Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

# Electronic Supplementary Information (ESI)

## Synthesis of nanostructured graphite via molten salt reduction of $CO_2$ and $SO_2$ at a relatively low temperature

Zhigang Chen, Yuxing Gu, Liangyou Hu, Wei Xiao, Xuhui Mao, Hua Zhu and Dihua Wang*

School of Resource and Environmental Science, Hubei International Scientific and Technological Cooperation Base of Sustainable Resource and Energy, Wuhan University, Wuhan 430072, China.

*Corresponding author. Email address: wangdh@whu.edu.cn (D. Wang); Tel.: +86 27 6877 4216; Fax: +86 27 6877 5799.

### Experimental

The experimental set-up of the MSCC-ET process was described previously.[14,29,29,32] A mixed melt of $Li_2CO_3$-$Na_2CO_3$-$K_2CO_3$-$Li_2SO_4$ (40:29:23:8 in molar ratio, analytic purity, Sinopharm Chemical Regent Co. Ltd., China) contained in an alumina crucible was used as the electrolyte for gas capture and electrochemical reaciton. $SnO_2$ (1.4 cm in diameter, 20 cm in length, Dyson Technical Ceramics, UK) or platinum plated titanium (Wuhan Kaida Science and Engineering Co. Ltd., China) and a U-shape Ni sheet (20 mm wide, 40 mm deep in the electrolyte, Sinopharm Chemical Regent Co. Ltd., China) were used as the anode and cathode, respectively. A simulated flue gas (14 vol% $CO_2$, 300 mg $m^{-3}$ $SO_2$, $N_2$ balance, Wuhan Newradar Special Gas Co. Ltd., China) was fed into the melt continously. The constant current electrolysis was conducted by a computer-controlled DC power supply (Shenzhen Neware Electronic Co. Ltd., China) at a cathode current density of 62.5 mA $cm^{-2}$ under predetermined temperatures of 475 $^oC$, 525 $^oC$, 575 $^oC$, 675 $^oC$, 725 $^oC$, 775 $^oC$ and 825 $^oC$ with an identical electrolysis charge ($Q$ = 7 Ah), respectively. Theoretically, the deposition of carbon could continue with feed of $CO_2$/flue gas and electricity. In our laboratory, the process can continuously be operated for more than one week. Subsequetly, the carbon product was deposited on the cathode. After electrolysis, the cathode was removed from the melt and the product was washed with dilute HCl and deionized water to remove adherent frozen electrolyte and then dried in a vacuum oven at 80 °C for 48 h.

X-ray diffraction (XRD) patterns were recorded on an X'Pert Pro PANalytical diffractometer using Cu-Kα radiation at λ=0.154 nm. Raman spectra were taken with an excitation wavelength of 514.5 nm (Confocal Raman Microspectroscopy, Renishaw RM-1000). The morphology of materials was recorded by field emission scanning electron microscope (FE-SEM, Zeiss SIGMA) and transmission electron microscopy (FEI tecnai G2 F30) operated at 300 kV accelerating voltage. X-ray photoelectron spectroscopy (XPS) analysis were carried out on an ESCALAB 250Xi spectrometer (Thermo Fisher) using an Al-Ka excitation source. The carbon, sulfur, and oxygen element contents of samples were determined using an Elemental Analyzer (Elementar, vario el cube, Germany). Transition metals of the carbon materials obtained at 675 °C, 725 °C, and 775 °C were analyzed by Inductively Coupled Plasma Mass Spectrometry on an Agilent 7500a ICP-MS instrument.

## Comparison of the XRD pattern and Raman Spectroscopy of carbon obtained in different electrolyte and under different atmosphere

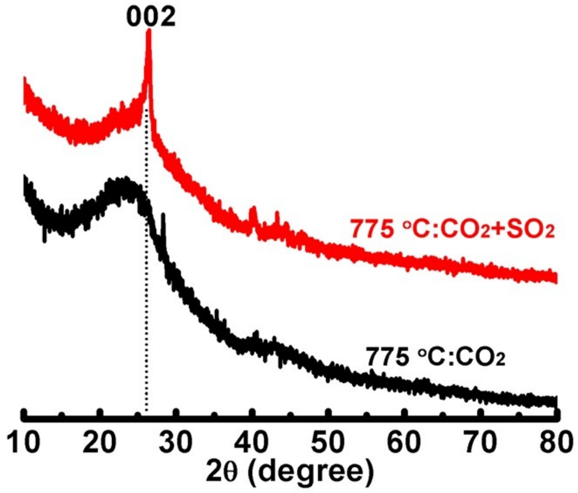

**Fig. S1** XRD pattern of the cathodic carbon obtained in molten $Li_2CO_3$-$Na_2CO_3$-$K_2CO_3$ without $Li_2SO_4$ under pure $CO_2$ atmosphere at 775 °C and a cathode current density of 62.5 mA $cm^{-2}$ (black line); XRD pattern of the cathodic carbon obtained in molten $Li_2CO_3$-$Na_2CO_3$-$K_2CO_3$-$Li_2SO_4$ under $CO_2$ and $SO_2$ atmosphere at 775 °C and a cathode current density of 62.5 mA $cm^{-2}$ (red line).

