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

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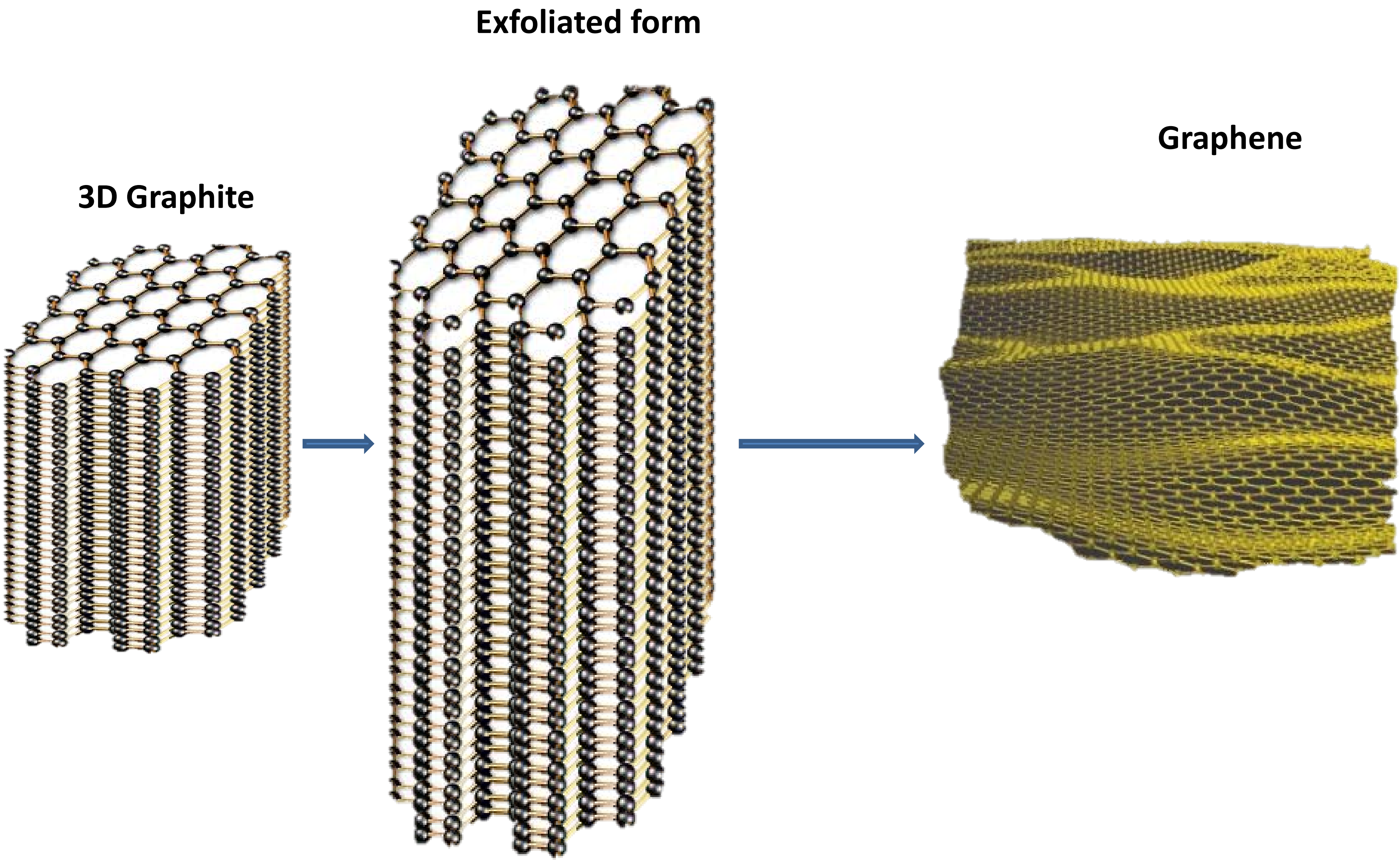
Novel properties

Graphene the perfect 2D system

- **Electronic Properties**
  - Novoselov *et al.* Electric Field Effect in Atomically Thin Carbon Films. *Science* 2004, *306*, 666–669.
  - Wu, J *et al.* Graphenes as Potential Material for Electronics. *Chem. Rev.* 2007, *107*, 718–747.
- **Charge carriers behave as massless Dirac fermions**
  - Novoselov *et al.* Two-Dimensional Gas of Massless Dirac Fermions in Graphene. *Nat. Phys.* 2005, *438*, 197–200.
- **Remarkable thermal conductivity**
  - Stankovich, S. et al. Graphene-Based Composite Materials. *Nature* 2006, *442*, 282–286.
- **Ambipolar field effect**
  - Novoselov *et al.* Electric Field Effect in Atomically Thin Carbon Films. *Science* 2004, *306*, 666–669.
- **Room-temperature quantum Hall effect**
  - Zhang, Y. et al. Experimental Observation of the Quantum Hall Effect and Berry's Phase in Graphene. *Nature* 2005, *438*, 201–204.

