

Supporting Information

For a novel interfacial synthesis of MnO-NiO-reduced graphene oxide hybrid as supercapacitor electrode with enhanced capacitive performance

Weidong Liu¹, Xiaobing Wang¹, Lishu Zhang and Jianshe Lian*

Supplementary Figures

The FESEM images of the as-obtained products prepared by common coprecipitation method with and without stirring condition are shown in Figure S1a and b. Obviously, no matter accompanied by stirring condition or not, both kinds of production show serious agglomeration problem in microscale. Although without stirring condition, the size of the synthetic decreases at certain extent, but is still in the range of sub-micrometer, not in nanometers (Fig. S1b). Compared to the morphology of MNO and MNG hybrids (Fig. S3 and Fig. 5), the homogeneous distribution, porosity, surface area and particle size of the common coprecipitation samples are all significantly without any comparability.

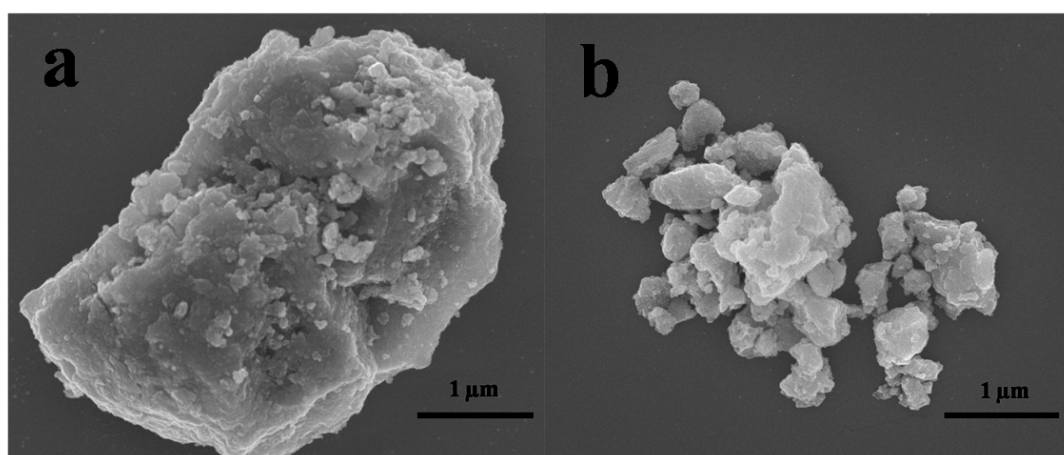
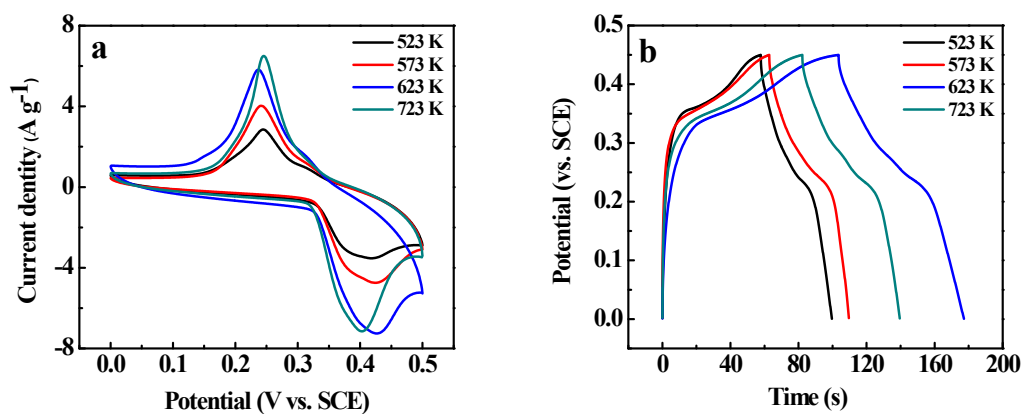


Fig. S1. FESEM images of common coprecipitation samples: (a) with magnetic stirring condition; (b) without magnetic stirring condition.

