

Supplementary Information

A General Approach towards the Efficient Catalysis in Pickering Emulsions Stabilized by Amphiphilic RGO-Silica Hybrid Materials**

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1. The synthesis of SBA-G-x and catalysts preparation

Graphene oxide was prepared according to the modified Hummer's method (*J Am Chem Soc* **1958**, *80*, 1339-1339). Powdered graphite (1 g) and sodium nitrate (0.5 g) were added to a 150 mL flask containing 25 mL conc. sulfuric acid with stirring at 0 °C. Potassium permanganate (3.8 g) was slowly added to the mixture in 2 h and the temperature was carefully controlled below 20 °C. Then the mixture was stirred for another 2 h at 35 °C and turned to dark brown and sticky. Addition of 45 mL water into the mixture was carefully handled and the temperature of the diluted mixture was kept at *ca.* 90 °C. When the mixture was cooled down to 45 °C, it was treated with 3 wt% hydro peroxide solution (30 mL), giving yellow suspension. After centrifugation, the yellow solid was washed with 100 mL water, 100 mL 30 wt% HCl and 100 mL ethanol for two times. Then 100 mL petroleum ether was used to precipitate the yellow solid and the filter cake was dried at 40 °C in vacuum.

To synthesize SBA-G-x, desired amount of 1 wt% GO aqueous solution and Pluronic 123 (P123, Aldrich Co. Ltd.) (4 g) were added to a round bottom flask with 3 wt% HCl (140 mL). After stirring for 2 h, tetraethoxysilane (TEOS) (8.4 g) was added and the mixture was heated to 40 °C with stirring for additional 24 h. Then the mixture was transferred to a Teflon-lined autoclave with hydrazine hydrate (3 mL) and aged at 120 °C for 24 h. After filtration, the resulting solid was calcined at 600 °C under Argon to remove template.

To prepare Pd@SBA-G-5, SBA-G-5 (1 g) was treated with PdCl₂ (84 mg) dissolved in 10 wt% HCl (20 mL). Then the suspension was stirred for 5 h at room temperature. After cooled to 0 °C, excess amount of NaBH₄ aqueous solution was added dropwise to reduce the Pd(II) species and the mixture was stirred for 12 h. After filtration, the catalyst was washed with water and dried under vacuum.

The SBA-G-x supported heteropolyacids (HPAs) were prepared according to the incipient wetness impregnation. SBA-G-x was soaked with HPAs solution and then calcined at 300 °C under Argon. For Cs substituted catalysts, the SBA-G-x was treated with Cs₂CO₃ solution prior to the HPAs solution.

2. Materials characterization

Atomic force microscopy (AFM) analysis of GO was conducted on a Bruker MultiMode 8 Atomic Force Microscope. Elemental analysis of GO with an Elementar Vario EL cube instrument showed 49.14 wt% C, 2.56 wt% H and 48.30 wt% O (by difference).

Nitrogen adsorption/desorption isotherms were measured by a NOVA-2000e analyzer or a Micromeritics ASAP 2020 analyzer at 77 K. The surface area was determined using Barrett-Emmet-Taller (BET) method and the average pore size and pore volume was determined by Barret-Joyner-Halenda (BJH) method.

X-ray powder diffraction (XRD) data were obtained on a JEOL-2010 diffractometer using Cu K α radiation at both small-angle and large-angle.

A Tecnai G220 transmission electron microscope and a Hitachi S-4800 scanning electron microscope were used to record the TEM and SEM images, respectively.

X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB MKII instrument using Al K α source to excite the photoelectrons.

Raman spectroscopies were measured on a Horiba Lador HR800 instrument and FTIR analysis was performed on a Bruker TENSOR 27 FTIR Spectrometer.

Prior to the decalin-water contact angle measurement, sample was compressed into pellet under 10 MPa. The pellet was immersed in decalin in a quartz cell and a water droplet was injected on the surface by a microsyringe. A Zhongchen JC2000D1 contact angle measuring instrument was used to record the images.

3. Catalytic Tests

For the chloromethylation of toluene, desired amount of catalyst, toluene (1.84 g), conc. HCl (10 mL) and paraformaldehyde (0.63 g) were added into a 50 mL three-necked flask. The mixture was vigorously stirred and reacted under HCl gas atmosphere at 80 °C for 8 h. After the reaction, the solid was filtrated and the organic phase was sampled and analyzed on a Shimadzu GC2010 gas-phase chromatography (GC).

