Supporting Information

Carbonaceous two-dimensional lattice with FeN_4 units

Jun Maruyama,[a,*] Taiji Amano,[b] Satoshi Inoue,[b] Yasuji Muramatsu,[b] Noriko Yoshizawa,[c] Eric. M. Gullikson[d]

[a]*Research Division of Environmental Technology, Osaka Research Institute of Industrial Science and Technology, 1-6-50, Morinomiya, Joto-ku, 536-8553 Osaka, Japan,* [b]*Graduate School of Engineering, University of Hyogo, 2167, Shosha, Himeji, Hyogo 671-2280, Japan,* [c]*Department of Energy and Environment, National Institute of Advanced Industrial Science and Technology, 16-1, Onoga-wa, Tsukuba 305-8569, Japan,* [d]*Center for X-ray Optics, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, United States of America*

Experimental

Materials

Iron phthalocyanine (FePc) was purchased from Tokyo Kasei and used as received. High-purity water was obtained by circulating ion-exchanged water through an Easypure water-purification system (Barnstead, D7403). Potassium hydroxide (99.99%, Alfa Aesar) was dissolved in the high-purity water to prepare 1 mol dm^{-3} KOH. The basal plane of the highly-oriented pyrolytic graphite (HOPG, NT-MDT, ZYB and ZYH grade) was carefully cleaved by adhesive tape and used as a substrate. The area was 12 × 12 mm and the thickness was about 1 mm. A commercially-available grid for transmission electron microscopy (TEM) with graphene supported on porous Si_3N_4 (EMJapan) was also used as a substrate.

Formation of carbonaceous thin film with a thickness around 70 nm from FePc

An aliquot of 1 g of the FePc powder was put inside of a 15-cm^3 crucible with a cap. The HOPG substrate was placed on the FePc powder with an alumina plate placed between them to avoid their direct contact. The alumina plate (13 × 13 × 1 mm) was cleaned by soaking in a 1:1 mixture of concentrated HNO_3 and H_2SO_4, followed by soaking in boiling high-purity water and drying before use. The crucible containing the substrate and the alumina plate on FePc was placed inside of a furnace and heat-treated at atmospheric pressure in an Ar atmosphere at T ºC (T = 600, 700, and 800) for 1 h after raising the temperature at 5 ºC min^{-1}. The sample obtained at T ºC was labeled FePc-T. The thickness was measured using an atomic force microscope (AFM, Nanopics, Seiko Instrument) with a Si cantilever in the DFM mode.

Formation of carbonaceous 2-dimensional lattice from FePc

The amount of FePc put in the crucible was reduced to 1 mg to form the 2-dimensional lattice and the substrate was HOPG or the graphene TEM grid. The heat treatment temperature was 800 ºC. The samples obtained using HOPG and the grid were labeled FePc-800-sm-HOPG and FePc-800-sm-graphene, respectively. A schematic diagram for the formation of the carbonaceous thin film and 2-dimensional lattice are shown in Fig. S1.

XANES measurements

The X-ray absorption near-edge structure (XANES) in the C *K* and N *K* regions was measured using synchrotron radiation (SR) at the beamline of BL-6.3.2[S1] of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The energy resolutions ($E/\Delta E$) of the XANES measurements were 5000 using a 1200 lines/mm grating and a 40 μm slit. All the powder samples were placed on an indium sheet of the sample holder in the vacuum measurement chamber. The sample photocurrent induced by the SR irradiation was them monitored during the SR photon energy scanning, which provided the total-electron-yield (TEY) XANES.[S2,S3]

DFT calculations

The XANES profiles were theoretically simulated by the first-principles calculation code, CASTEP.[S4] An individual molecular model was placed in a sufficiently large super cell. After structure optimization by the Material Studio code, calculations in the ground state were achieved in CASTEP. Calculations in an excited state with a $1s^{-1}$ core hole were then performed for each atom. The transition energy of the calculated XANES was corrected by considering the energy differences at the valence and core levels in the ground and excited states.[S5]

Characterization of 2-dimensional carbonaceous lattice

A transmission electron microscope (TEM) image was obtained using a JEM-2100IM (JEOL) at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out using a PHI ESCA 5700 system (Physical Electronics) with Al Kα radiation (1486.6 eV).

Electrochemical measurement

The surface of FePc-800-sm-HOPG was masked using an adhesive tape made of polytetrafluoroethylene (PTFE) with a 6 mm diameter hole to expose the surface of 0.283 cm^2 functioning as the working electrode. The measurement of the current-potential relationships was performed at 25 ºC using an electrochemical analyzer (BAS, 100B/W) and a three-electrode perfluoroalkoxy alkane (PFA) cell. The PFA cell was cleaned by soaking in a 1:1 mixture of concentrated HNO_3 and H_2SO_4, followed by soaking in boiling high-purity water. The electrolyte was Ar or O_2-saturated 1 mol dm^{-3} KOH, the counter electrode was a Pt wire, and the reference electrode was Hg/HgO/1 mol dm^{-3} KOH.

