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Light Driven Epoxidation of Olefins with Graphene Oxide/g-C_3N_4 Supported Mo (Salen) Complex

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Experimental Section

Chemicals

The flake graphite (particle diameter ~44 µm) was purchased from Qingdao Jinrilai Graphite Co. (China) and molybdenyl acetylacetonate ($[CH_3COCH{=}C(O)CH_3]_2MoO_2$) was from Shanghai Aladdin Biological Technology Co. (China). Other Reagents (3-(Aminopropyl) trimethoxysilane (APTMS), salicydehyde, olefins, etc.) were all obtained from Sinopharm Chemical Reagent Co. and all the chemicals were used without further treatment or purification.

Preparation of GO, g-C_3N_4 and Mo-GO/g-C_3N_4

Graphene Oxide (GO) was synthesized from the flake graphite by a modified Hummers method as mentioned in our previous research.[1] The graphitic carbon nitride nanosheets (g-C_3N_4) were prepared according to our group's previous work.[2] The Mo-GO/g-C_3N_4 was prepared by two steps. Firstly, GO (200 mg) was dispersed in ethanol (150 mL), followed by stirring and ultrasonication (40 KHz, 100w) for each 0.5 h to get a uniform suspension. Then, APTMS (360 µL, 2 mmol) was dropwise added into the mixture, along with stirring and reflux for 6 h. The solution was centrifuged and washed with DI water and ethanol three times, respectively. Subsequently, the mixture was dispersed into 50 mL ethanol, followed by 0.5 h ultrasonication. Afterwards, salicyladehyde (316 µL, 3 mmol) and certain amount acetic (accelerant) were added into the suspension. After refluxing for 5 h, the mixture was centrifuged and washed with ethanol and methanol twice, respectively. Immediately, the obtained paste was mixed with molybdenyl acetylacetonate (652 mg, 2 mmol) in methanol and stirred for 10 h at 50 ^oC. The resulting mixture was centrifuged and washed with methanol and ethanol twice respectively, followed by dissolving in ethanol (50 mL) for further use. Secondly, the as-prepared g-C_3N_4 (400 mg) was dispersed into the above ethanol mixture and ultrasonicated 1 h for complete decentralization. After stirring and refluxing for 6 h, the mixture was centrifuged and washed with ethanol and DI water three times, respectively, accompanied by a freeze-drying procedure to get the final product (916 mg, Mo %≈4.2 wt%, effective immobilizing rate of Schiff base-Mo ligand≈20 %). As a contrast, GO/g-C_3N_4 were prepared similarly without adding molybdenyl acetylacetonate.

Characterization

FT-IR spectra were obtained on the NICOLET 6700 FT-IR thermoscientific spectrometer in the region of 500-4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was investigated on a Kratos Ultra DLD imaging spectrometer (UK) with the Al Kα Radiation (1484.6 eV) in TRW research collaboration centre. The powdered samples were pressed into pellets before XPS studies. Field-emission scanning electron microscope (FE-SEM) and scanning electron microscope-energy dispersive spectrometer (SEM-EDS) were both operated at S-4800 machine (Hitachi) with an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) images were recorded using a JEOL JEM 2100 electron microscope under an accelerating voltage of 200 kV. Samples for TEM were prepared by ultrasonically dispersing the powders in ethanol over 2 h, and then dropwise added onto a carbon coated copper grid. Surface photovoltage (SPV) measurement was conducted in a sandwich cell (ITO/sample/ITO) using the light source-monochromator-lock-in detection technique within a range of 200-600 nm.

Photocatalytic tests

The photocatalytic reactions were carried out in a photoreaction generator (50 mL) with a circulation condensed water jacket at ambient temperature. A Xe lamp (300 W) with an AM 1.5G filter (85 mW·cm^{-2}) was employed as the light source. Typical conditions for the epoxidations were as follows: olefin (10 mmol), acetonitrile (10 mL), chlorobenzene (5mmol, a GC internal standard) and catalyst (10 mg) were added to the reactor with a magnetic stirrer. After sonicating 5 min, the mixture was purged by oxygen gas for 30 min, which served as oxidant in epoxidation. Then the mixture was continuously stirred under the illuminant for 6h. After the reaction, the solid was centrifuged and washed with DI water and acetonitrile twice, respectively, dried at 80°C over night for next use. The stability were investigated with the recovered catalyst. Products of epoxidation were analysed with a gas chromatograph (Shimadzu GC-8A). Both the conversion and selectivity were obtained through the internal standard method according to the GC data, which was further confirmed by GC-MS. The formula was listed below and GC data of cyclooctene was given in Fig. S1 as a demonstration.

