Electronic Supplementary Material (ESI) for RSC Advances

Supporting online information

Influence of CO_2 on the stability of discharge performance for Li-air batteries with hybrid electrolyte based on the graphene nanosheets

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Experimental

Graphene naosheets is obtained using precursor graphite as a starting material through the chemical reduction of graphene oxide in solution.[1,2] The reduction of graphite oxide is carried out stirring with hydrazine hydrate at room temperature for 24 h, then wash with distilled water until neutral and dried at room temperature for 24 h to obtain the graphene nanosheets.

The catalyst paste is prepared from the different graphene nanosheets by the following procedure. The carbon materials (graphene nanosheets) (90%), polytetrafluoroethylene (PTFE) (7%) and Acetylene Black (AB) (3%) is well mixed, and then is roller-pressed into a sheet to form catalytic layer. The gas diffusion layer is prepared by mixing the acetylene black (60%) and PTFE (40%), and then is rolled to form film. Consequently, the air catalytic layer is prepared by pressing the catalytic layer and gas diffusion layer onto nickel mesh.

The electrochemical test set up for Li-air battery with hybrid electrolyte is described in previous work of our group.[3] 1 M $LiClO_4$/ED/DEC are used as the organic electrolyte and 1 M $LiNO_3$+0.5 M LiOH is used as the aqueous electrolyte. Then, the solid state electrolyte $Li_{1+x+y}Al_x(Ti,Ge)_{2-x}Si_yP_{3-y}O_{12}$ (LISICON) film is used as the separating membrane between organic electrolyte and aqueous electrolyte to prevent intermixes between the two solutions. The cells is discharged at the current density of 0.5 $mAcm^{-2}$ until the experiment is finished in three different atmospheres: air (about 400 $ppmCO_2/O_2$), and 1000 $ppmCO_2/O_2$. The galvanostatic intermittent titration technique (GITT) is carried out discharging at the current density of 0.5 $mAcm^{-2}$ for 30 min, and then rest for 3 h, 50 cycles.

The discharge products are characterized by X-ray photoelectron spectroscopy (XPS) (S-Probe ESCA Model 2803), XRD and optical microscopy. The graphene nanosheets are characterized by X-ray photoelectron spectroscopy (XPS) (S-Probe ESCA Model 2803), BET and scanning electron microscopy (SEM) (JEOL, JEM-2010F).

Reference:

1 Hummers, W. S., & Offeman, R. J. Preparation of graphitic oxide. J. Am Chem Soc **80**, 1339 (1958).

2 Yoo, E.J. et al. Enhanced electrocatalytic activity of Pt subnanoclusteres on graphene nanosheet surface. Nano Letters **9**, 2255-2259 (2009).

3 Wang, Y. & Zhou, H. A lithium-air battery with a potential to continuously reduce O_2 from air for delivering energy. Journal of Power Sources **195**, 358-361 (2010).

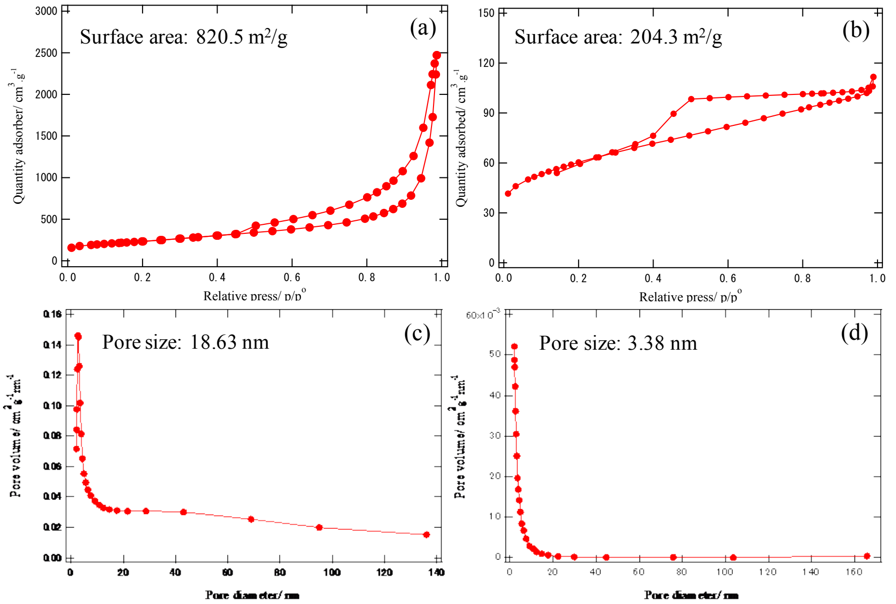

Fig. S1 Nitrogen adsorption isotherms of commercial graphene sheets (a) and graphene nanosheets (b). Pore size distribution of commercial graphene sheets (c) and graphene nanosheets (d).

