Framework substitution of graphene to form metal-oxide nanolamellas

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Graphene, the 2D carbon nanomaterial and the mother of all graphitic forms, has become an exciting topic of research during the last five years. Graphene was first obtained in 2004 by Geim's group from a simple micromechanical cleavage of highly oriented pyrolytic graphite[1,2]. For their 'ground breaking' studies on graphene, Geim and Novoselov were awarded 2010 Physics Nobel Prize. After the large-scale preparation of graphene by chemical reduction of graphene oxide was reported[3,4] in 2006, there have been tremendous activities in the research and applications of graphene[5–9]. Graphene is a flexible carbon sheet having long-range π-conjugation and high mechanical strength. Its surface area is nearly twice that of carbon nanotubes. Also, it possesses high electrical and thermal conductivity with a charge carrier mobility as high as 2×10^5 cm^2 V^{-1} s^{-1}. As a result, graphene has opened up new avenues for several interesting applications.

It is of great interest to study the possibility of replacing all the carbon atoms in the framework of graphene by atoms of other elements. If that can be accomplished, then it should be possible to obtain some interesting, novel, planar, nanostructured materials presumably endowed with exceptional properties.

In a recent report, Chen *et al.*[10] have successfully addressed this challenging issue of the framework substitution of graphene to form metal-oxide nanolamellas by a simple chemical procedure. Their approach involved *in situ* replacement of carbon atoms in the graphene framework, thereby transmitting the morphology of the layered structure from graphene to the prepared metal oxides. The generality of the method was demonstrated with the preparation of nanolamellas of MnO_2, Co_3O_4 and Cr_2O_3.

In a typical experiment to prepare nanolamellas of MnO_2, graphene sheets were first produced by dispersion and exfoliation of bulk graphite in *N*-methylpyrrolidone at a starting concentration of 0.1 mg/ml. About 100 ml of the graphene dispersion was vigorously stirred, and 5 ml of $KMnO_4$ solution (80 mg of $KMnO_4$ dissolved in 5 ml of deionized water) was introduced rapidly.

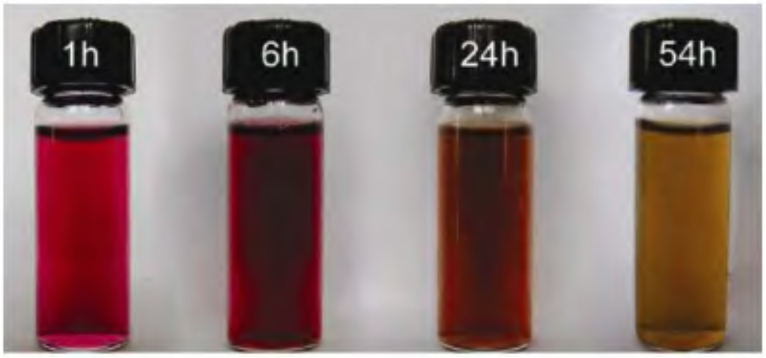

Figure 1. Digital pictures of the reacting solution from 1 to 54 h to form nanolamellas of MnO_2 (note: 1 ml of reacting mixture was diluted with 4 ml of deionized water for reliable comparison). Reprinted with permission from Chen *et al.*[10]. Copyright (2010) from American Chemical Society.

