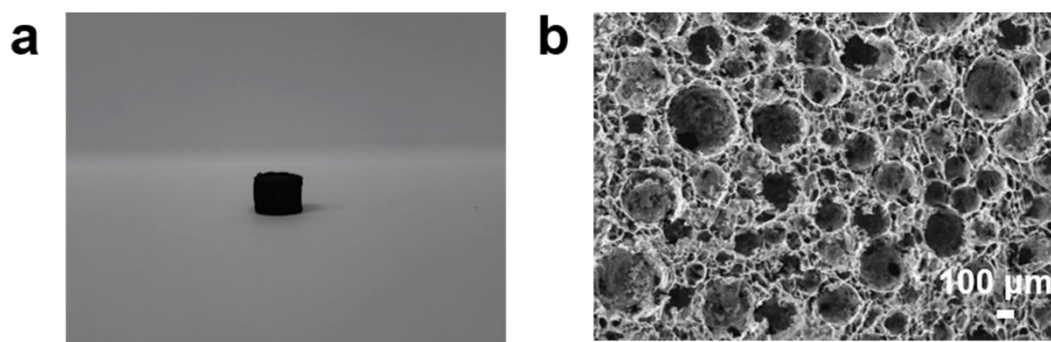


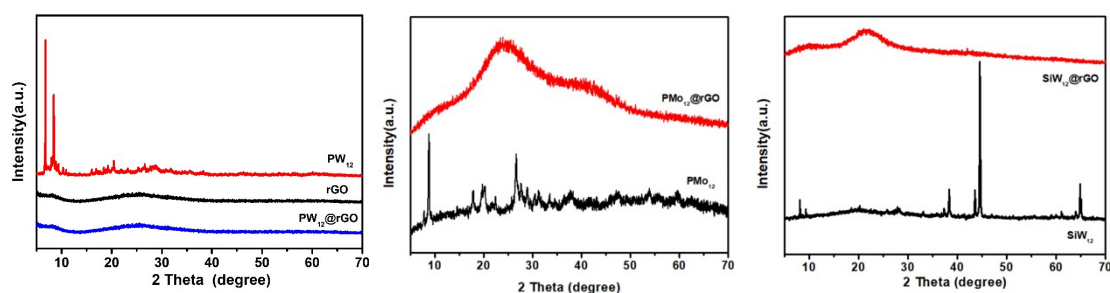
Supplementary Information

**Polyoxometalate-modified reduced graphene oxide foam as  
monolith reactor for efficient flow catalysis of epoxide ring-  
opening reactions**

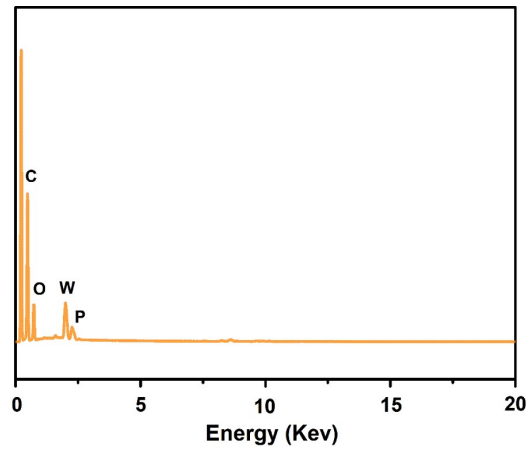
Xiaoting Jing, Zhen Li, Weijie Geng, Yingnan Chi,\* Hongjin Lv,\* Changwen Hu



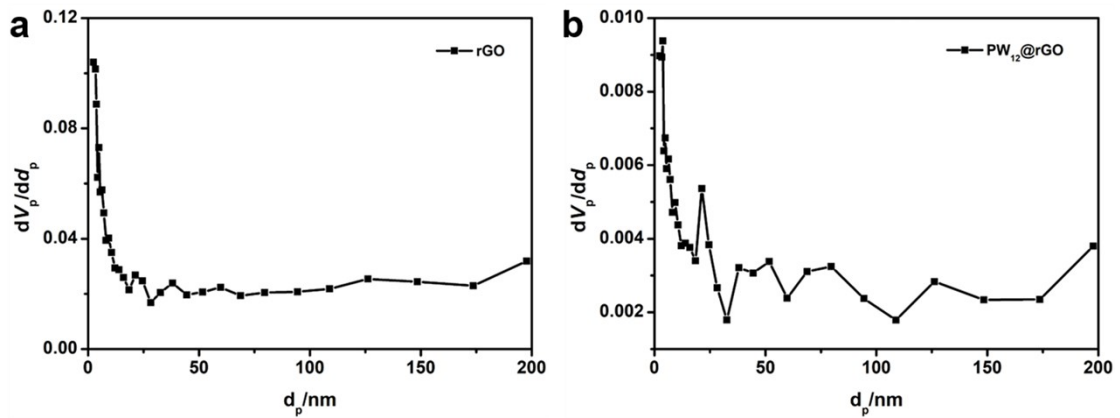
**Figure S1.** The (a) digital photograph and (b) SEM image of  $PW_{12}@rGO$  monolith.



