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Highly efficient nanoporous graphitic carbon with tunable textural properties for dye-sensitized solar cells

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S1: Fabrication of dye-sensitized solar cell

A nanocrystalline TiO₂ photoelectrodes of 20 μ m thickness (area: 0.25 cm²) was prepared by screen-printing on conducting glass as previously described. The films were further treated with 0.05 M TiCl₄ and 0.1 M HCl aqueous solutions before examination. Coating of the TiO₂ film was carried out by immersing for 45 h in a sensitizer solution (N719) of 3 × 10⁻⁴ M acetonitrile/*tert*-butyl alcohol (1/1, ν/ν) solution. Deoxychloric acid (20 mM) was added to the dye solution as a co-adsorbent to prevent aggregation of dye molecules. Photovoltaic measurements were performed in a two-electrode sandwich cell configuration. The dye-deposited TiO₂ film and a nanoporous graphitic carbon (NGC) on conductive glass were used as the working electrode and the counter electrode respectively. The two electrodes were separated by a surlyn spacer (40 μ m) and sealed by heating the polymer frame. The electrolyte was composed of 0.6 M dimethylpropyl-imidazolium iodide (DMPII), 0.05 M I₂, TBP 0.5 M and 0.1 M LiI in acetonitrile.

S2: Preparation of mesoporous carbon

Large pore mesoporous carbon was synthesized by pyrolysis of sucrose inside the mesoporous silica. In a typical synthesis of mesoporous carbon, 1 g of SBA-15 silica template was added to a solution obtained by dissolving 1.2 g of sucrose and 5.0 g of water, and keeping the mixture in an oven for 6 h at 100 °C. Subsequently, the oven temperature

was raised to 160 °C for another 6h. In order to obtain fully polymerized and carbonized sucrose inside the pores of silica template, 0.9 g of sucrose, 0.08 g of H₂SO₄ and 5.0 g of water were again added to the pretreated sample and the mixture was again subjected to thermal treatment described above. Carbonization was performed at 900 °C for 5 h under N₂-atmosphere. The resulting carbon/silica composite was treated with HF acid (5 wt %) at room temperature to selective removal of silica. The obtained mesoporous carbon is denoted as LPC.

S3: Techniques of characterization

Nitrogen adsorption-desorption isotherms of NGC materials synthesized at different pyrolysis temperature were measured at 77 K on a Quantachrome Autosorb 1 volumetric analyzer and at relative pressure up to ~0.99. Prior to the nitrogen sorption analysis, all the materials were out gassed for 10 h at 513 K to remove moisture and gasses adsorbed on solid surface. The external specific surface area was calculated from BET method and mean pore sized from adsorption-desorption branch of the isotherm was obtained by BJH method. Powder XRD patternS of the NGC material were measured using Cu $k_{\alpha 1}$ radiation with Rigaku RINT-2000 x-ray diffractometer. The HR-TEM mapping of NGC material was obtained on JEOL JEM-2100F after dispersing the ethanolic solution of the material onto a carbon coated copper grid.

S4: HR-TEM images of NGC-1000-5



(a) Graphitic pore channels and (b) graphitic layers





S6: XPS spectra of NGC materials



(a) NGC-1000-5, (b) NGC-800-5 and (c) NGC-800-2

The deconvoluted C1s X-ray Photo Emission Spectroscopy (XPS) of NGC materials manifest three curves with binding energy centered at 284.6, 285.8, and 287.6 eV, which indicate the presence of three chemically different carbons. The lowest energy of the peak at 284.6 eV can be assigned to C-C bond of sp² graphitic carbon, whereas the peaks centered at 285.8 eV and 287.6 eV are corresponds to C-O and C=O bonds respectively. As shown in the figures, the peak intensity of C-C bond for NGC-1000-5 material significantly increases compare to the materials of NGC-800-5 and NGC-800-2. The above results demonstrate that the increase in pyrolysis temperature from 800 to 1000 °C reflect an increase in the content of C-C bonds of graphitic carbon. The changes in graphitic nature of NGC materials are also reflected strongly in their XRD pattern and Raman spectra.