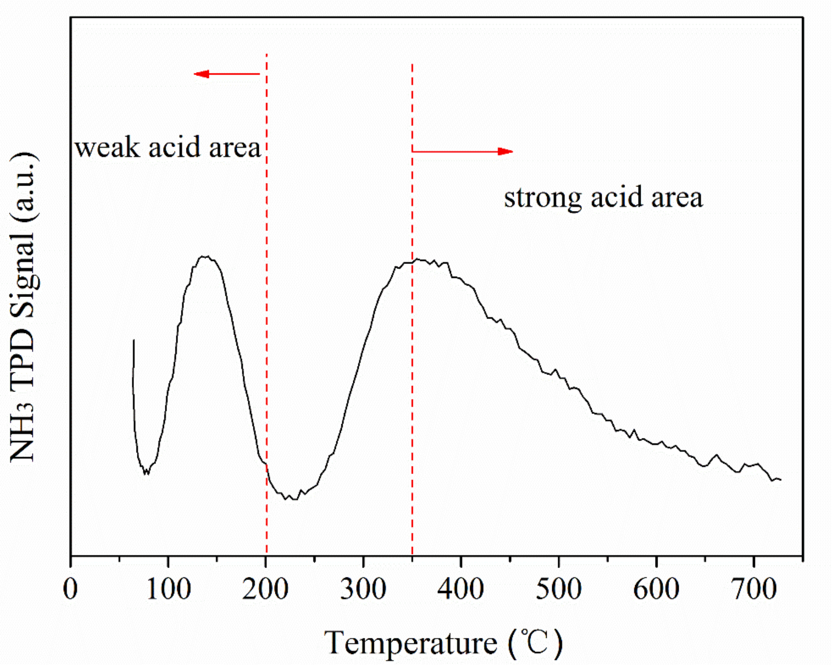


**Figure. S11** $NH_3$-TPD profiles of prepared $SnO_2$/m-ZSM-5 nanocomposite.

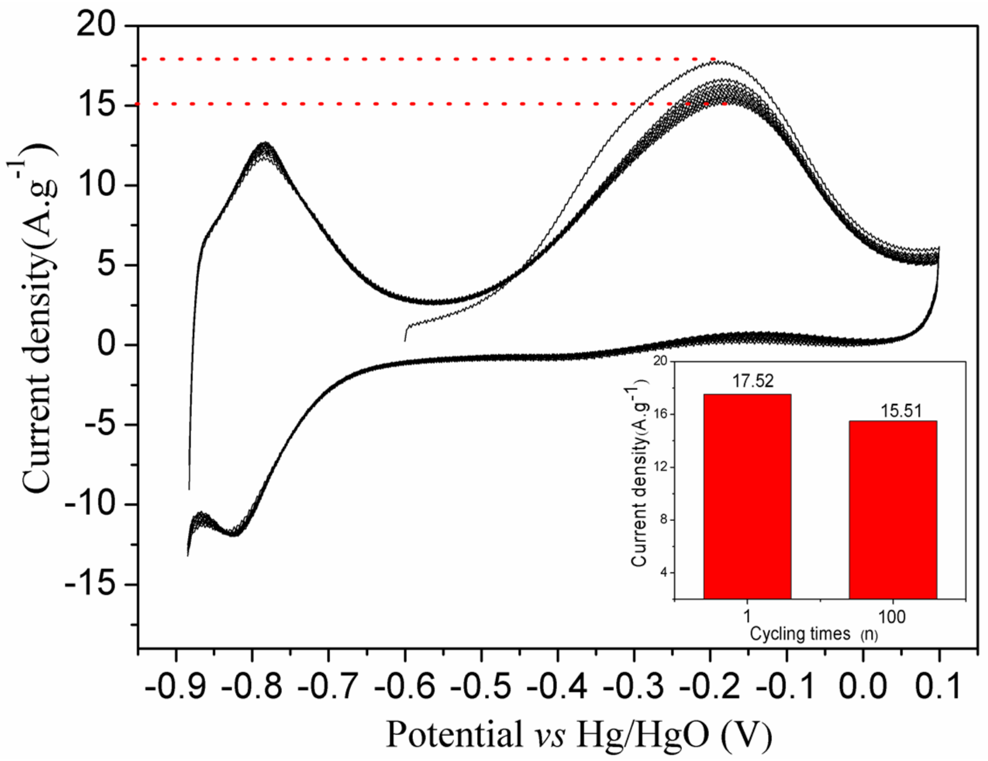


**Figure. S12** CV results of methanol oxidation on commercial catalyst 20wt% Pt/C-JM for cycling 100 times in electrolyte solution of 0.5 M NaOH + 0.8 M $CH_3OH$ at a scan rate of 0.05 $Vs^{-1}$ under 20°C, and the current density *vs* cycling time histograms in the inset.

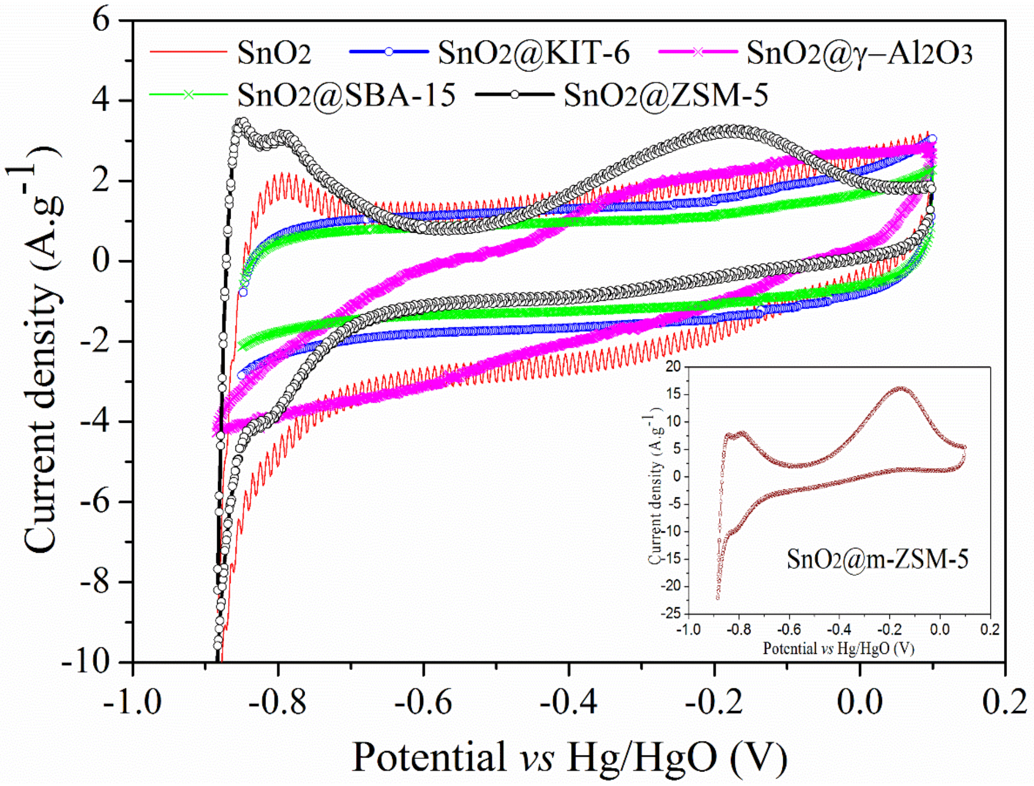


**Figure. S13** CV results of samples for methanol oxidation in 0.5 M NaOH + 0.8 M $CH_3OH$ solution at a scan rate of 0.05 Vs$^{-1}$ under 20°C, and the methanol oxidation result of $SnO_2$@m-ZSM-5 (in the inset) at the same test condition.