Supporting information for

Novel synthesis of graphene foils in the mesostructured silica between lamellar and hexagonal phases

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This supplementary information includes Experimental method and Figures S1-S3.

Experimental method

(a) Reagents. The chemicals employed in this work are expressed as follow: Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, MW = 12600, BASF, Germany); $CoCl_2$ (assay ≥ 95%, Hayashi, Japan); CH_3OH (assay ≥ 99.5%, Hayashi, Japan); HCl (assay ≥ 37%, Sigma-Aldrich, Germany); tetraethyl-ortho-silicate (assay ≥ 99%, Fluka, Germany); NaOH (assay ≥ 96%, Hayashi, Japan); $ZnCl_2$ (assay ≥ 95%, Hayashi, Japan); $MnCl_2$ (assay ≥ 99%, Acros, USA).

(b) Preparation. In preparing single-layer and bi-layer graphene sheets (GS), 0.9 g Pluronic F127 and 0.5 ml of 0.05 M cobalt chloride were dissolved in methanol. 0.011 ml HCl was added into the above methanol solution under stirring at room temperature for 25 min. Then, 2.08 ml tetraethyl-ortho-silicate (TEOS) was added into the above mixture under stirring for 30 min. In order to carry out the self-assembly reaction, the mixtures were subsequently aged at room temperature for 24 h. The self-assembled mixture was put into a quartz tube, which was filled with nitrogen gas for 30 min and then vacuumed before graphitization process. The aged mixtures were heated from room temperature to 600 ^{o}C at a ramping rate of 1 ^{o}C/min, and were held at 600 ^{o}C for 4 h for GS growth. The GS was collected and dispersed in methanol or ethanol after removing the silica template by using 2 M NaOH. The metaphase silica templates were prepared by following the above procedure but the silica mixtures were annealed under the air surrounding instead of vacuum condition.

(c) Textural analyses. The microstructure of silica templates and GS were examined by means of a field-emission transmission electron microscope (FE-TEM, Philips Tecnai) coupled with STEM elemental mapping. For preparation of TEM samples, the silica and GS powders were uniformly dispersed in an ethanol solution under an ultrasonic bath for 20 min. Then, some of the above solutions were dropped onto copper grids by a 50-μL micropipet for several times and followed by solvent evaporation in air at 85 °C overnight. The coexistence of lamellar and hexagonal structures of silica templates was identified by small-angle x-ray scattering analysis (SAXS, Osmic PSAXS). The thickness of GS was identified by an atomic force microscope (AFM, Digital Instrument D3100). The preparation procedure of AFM sample was completely following the literature.[1] The structure of graphene nanosheet was determined through a high-resolution micro-Raman analysis (Lab RAM HR-Raman Microscope, Horoba). The density of surface functional groups was measured by an X-ray photoelectron spectrometer (XPS, Kratos Axis Ultra DLD), employed Al monochromator ($h\nu$=1486.69 eV) irradiation as the photosource. The ratio of surface functional groups was obtained from the area ratio of fitting peaks by the XPSPeak 4.1 program with Shirley baseline and asymmetric Lorentzian–Gaussian sum function.