The hydrolysis of chloromethyl benzene (1.02 g) was carried out in toluene (5 mL) and water (10 mL) at 83 °C for 8 h. The yield of benzyl alcohol was determined by GC.

The typical procedure for nitrobenzene reduction is that SBA-G-5 (100 mg), nitrobenzene (0.31 g) and Na₂S (0.58 g) were added into a 50 mL flask with 20 mL water-decalin mixture. Then the suspension was heated to 80 °C with stirring. After the reaction, the solid was filtrated and the aqueous phase was extracted with 10 mL decalin for 3 times. Then the decalin phase was analyzed by GC.

To hydrogenate vanillin, vanillin (0.21 g), water (15 mL), decalin (15 mL) and Pd@SBA-G-5 (0.1 g) were added to a 50 mL autoclave. Before heating, the autoclave was purged with H₂ and charged with 1 MPa H₂ at room temperature. Then it was heated to desired temperature with vigorous stirring. After the reaction, both the water and decalin phases were sampled and analyzed by GC. For the oxidative desulfurization, dibenzothiophene (25 mg) was dissolved in decalin (7 mL) and diluted H₂O₂ (0.5 M, 3 mL) was used as oxidant. After addition of catalyst, the mixture was vigorously stirred for 3 h at reaction temperature. Then the aqueous phase was removed and the organic phase was washed with 5 mL water for 3 times. The dibenzothiophene content was measured by a Shimadzu UV-2550 ultraviolet visible spectrophotometer (UV-Vis).

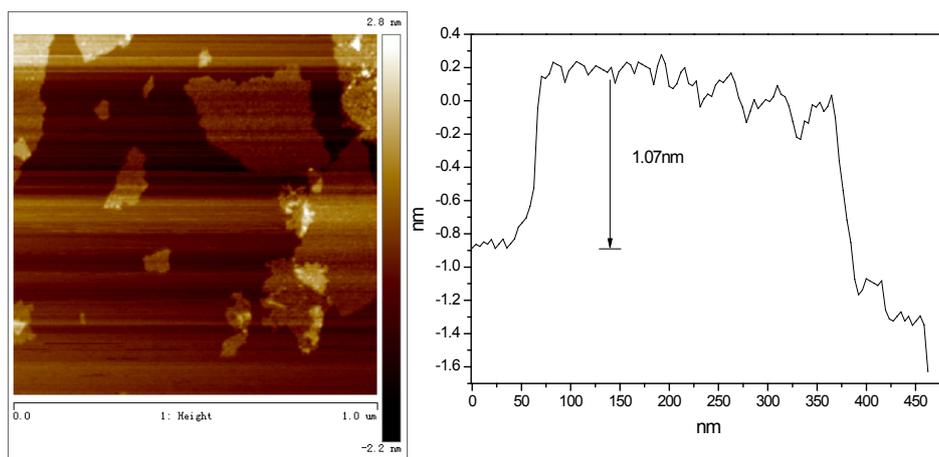


Figure S1. Atomic force microscopy (AFM) of the graphene oxide.