Fig. S2a and b displayed the CV and GCD curves of the common coprecipitation samples varying with annealing temperature. Similar to the curves of the MNO and MNG hybrids, the typical redox peaks in the CVs and the nonlinear variation in the GCDs indicated the same pseudocapacitance nature of common coprecipitation samples. The specific capacitance calculated from the discharge curves was showed in Fig. S2c. Among the various annealing temperatures, the sample annealed at 623 K exhibited the highest specific capacitance as 155.3 F g^{-1} at a current density of 1 A g^{-1} . Thus, we can confirm 623 K as the optimum annealing temperature.



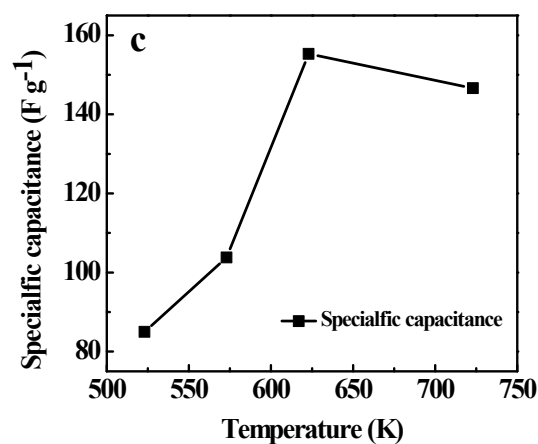


Fig. S2. Common coprecipitation samples annealed at different temperatures: (a) CV curves; (b) GCD curves; (c) specific capacitance values.

The obtained MNO particles are disperse without large-scale agglomeration and are in nanoscale (Fig. S3a). As shown in Figure S3b, many nanospheres of MNO hybrid with an average diameter of 20~30 nm are assembled to form a netlike porous nanostructure. The detail TEM image of the MNO nanoparticles is displayed in Figure S3c, where the particle size is clearly observed. Compared to common coprecipitation samples (Fig. S1), the particle size and morphology of the as-obtained products have been largely improved and a nanostructure is obtained. Moreover, the corresponding diffraction rings (Fig. S3d) identify the nanocrystalline nature of the MnO and NiO in the MNO hybrid.