References

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Formation of carbonaceous thin film and 2-dimensional lattice

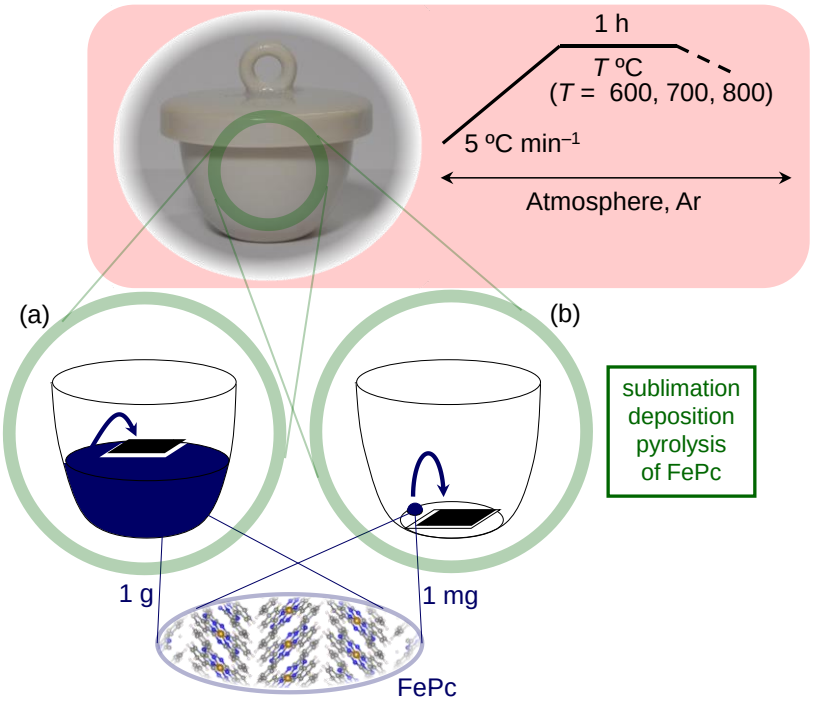

Fig. S1. Schematic diagram for formation of (a) carbonaceous thin film and (b) 2-dimensional lattice.