Synthesis

- Physical method : Low yield
  - Novoselov *et al.* Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.



- Liquid-phase exfoliation of graphite
  - Hernandez, Y. *et al.* High-Yield Production of Graphene by Liquid-Phase Exfoliation of Graphite. *Nat. Nanotechnol.* **2008**, *3*, 563–568.
  - Athanasios, B. B. *et al.* Liquid-Phase Exfoliation of Graphite Towards Solubilized Graphenes. *Small* **2009**, *5*, 1841–1845.
- Chemical vapor deposition
  - Park, H. J. *et al.* Growth and Properties of Few-Layer Graphene Prepared by Chemical Vapor Deposition. *Carbon* **2010**, *48*, 1088–1094.
- Selfassembly approach
  - Weixia, Z. *et al.* A Strategy for Producing Pure Single-Layer Graphene Sheets Based on a Confined Self-Assembly Approach. *Angew. Chem., Int. Ed.* **2009**, *48*, 5864–5868.
  - Li, X . *et al.* Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science* **2009**, *324*, 1312–1314.
- Chemical reduction of graphite oxide
  - Li, D. *et al.* Processable Aqueous Dispersions of Graphene Nanosheets. *Nature* **2008**, *3*, 101–105.
- Nanomaterial based reduction of GO
  - Williams, G. *et al.* TiO_2Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide. *ACS Nano* **2008**, *2*, 1487–1491.
  - Sreeprasad, T. S. *et al.* Tellurium Nanowire-Induced Room Temperature Conversion of Graphite Oxide to Leaf-like Graphenic Structures. *J. Phys. Chem. C* **2009,** *113,* 1727–1737.

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 $KMnO_4$, $K_2Cr_2O_7$, Na_2CrO_4, $Co(NO_3)_2 \cdot 6H2O$, *etc.*, yielding corresponding metal oxide materials by means of sacrificing graphene itself.
- MnO_2 is known as a promising electrode material for applications in supercapacitors.
- The MnO_2 material obtained from the traditional coprecipitation method has a low specific capacitance owing to its low specific surface area. Nanoscale MnO_2 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 MnO_2, Co_3O_4, and Cr_2O_3 with nanolamella structure can be prepared. The as-obtained MnO_2 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 MnO_2, Co_3O_4, and Cr_2O_3 nanowires from SWNTs.

Experimental

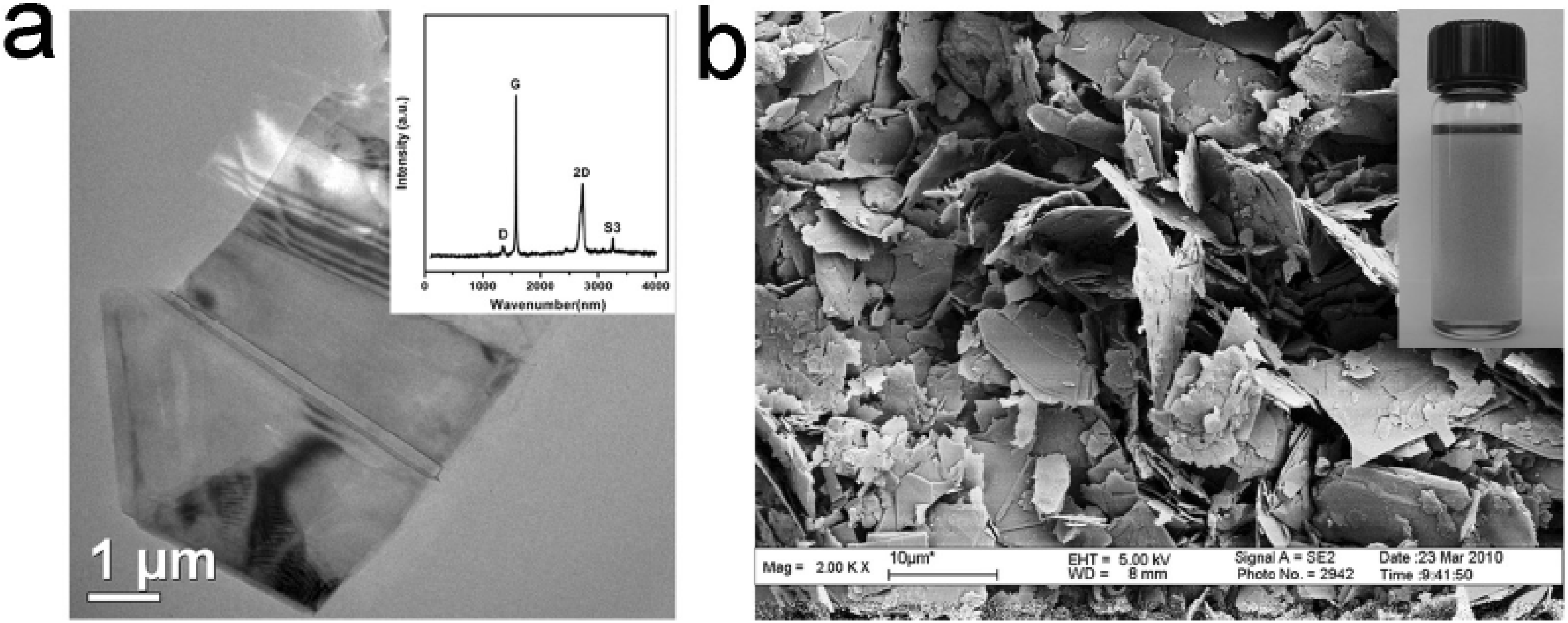
- Graphene sheets were produced by dispersion and exfoliation of bulk graphite in N-methyl-pyrrolidone (NMP) at a starting concentration of 0.1 mg/mL