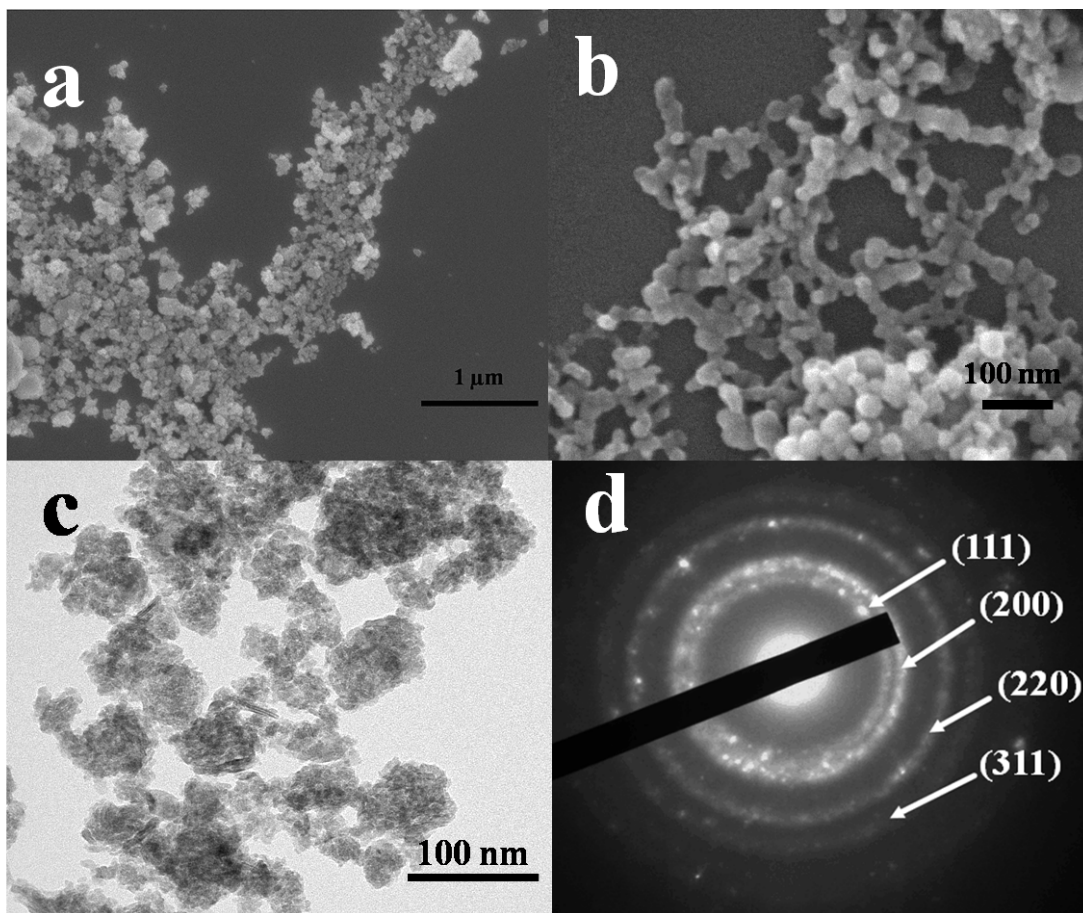


Fig. S3. MNO: (a, b) FESEM images; (c) TEM image; (d) the corresponding SAED pattern.

Fig. S4a and b showed the typical CV curves and galvanostatic discharge curves of our symmetric supercapacitor at different scan rates and current densities in 3M KOH aqueous solution. When the current densities were 0.5, 1, 2 and 4 A g⁻¹, the specific capacitance values can be calculated from the discharge curves to be 316, 174, 152 and 140 F g⁻¹. Fig. S4c demonstrated the Ragone plot of the as-prepared symmetric supercapacitor measured in the voltage window of 0–0.5 V at different current densities. Specific energy and power densities were calculated by the formulas $E = CV^2/2$ and $P = E/t$, where E is the energy density, C is the specific capacitance, V is the potential window of discharge, P is the power density, and t is the discharge time in the potential window.¹ While the energy density reduced from 10.97 W h kg⁻¹

to 4.86 W h kg^{-1} , the power density increased from 125 W kg^{-1} to 1000 W kg^{-1} , as the current density increased from 0.5 A g^{-1} to 4 A g^{-1} . The galvanostatic charge-discharge cycle test was also studied in a symmetric supercapacitor for 2000 cycles at 1 A g^{-1} (Fig. S4e), and parts of the charge-discharge curves during the test were shown as Fig. S4d. In the initial stage of the cycle test, the specific discharge capacitance was calculated as 350.64 F g^{-1} . But during the subsequent cycles, the capacitance dropped in a certain extent, and finally stabilized at about 138 F g^{-1} . However, the coulombic efficiency has been always keeping at a high rate about 99%. The capacitance decline might be attributed to the irreversible recovery of the active materials during cycling, and sluggish kinetics of the device. As for the distinction of capacitance with the three-electrode system, it is likely due to the matching problem arisen from utilizing the same metal oxide electrodes with a narrow electrochemical window.²