Figure S1 shows the Brunauer-Emmett-Teller (BET) nitrogen adsorption isotherms of commercial graphene sheets and graphene nanosheets. Both samples exhibit Type I + Type II behavior. The specific surface area is estimated to be 820.5 and 204.3 m^2/g for commercial graphene sheets and graphene nanosheets, respectively. Furthermore, the pore size of both samples also is estimated to be 18.63 and 3.38 nm for commercial graphene sheets and graphene nanosheets, respectively.

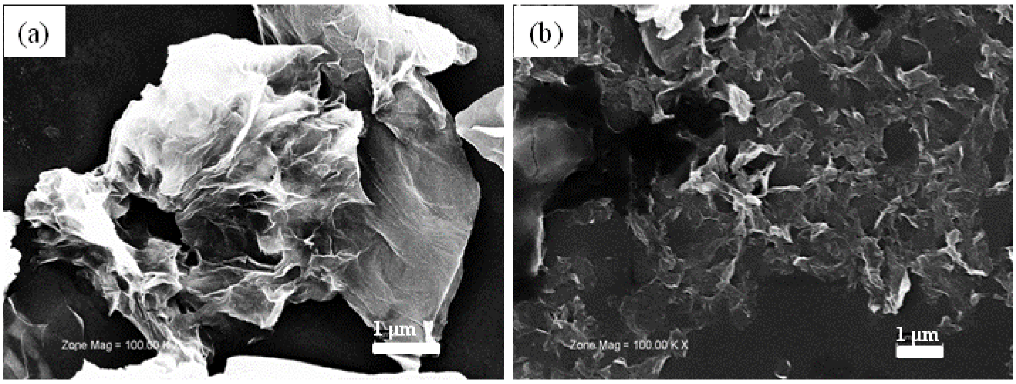

Fig. S2 SEM images of commercial graphene sheets (a) and graphene nanosheets (b)

Figure S2 shows SEM images of commercial graphene sheets and graphene nanosheets. As can be seen in Figure S2, the commercial graphene sheets and graphene nanosheets have a curled morphology with a winkled and paper-like structure.

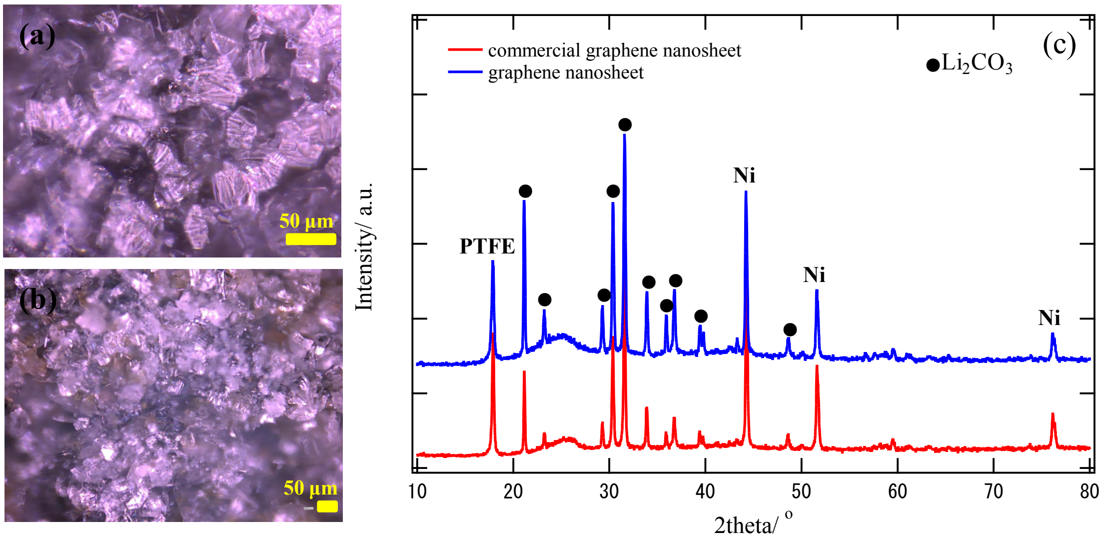

Fig. S3 Optical images of commercial graphene sheets (a) and graphene nanosheets (b) after discharge process for 100 and 150 h, respectively. XRD patterns of commercial graphene sheets and graphene nanosheets after discharging in 1%CO_2/O_2 (c).

