

## Supporting Information

### **Copper nanoparticles spaced 3D graphene films for binder-free lithium-storing electrodes**

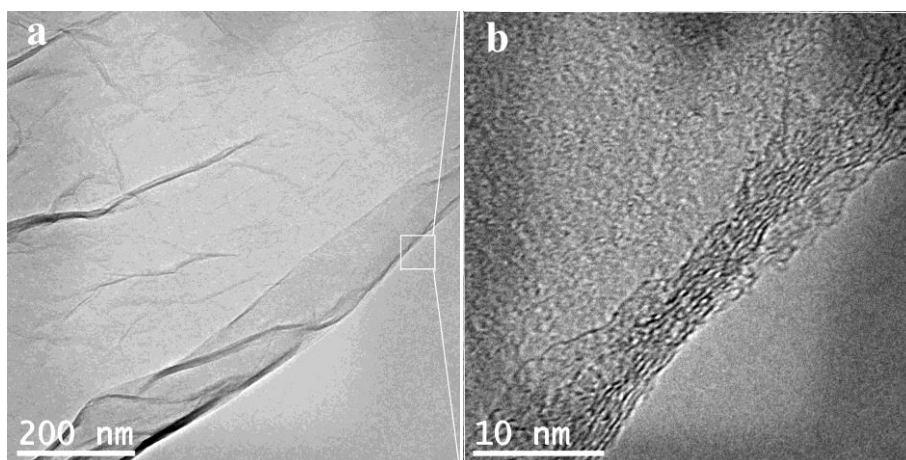
Dong-Jie Guo,<sup>a</sup> Zi-Ying Wei,<sup>a</sup> Bo Shi,<sup>b</sup> Shi-Wen Wang,<sup>a</sup> Li-Zhen Wang,<sup>a</sup> Wei Tan<sup>c</sup> and  
Shao-Ming Fang<sup>\*a</sup>

<sup>a</sup> State Laboratory of Surface & Interface, Zhengzhou University of Light Industry,  
Zhengzhou, China, 450002

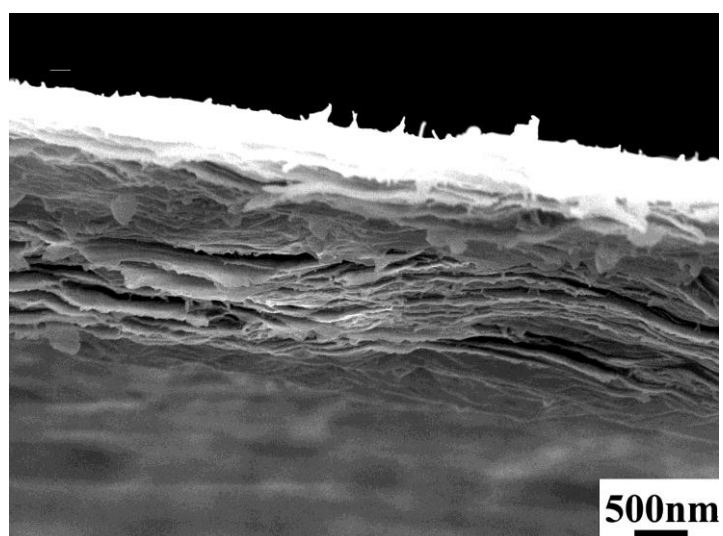
<sup>b</sup> College of Energy and Power Engineering, Nanjing University of Aeronautics and  
Astronautics, Nanjing, China, 210016

<sup>c</sup> Department of Mechanical Engineering, University of Colorado, Boulder, USA,  
80309