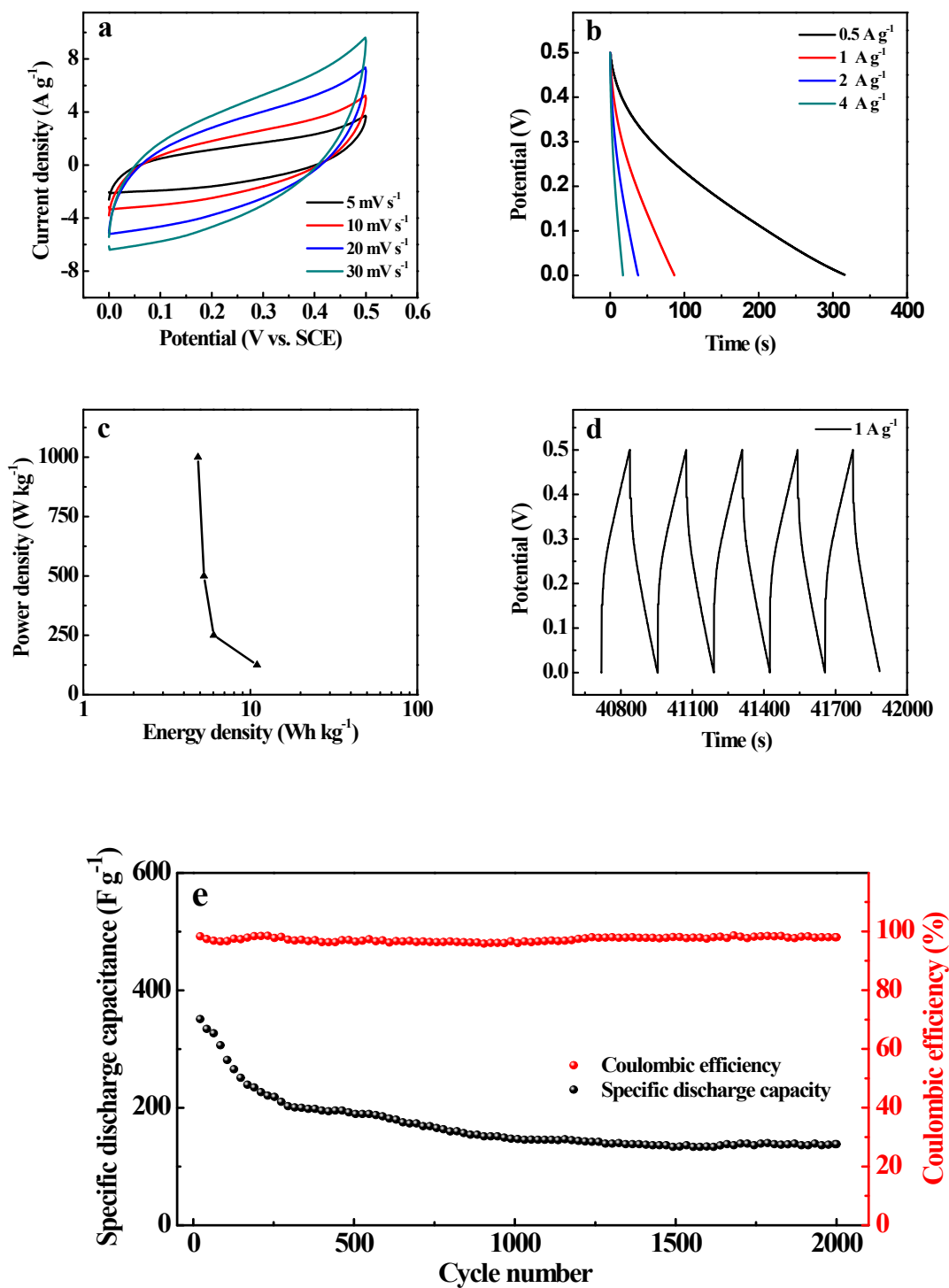


Fig. S4. The electrochemical performance of the MNG hybrid electrode in a two-electrode system measured in 3 M KOH solution. (a) CV curves at different scan rates; (b) Galvanostatic discharge curves at different current densities; (c) Ragone plot related to energy and power densities of MNG//MNG symmetric supercapacitor; (d) GCD curves of the symmetric supercapacitor during the cycle testing; (e) The cycle stability measured at 1 A g^{-1} (the black points show the change trend of specific capacity during the cycle testing, and the reds show the change of coulombic efficiency).

References

1. J. Yan, Z. Fan, W. Sun, G. Ning, T. Wei, Q. Zhang, R. Zhang, L. Zhi and F. Wei, *Advanced Functional Materials*, 2012, 22, 2632-2641.
2. H. Wang, C. M. B. Holt, Z. Li, X. Tan, B. S. Amirkhiz, Z. Xu, B. C. Olsen, T. Stephenson and D. Mitlin, *Nano Research*, 2012, 5, 605-617.