Electronic Supplementary Material (ESI) for RSC Advances.

Support Information

Preparation of SnO_2/graphene nanocomposite and its application to the catalytic epoxidation of alkenes with H_2O_2

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1. Experimental

1.1 Synthesis of SnO_2/RGO nanocomposite

SnO_2/RGO nanocomposites were synthesized via an in situ hydrothermal method. Graphite oxide, the precursor of graphene, was obtained by a modified Hummer method from graphite powder. $SnCl_2{\cdot}2H_2O$ (1.30 g) was dissolved in 0.4 M HCl solution (20 mL). Subsequently, the above solution was mixed with graphene oxide aqueous solution (0.5 mg mL^{-1}, 20 mL) and urea (1.30 g) under vigorous stirring to make a homogeneous solution. The precursor solution was treated by ultrasonic for 30 min and then heated up to 353 K in the Teflon-lined stainless steel autoclave (100 mL) for 12 h and filtered. The precipitates were washed with deionized water several times. Finally, the black solid products were obtained after drying at 333K overnight.

1.2 General reaction procedure

Typical procedure for epoxidation of alkene was carried out using 10 mmol (0.84g) cyclohexene and 5 mol% catalyst (amount of substrate) in 5 mL acetonitrile and 5 mL 0.2M $NaHCO_3$, and then heated to 50 °C for 3 h with 12mmol (1.36g) 30 wt% H_2O_2. After reaction, the catalyst was separated by filtration and the reaction process was detected by gas chromatograph.

1.3 Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer using Cu Kα radiation (λ= 1.542 Å). The data were collected 2θ from 5˚ to 80˚at a scanning rate of 10°/min. Fourier transform infrared (FTIR) spectra in the frequency range of 400~4000 cm^{-1} were performed on a Nexus 670 spectrometer using KBr pellets. X-ray Photoelectron Spectroscopy (XPS) measurements were carried out on an ESCALAB 250Xi electron spectrometer from Thermo Scientific using Al Kα radiation. The morphology and structure of the presented composite were characterized by TEM and HRTEM techniques using a JEM-2010 (HR) transmission electron microscope operating at 200 kV. The amount of graphene was obtained from a simultaneous TG/DSC (SDT Q600) apparatus. The sample was heated from room temperature up to 750°C with heating rate of 10 °C /min and under air atmosphere. The chemical compositions of filtrate was analysed by ICP-AES (Iris intrepid II XSP).