Figure S3 (a), (b) shows the optical images of commercial graphene sheets and graphene nanosheets after discharge for 100 and 150 h, respectively in air condition. It is shown that Li_2CO_3 crystal is formatted on a whole air electrode surface for both samples. Moreover, it is also confirmed the formation of Li_2CO_3 of both samples after long-term discharge process in 1%CO_2/O_2 by XRD result (Figure S2 (c)).

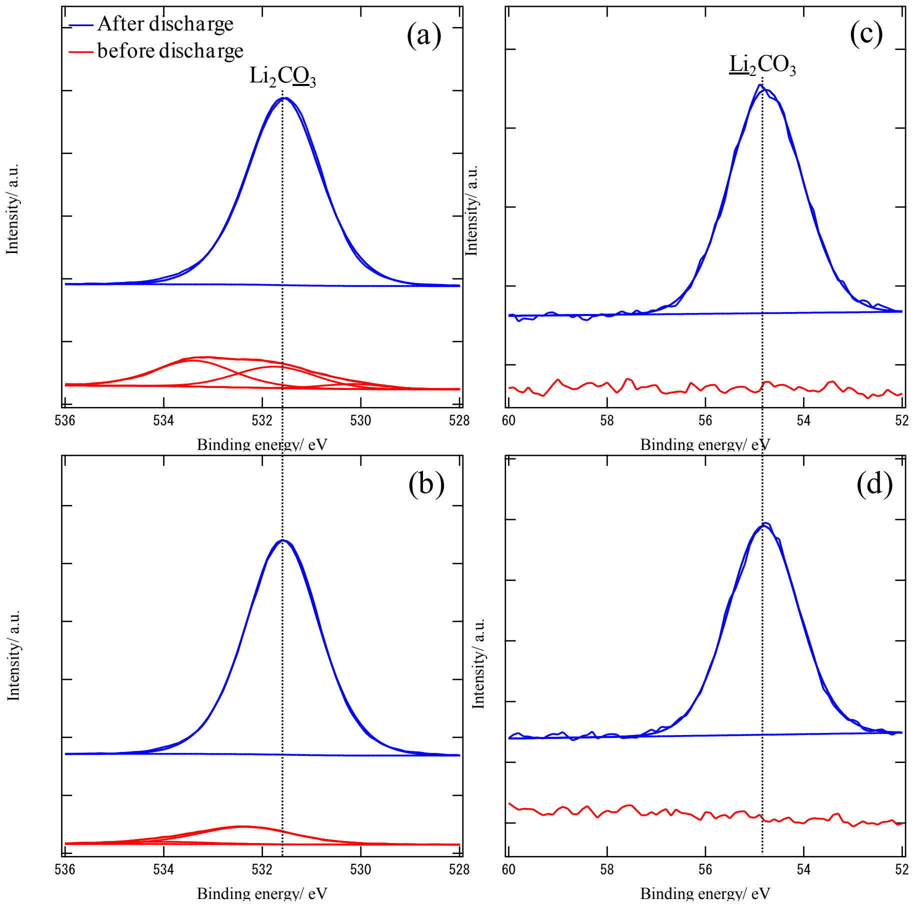

Fig. S4 the O1s XPS spectra of commercial graphene sheets (a) and graphene nanosheets (b). The Li1s XPS spectra of commercial graphene sheets (c) and graphene nanosheets (d).

Fig. S4 shows the O1s and Li1s of XPS spectra of commercial graphene sheets and graphene nanosheets before and after long-term discharge process. The main O1s XPS peak from the Li_2CO_3 after long-term discharge process is located at 531.8 eV, which is in reasonable agreement with reported binding energy for Li_2CO_3 (532.2 eV). The Li 1s peak of Li_2CO_3 at 54.8 eV after discharge process is in agreement with reported value for Li2CO3 (55 eV).