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# Supporting Information

## Synthesis and Characterization of Titanium(IV)/Graphene Oxide Foam: A Sustainable Catalyst for the Oxidation of Benzyl Alcohol to Benzaldehyde

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## 1. General Information

All reactions were carried out under different conditions in round-bottom flask. All solvents and reactants were directly bought from commercial sources without further purification. General procedure for the oxidation of BnOH: A round-bottom flask equipped with a stir bar was charged with BnOH (720 mg, 6.66 mmol), $Ti(SO_4)_2$/GOF (400 mg). solvent (10 mL) was added at room temperature and stirred for 5 min. $H_2O_2$ was added into the reaction system at reflux temperature. The reaction was monitored by HPLC (monitoring wavelength: 254 nm, mobile phase: water/acetonitrile=4:1, with 0.05% $Et_3N$, Flow rate: 1.0 mL/min, Retention time: Benzoic acid=1.9 min, BnOH=10.1 min, BzH=24.1 min. Specific surface areas (BET) and TGA analysis of $Ti(SO_4)_2$/GOF were determined by $N_2$ physisorption at 77 K using Quantachrome NOVA4000 and Mettler star e STA respectively. SEM, EDS and XRD patterns were obtained by Hitachi S-4700 (HV=25.00 Kv) and Pert PRO MRD. IR spectra were measured by EQUINOX55 (Resolution: 2 $cm^{-1}$, Frequency Range: 4000-400 $cm^{-1}$). $^{13}C$-SSNMR was recorded by 400 MHz Bruker Avance III (direct $^{13}C$ onepulse, ro=4.0 kHz).

## 2. The procedure for the synthesis of $Ti(SO_4)_2$/GOF

GO was synthesized by modified Hummers and Offeman's method. In detail, nature graphite (2 g) was ground with NaCl (80 g) for 30 minutes until the graphite well-dispersed on the surface of NaCl. The mixture was dissolved in the deionized water (DI water) and then filtered and washed by large amount of deionized water. The filter cake was dried overnight at 60 ℃ *in vacuo*. Next, the graphite was put into a mixture of concentrated $H_2SO_4$ (12 mL), $K_2SO_8$(2.5 g) and $P_2O_5$(2.5 g). The solution was stirred at 80 ℃ for 24 h. Then the mixture was slowly diluted with 250 mL DI water, filtered, and washed with DI water until the filtrate displayed neutral. The filter cake was dried overnight at 60 ℃ *in vacuo*. The pre-oxidized graphite was then stirred in concentrated $H_2SO_4$ (46 mL) under vigorous stirring for 24 h. And then $NaNO_3$ (1.0 g) was added, 5 minutes later, $KMnO_4$ (10 g) was slowly added into the mixture while keeping the temperature < 20 °C. The mixture was then kept in an oil-bath of 35 ± 5 °C for 30 minutes. 30 minutes later, DI water (6 mL) was gradually added to the solution while keeping the temperature < 40 °C. 5 minutes later, DI water (6 mL) was gradually added again.

Another 5 minutes later, DI water (80 mL) was slowly added into the mixture. When water adding finished, the mixture was transferred into an oil-bath of 90 ± 5 °C and kept for 15 minutes. 15 minutes later, DI water (280 mL) was added. Finally, $H_2O_2$ (20 mL) was added to quench the excess $KMnO_4$. After the oxidation process, the mixture was filtered and washed with 5 wt% HCl for three times followed by large amounts of DI water until the pH of rinse water was close to neutral. The final sediment was re-dispersed in DI water and underwent sonication to get the exfoliated graphene oxide (GO). The exfoliated graphene oxide (GO) was then dried at 30 °C *in vacuo*. As-synthesized 400 mg GO was dispersed in 800 mL $Ti(SO_4)_2$ aqueous solution ($4\times10^{-3}$ mol/L) and put under ultrasonic irradiation for 1 hour followed by freeze drying lead to $Ti(SO_4)_2$/GOF.

**Figure S1. $Ti(SO_4)_2$/GOF**

### 3. Large-scaled synthesis of BzH under solvent-free condition

50 mL BnOH and 1.0 g $Ti(SO_4)_2$/GOF were added into 500 mL three-neck flask, the reaction mixture was heated to 70℃. 165 mL $H_2O_2$ (30wt%) was added into the reaction dropwise. The reaction mixture was stirred at 70℃ for 10 h. Then the reaction mixture was cooled into room temperature and an aqueous solution of $Na_2S_2O_3$ (1%) was added to quench the residual $H_2O_2$. The reaction mixture was distilled *in vacuo* to collect the colorless distillate as BzH (Pa =$2.6\times10^3$, Temperature=75 ℃). After the completion of distillation, a certain amount of DCM was added into the viscous liquid, which was filtered to remove the catalyst followed by distillation of the filtrate with aforementioned

conditions. Totally 40 mL BzH was obtained after twice distillation.

**4. Recycling tests of $Ti(SO_4)_2$/GOF**

The oxidation was carried out under identical reaction conditions as described in the general procedure for the oxidation of BnOH. After the completion of each run, the reaction mixture was allowed to reach room tempeture and was filtrated. The remaining solid was washed by $CH_2Cl_2$ (3×20 mL), dried and reused in the following run.

**Table S1. Recycling tests of $Ti(SO_4)_2$/GOF for oxidation of BnOH[a]**

| Circle number | Conversion (%) | Selectivity (%) |
|---|---|---|
| 1 | 90.1 | 98.8 |
| 2 | 91.0 | 98.9 |
| 3 | 90.7 | 99.2 |
| 4 | 91.8 | 98.9 |
| 5 | 90.4 | 99.2 |
| 6 | 91.9 | 98.6 |
| 7 | 90.6 | 98.1 |
| 8 | 91.7 | 98.7 |
| 9 | 90.1 | 98.6 |
| 10 | 90.7 | 98.7 |

[a]reaction conditions: BnOH (720 mg, 6.66 mmol), $Ti(SO_4)_2$/GOF (400 mg), THF (10 mL) and 30wt% $H_2O_2$ (0.82 mL, 8.0 mmol) under reflux condition.

## 4. SEM spectroscopy of recycled 10 times of $Ti(SO_4)_2$/GOF for the oxidation