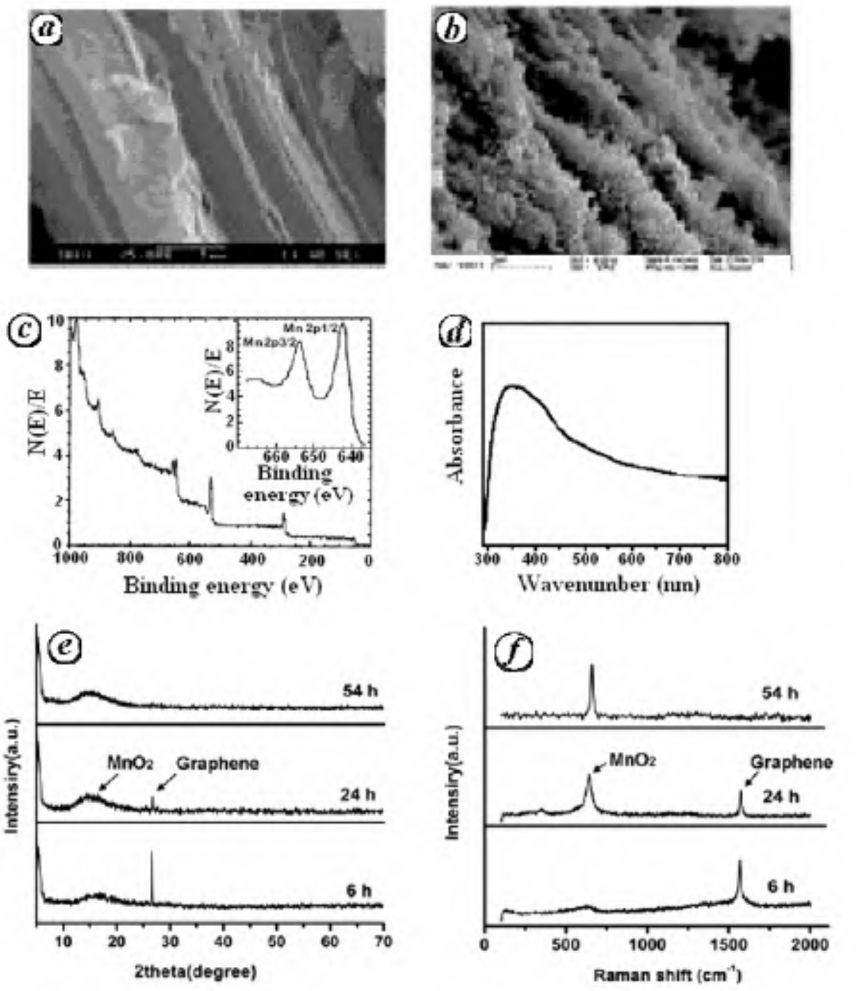

Figure 2. ***a***, FESEM image of graphene. ***b***, FESEM image. ***c***, X-ray photoelectron spectrum (inset) Mn (2p) peaks. ***d***, UV-visible absorption of as-obtained MnO_2-lamellas. ***e***, X-ray diffraction and ***f***, Raman analysis of samples taken at different time intervals. Reprinted with permission from Chen *et al.*[10]. Copyright (2010) from American Chemical Society.

The mixture was kept standing under ambient conditions until the purple colour turned to golden-brown, which took about 54 h (Figure 1). No precipitation occurred during and after the reaction and the mixture was finally centrifuged and washed with deionized water and ethanol respectively, to obtain the product. The reaction could be made faster upon heating the mixture. Likewise, Co_3O_4 and Cr_2O_3 were obtained using appropriate concentrations of $Co(NO_3)_2 \cdot 6H_2O$ and Na_2CrO_4 as the reagents respectively.

The product was subjected to analysis by several techniques to get credible evidence for the atom-by-atom framework substitution of graphene to form the MnO_2 nanolamellas. Figure 2 *a* and *b* shows the field emission scanning electron microscope (FESEM) images of the graphene before and after treatment with $KMnO_4$. The transfer of the lamellar structure to the product was clearly observed. Interestingly, the authors suggested the *in situ* growth of MnO_2 from the carbon atoms as the lamellas were constituted by many nanoscale particles. X-ray photoelectron spectral data indicated that the product contained Mn and O as the two main components (Figure 2 *c*). The UV–visible absorption spectrum showed a broad peak at 360 nm corresponding to d–d transitions of Mn ions in MnO_2 nanocrystals (Figure 2 *d*). X-ray diffraction and Raman data of the product collected at various time intervals clearly illustrated the transformation process from graphene to MnO_2 nanolamellas (Figure 2 *e* and *f*). The conventional double titration method indicated that most of the Mn was in the oxidation state + 4.