Reference

1. A.A. Green, M.C. Hersam, *Nano Lett.* **2009**, *9*, 4031.

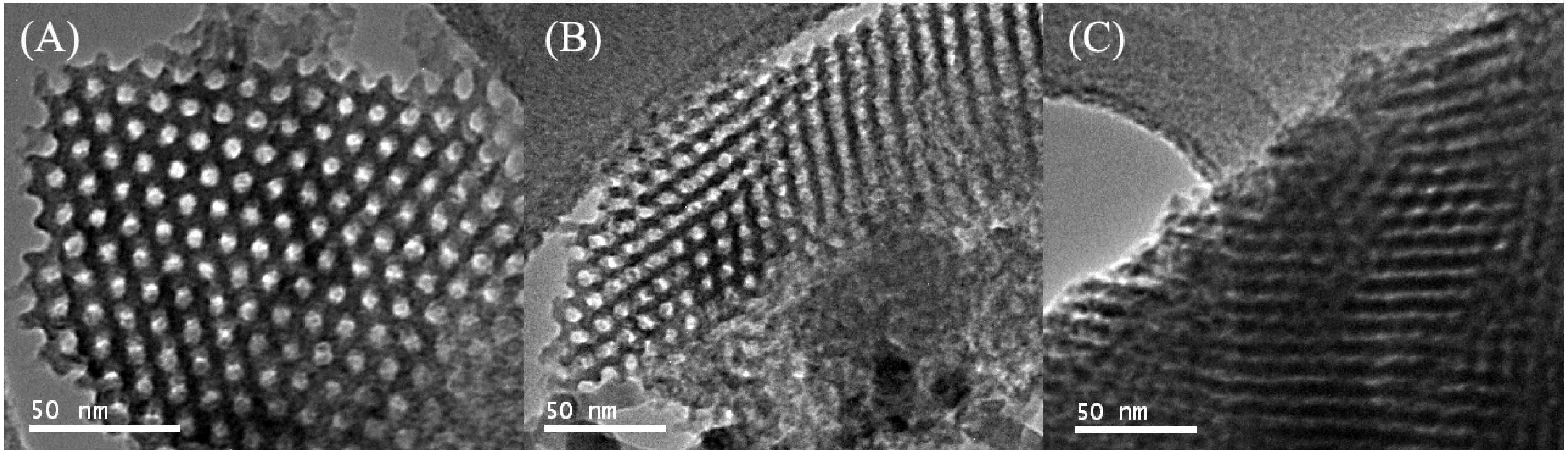

Fig. S1 (A) The hexagonal structure of SiO_2 template prepared from self-assembly TEOS/Pluronic F127 mixture without addition of metal salts. (B,C) The mesophase structures of SiO_2 templates prepared from self-assembly TEOS/Pluronic F127 mixture with addition of (B) $MnCl_2$ and (C) $ZnCl_2$. The hexagonal pillars with its c axis perpendicular to the image was destroyed and pinned at the mesophase structure between hexagonal and lamellar phases by adding $MnCl_2$ and $ZnCl_2$.

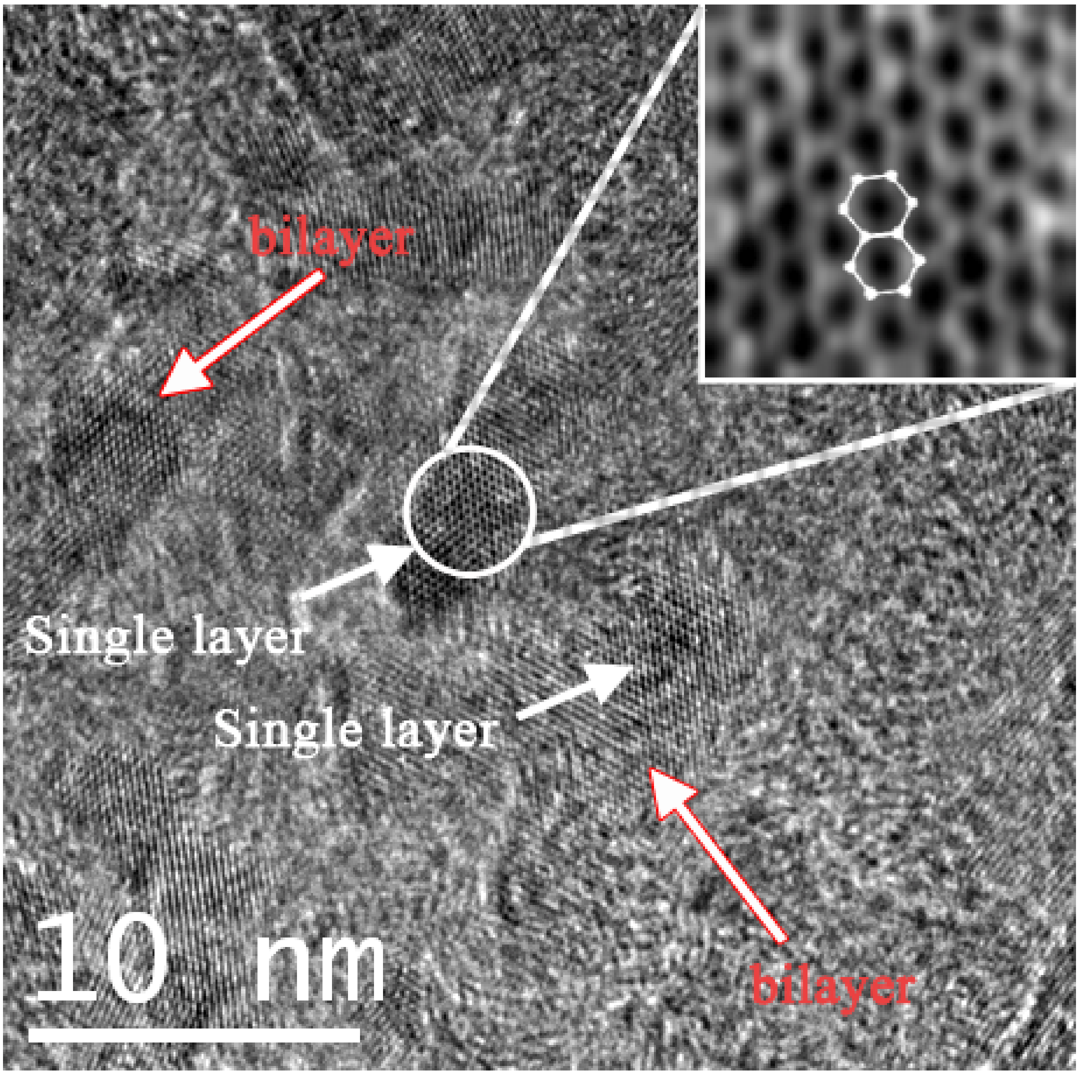

Fig. S2 A HR-TEM image of graphene. Inset is the atomic image of a single-layer graphene. The clear lattice image of single-layer and bi-layer graphene sheets reveals that growth of graphene sheets is catalyzed by the addition of iron-group catalysts within the confined environment of SiO_2 templates.