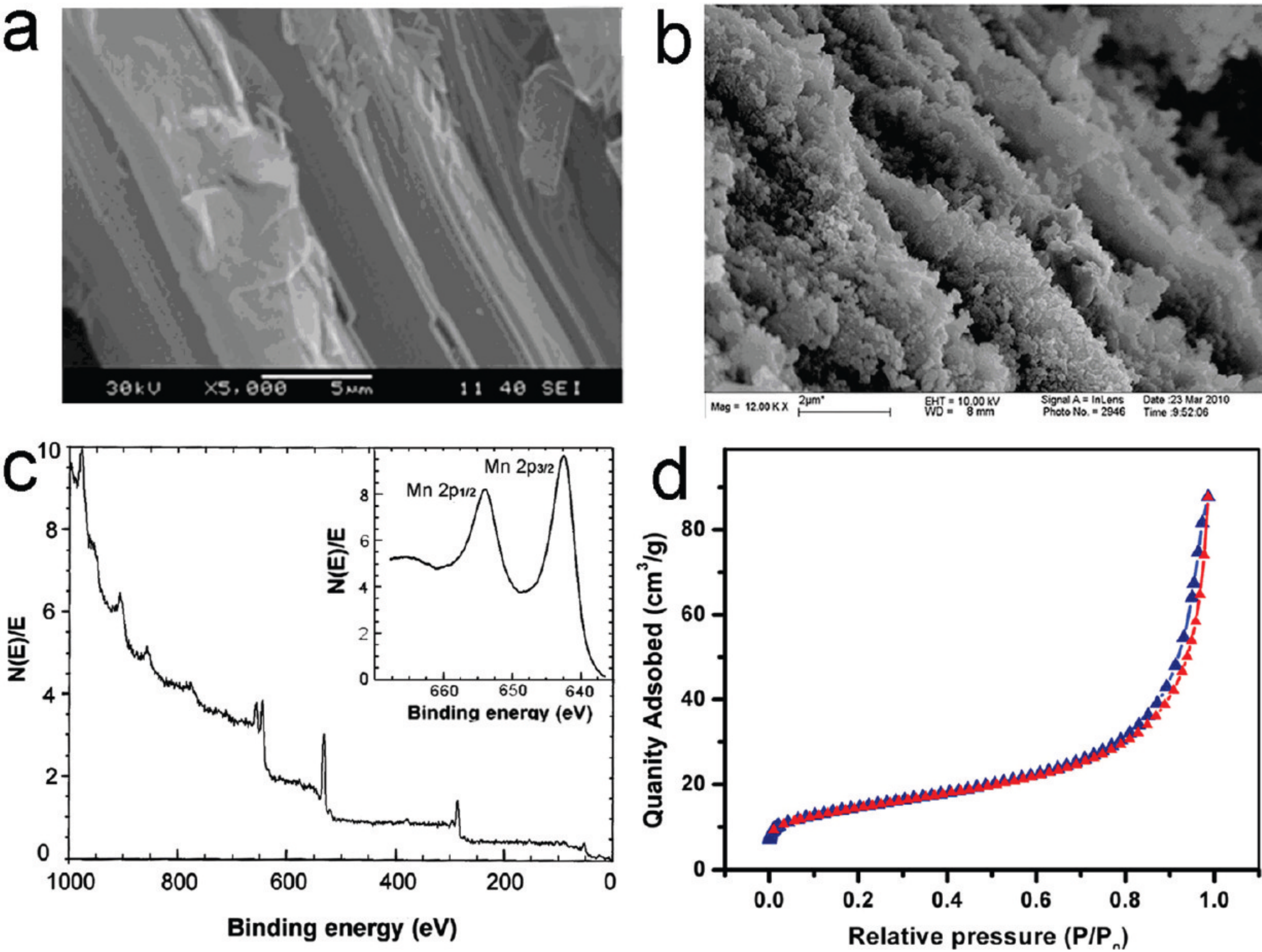
  Colman *et al*. Nat. Nanotechnol. 2008, 3, 563–568.