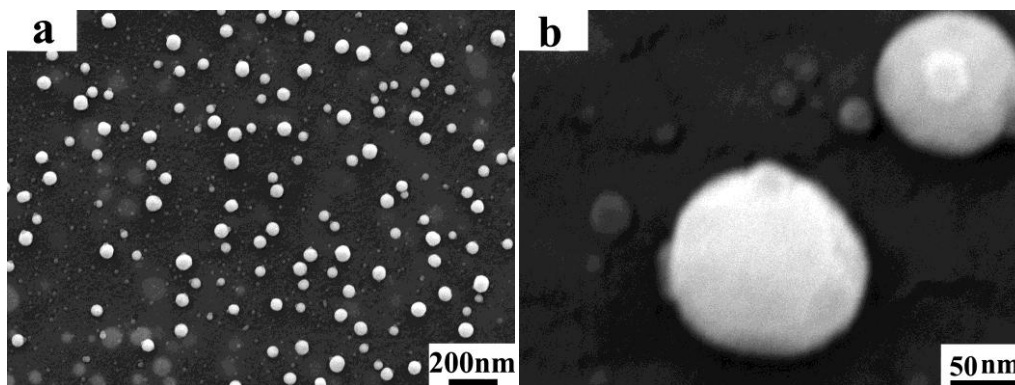
\* Corresponding Author, Correspondence should be sent to: [mingfang@zzuli.edu.cn](mailto:mingfang@zzuli.edu.cn)



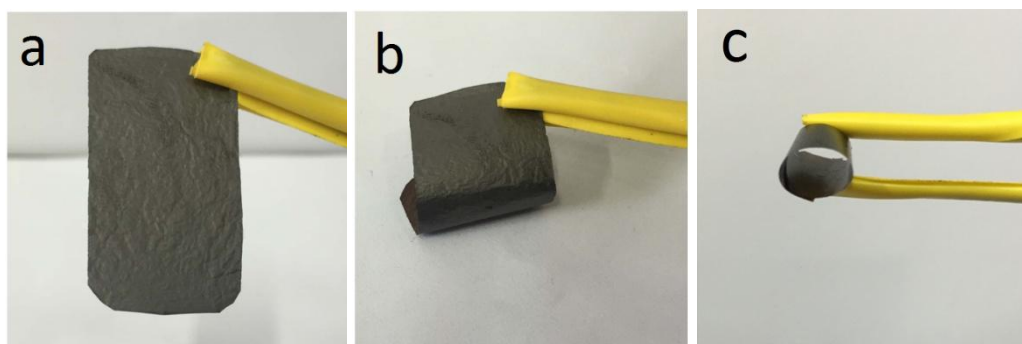
**Figure S1.** *a* is a TEM image of GO flake with a flexible sheet structure and small wrinkles on the surface, *b* is its HRTEM image shows that there are 8-13 layers of GO flakes stacking at the edge.



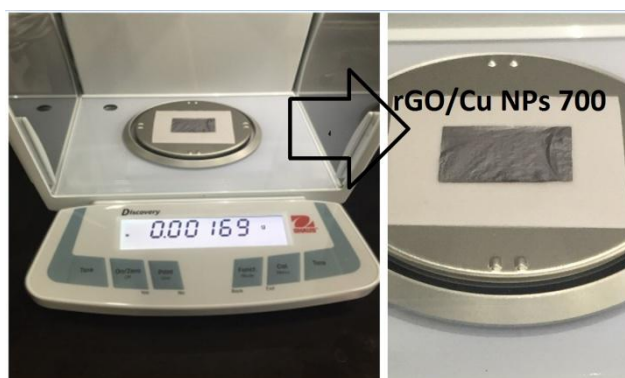
**Figure S2.** Cross-sectional SEM view of GO-EPD film. The entire film is around 2  $\mu\text{m}$  thick, showing a highly porous texture.



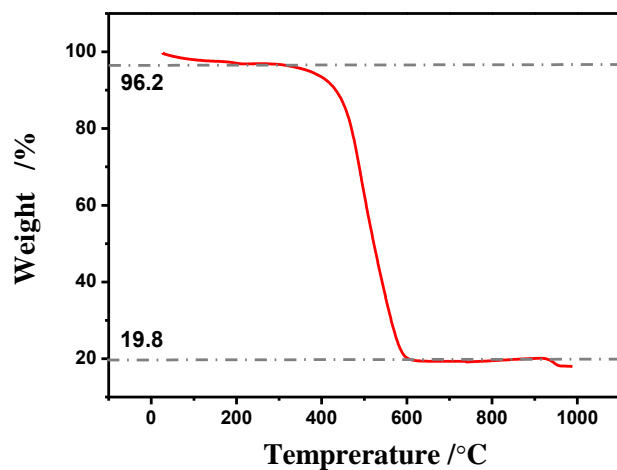
**Figure S3.** Top-view SEM images of the rGO/Cu NPs 700 with magnification of 10,000 (a) and 300,000 (b) times. *a* shows that a large number of Cu NPs uniformly distribute on the graphene surface, some Cu NPs locate below the surface, showing light white color; *b* shows high resolution images of spherical Cu NPs and un-grown Cu NPs.



