Synthesis of graphene nanosheets with good control over the number of layers within the two-dimensional galleries of layered double hydroxides†

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Received 26th May 2012, Accepted 27th June 2012
DOI: 10.1039/c2cc33782g

Graphene nanosheets have been generated in the confined space of the two-dimensional galleries of a layered double hydroxide (LDH) and good control over the number of graphene layers can be achieved by adjusting the amounts of intercalated carbon source.

Graphene, a two-dimensional material with less than ten stacked layers of an sp²-hybridized C lattice, has fascinating electronic, thermal conductivity and mechanical properties. Owing to their distinct electronic band structures, graphene materials with different layer numbers have extraordinary physicochemical properties and tremendous potential for applications in nanoelectronic and nanophotonic devices. Therefore, the synthesis of graphene with controllable number of layers has been intensively explored in recent years. Monolayer and few-layer graphene were originally obtained via mechanical cleavage of highly oriented pyrolytic graphite. Some research have focused on the synthesis of monolayer or bilayer graphene by chemical vapour deposition (CVD) from gaseous carbon sources (such as CH₄ or C₂H₂) on some special substrates. In addition, large area, high-quality graphene samples with controllable thickness have been synthesized from a polymer film deposited on a metal catalyst substrate. Recently, Li et al. have shown a confined self-assembly approach to generate monolayer graphene, which is derived from lamellar mesoporous silica produced using a lysine-based surfactant bearing a terminal pyrrole moiety as the structure-directing agent. Here, we demonstrate a new method to synthesize graphene nanosheets in the two-dimensional interlayer galleries of a rigid host-layered double hydroxide (LDH), using methyl methacrylate (MMA) as the liquid carbon source. Furthermore, a well-controlled number of layers can be realized by adjusting the quantity of MMA.

LDHs are a class of anionic clays whose structure is based on brucite-like layers in which some of the divalent metal cations have been replaced by trivalent ions giving positively-charged sheets. This positive charge is balanced by intercalation of anions, here we used dodecyl sulfonate (DSO) as anions to support the layers and provide space for a neutral guest molecule – MMA. We synthesized a series of MgAl-LDH host containing co-intercalated DSO anions and MMA in a one-step reaction (Step I in Fig. 1), denoted LDH-1 (with a MMA : DSO molar ratio of 1.2), LDH-2 (with a MMA : DSO molar ratio of 3.2) and LDH-3 (with a MMA : DSO molar ratio of 8.0), respectively. Details of the preparation method are given in the ESI. In addition to balancing the positive charge on the layers, the DSO anions provide a hydrophobic environment allowing co-intercalation of neutral MMA which acts as the carbon source for the subsequent fabrication of graphene nanosheets in situ. Subsequent calcination of the material under a reducing atmosphere results in a collapse and shrinkage of the inorganic layered structure and growth of graphene nanosheets in the confined space between the inorganic sheets, as illustrated in Step II (Fig. 1). Finally, the MMA-derived graphene nanosheets with various layer numbers can be obtained by acid etching of the calcined LDH materials (Step III).

As shown in Fig. 2a–c, high resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM) (Fig. S1 in the ESI†) images show the expected platelet morphology of LDH. The layered structure is confirmed by X-ray diffraction (XRD) which shows the characteristic series of basal and higher order (00l) reflections at low angles (Fig. 2d), corresponding to the typical basal spacing of a LDH containing intercalated DSO. The interplanar spacings

Fig. 1 Schematic illustration of the formation of MMA-derived graphene nanosheets with various layer numbers in the interlayer galleries: (a) monolayer, (b) bilayer/trilayer and (c) multilayer (<6 layers) graphene nanosheets obtained from LDH-1, LDH-2 and LDH-3, respectively.

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† Electronic supplementary information (ESI) available: Preparation, characterization, SEM and HRTEM images, TG-MS, AFM images, digital photograph, XRD, XPS and elemental analysis. See DOI: 10.1039/c2cc33782g
of LDH-0 (intercalated with DSO alone), LDH-1, LDH-2 and LDH-3 decrease with increasing quantity of intercalated MMA. The differences can be also observed in the HRTEM images (Fig. 2a–c). Since the crystallographic thickness of the LDH layer is 0.48 nm,9 the interlayer gallery heights of LDH-1, LDH-2 and LDH-3 vary in the range 1.72–2.02 nm. Comparison of the infrared spectra of the materials with those of sodium dodecyl sulfonate (SDSO) and MMA (Fig. 2e) confirms that the interlayer galleries are occupied by both DSO anions and MMA, as shown by the bands at ca. 1184 cm\(^{-1}\) (S=O asymmetric stretch of DSO) and 1733 cm\(^{-1}\) (C=O vibration of MMA), respectively. These results confirm that the desired LDH precursors co-intercalated with DSO anions and MMA have been successfully synthesized.