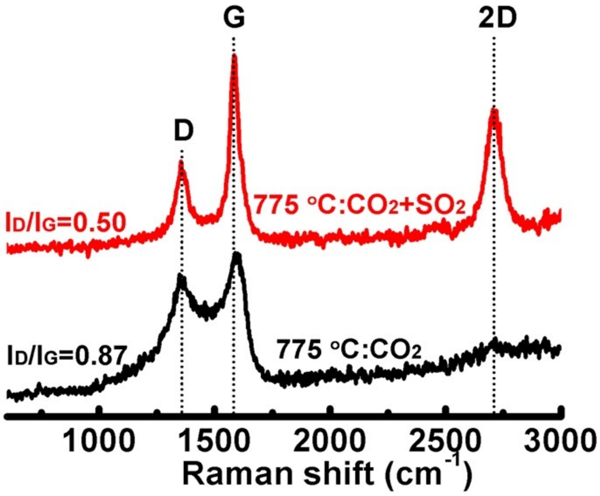

**Fig. S2** Raman spectra of the cathodic carbon obtained in molten $Li_2CO_3$-$Na_2CO_3$-$K_2CO_3$ without $Li_2SO_4$ under pure $CO_2$ atmosphere at 775 °C and a cathode current density of 62.5 mA cm$^{-2}$ (black line); Raman spectra of the cathodic carbon obtained in molten $Li_2CO_3$-$Na_2CO_3$-$K_2CO_3$-$Li_2SO_4$ under $CO_2$ and $SO_2$ atmosphere at 775 °C and a cathode current density of 62.5 mA cm$^{-2}$ (red line).

**Table S1** Elemental analysis on the electrolytic carbon materials obtained under different temperatures.

| Temperature (°C) | Measured (wt%) | | |
|---|---|---|---|
| | C | S | O |
| 475 | 70.32 | 2.782 | 23.534 |
| 575 | 75.33 | 2.427 | 18.076 |
| 675 | 83.34 | 0.989 | 10.357 |
| 775 | 83.94 | 0.887 | 6.532 |
| 825 | 88.17 | 0.611 | 6.242 |

**Table S2** Content of metallic impurities (ppm) in carbon materials obtained at 675 $^{o}$C (non-graphitization), 725 $^{o}$C (partial graphitization), and 775 $^{o}$C (graphitization) as determined by ICP-MS analysis.

| Metal | 675 $^{o}$C (non-graphitization) | 725 $^{o}$C (partial graphitization) | 775 $^{o}$C (graphitization) |
|---|---|---|---|
| Cu | - | - | - |
| Fe | - | - | - |
| Mn | - | - | - |
| Zn | - | - | - |
| Co | 18.2 | 5.7 | 4.5 |
| Ni | - | - | 1.8 |
| Ga | 0.2 | 0.3 | - |
| Mo | 34.3 | - | - |
| Pt | 5.6 | 1.5 | - |
| Ru | - | - | - |
| Sn | 88.8 | 0.8 | 0.05 |
| Ti | 32.1 | - | 8 |
| Zr | - | - | 0.01 |
| Cr | - | - | 1.8 |

## Thermodynamics of sulfur involved reactions

**Table S3** Gibbs energy change *ΔG* (kJ mol$^{-1}$) of the reactions under different temperature (data from HSC 5.0)

| Temperature ($^{o}$C) | 475 | 525 | 575 | 675 | 725 | 775 | 825 |
|---|---|---|---|---|---|---|---|
| $4Li_2O + 4SO_2$ (g) = $3Li_2SO_4 + Li_2S$ | -625.6 | -590.8 | -556.4 | -497.8 | -469.2 | -441.0 | -413.2 |
| $4Li_2CO_3 + 4SO_2$ (g) = $3Li_2SO_4 + Li_2S + 4CO_2$ (g) | -197.9 | -191.6 | -185.4 | -181.8 | -179.2 | -168.4 | -157.6 |
| $4S + 4Li_2CO_3 = Li_2SO_4 + 3Li_2S + 4CO_2$ (g) | 77.5 | 53.7 | 30.4 | -17.7 | -40.2 | -54.0 | -67.4 |
| $C+2S =CS_2$(g) | 0.9 | -5.7 | -12.1 | -24.8 | -31.0 | -37.2 | -43.3 |