  - Energy required to exfoliate graphene is balanced by the solvent–graphene interaction for solvents whose surface energies match that of graphene.

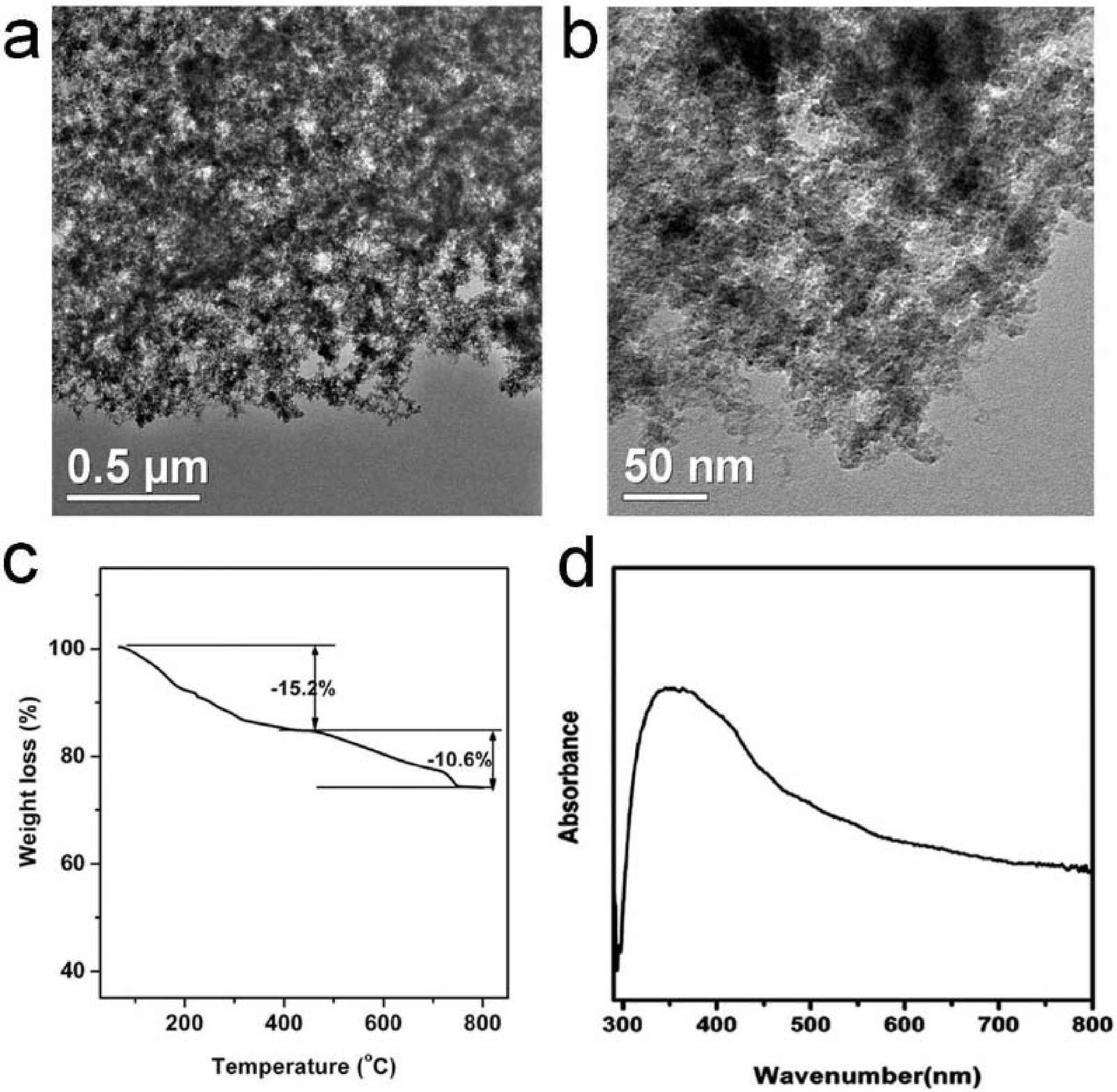
- ✓ Graphene dispersion (100 mL) was vigorously stirred, while 5 mL of $KMnO_4$ solution (80 mg of $KMnO_4$ dissolved in 5 mL of deionized water) was introduced rapidly. The mixture was kept standing in a covered beaker under ambient conditions until the purple color turned to a golden brown.
- ✓ To prepare Co_3O_4 nanolamellas, $Co(NO_3)_2 \cdot 6H_2O$ (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 Na_2CrO_4 (400 mg).