$$Conversion(\%) = \left\{ \left[\frac{S_{Olefin}}{S_{chlorobenzene}} \right]_{t_0} - \left[\frac{S_{Olefin}}{S_{chlorobenzene}} \right]_{t_x} \right\} \times \frac{100}{\left[\frac{S_{Olefin}}{S_{chlorobenzene}} \right]_{t_0}}$$

$$Selectivity(\%) = S_{product} \times \frac{100}{\left[S_{product} + S_{by-product} \right]}$$

---S: Peak area of detecting object

---t_0: Initial time

---t_x: Reaction time

Characterizations

Gas chromatography

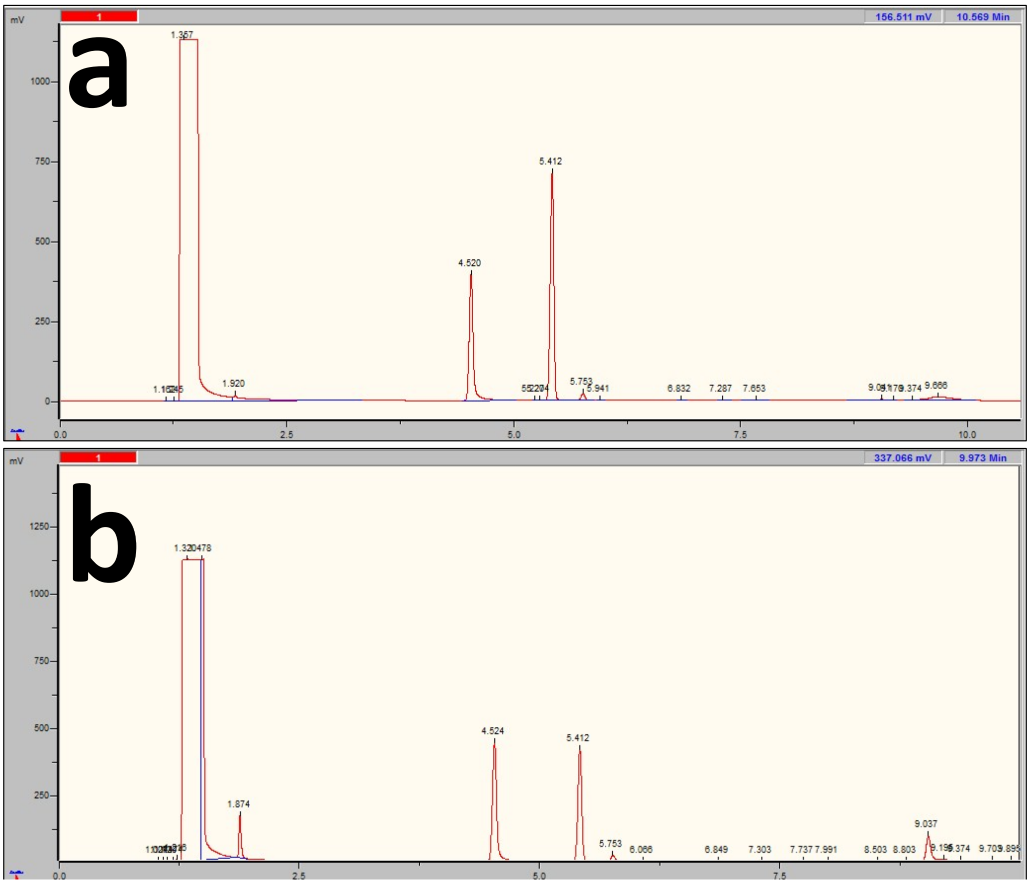

Fig. S1 Gas chromatography spectra of the products in cylooctene epoxidation[a] from different time: (a) 0 h; (b) 6 h.

[a]Reaction conditions: cyclooctene (10 mmol), CH_3CN (10 mL, solvent), chlorobenzene (5 mmol), catalyst (10 mg) and O_2. The mixture was continuously stirred under AM 1.5 G for 6 h.

References

1. G. Bian, P. Jiang, H. Zhao, K. Jiang, L. Hu, Y. Dong and W. Zhang. *ChemistrySelect*, 2016, **1**, 1384.
2. L. Kong, Y. Dong, P. Jiang, G. Wang, H. Zhang and N. Zhao. *J. Mater. Chem. A*, 2016, **4**, 9998.