Upon calcining the three LDHs in a reducing atmosphere at 900 °C, the XRD patterns (Fig. 3a) show that LDH structures have been destroyed and are consistent with previous studies of the thermal decomposition of LDHs, which have shown that cubic metal oxide (periclase-like) phases are formed by a topotactic transformation of the close-packed oxygen layers.10 In the XRD patterns of the three calcined LDHs (c-LDH), the peaks marked (111), (200) and (220) correspond to the characteristic reflections of a periclase-like phase. HRTEM (Fig. 3b-d) and SEM images (Fig. S2, ESI\(^{\dagger}\)) show that the lamellar morphologies are preserved.10 Interestingly, as shown in Fig. 3b-d, the monolayer, bilayer/trilayer and multilayer graphene nanosheets formed in the interlayer galleries of periclase-like layers can be seen as types of graphite intercalation compounds\(^{11}\) (GICs) from stage-1 to stage-6 (in Scheme S1, ESI\(^{\dagger}\)), respectively. In the inset of Fig. 3a, the diffraction peaks in the low angle region may belong to the stage structures of GICs. The diffraction peak at 19.8° in the pattern of c-LDH-1 (Fig. 3a) corresponds to a basal spacing of 0.45 nm, which is also observed in the HRTEM image (Fig. 3b), consistent with the presence of monolayer graphene nanosheets. For c-LDH-3, the HRTEM image (Fig. 3c) shows that the spacing between the host layers decreased to 1.3–1.6 nm, suggesting that bilayer and trilayer graphene nanosheets (denoted by yellow lines) have been formed between the layers of the host in the marked region. The XRD peak at ~25° in the diffraction patterns of c-LDH-2 and c-LDH-3 (Fig. 3a) corresponds to the characteristic interplanar distance of graphene (~0.35 nm), as shown in Fig. 3c and d. This peak is absent in the diffraction pattern of c-LDH-1, consistent with the presence of monolayer graphene nanosheets. The mechanism of formation of graphene nanosheets within the two-dimensional galleries is described in Fig. S3 and S4 (ESI\(^{\dagger}\)).

The graphene nanosheets were easily isolated by dissolving the metal oxide phase in hydrochloric acid. HRTEM, AFM images and digital photograph (Fig. S5 and S6, ESI\(^{\dagger}\)) showed that LDH-1 gave monolayer graphene nanosheets (Fig. 4a), LDH-2 gave a mixture of bilayer (Fig. 4b) and trilayer (Fig. 4c) graphene nanosheets (as discussed above), whilst LDH-3 afforded multilayer graphene nanosheets. The XPS and elemental analysis data for the graphene nanosheets with various layer numbers (Fig. S7 and Table S1, ESI\(^{\dagger}\)) are consistent with a small proportion of oxygenated surface functional groups, as expected.

Raman spectroscopy (Fig. 4e), which gives a more macroscopic characterization of graphene than electron microscopy, gave results which are consistent with the HRTEM images. The Raman spectra of the different samples (Fig. 4e) all showed a strong G band at ~1580 cm\(^{-1}\) characteristic of the in-plane vibration of a layer of sp\(^2\)-hybridized carbon atoms and a weaker D band at around ~1350 cm\(^{-1}\) resulting from defects or imperfections.12 The G/D intensity ratio is around 3, suggesting that the
the layered precursor, allowing monolayer, bilayer/trilayer or multilayer graphene nanosheets to be synthesized as required. Furthermore, this method is simple and requires cheap materials which are readily available, and the synthesis of the MMA-intercalated LDH precursor should be easy to scale-up, as we have already produced similar LDHs on a large scale.

This work was supported by the National Basic Research Program of China (Grant No. 2011CBA00508), the National Natural Science Foundation of China (Grant No. 20971011), the Excellent PhD Thesis Fund of Beijing (YB20101001001) and the Program for New Century Excellent Talents in Universities (Grant No. NCET-08-0713).

Notes and references