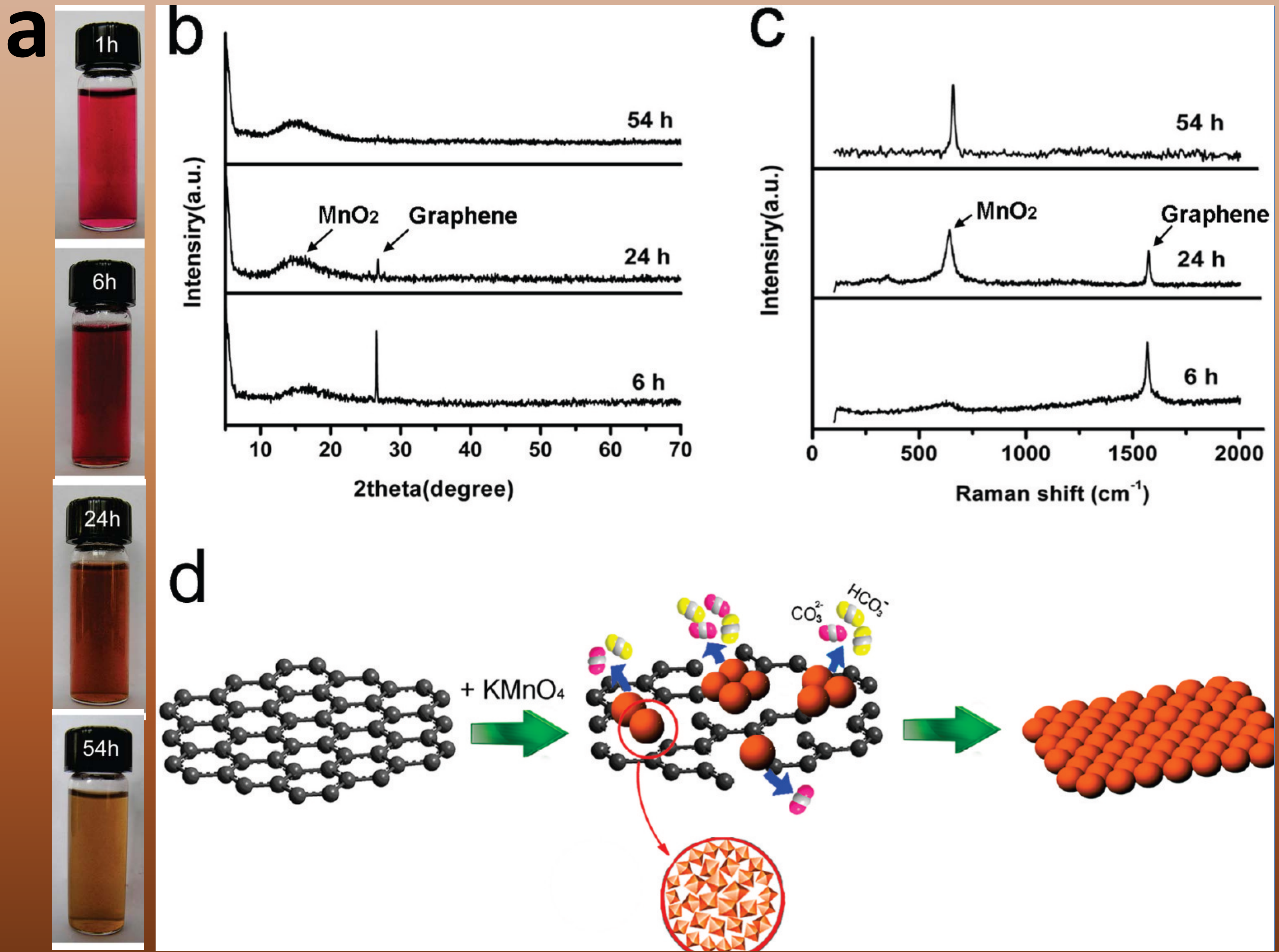
Results and Discussion





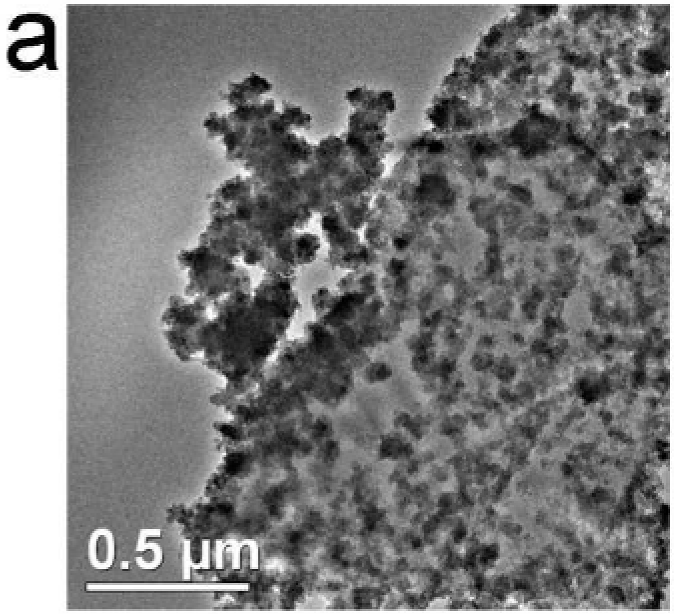
a
30kV X5,000 5μm 11 40 SEI
b
Mag = 12.00 K X
2μm*
EHT = 10.00 kV
WD = 8 mm
Signal A = InLens
Photo No. = 2946
Date :23 Mar 2010
Time :9:52:06
c
N(E)/E
Binding energy (eV)
Mn 2p1/2
Mn 2p3/2
d
Quanity Adsobed (cm3/g)
Relative pressure (P/Po)

