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Electronic Supplementary Information

Bio-derived calcite as a sustainable source for graphenes as high-performance electrode material for energy storage

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Experimental Section

Synthesis of graphene materials

Eggshell were soaked in acetone for 2h, rinsed and then calcined in a muffle furnace at 500°C for 2 h in order to remove organic component. Then 1 g calcined eggshell and 1 g magnesium flake (Sinopharm Chemical Reagent Co. Ltd, 200 mesh) were sealed separately at the two ends of a steel ampoule in an argon-filled glovebox. The sealed ampoule was heated to 700°C with a heating rate of 5 °C/min and kept at that temperature for 5 h in an argon flow. The ampule was then cooled and opened. The obtained black product was etched in 2 M HCl aqueous solution for 5 h, filtered out and rinsed with de-ion water for several times. It was finally vacuum-dried at 50°C for 12 h to obtained graphene product. The yield of graphene product was about 60%.

Materials Characterizations

X-ray diffraction (XRD) patterns were obtained by a X-ray diffractometer (Bruker D8 Discover) with Cu Kα radiation (λ = 1.5418 Å, 40 kV, 40 mA). The chemical compositions of sample were examined by a X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Escalab 250XI). Raman spectra were recorded on a Labram HR-800 spectrometer employing a 514 nm laser beam. The morphology of samples was observed by a field-emission scanning electron microscopy (FESEM, Hitachi S-4800) and high-resolution transmission electron microscopy (HRTEM, JEOL 2100F). The surface morphologies of samples were studied using atomic force microscopy (AFM, Veeco DI Multimode V SPM) in tapping mode. The decomposition temperature of eggshell was determined by a thermogravimeter (NETZSCH STA 449C) and the measurements were carried out in air between room temperature and 1000°C with a ramp rate 10°C/min.

Electrochemical Measurements

Graphene materials as active materials, Super P carbon black and polyvinyldifluoride (weight ratio 80:10:10) were mixed in N-Methylpyrrolidone (NMP) solvent to produce a slurry. The slurry was coated onto a copper foil using the doctor-blading method and then dried to form the working electrode. The electrochemical tests were performed using two-electrode coin-type cells (CR 2016) with lithium as the counter electrode. One molar LiPF6 in a 1:1:1 (volume ratio) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) and dimethyl carbonate (DMC) was used as the electrolyte. The mass of the active materials loaded each electrode was in the range of 0.50-0.60 mg. Cell assembling was carried out in an argon-filled glove box. Galvanostatic charge–discharge cycling was conducted using a battery tester (Land, CT2100A) with a voltage window of 0.01-3 V at various current density. All galvanostatic charge–discharge cycling test were performed at 25°C. An Autolab PGSTAT 302 N electrochemical workstation was used to obtain the cyclic voltammograms of the samples in the voltage range (0.01-3 V) with a scanning speed of 0.5 mV/s.

Calculation of equilibrium pressures of Mg and CO_2

Table S1. The formation Gibbs energies for $CaCO_3$, CO_2, CaO, Mg at 900.00, 1000.00 and 973.15 K, respectively.

T (K)	$\Delta G^0_{f\text{-}CaCO3(s)}$ (kJ)	$\Delta G^0_{f\text{-}CO2(g)}$ (kJ)	$\Delta G^0_{f\text{-}CaO(s)}$ (kJ)	$\Delta G^0_{f\text{-}Mg(l)}$ (kJ)	$\Delta G^0_{f\text{-}Mg(g)}$ (kJ)
900.00[a]	-976.009	-395.680	-541.345	-	44.438
1000.00[a]	-951.253	-395.810	-531.087	0	34.436
973.15[b]	-957.900	-395.775	-533.841	0	37.121

Note: [a] Thermochemical data 900K and 1000K were from Barin, I.; Platzki, G. Thermochemical data of pure substances; VCH Weinheim, 1995. [b] Thermochemical data at 700 °C(973.15 K) were linearly interpolated from data at 900 and 1000 K.