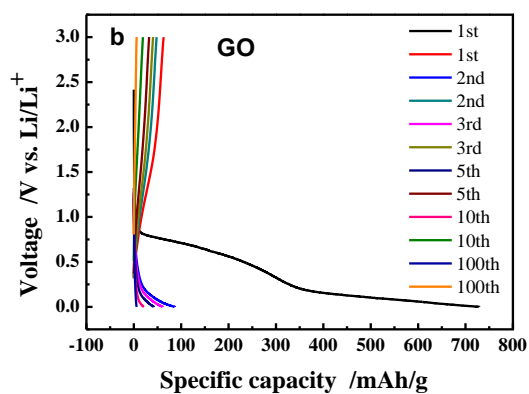
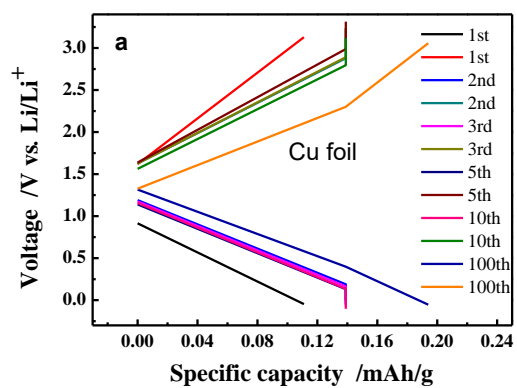
**Figure S4.** Optical images of graphene composite “tube”. A sample of rGO/Cu NPs 700 film was put into a package by a tweezer.

