Electronic Supplementary Information

Selective surface functionalization at regions of high local curvature in graphene

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Synthesis and Transfer of Graphene. Large-area, high-quality graphene monolayers were synthesized using the CVD method reported previously (*Science*, 2009, **324**, 1312) and transferred to 10 different substrates (*Nano Lett.*, 2009, **9**, 4359). In a typical process, a solution of PMMA in chlorobenzene (350 kDa, 46 mg/mL) was spin-coated on the surface of graphene. Then, after the Cu substrate was completely dissolved in (NH₄)₂S₂O₈ aqueous solution (0.5 M), the PMMA-graphene material was transferred to the surface of a Si substrate (280-nm thick SiO₂ layer) or onto the same type of Si substrate decorated with SiO₂ nanoparticles of ~50 nm diameter. The PMMA-graphene-Si 15 samples were dried in air for 30 min and then under vacuum (10⁻² Torr) for 30 min to remove residual water. Finally, the PMMA was removed for each type of sample using acetone.

Chemical Treatment of Graphene. In a typical process, graphene on the Si wafer substrate was immersed into an acetonitrile solution of 4-nitrophenyl diazonium tetrafluoroborate at known concentrations and for known periods of times. The chemical reaction between graphene and this 20 diazonium salt was carried out at room temperature in the dark and in a glove box (Ar atmosphere). Afterward, the sample was washed with acetonitrile several times and dried.

Microscopy and Spectroscopy. All substrates supported with graphene were characterized via optical microscopy (Zeiss Axioskop), scanning-transmission electron microscopy (Hitachi S-5500), and micro-Raman spectroscopy (WITEC Alpha 300, λ=488 nm, 100× objective lens). The elemental 25 analysis (C, N, B, F) and chemical bonding analysis of graphene was conducted using a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer.

Density Functional Theory (DFT) Calculations. The calculations were performed for large supercells (128 carbon atoms) that provided a proper separation of the ripples. All technical details of the calculations may be found in the following reference: *J. Phys. Chem.* C 2009, **113**, 14176-14178.

The pyramidization angle calculations were performed using the method described in *J. Phys. Chem. A* 2001, **105**, 4164-4165. The calculations demonstrate that increasing the pyramidization angle (i.e., increasing the curvature of the ripples) increases binding energies and decreases the covalent bond formation energy (Fig. S3b). The changes in the total energy of graphene under the formation of small 5 ripples were comparable with the strain energy above 5% (see *ChemPhysChem* 2012, **13**, 1463–1469). The value of the binding energies for a pair of nitrophenyl groups to flat graphene was about 2.5 eV, which is comparable to that calculated for hydrogen (to form graphane from graphene). Increasing the pyramidization angles lead to increased binding energies such that the values were comparable to the calculated values of the vacancy formation in flat graphene (about 7 eV). Estimated temperature 10 required for the desorption of nitrophenyl groups from the top of the ripples was > 1000 K.



Figure S1. Raman maps of the D/G ratio of graphene on a Si substrate (a) before and (b) after treatment with 10 mg/mL of the diazonium salt in acetonitrile for 60 min.



15 Figure S2. Raman maps of the D/G ratio of graphene on a Si substrate decorated with SiO₂ nanoparticles (a) before and (b) after treatment with 10 mg/mL of the diazonium salt in acetonitrile for 60 min.

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Figure S3. (a) Calculated pyramidization angles (solid red line) and total energy per carbon atom of pure graphene as function of the height (h)/radii (R) ratio of the ripples. (b) Binding energy for a pair of p-nitrophenyl groups as a function of the pyramidization angle. The bond formation energy of the p-5 nitrophenyl groups to flat graphene was set to zero. The structure shown in the inset reflects the optimized atomic structures of the p-nitrophenyl groups on the ripple with h/R = 0.15.

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