Taking a clue from the increase in pH of the reaction mixture with time, the whole process of formation of MnO_2 nanolamellas was proposed (Figure 3) to involve the reaction of graphene carbon with $KMnO_4$ in the aqueous solution according to the reaction:

$$4KMnO_4 + 3C + H_2O \rightarrow$$
$$4MnO_2 + K_2CO_3 + 2KHCO_3.$$

The MnO_2 nanolamellas were found to have a surface area of 50.3 $m^2\ g^{-1}$, with pore volume of 0.135 $cm^2\ g^{-1}$, which are remarkably higher than the MnO_2 produced by the traditional co-precipitation of $KMnO_4$ and Mn^{2+}. The MnO_2 nanolamellas were fabricated to electrodes for evaluation in supercapacitors. At a discharge current of 500 mA g^{-1}, the estimated specific capacitance for MnO_2 nanolamellas was 191 F g^{-1}, which is larger than MnO_2 with many other morphologies such as flowers (168 F g^{-1}), hollow urchins (147 F g^{-1}), clews (120 F g^{-1}) and nanorods (140 F g^{-1}). Also the nanolamellas exhibited high electrochemical stability with less than 10% decrease in capacitance even after 3000 charge–discharge cycles.

The generality of the procedure is striking when the study also demonstrated the possibility to prepare nanolamellas of other metal oxides like Co_3O_4 and Cr_2O_3 (Figure 4 *a* and *b*). The adaptability of the reported procedure to form nanowires of these metal oxides from single-walled carbon nanotubes has added value to the versatility of the method (Figure 4 *c*).

The significance of the study is the new perspective it has generated on graphene chemistry in that graphene is not only a building block of other carbon nanomaterials, but can be exploited as a common template to form many interesting nanolamellar structures which can find potential applications in directed self-assembly, gratings, nanotemplates, and catalysis.

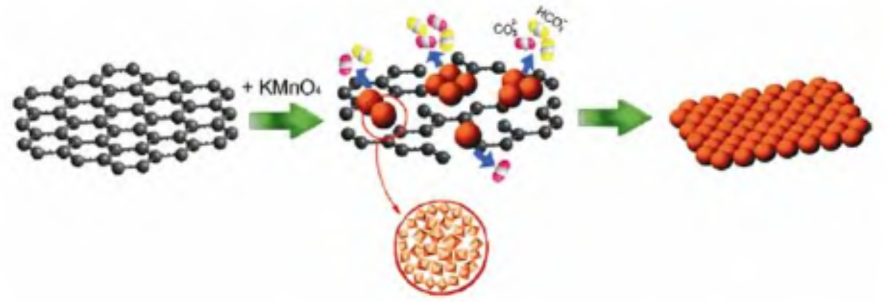

Figure 3. Illustration of the process of formation of MnO_2 nanolamellas from graphene. Reprinted with permission from Chen *et al.*[10]. Copyright (2010) from American Chemical Society.

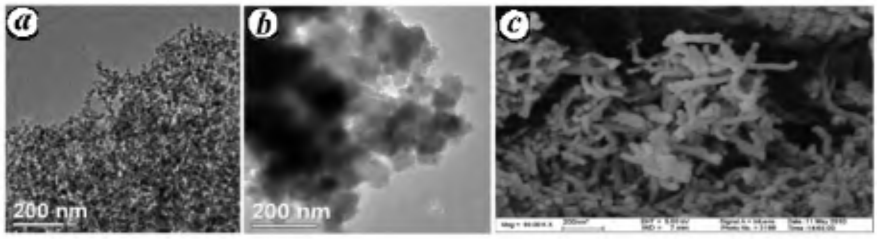

Figure 4. ***a***, ***b***, TEM images of the as-prepared Co_3O_4 and Cr_2O_3 nanolamellas. ***c***, FESEM image of the as-prepared MnO_2 nanowires from single-walled carbon nanotubes. Reprinted with permission from Chen *et al.*[10]. Copyright (2010) from American Chemical Society.

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