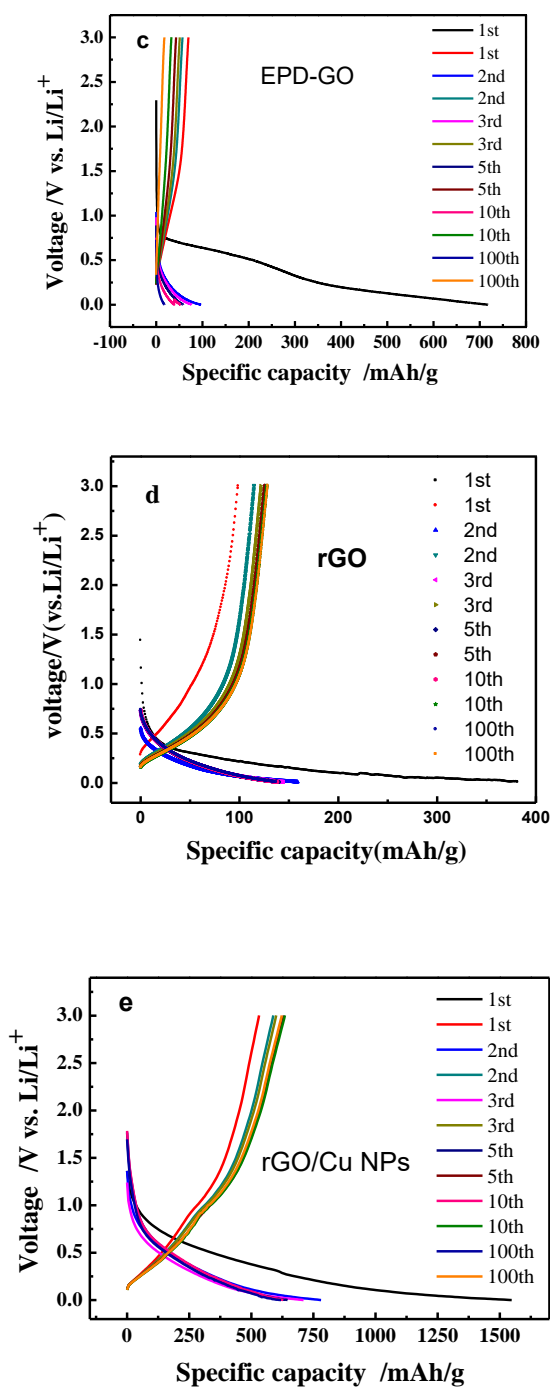


**Figure S5.** Demonstration of the measurement of the sample mass. A balance (Ohaus Discovery, DV215CD) with a sensitivity of 0.0001g was used to determine the mass of graphene electrode. The displayed value of 1.69 mg was the net mass of rGO/Cu NPs 700 membrane with an area of 6.25 cm<sup>2</sup>. To obtain accurate measurement with the balance, a sample with a larger area was measured, which was used to determine the mass per unit area. Therefore, the mass of an electrode with an area of 1.18 cm<sup>2</sup> can be obtained by calculation.

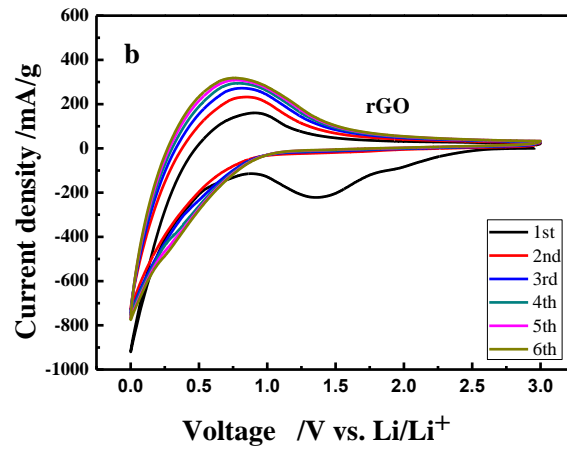
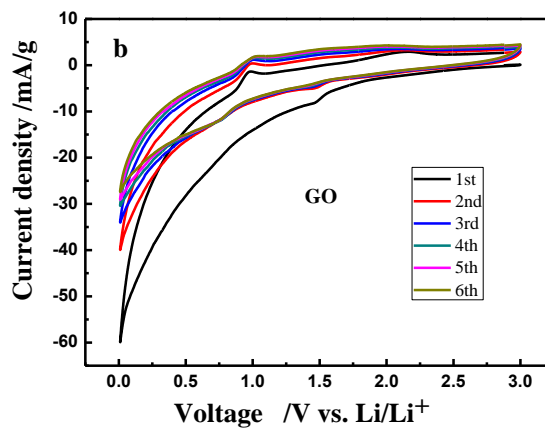
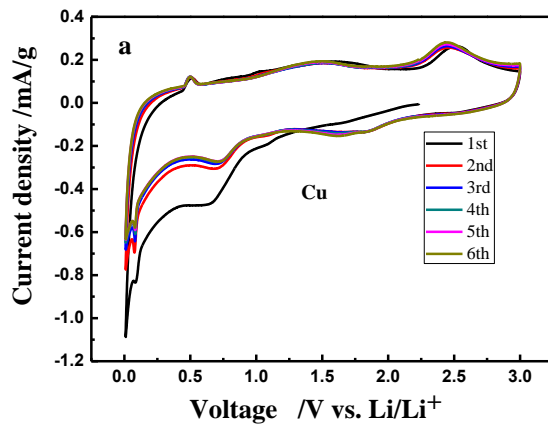