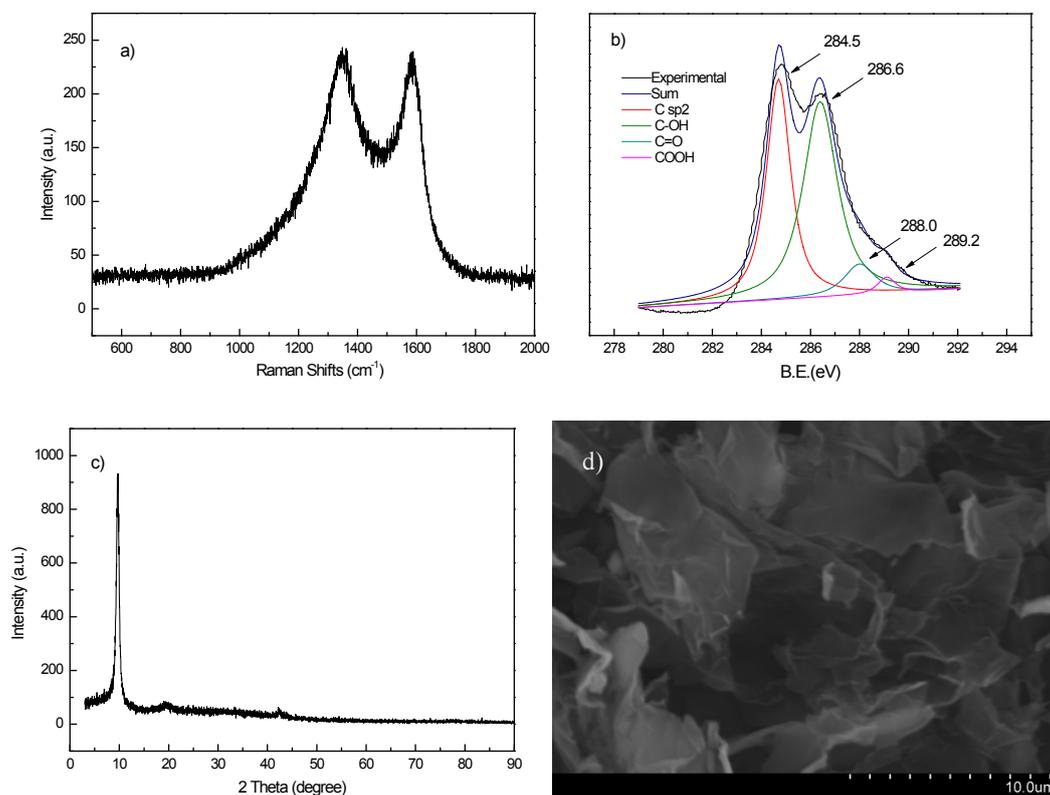


Figure S2. a) Raman spectroscopy, b) XPS, c) XRD and d) SEM image of the graphene oxide.

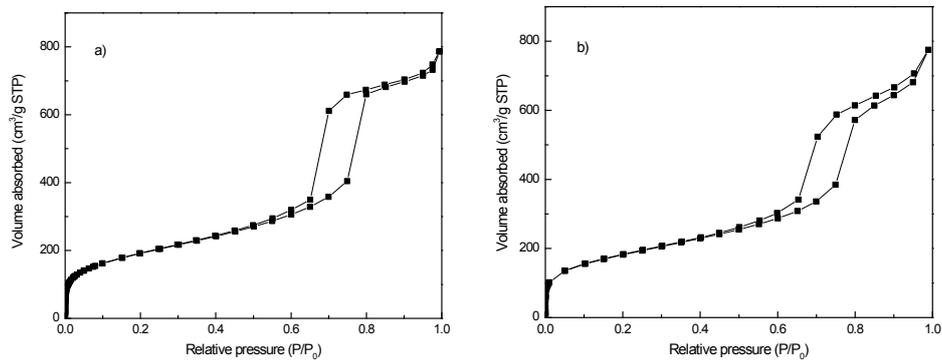


Figure S3. N_2 isothermal adsorption-desorption isotherms of a) SBA-G-1 and b) SBA-G-10.

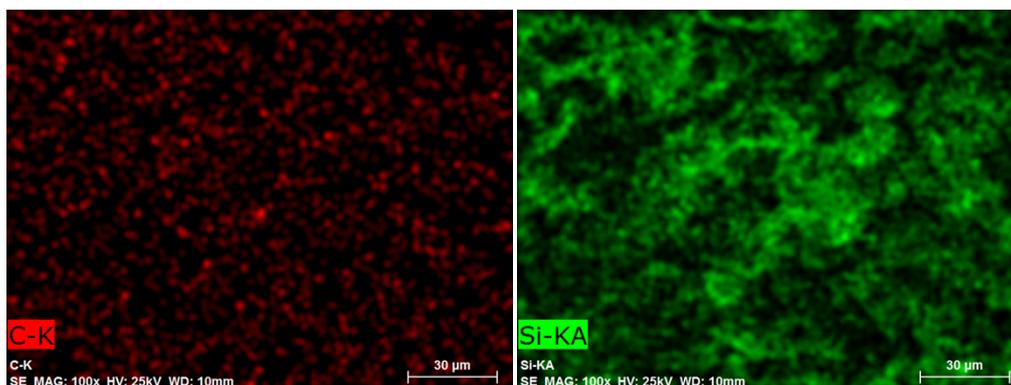


Figure S4. EDS analysis of SBA-G-5.

