Supporting Information

Covalently-grafted Polyethyleneimine on Hydroxylated Three-dimensional Graphene for Superior CO₂ Capture

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**Preparation of MCM-41.** The conventional MCM-41 was hydrothermally synthesized at 100 °C for 40 h using Cab-O-Sil fumed silica as the silica source, 25% solution of tetramethylammonium hydroxide in water (TMAOH) for pH adjustment, and cetyltrimethylammonium bromide (CTAB) as the surfactant template. The molar composition of the mixture was: 1.0 SiO$_2$ : 0.32 TMAOH : 0.45 CTAB : 67 H$_2$O. After the synthesis, the solid product was recovered by filtration, washed several times with deionized water, dried at 100 °C overnight, and calcined at 550 °C for 5 h to remove the template.

**Preparation of PEI-Impregnated MCM-41-PEI (MCM-41-PEI 70K and MCM-41-PEI 600).** The desired amount of PEI (either high molecular weight ~70000 or low molecular weight ~600) was dissolved in methanol and stirred for 30 minutes. Subsequently, 0.5 gram of MCM-41 was added and stirred for an additional 60 minutes. The methanol was removed under vacuum. The resulting MCM-41-PEI was dried overnight at 60 °C.

**Preparation of chemically tethered MCM-41-PEI (MCM-41-PEI-CT).** Typically, 990 mg of aziridine was added to a suspension of 0.5g dried MCM-41 in toluene. Approximately 120 mg of glacial acetic acid was added to the suspension to catalyze the surface polymerization. The mixture was vigorously stirred at RT for 48 h in a sealed vessel. After completion, the powder was filtered and washed with toluene and finally dried in vacuum.
Fig. S1 TEM image of HG.
Fig. S2 EDS carbon mapping (a) and oxygen mapping (b) of HG.
Fig. S3  SEM image of HG-PEI-0.51.
Fig. S4 Full survey XPS spectrum of HG and HG-PEI-0.51.
Fig. S5 XRD patterns of HG before and after the polymerization of PEI.
Fig. S6 Nitrogen adsorption/desorption isotherms of HG and HG-based adsorbents.
Fig. S7 Pore size distribution calculated from the desorption branch for HG and HG-based adsorbents.
Fig. S8 TGA thermograms of HG, HG-based adsorbents, and commercial PEI.
Fig. S9 TEM image of HG-PEI-0.51.
Fig. S10 CO₂ adsorption isotherms measured at 25 °C / 0-7 atm.
Fig. S11  DSC heatflow profiles during adsorption process of the HG-PEI adsorbents. The adsorption temperature is 25 °C.
Fig. S12  (a) CO$_2$ capture kinetics of HG-PEI adsorbents in 10% CO$_2$ at 25 °C. (b) Adsorption halftimes of the HG-PEI adsorbents in 10% CO$_2$ at operating temperatures of 25, 50, and 75 °C.
Fig. S13  The CO$_2$ adsorption/desorption profile of HG-PEI-1.98. Experimental conditions: adsorption at 25 °C for 60 min in 10% CO$_2$ and desorption at 100 °C for 60 min in 100% argon.
Fig. S14  Powder X-ray diffraction pattern of MCM-41.
Fig. S15  Nitrogen adsorption/desorption isotherms of MCM-41 and MCM-41-based adsorbents.
Fig. S16 Pore size distribution calculated from the desorption branch for MCM-41 and MCM-41-based adsorbents.

References