Structure models

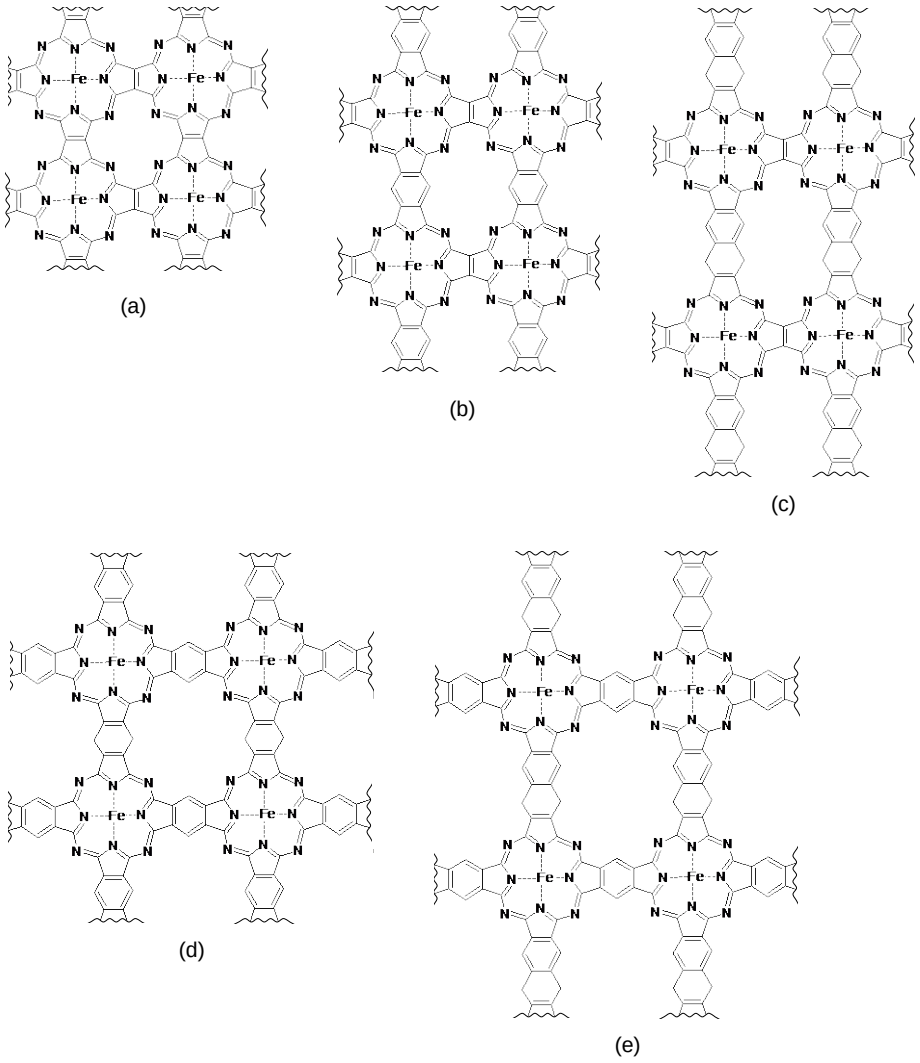

Fig. S2. Potential structures of carbonaceous two-dimensional lattice based on N *K*-XANES and DFT calculations. Theoretical weight losses during the pyrolysis (%) are: a, 45.1; b, 36.3; c, 23.2; d, 27.5; e, 14.4.