$CaCO_3(s) \leftrightarrow CaO(s)+CO_2(g)$ (1) $Mg(l) \leftrightarrow Mg(g)$ (2)

The standard Gibbs energy changes for reaction (1) and (2) can be calculated to be 28.284 and 37.121 kJ/mol according to following equation (S1)

$$\Delta G_r^0 = \sum \Delta G_{fproduct}^{\ 0} - \sum \Delta G_{freactants}^{\ 0} \quad \text{(S1)}$$

Under moderate pressure, the equilibrium pressure at 700 °C can be calculated by equation (S2)

$$P = e^{\frac{-\Delta G_r^0}{RT}} \quad \text{(S2)}$$

The equilibrium pressures can be calculated to be 0.030 and 0.010 atm at 700 °C (973.15K) for CO_2 and Mg vapor, respectively, assuming the overall pressure was 1 atm and the reactor was not completely sealed.

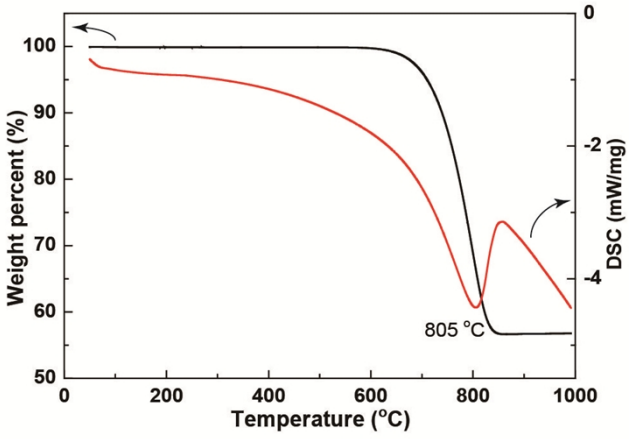

Figure S1. TG-DSC analysis of commercial available $CaCO_3$ (Aladdin Reagent, China).

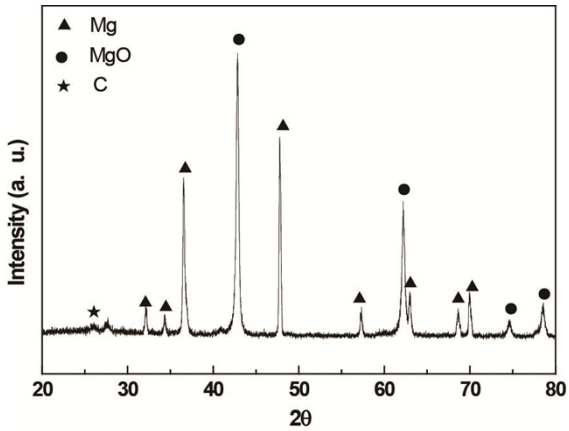

Figure S2. XRD pattern of the product at the location of Mg flakes after the magnesiothermic reduction process.

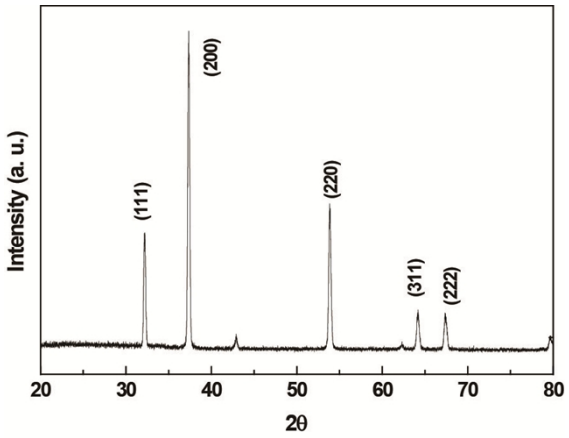

Figure S3. XRD pattern of the product at the location of bio-calcite after the magnesiothermic reduction process. The pattern fit well with CaO phase (PDF card No. 48-1467).

