

One-step Hydrothermal Amino-grafting of Graphene Oxide as an Efficient Solid Base Catalyst

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1 Experimental Details

1.1 Catalyst preparation

Graphite powder (99.9999 % metals basis), 30 % H₂O₂, 30 % methylamine, 70 % ethylamine, propylamine (99.9 %), n-butylamine (99.9 %), benzaldehyde (99.9 %), nitromethane (99.9 %), and methylacrylate (99.9 %) were purchased from Alfa Aesar.

Graphite oxide was synthesized from graphite based on the method developed by Hummers and co-workers with some modifications. In a typical process, 69 mL concentrated H₂SO₄ was added to a mixture of 3 g graphite and 1.5 g NaNO₃, cooled to 273 K and stirred for 30 min. Then, 9 g KMnO₄ was slowly added with vigorous stirring to keep the reaction temperature below 293 K. The system was heated to 308 K and stirred for 4 hours before the addition of 138 mL deionized water. The suspension was maintained at 370 K for 30 min and diluted with 20 mL deionized water and 10 mL 30% H₂O₂. The suspension was filtered and washed successively with 200 mL of 30 % HCl and 200 mL of ethanol for 5 times. The filter cake was dispersed in deionized water and centrifuged at 4000 rpm for several times until the pH value was higher than 4. The filter residue was vacuum-dried overnight at room temperature and graphite oxide was obtained.

Graphite oxide was exfoliated into graphene oxide (GO) by ultrasonication in aqueous mediate. To obtain amine-functionalized GO, 0.5 g GO was redispersed in 100 mL 1.5 M aqueous solution of amine (methylamine, ethylamine, propylamine or butylamine) by ultrasonication for 1 h in a sealed container. The homogeneous suspension was transferred to a Teflon-lined autoclave and subjected to hydrothermal treatment at different temperatures for 3 days. A black cylinder was obtained and subjected to

vacuum freeze drying. The product was vacuum-dried at 353 K for 12 h and amine-functionalized GO was obtained. The amine-functionalized GO materials were labeled as MAGO (methylamine functionalized GO), EAGO (ethylamine functionalized GO), PAGO (propylamine functionalized GO) and BAGO (butylamine functionalized GO), respectively, based on the specific amine employed.

1.2 Sample characterization

Nitrogen adsorption/desorption of the samples were measured at 77 K on Quantachrome iQ-MP gas absorption analyzer after outgassing at 473K under vacuum for 12 h. The specific surface area was calculated with the Brunauer-Emmett-Teller (BET) equation.

CHN element analysis of samples was performed on an Elementar vario EL CUBE analyzer.

Atomic force microscopy (AFM) images were recorded on a Veeco Nanoscope IV with a silicon cantilever by using the tapping mode. For AFM measurement, the diluted colloidal suspension (0.01 mg mL^{-1}) was sprayed onto a freshly cleaved mica surface and then dried in air for 1 h.

Transmission electron microscopy (TEM) images were taken on a Philips Tecnai G² 20 S-TWIN electron microscope at an acceleration voltage of 200 kV. A few drops of alcohol suspension containing the sample were placed on a copper grid, followed by evaporation at ambient temperature.

Raman spectra of samples were recorded on a Renishaw InVia Raman spectrometer with the green line of an Ar-ion laser (514.5 nm) in micro-Raman configuration.

X-ray photoelectron (XP) spectra of the samples were recorded on a Kratos Axis Ultra DLD spectrometer with a monochromated Al-K α X-ray source ($h\nu = 1486.6 \text{ eV}$), hybrid (magnetic/electrostatic) optics and a multi-channel plate and delay line detector (DLD). The high-resolution spectra were recorded with pass energy of 40 eV using an aperture slot of $300 \times 700 \mu$. Accurate binding energies ($\pm 0.1 \text{ eV}$) were determined with respect to the position of the adventitious C 1s peak at 284.8 eV.

Thermogravimetric (TG) analysis of the samples was performed on TA SDT-Q600 thermogravimetric analyzer. In a typical measurement, 0.05 g of the sample was heated

in an Al₂O₃ crucible with a constant heating rate of 5 K min⁻¹ and under He purging using a flow rate of 20 mL min⁻¹. The products from TG were synchronously analysed by a Pfeiffer Omni Star TM GSD320 mass spectrometer (MS).

The basicity of amino-functionalized GO, expressed as H value, was determined by using Hammett indicator method. The basicity is quoted as being stronger than the weakest indicator with a color change, but weaker than the strongest indicator without a color change. In a typical experiment, the mixture of 50 mg sample and 3 mL Hammett indicator was sealed in a bottle and purged with Ar. For comparison, the Hammett indicator itself was also sealed in a bottle and purged with Ar. Then the sealed bottles were kept at constant temperature of 298 K for up to 9 days to reach equilibrium when no further color changes could be observed. The following Hammett indicators were used: 4-nitroaniline (H value =18), aniline (H value =27), triphenylmethane (benzene as solvent, H value =33), isopropyl benzene (H value =37) and dimethylbenzene (H value =39).

Solid superbases are defined for substances that possess basic sites with strength stronger than H = 26 (H corresponding to the pK_a value of the indicator).^{S1}

[S1] K. Tanabe, M. Misono, Y. Ono and H. Hattori, *New Solid Acids and Bases*, Kodansha-Elsevier, Tokyo, 1989, p. 3

1.3 Catalytic evaluation

All catalytic reactions were carried out in a flask immersed in oil bath with a water-cooled condenser under argon protection. No solvent was used for all reactions and the products were identified by mass spectrometry (Shimadzu GCMS-QP2010SE, with a 20 m DB-5 capillary column) and quantitatively analyzed by gas chromatography (Shimadzu GC-2010 Plus, flame ionization detector, He carrier and 60 m DB-5 capillary column).