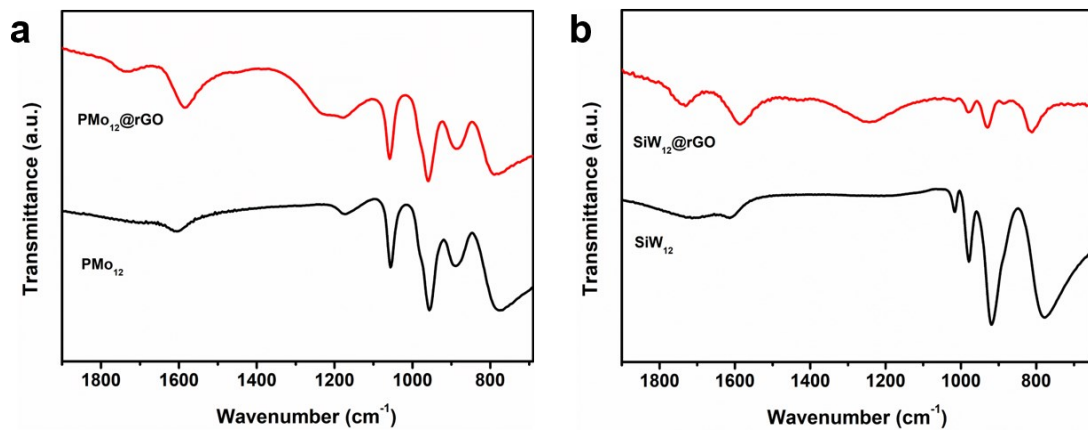
**Figure S2.** Powder XRD patterns of rGO, POMs, and POM@rGO composites.



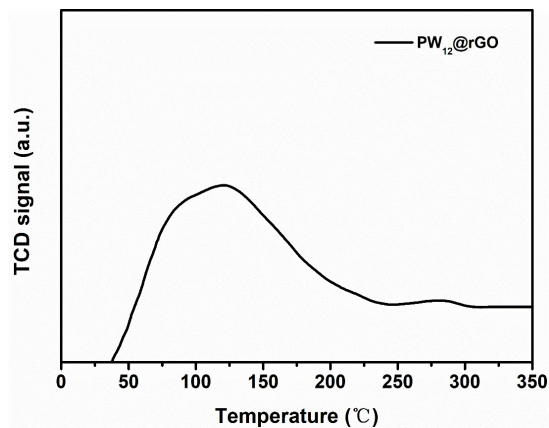
**Figure S3.** EDS spectra of  $\text{PW}_{12}@r\text{GO}$ .



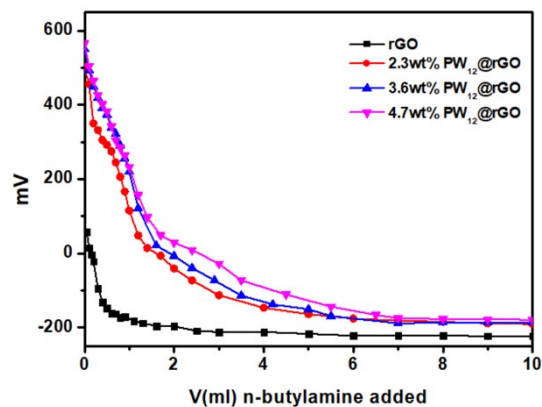
**Figure S4.** Pore size distributions of (a) rGO and (b)  $\text{PW}_{12}@r\text{GO}$  by BJH method desorption branch.