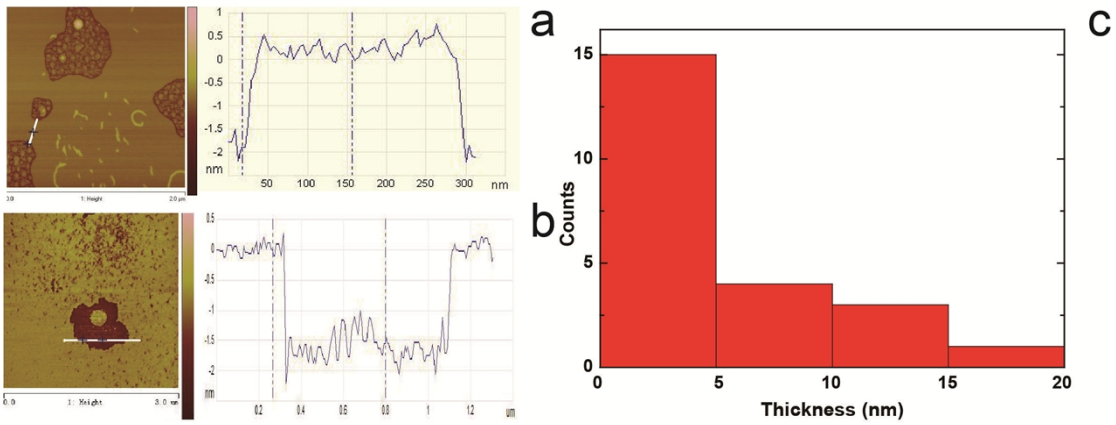

Figure S4. (a) and (b) AFM images of synthesized graphene nanosheets with thickness of a few nanometers. (c) Thickness distribution of graphene materials based on the AFM images and TEM cross section images.

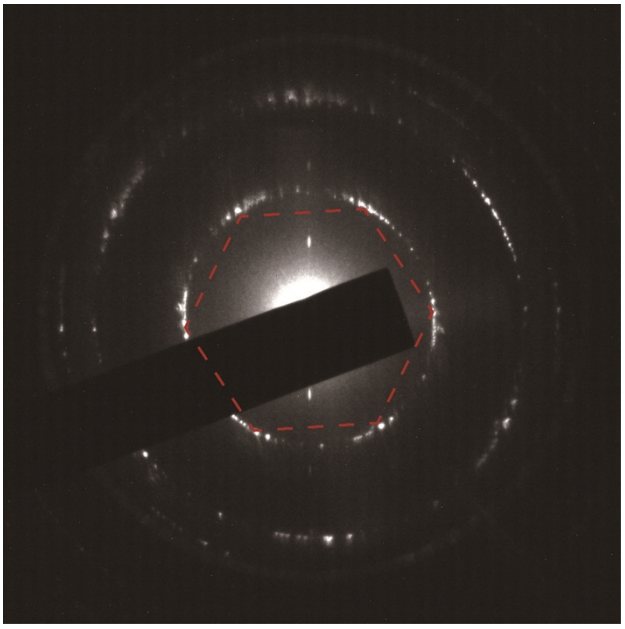

Figure S5. SAED pattern of the synthesized graphene.

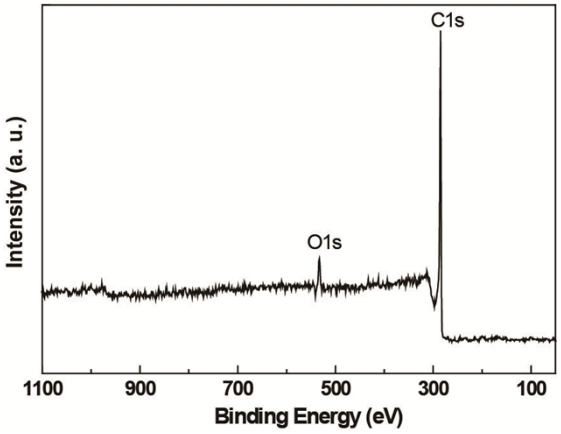

Figure S6. XPS survey spectrum of the synthesized graphene product.