2. TG/DSC curves of SnO_2/RGO composite

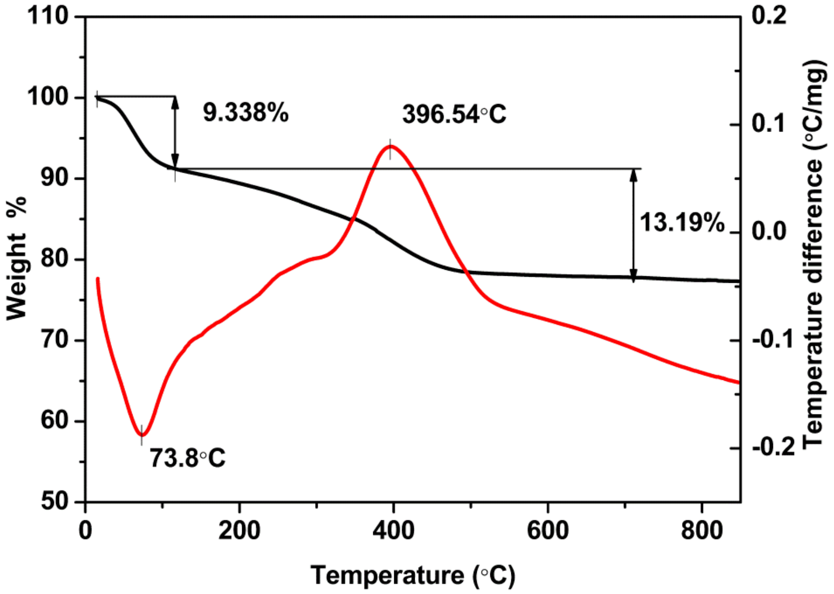
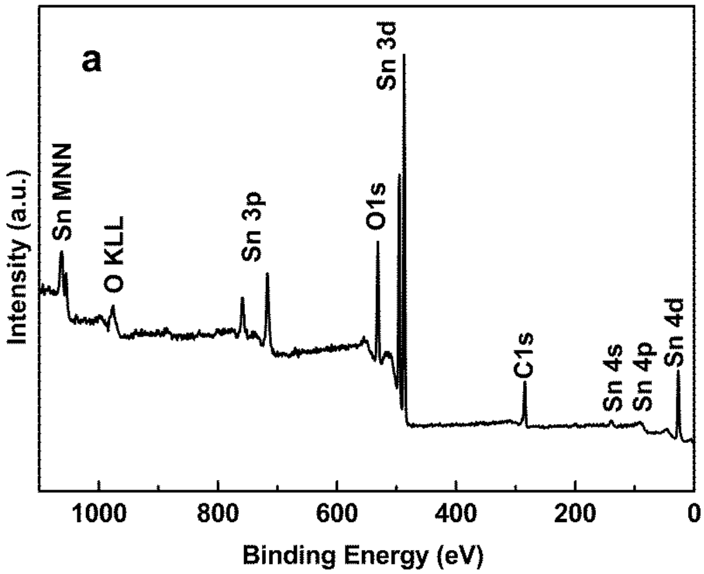


Fig. S1 TG/DSC curves of SnO_2/RGO composite

TGA was employed to quantify the amount of graphene present in the composite under air atmosphere. As shown in the curves (Fig. S1), the 13.19 wt% weight loss occurred mainly from 100 to 500 °C with an exothermal peak at 396.54°C, which was associated with the burning of graphene in air. Therefore, according to the change of weight, the mass loading of SnO_2 was calculated to be 77 wt% in the SnO_2/RGO composite.