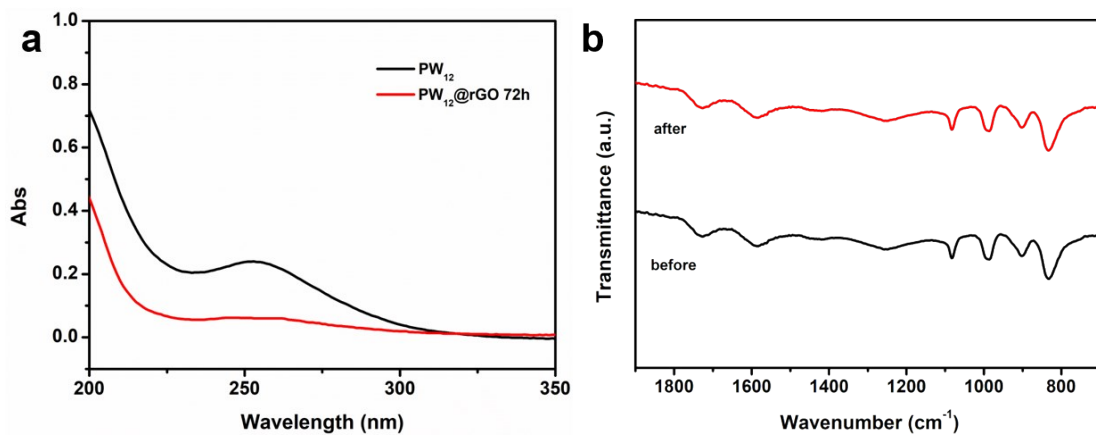
**Figure S5.** FT-IR spectra of  $\text{PMo}_{12}@r\text{GO}$  and  $\text{SiW}_{12}@r\text{GO}$ .



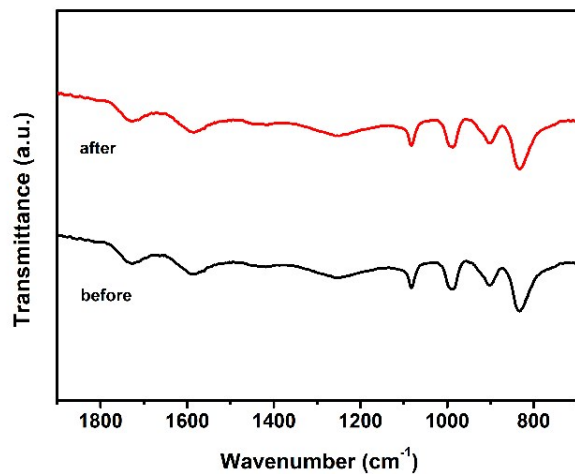
**Figure S6.** NH<sub>3</sub>-TPD for PW<sub>12</sub>@rGO.



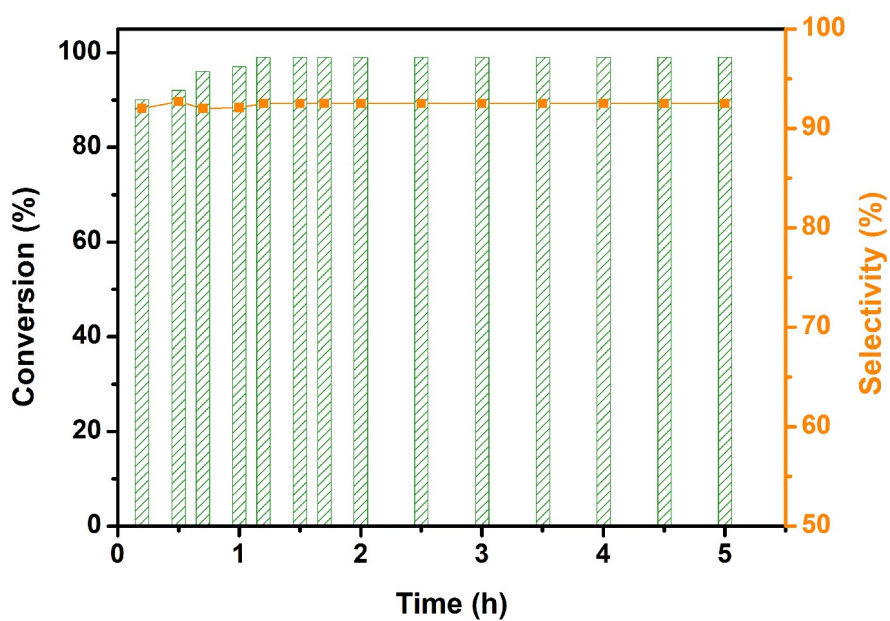
**Figure S7.** Potentiometric titration curves of n-butylamine in acetonitrile for different PW<sub>12</sub>@rGO composites.