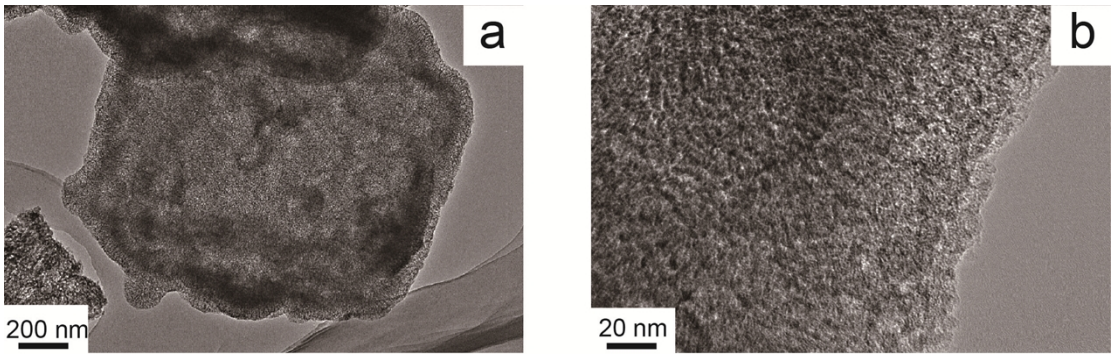

Figure S7. TEM images of carbon product obtained through the magnesiothermic reduction reaction at 600 ^{o}C for 12 h.

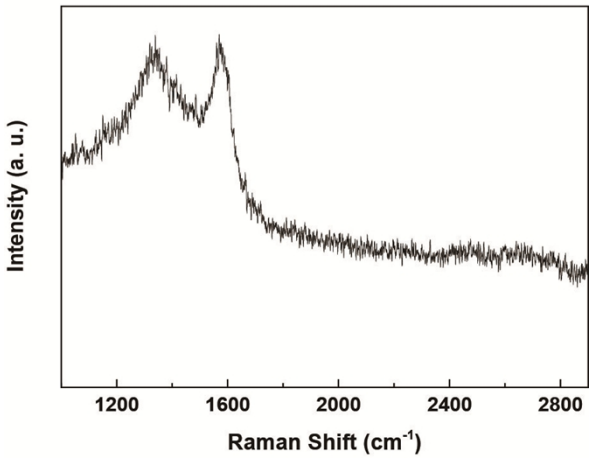

Figure S8. Raman spectrum of carbon product obtained through the magnesiothermic reduction reaction at 600 °C for 12 h.

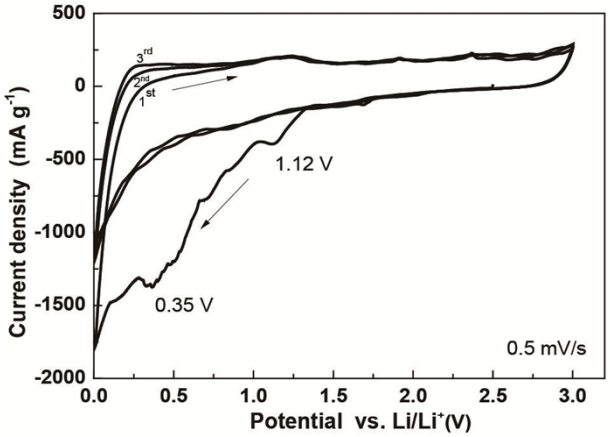

Figure S9. . Cyclic voltammograms (CV) of the synthesized graphene at the first three cycles.

Table S2. Comparison of the specific capacities of reported graphene nanosheets with this work.

No	Materials	Current density	Cycle number	Capacity (mA h g^{-1})	Ref. No.
1	graphene nanosheets	0.05 A g^{-1}	20	290	1
2	Graphene nanosheets with carbon nanotubes	0.05 A g^{-1}	20	480	1
3	Graphene nanosheets with C_{60}	0.05 A g^{-1}	20	600	1
4	Hydrazine reduced GO	0.05 A g^{-1}	15	185	2
5	600 °C pyrolytic GO	0.05 A g^{-1}	15	690	2

6	graphene nanosheets	0.372 A g^{-1}	100	460	3
7	graphene nanosheets	0.2mA cm^{-2}	30	502	4
8	Porous graphene nanosheets	0.1 A g^{-1}	160	678.4	This work

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