3. XPS spectra of SnO_2/RGO composite



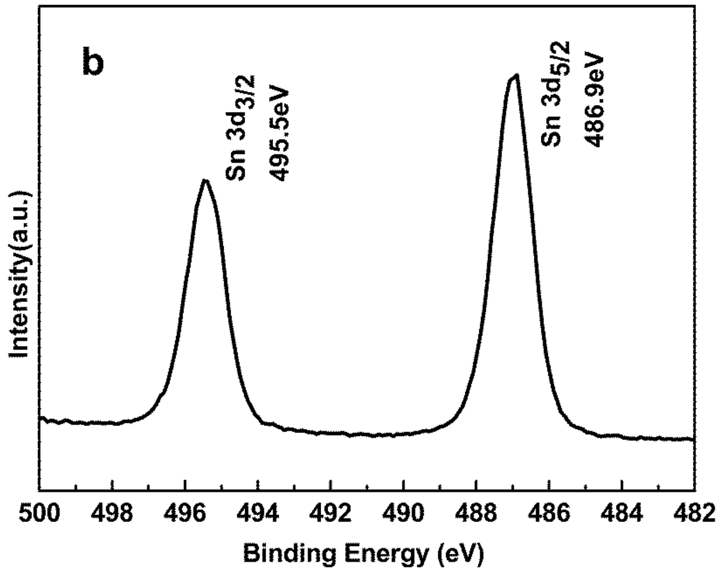


Fig. S2 (a) XPS spectrum and (b) Sn 3d spectrum of SnO_2/RGO composite

4. FTIR spectra of the GO, prepared SnO_2 and SnO_2/RGO nanocomposite

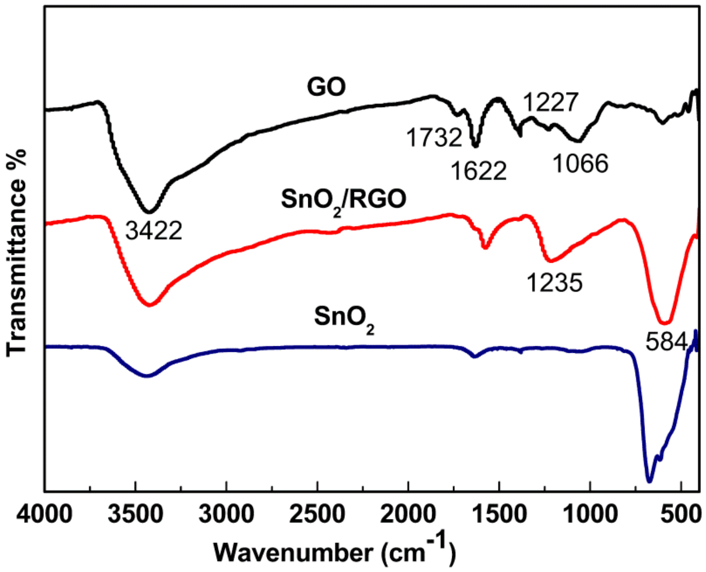


Fig. S3 FTIR spectra of GO, prepared SnO_2 and SnO_2/RGO nanocomposite

5. The full sets of selectivity data

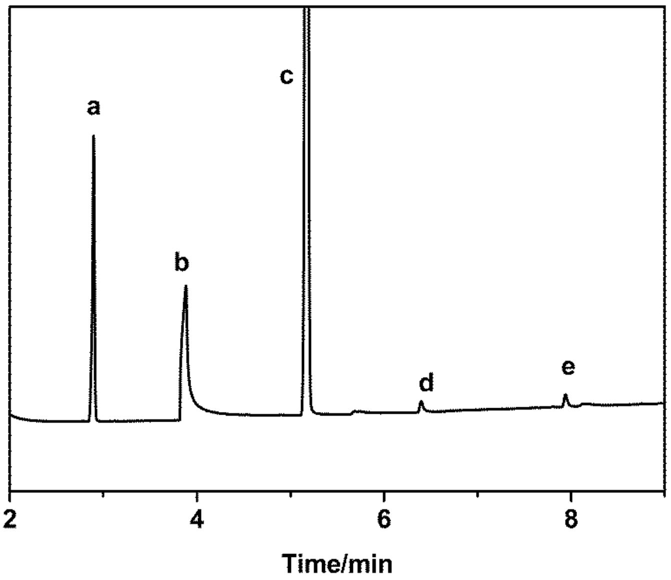
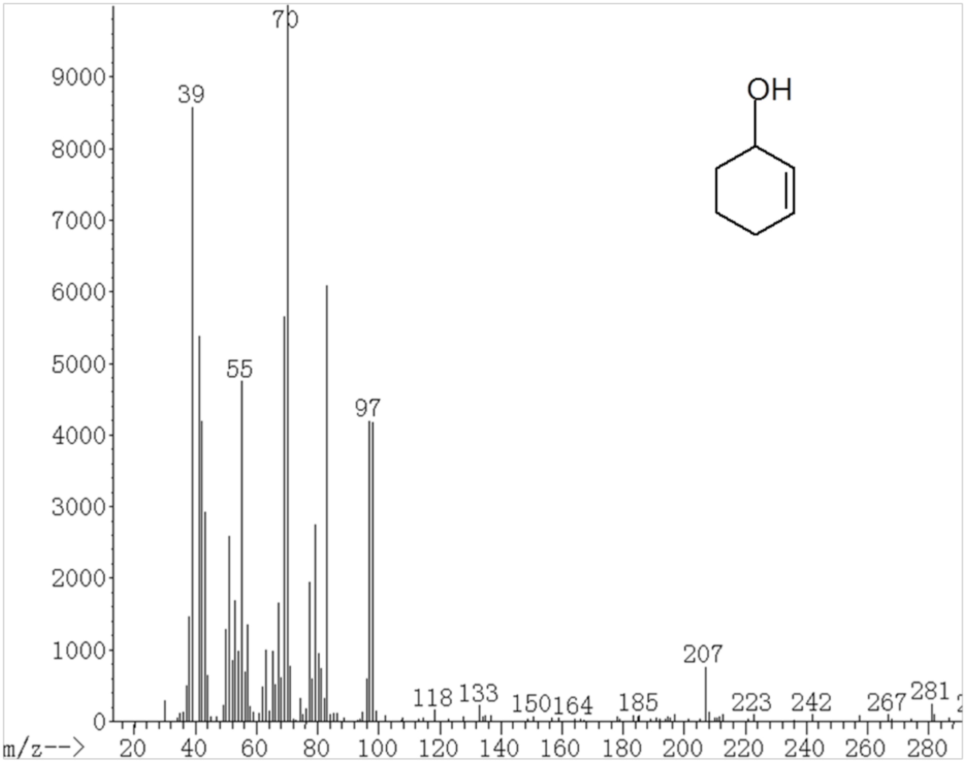