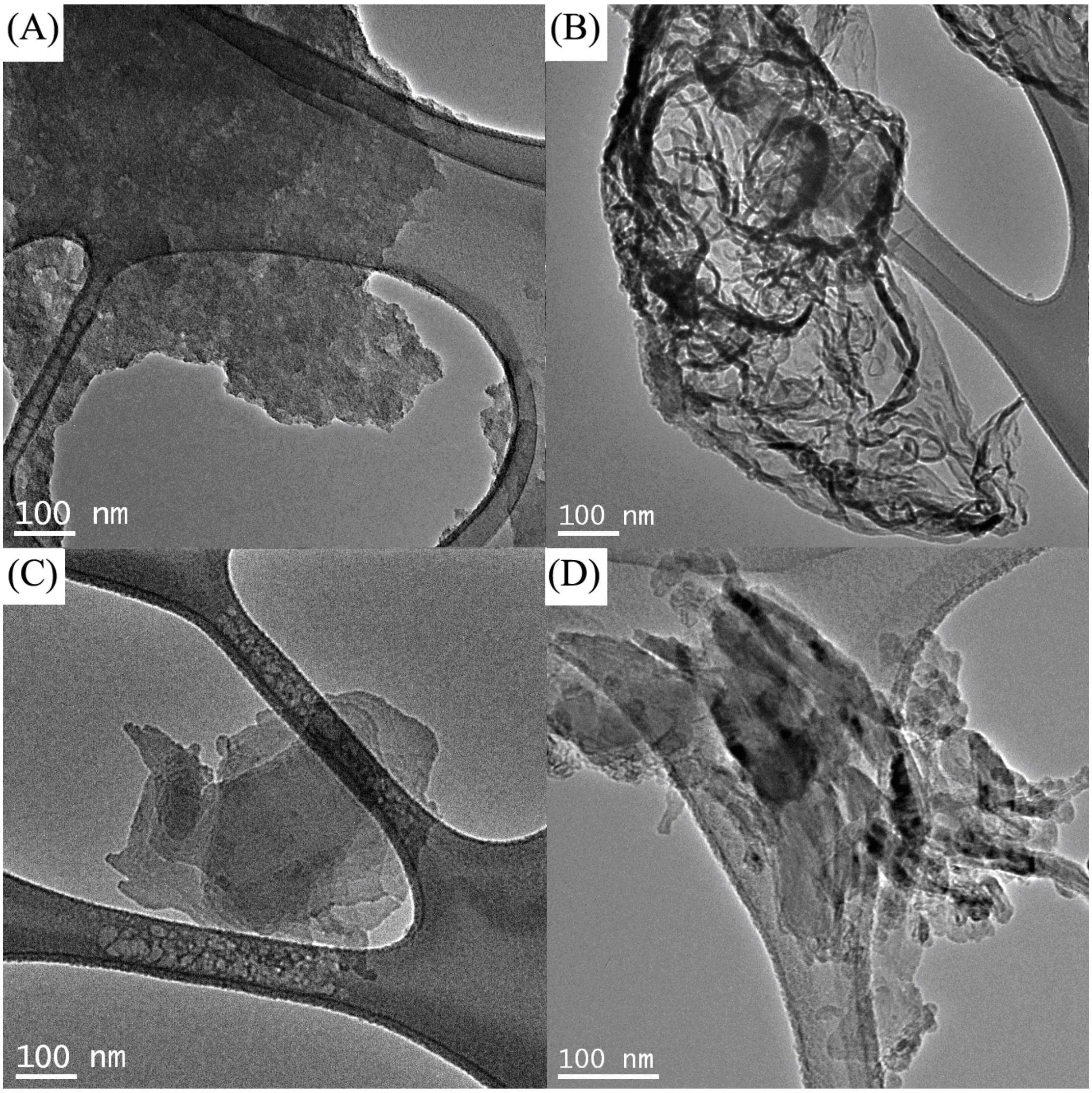

Fig. S3 TEM images of (A) activated carbon and (B-D) graphite obtained from self-assembled TEOS/Pluronic F127 mixtures (A,B) without addition of metal salts and with addition of (C) $MnCl_2$ and (D) $ZnCl_2$. Although activated carbon is the main product derived from the self-assembled TEOS/Pluronic F127 mixture without addition of $CoCl_2$, some graphite-like carbons can be observed (e.g., Fig. S3B). Moreover, due to the significant amount of mesophase structure between hexagonal and lamellar phases when $MnCl_2$ and $ZnCl_2$ were added in the self-assembled TEOS/Pluronic F127 mixture, more graphite-like carbons can be obtained (see Fig. S3C and S3D). The above results reveal that graphitization without iron-group catalysts does occur at relatively low temperatures (600^{o}C) under the confined spaces in the SiO_2 template.