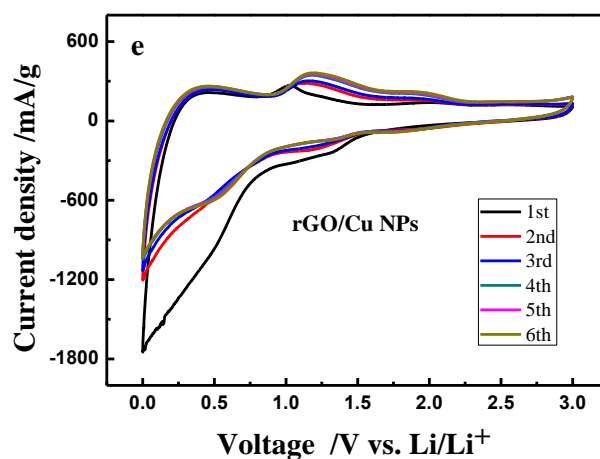
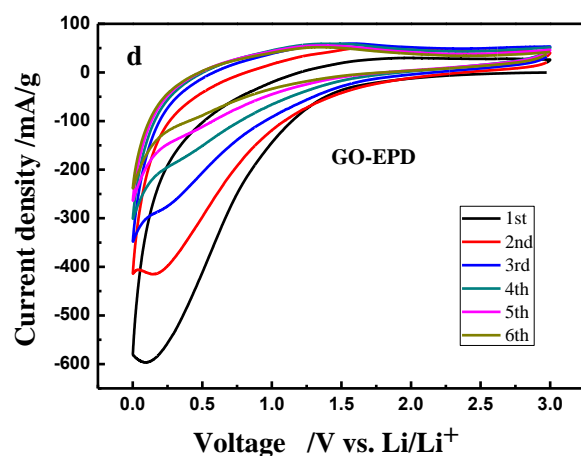
**Figure S6.** Thermogravimetric curve of rGO/Cu NPs 700 film. Under O<sub>2</sub> atmosphere, graphene skeleton completely decomposes at 616 °C. After full removal of C element, Cu element remains. Therefore, the mass ratio of Cu element is 15.6%.





**Figure S7.** The 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, 5<sup>th</sup>, 10<sup>th</sup>, and 100<sup>th</sup> cycles of the Cu foil (a), GO (b), GO-EPD (c), rGO (d), and rGO/Cu NPs 700 (e) films at a current density of 0.2 A/g (vs Li/Li<sup>+</sup>).





**Figure S8.** Cyclic voltammogram curves of the Cu foil (a), GO (b), rGO (c), GO-EPD (d), and rGO/Cu NPs 700 (e) films at a scan rate of  $0.1 \text{ mVs}^{-1}$ .

**Table S1.** Mass and size parameter of battery electrode

	Film mass /mg	film size /cm <sup>2</sup>	mass per unit area /mg/cm <sup>2</sup>	radius of electrode /cm	electrode area /cm <sup>2</sup>	mass of electrode /mg
GO	6.12	14.21	0.431	0.613	1.18	0.508
rGO	4.32	13.25	0.326	0.613	1.18	0.384
GO-EPD	3.53	12.23	0.289	0.613	1.18	0.341
rGO/Cu NPs 400	2.02	6.72	0.301	0.613	1.18	0.355
rGO/Cu NPs 550	2.33	8.20	0.284	0.613	1.18	0.335
rGO/Cu NPs 700	1.69	6.25	0.270	0.613	1.18	0.319
rGO/Cu NPs 850	2.01	7.78	0.258	0.613	1.18	0.304

**Table S2.** Surface area, pore volume, and other related parameters of graphene families derived from nitrogen porosimetry analyses.

	sample mass /g	surface area /m <sup>2</sup> /g	mean pore size /nm	pore capacity /cm <sup>3</sup> /g	adsorption type
GO	0.1086	9.61	26.676	0.063	Type IV
rGO	0.1305	5.29	14.922	0.020	Type IV
GO-EPD	0.1298	3.36	33.075	0.041	Type IV
rGO/CuNPs 400	0.1414	28.19	36.854	0.175	Type IV
rGO/CuNPs 550	0.1913	25.54	41.750	0.184	Type IV
rGO/CuNPs 700	0.1568	22.25	49.308	0.204	Type IV
rGO/CuNPs 850	0.1378	21.01	45.940	0.216	Type IV

**Table S3.** Interlayer spaces of graphene families. The interlayer distance between crystalline planes is calculated by the following Bragg's equation:  $2d\sin\theta=n\lambda$ ; where,  $d$ : interlayer distance,  $\theta$ : scattering angle,  $\lambda$ : wavelength of incident X-ray (= 1.54 Å).

Samples	$\lambda$	$\theta$	$\sin\theta$	d /nm
GO	0.154	5.855	0.1020	0.7503
GO-EPD	0.154	5.905	0.1028	0.7412
rGO	0.154	12.905	0.2233	0.3448
rGO/CuNPs 400	0.154	12.051	0.2087	0.3694
rGO/CuNPs 550	0.154	12.554	0.2173	0.3544
rGO/CuNPs 700	0.154	12.646	0.2189	0.3517
rGO/CuNPs 850	0.154	12.714	0.2201	0.3499
NFG	0.154	13.091	0.2265	0.3390