Fig. S4 GC analysis spectrum of cyclohexene epoxidation over the SnO_2/RGO catalyst.
(a) cyclohexene, (b) acetamide, (c) cyclohexene oxide, (d) cyclohexenol and (e) cyclohexenone

The main product (c) had been validated by the comparison with commercial sample. Other by-products were identified through the GC-MS database.



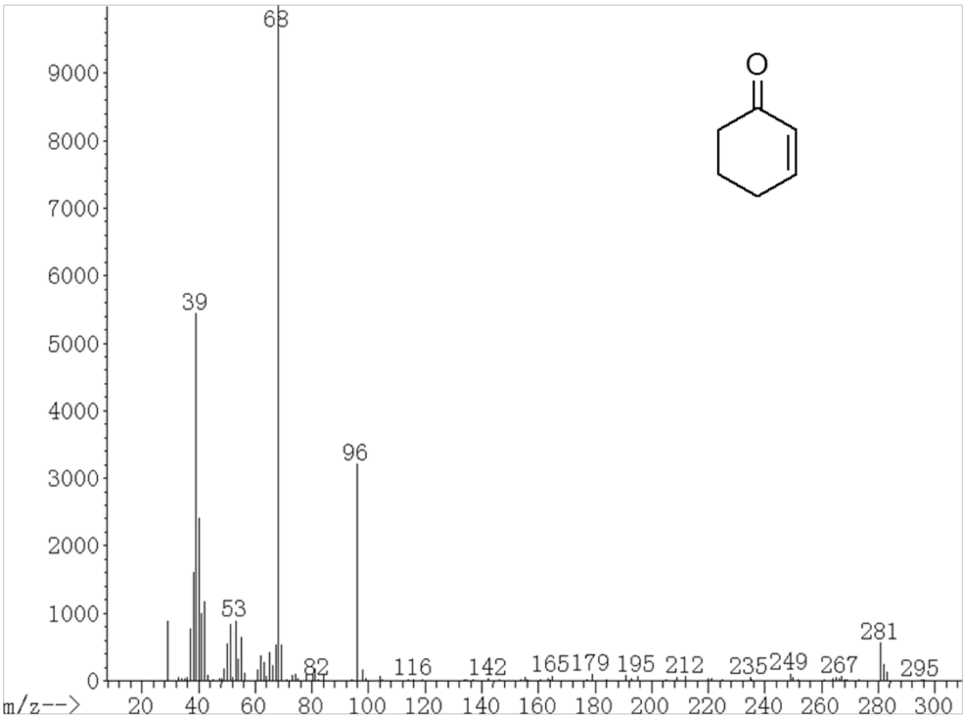


Fig. S5 GC-MS analysis spectra of cyclohexenol and cyclohexenone

6. Epoxidation of cyclohexene catalyzed by SnO_2/RGO catalyst under different conditions

Table S1 Epoxidation of cyclohexene catalyzed by SnO_2/RGO catalyst under different conditions[a]