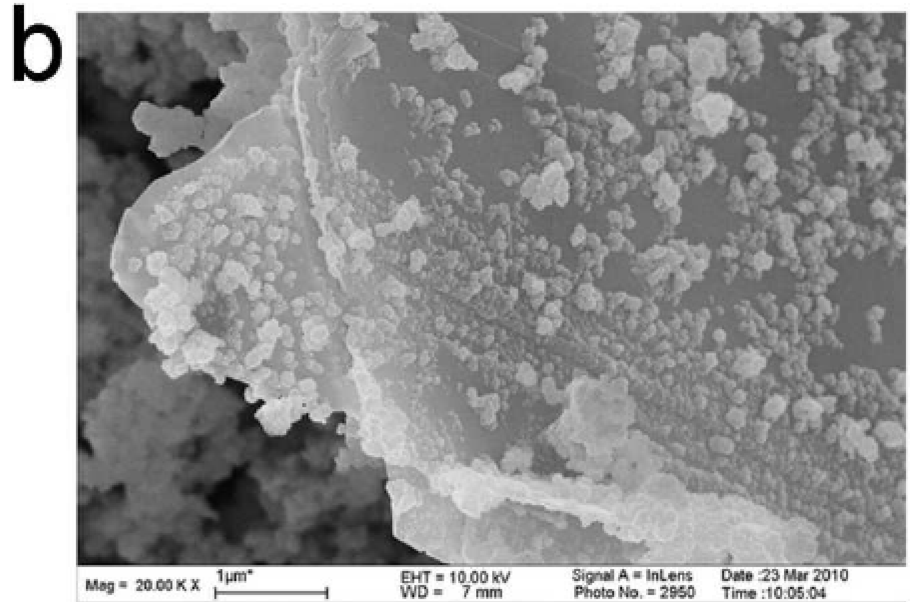

a
0.5 μm
b
50 nm
c
-15.2%
-10.6%
Weight loss (%)
100
80
60
40
200
400
600
800
Temperature (°C)
d
Absorbance
300
400
500
600
700
800
Wavenumber(nm)



