Supplementary Materials:

Materials

All solvents and chemicals were used as received from commercial supplies and were used as received, unless otherwise stated. Hydrogen peroxide (H₂O₂) (30wt%, AR, Beijing Chemical Works); acetonitrile (AR, Tianjin Chemical Works); toluene (AR, Tianjin Fuyu Fine Chemical Co., Ltd.); *N*,*N*-dimethylhexadecan-1-amine (99.1%, TCI); sodium phosphotungstate (AR, Aladdin Chemistry Co., Ltd.); cyclooctene (95%, Aladdin Chemistry Co. Ltd).

Analytical Methods

FTIR spectra (4000-400 cm⁻¹) were recorded in KBr discs on a Nicolet 6700 IR spectrometer. The elemental analysis was conducted t using a Leeman ICP-AES Prodigy elemental analyzer. Scanning electron microscope (SEM) analysis was performed using ESEM-FEG XL30 scanning electron microscope and an energy-dispersive X-ray spectrometer (EDS, 30 mm², EDAX). XPS spectra of the catalyst were recorded using an ESCALAB 250 spectrometer with a monochromated Al K α radiation source. Detailed spectra were recorded for the following regions: C_{1s}, N_{1s}, O_{1s}, P_{2p}, and W_{4f} (20.00 eV pass energy, 0.1 eV step, 0.2 s step⁻¹). The XPS spectra of W_{4f} were fitted into peak doublets with parameters of spin-orbit separation $\Delta E_P(4f_{5/2}-4f_{7/2}) = 2.15$ eV and an intensity ratio $I_{W4f5/2}/I_{W4f7/2} = 0.75$ using XPS Peak software. Conversion, selectivity and yield were determined by gas chromatography coupled with a flame ionization detector [GC-FID, SHIMADZU GC-14C equipped with a capillary column (TM-1, 30m×0.25mm i.d.×0.5µm)].

Experimental

Preparation of the Grapheme/Peroxotungstate Complex

GO was prepared by the improved Hummers' method¹. Na₂WO₄·2H₂O (2 mmol, 0.660g) was dissolved in 50 mL of mixture containing (2 mg/mL) graphene oxide at 50 °C with stirring for 10 min, followed by the addition of H₂O₂ (30%, 2mL). After stirring for another 1 h, H₃PO₄ (85%, 0.231g) was added to the above mixture with stirring for an additional 30 min. Next, 0.539g of *N*,*N*-dimethylhexadecan-1-amine (DMA16) was dissolved in 50 mL of distilled water at 50 °C with stirring for 10 min. The graphene mixture was then added into the DMHA solution with stirring for 10 min. H₂O₂ (30%, 2mL) was added to the mixture and stirred at 50 °C for another 1 h. The resulting reaction mixture was cooled to room temperature. The brown precipitate was decanted and washed with 20ml of distilled water (once). Yield: 0.78g.

Epoxidation of Cyclooctene

The catalyst (0.052 g) was added into 5 mL of water at 323 K with stirring for 10 min, followed by the addition of H₂O₂ (30%, 2mmol) and cyclooctene (1 mmol). After stirring for 12 h, the resulting reaction mixture was cooled to room temperature. The GO-POM catalyst was decanted to the bottom of the reactor to and was easily separated for reuse without any treatment. The epoxide was extracted by diethyl ether. The conversions and selectivities were determined by gas chromatography using an internal standard technique.

References

1. D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, ACS Nano, **2010**, 4, 4806-4814.