Entry	Effect	Solvent	Temperature (°C)	Molar ratio[b]	Conversion (%)[c]	Epoxide selectivity (%)
1	Solvent	DCM	50	1.2	0	0
2		MeCOEt	50	1.2	6	100
3		EtOH	50	1.2	28.1	20.1
4	Temperature	MeCN	0	1.2	66.8	92.8
5		MeCN	25	1.2	88.2	95.1
6		MeCN	50	1.2	92.5	98.2
7		MeCN	70	1.2	94.1	82.6
8	Molar ratio	MeCN	50	1	87.4	93.2
9		MeCN	50	1.2	92.5	98.2
10		MeCN	50	1.5	93.6	95.3
11		MeCN	50	2	93.6	96.2

a Reaction conditions: cyclohexene (10 mmol), SnO_2/RGO nanocomposite (100mg, 5 mol% of substrate), solvent (5 mL), $NaHCO_3$ (0.2M, 5mL), 30 wt%H_2O_2 as oxidant, 3 h. *b* The molar ratio of H_2O_2 to cyclohexene. *c* Conversion and selectivity were determined by GC and identified by GC-MS.

As can be seen in Table S1, the oxidation hardly occurred in other solvents, which suggested the major role of acetonitrile in this reaction. The conversion of cyclohexene increased with increasing the reaction temperature especially range from 0 °C to 50 °C because higher temperature is favor to activate reaction molecules. However further increase in temperature increased the conversion but caused poor epoxide selectivity, which might be due to the generation of more side reactions at higher temperature. Thus modestly elevated temperatures are required to obtain a significant increase in both conversion and selectivity of desired epoxide. Interestingly, the oxidant/substrate molar ratio had no remarkable effect on this production. Taking into account the atom economy, 1.2 molar equivalents H_2O_2 per mole of the substrate are appropriate.

7. Reusability of SnO_2/RGO in the epoxidation of cyclohexene

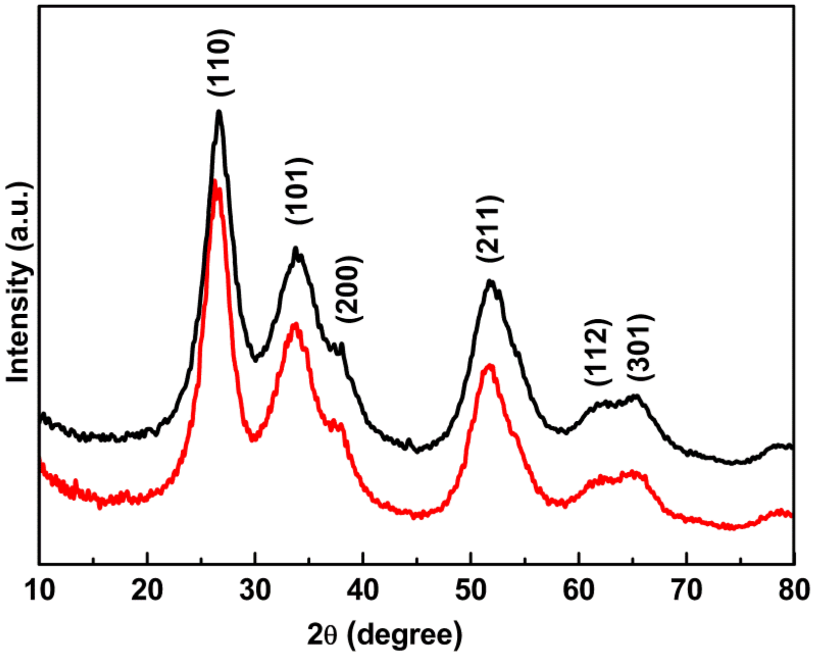


Fig. S6 XRD patterns of the fresh (black line) and reused catalyst (red line).