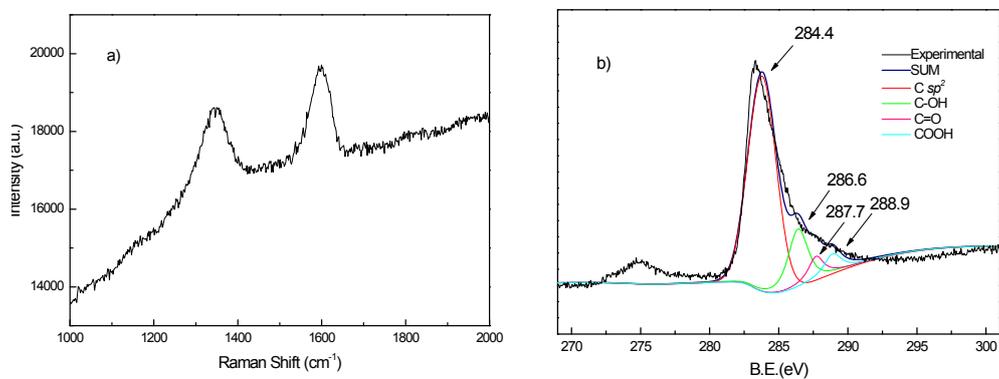


Figure S5. a) Raman spectroscopy and b) XPS of SBA-G-5.

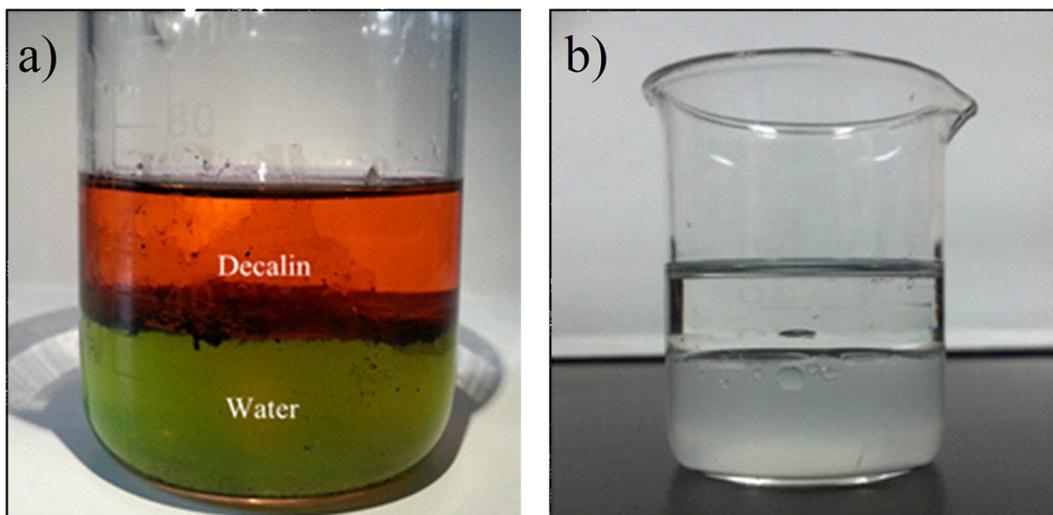


Figure S6. Comparison the behavior of a) SBA-G-5 and b) SBA-15 in the water-decalin biphasic system.

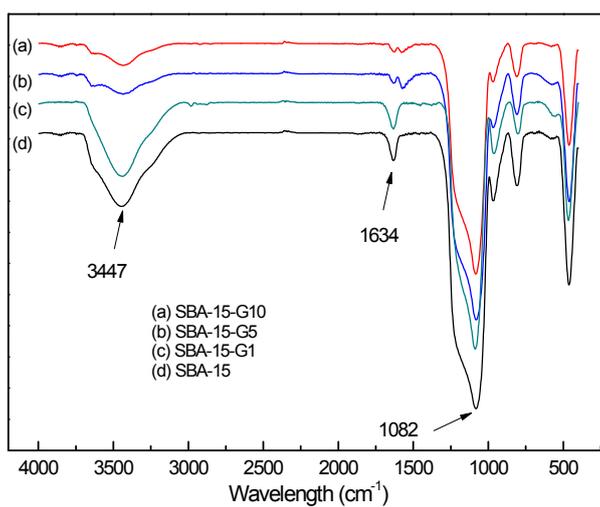


Figure S7. FTIR spectra of SBA-G-x.

