From Graphene to Metal Oxide Nanolamellas: A Phenomenon of Morphology Transmission

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Novel properties

Electronic Properties


Charge carriers behave as massless Dirac fermions


Remarkable thermal conductivity


Ambipolar field effect


Room-temperature quantum Hall effect

Physical method: Low yield

Liquid-phase exfoliation of graphite


Chemical vapor deposition


Selfassembly approach


Chemical reduction of graphite oxide


Nanomaterial based reduction of GO

The main interests in graphene are centered on two aspects:

- Pursuing for feasible approaches to produce graphene sheets
- Exploring peculiar properties of individual graphene nanosheets or graphene-based nanocomposites

The basic framework of graphene remains unchanged.

Relatively little attention has been paid so far to explore the framework substitution of graphene.
In this work

Graphene as a template.

- Taking into account that graphene is a 2-dimensional network of carbon atoms, it can be oxidized with some oxidizing reagents, such as KMnO₄, K₂Cr₂O₇, Na₂CrO₄, Co(NO₃)₂ · 6H₂O, etc., yielding corresponding metal oxide materials by means of sacrificing graphene itself.
- MnO₂ is known as a promising electrode material for applications in supercapacitors.
- The MnO₂ material obtained from the traditional coprecipitation method has a low specific capacitance owing to its low specific surface area. Nanoscale MnO₂ particles possess large surface area and relatively high specific capacitance, the microstructure is easily damaged during electrochemical cycling, giving a relatively poor electrochemical stability.

Here ....

Report a general procedure to prepare nanoscale metal oxides by *in situ* replacement of carbon atoms in the graphene framework and also demonstrate, for the first time, that MnO₂, Co₃O₄, and Cr₂O₃ with nanolamella structure can be prepared. The as-obtained MnO₂ product has exhibited a large surface area and excellent electrochemical properties in neutral electrolyte, displaying satisfactory specific capacitance and high electrochemical stability.

Single-walled carbon nanotube (SWNT) - rolled up graphene sheet- this methodology consequently is readily adaptable to fabricating MnO₂, Co₃O₄, and Cr₂O₃ nanowires from SWNTs.
Experimental

- Graphene sheets were produced by dispersion and exfoliation of bulk graphite in N-methyl-pyrrolidone (NMP) at a starting concentration of 0.1 mg/mL. Colman et al. Nat. Nanotechnol. 2008, 3, 563–568.
  - Energy required to exfoliate graphene is balanced by the solvent—graphene interaction for solvents whose surface energies match that of graphene.

✓ Graphene dispersion (100 mL) was vigorously stirred, while 5 mL of KMnO4 solution (80 mg of KMnO4 dissolved in 5 mL of deionized water) was introduced rapidly. The mixture was kept standing in a covered beaker under ambient conditions until the purple color turned to a golden brown.

✓ To prepare Co₃O₄ nanolamellas, Co(NO₃)₂ · 6H₂O (200 mg) were dissolved in 5 mL of deionized water and then introduced into graphene dispersion (100 mL) vigorously stirring. The as-obtained mixture was loaded into a Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. The autoclave was allowed to cool to room temperature. Then, the powders obtained were collected and washed repeatedly and finally dried.

✓ This procedure is also adaptable to chromium oxide nanolamellas starting with Na₂CrO₄ (400 mg).
Results and Discussion
4KMnO₄ + 3C + H₂O → 4MnO₂ + K₂CO₃ + 2KHCO₃.
Solution pH value was increasing with the reaction, probably as a result of the formation of $\text{CO}_3^{2-}$ or $\text{HCO}_3^-$.

Reaction was much faster upon heating.
Conclusions

- A general procedure by *in situ* substitution of the framework of graphene to produce metal oxide nanolamellas has been reported.
- Electrochemical properties of the as-prepared MnO₂ nanolamellas are more competitive than MnO₂ with many other morphologies.
- Only a slight decrease in capacitance of less than 10% even after 3000 cycles, demonstrating a great stability.
- Methodology is easily adaptable to SWNTs to form metal oxide nanowires.
- Method can be extended to different metals like Co, Cr, etc.
- Provided evidence to verify that graphene is not just a common union of carbon atoms, but rather, it is unique, having valuable properties and diverse potential applications.
Thank You!