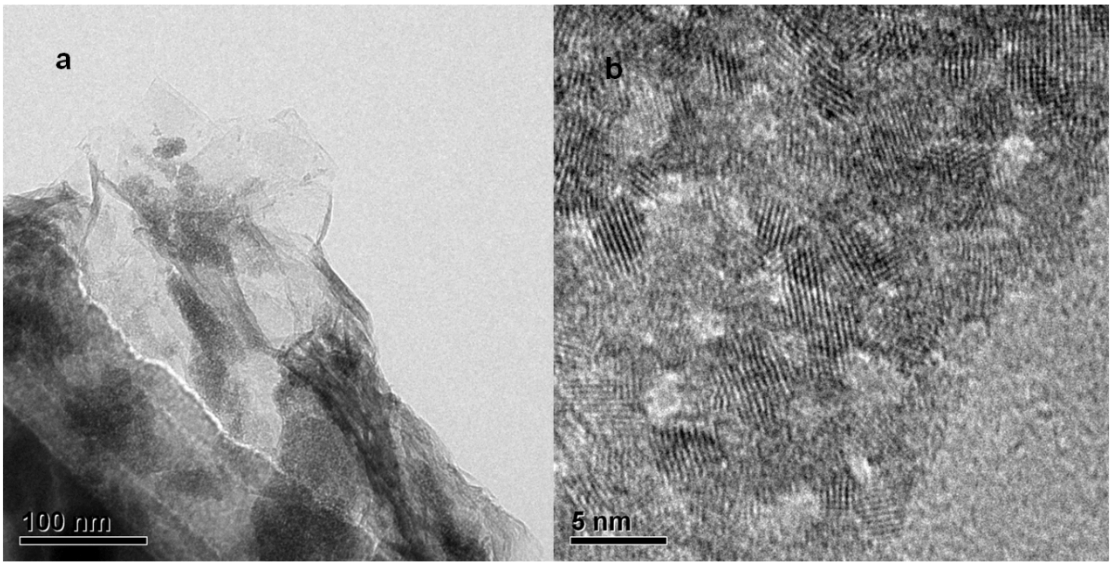


Fig. S7 (a) Low magnification TEM image of the reused SnO_2/RGO composite; (b) high magnification TEM image of the reused SnO_2/RGO composite.

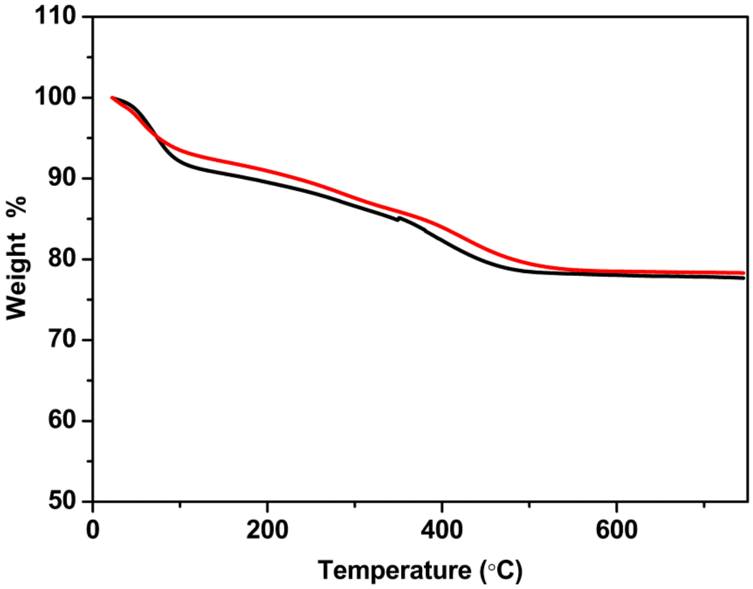


Fig. S8 TG curves of the fresh (black line) and reused catalyst (red line).