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

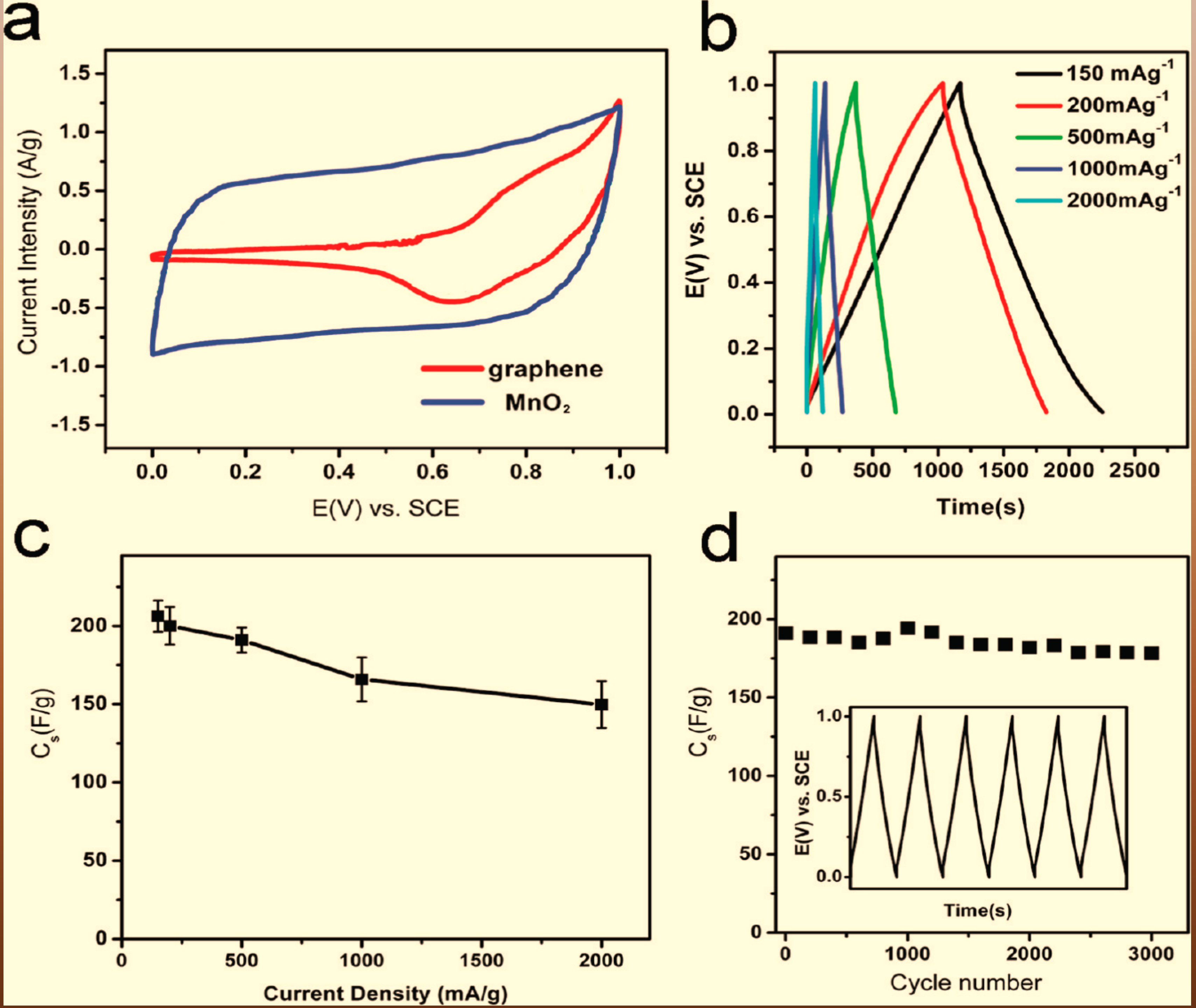
TEM and FESEM after 24 h



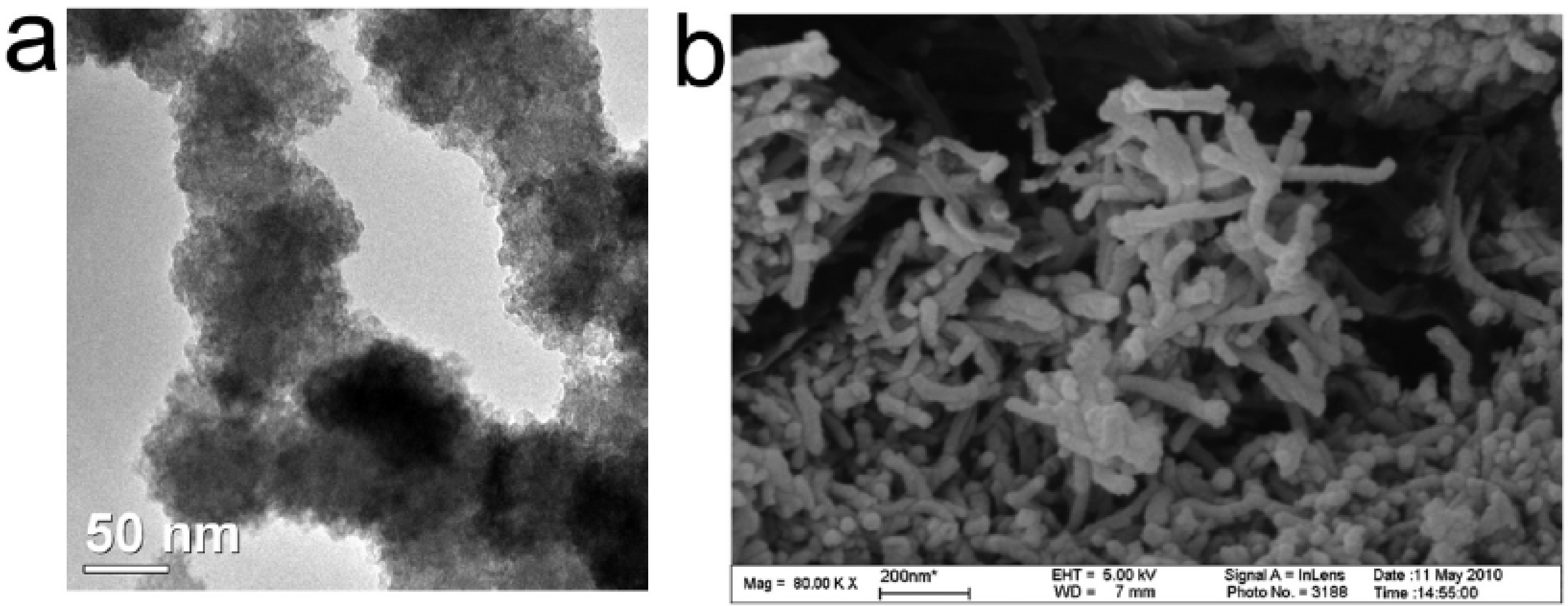


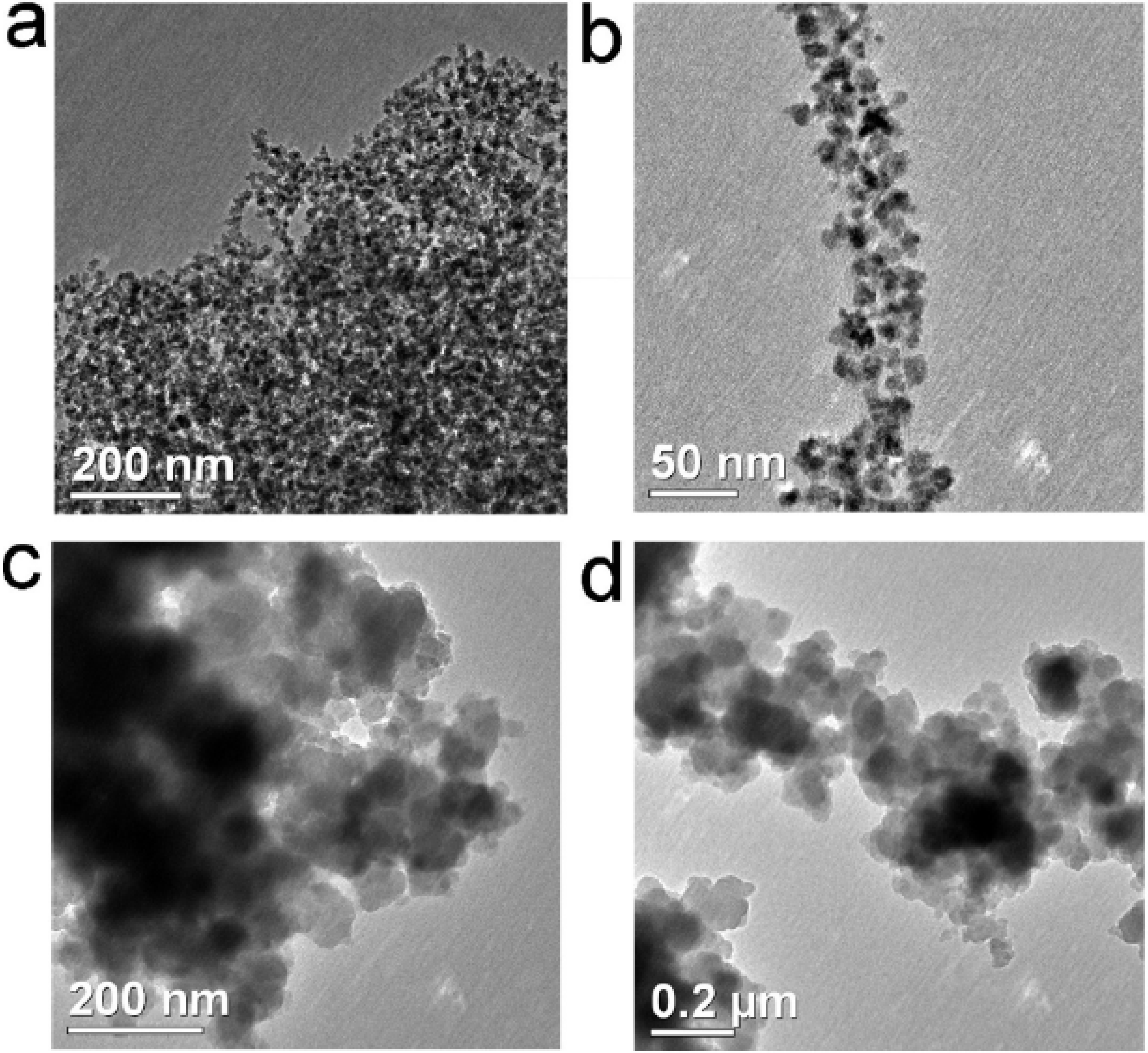
Solution pH value was increasing with the reaction, probably as a result of the formation of CO_3^{2-} or HCO_3^-

Reaction was much faster upon heating



a
Current Intensity (A/g)
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
0.0
0.2
0.4
0.6
0.8
1.0
E(V) vs. SCE
graphene
MnO2
b
E(V) vs. SCE
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
2500
Time(s)
150 mAg-1
200mAg-1
500mAg-1
1000mAg-1
2000mAg-1
c
Cs(F/g)
200
150
100
50
0
0
500
1000
1500
2000
Current Density (mA/g)
d
Cs(F/g)
200
150
100
50
0
0
1000
2000
3000
Cycle number
E(V) vs. SCE
1.0
0.5
0.0
Time(s)


a
50 nm
b
Mag = 80.00 K X
200nm*
EHT = 5.00 kV
WD = 7 mm
Signal A = InLens
Photo No. = 3188
Date :11 May 2010
Time :14:55:00


a
200 nm
b
50 nm
c
200 nm
d
0.2 µm

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 MnO_2 nanolamellas are more competitive than MnO_2 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!