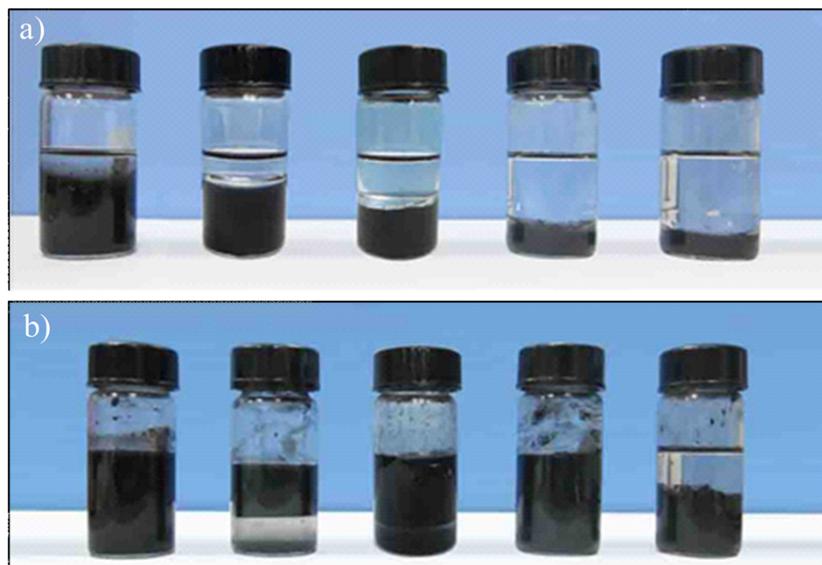


Figure S8. Photos of SBA-G-5 (0.1 g) in water-decalin mixtures a) before and b) after sonication. From left to right: the volume ratios of water to decalin (mL : mL) are 8:2, 6:4, 5:5, 4:6 and 2:8.

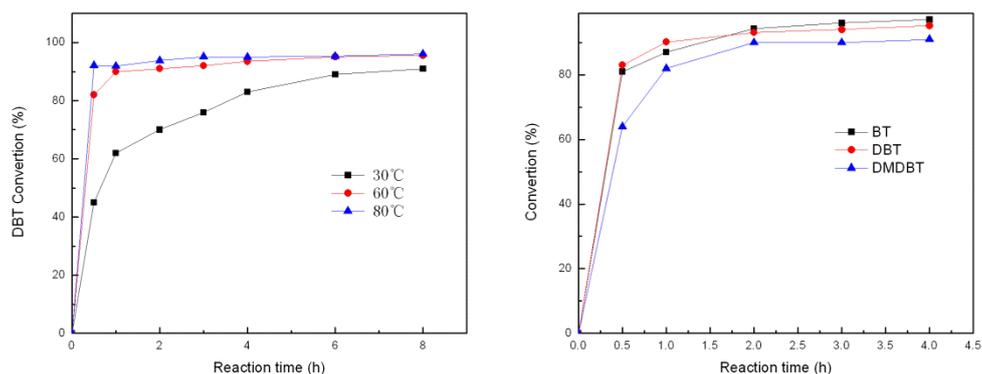


Figure S9. Conversion of thiophenes in the presence of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}@SBA-G-5$ as a function of reaction time.

Reaction condition: thiophenes (0.11 mmol) in decalin (7 mL), H_2O_2 (0.5 M, 3 mL) and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}@SBA-G-5$ (80 mg) (Right: BT: benzothiophene, DBT: dibenzothiophene, DMDBT: 4,6-dimethyldibenzothiophene, reaction temperature: 60 °C)

Table S1. The porous structure of SBA-G-x.

Entr y	Sample	BET surface area (m^2/g)	Pore size (\AA)	Pore volume (cm^3/g)
1	SBA-15-G1	622.873	65.61	1.162
2	SBA-15-G5	582.117	77.07	1.157
3	SBA-15-G10	567.425	66.19	1.138

Table S2. Chloromethylation of toluene.

Entry ^[a]	Emulsifier	Yield of chloromethyl toluene (mol%)	Ratio of <i>m</i> -isomer : <i>p</i> -isomer
1	0.1 g SBA-G-5	98	0.84
2	0.1 g SBA-15	72	0.82
3	5 mg RGO	81	0.84
4	5 mg PEG-1000	85	0.87
5	5 mg OTAC	80	0.86

[a] Reaction condition: toluene (1.84 g) reacted with conc. HCl (10 mL) and paraformaldehyde (0.63 g) at 80 °C with HCl gas bubbling for 8 h.

Table S3. Hydrolysis of chloromethylbenzene.

Entry ^[a]	Emulsifier	Additive	Yield of benzyl alcohol (mol%)
1	0.1 g SBA-G-5		34
2	--		19
3	0.1 g SBA-15		20
4	0.1g SBA-G-5	2 g HCOONa	78
5	--	2 g HCOONa	65
6	0.1 g SBA-15	2 g HCOONa	68

[a] Reaction condition: benzyl chloride (1.02 g) in toluene (5 mL) and water (10 mL) at 83 °C for 8 h.