DFT calculation for C *K*-XANES

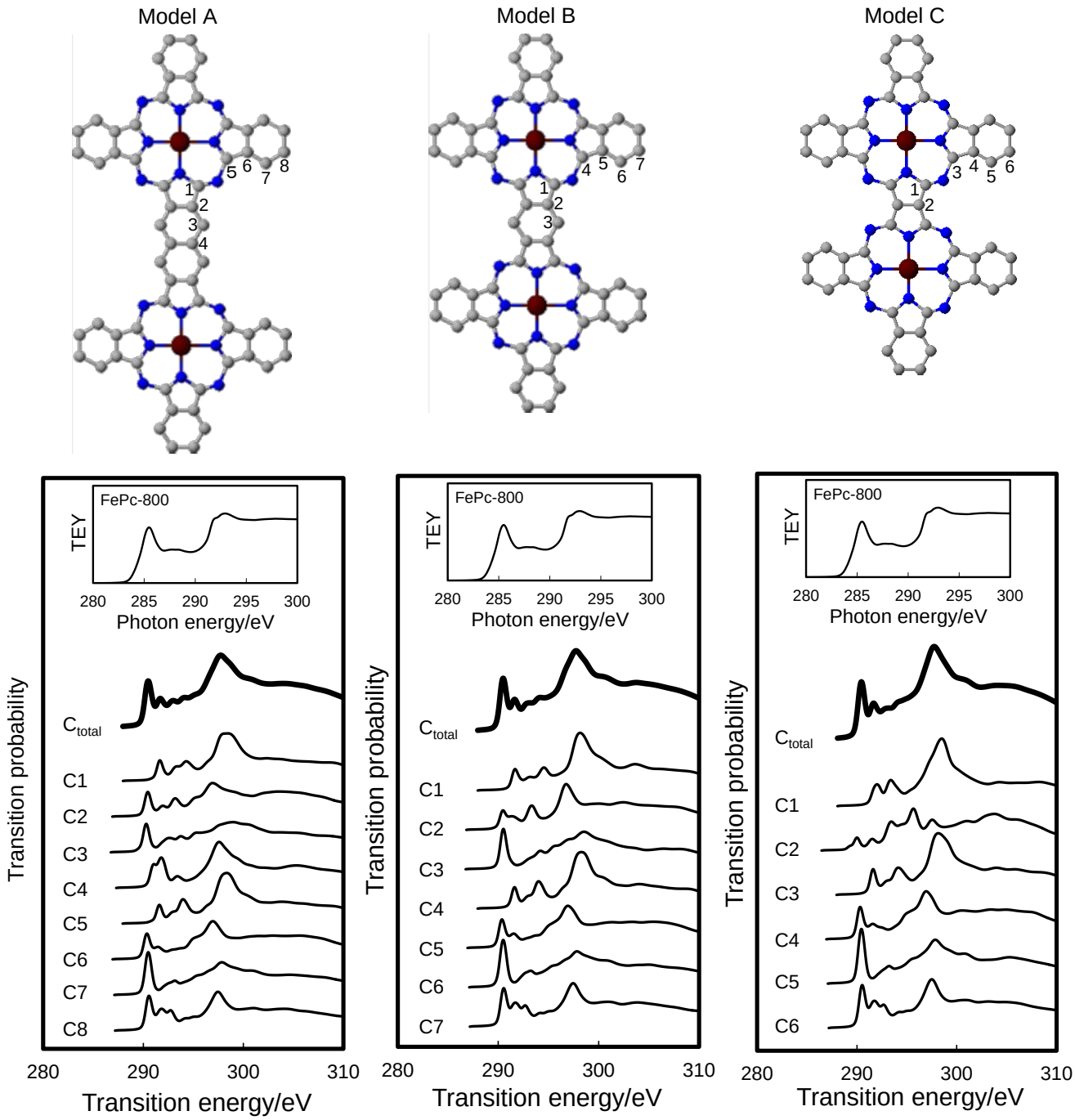

Fig. S3. Molecular models used for the DFT calculations for the C *K*-XANES spectrum of FePc-800, simulated C *K*-XANES spectrum (C_{total}) obtained by summing each spectrum of the C atom in the corresponding model, and C *K*-XANES of FePc-800 (inset). The carbon, nitrogen, and iron atoms are displayed in grey, blue, and brown, respectively. The hydrogen atoms are omitted.

TEM images

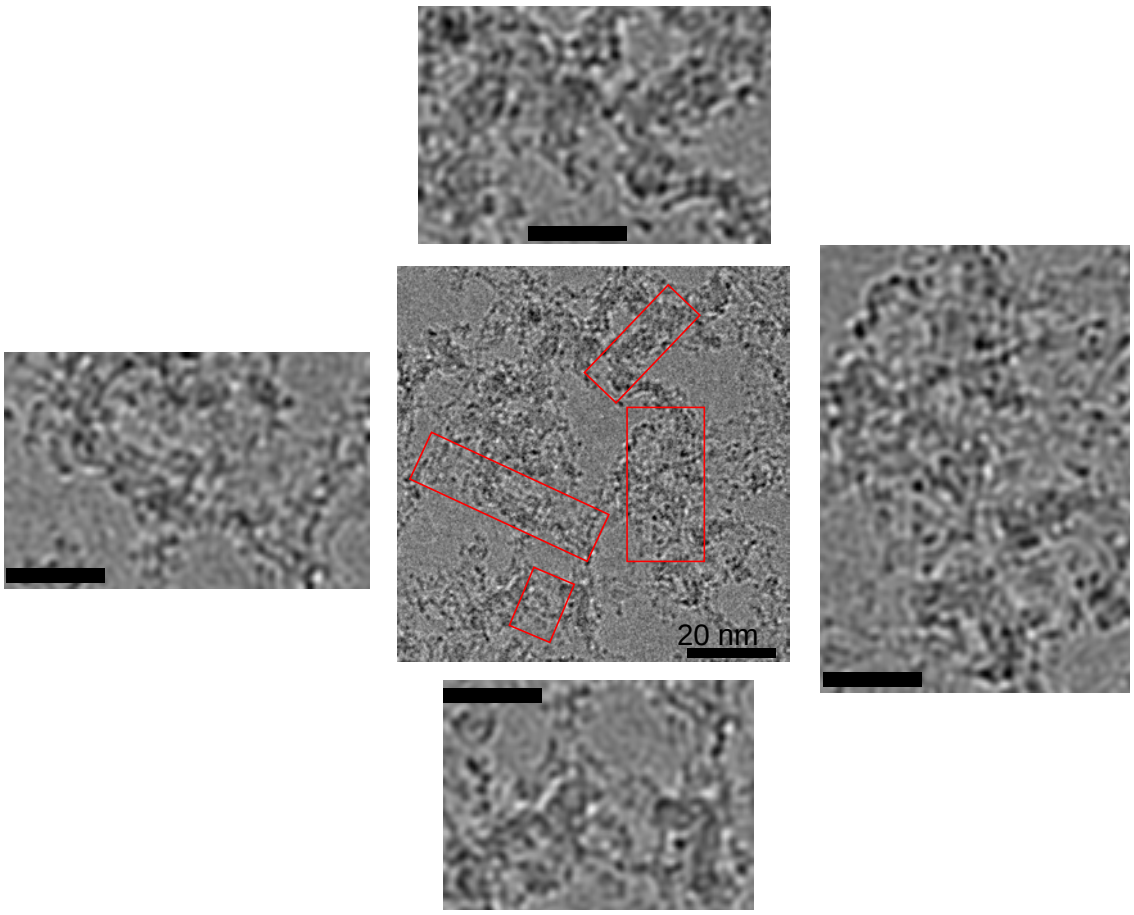

Fig. S4. Enlarged views of the regions designated by the red rectangles in Fig. 3(a) (shown in the center). All the scale bars in the enlarged views are 10 nm.