Knoevenagel condensation reaction: 6 mmol benzaldehyde, 20 mg catalyst and 9 mmol malononitrile or diethyl malonate were added in turn into a 25 mL round bottom flask. The mixture was heated to 353 K under stirring. The progress of the reaction was monitored by periodically withdrawing 0.2 µL of liquid samples with a filtering syringe.

Michael addition reaction: 20 mg catalyst was added into 12 mmol nitromethane and stirred for 30 min. Then 6 mmol methylacrylate was added dropwise. The mixture was heated to 323 K under stirring. The progress of the reaction was monitored by periodically withdrawing 0.2 μL of liquid samples with a filtering syringe.

Transesterification reactions: 0.2 mol glycol and 0.2 g catalyst were mixed in the flask and heated to 413 K. After stirring 30 min, 0.04 mol methyl benzoate was rapidly added into the reactor. The progress of the reaction was monitored by periodically withdrawing 0.5 μL of liquid samples with a filtering syringe.

2. Supporting Figures

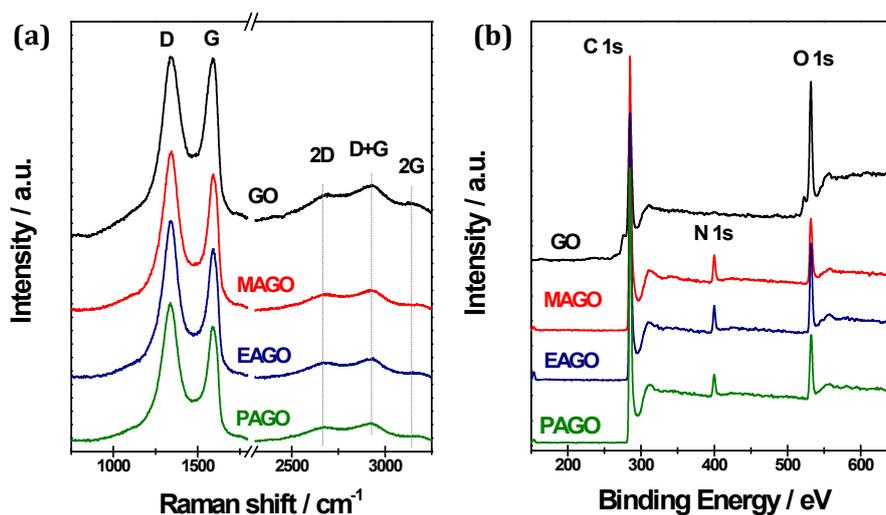


Figure S1 Raman (a) and survey XP spectra (b) of GO and amine-grafted GO

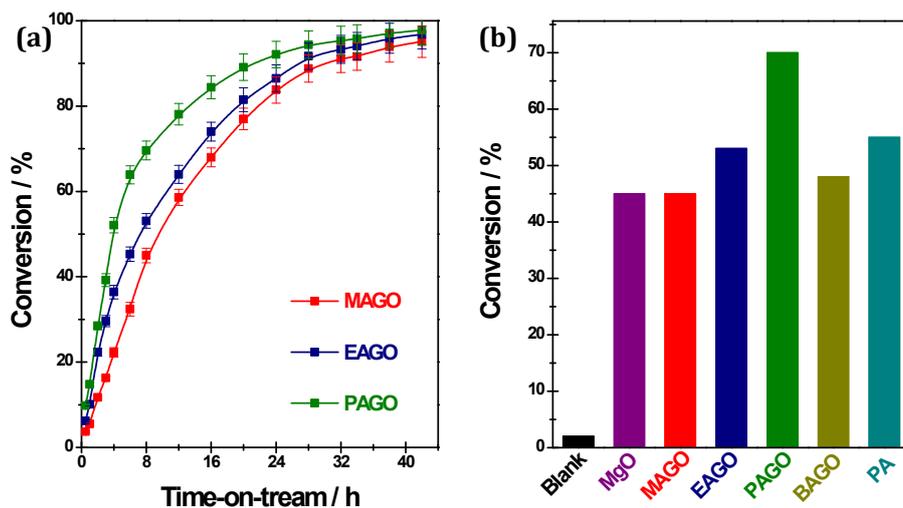


Figure S2 Time-on-stream (TOS) profile of transesterification over amine-functionalized GO (a) and the comparison of conversion after reaction for 8 h (b)

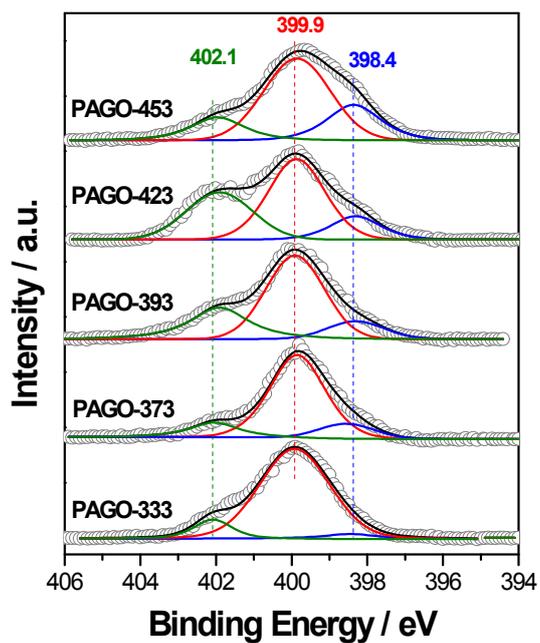


Figure S3 High-resolution N1s XP spectra of PAGO synthesized at different temperatures