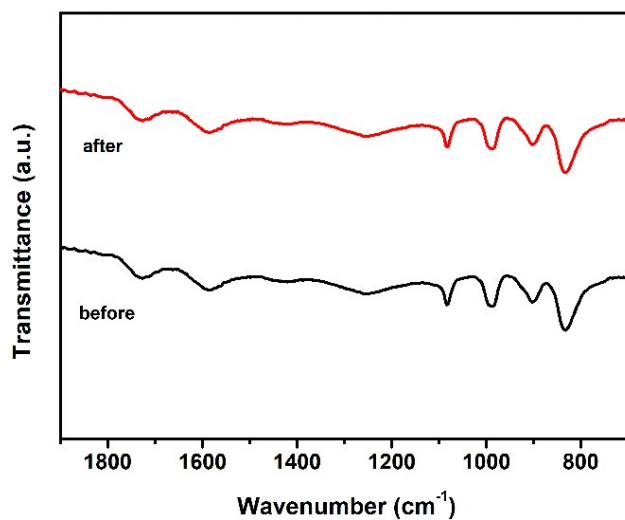
**Figure S8.** (a) Liquid-phase UV-vis spectra from leaching test of PW<sub>12</sub>@rGO immersed in methanol for 72 h. (b) FT-IR spectra of PW<sub>12</sub>@rGO before and after the leaching test.



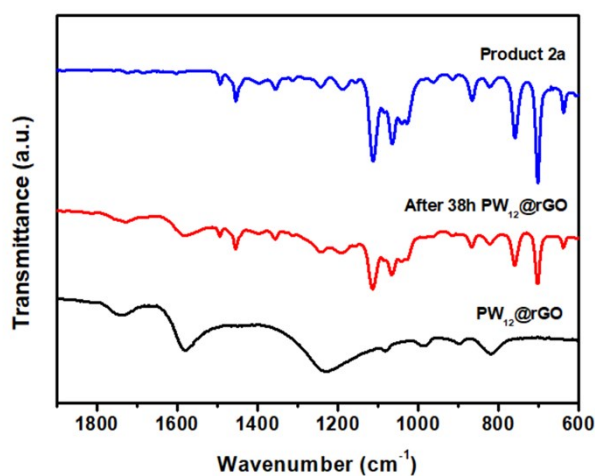
**Figure S9.** FT-IR spectra of recycled and fresh PW<sub>12</sub>@rGO in batch reaction.



**Figure S10.** PW<sub>12</sub>@rGO catalyzed epoxide ring-opening reaction in a continuous flow mode in the first 5 h.



**Figure S11.** FT-IR spectra of  $\text{PW}_{12}@r\text{GO}$  before and after the continuous flow catalysis.



**Figure S12.** FT-IR spectra of fresh  $\text{PW}_{12}@r\text{GO}$ , product 2a, and  $\text{PW}_{12}@r\text{GO}$  after 38 hours' reaction.

**Table S1.** Surface acidities of  $\text{PW}_{12}@r\text{GO}$  determined by potentiometric titration with n-butylamine.

| Sample                             | $E_i$ (mV) | Acid amount (mmol n-butylamine $\text{g}^{-1}$ ) |
|------------------------------------|------------|--|
| rGO                                | 59         | 0.25   |
| 2.3wt% $\text{PW}_{12}@r\text{GO}$ | 499        | 1.48   |
| 3.6wt% $\text{PW}_{12}@r\text{GO}$ | 551        | 1.96   |
| 4.7wt% $\text{PW}_{12}@r\text{GO}$ | 566        | 2.47   |

**Table S2.** Comparison of heterogeneous catalysts for methanolysis of epoxide ring-opening reactions.

| Catalyst                                | mole%<br>catalyst versus<br>styrene oxide | Temp.<br>(°C) | Time<br>(h) | Conv<br>(%) | TOF<br>(h <sup>-1</sup> ) | Ref.      |
|---|---|---------------|-------------|-------------|---------------------------|-----------|
| MIL-101(HPW)                            | 0.7                                       | 40            | 0.33        | 99.8        | 98.5                      | 1         |
| CuO / SiO <sub>2</sub>                  | 0.5                                       | 60            | 8.5         | 97          | 21.9                      | 2         |
| PANF <sub>DTA</sub> @Fe(III)            | 5   | RT            | 1           | >99         | -                         | 3         |
| MIL-101-NH <sub>2</sub> -PC-<br>Ru(III) | 0.1                                       | RT            | 30          | 100         | 2325                      | 4         |
| Co-POM@MIL-101                          | 0.1                                       | RT            | 0.5         | 100         | 1504                      | 5         |
| PW <sub>12</sub> @rGO                   | 0.066                                     | RT            | 0.17        | 99          | 8932                      | This work |

## References

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