One pot synthesis of Nickel foam supported self-assembly of $NiWO_4$, $CoWO_4$ nanostructures that act as high performance electrochemical capacitor electrodes

Guanjie He[a], Jianmin Li[b], Wenyao Li[c], Bo Li[d], Nuruzzaman Noor[a], Kaibing Xu[b], Junqing Hu[b]* and Ivan P. Parkin[a]*

[a]*Materials Chemistry Centre, Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K., E-mail:i.p.parkin@ucl.ac.uk*

[b]*State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China. E-mail: hu.junqing@dhu.edu.cn*

[c]*School of Material Engineering, Shanghai University of Engineering Science, Shanghai 201620, China*

[d]*Department of Chemistry, Duke University, NC 27708, U.S.A.*

Preparation of the working electrodes for powder samples

Working electrodes were prepared by mixing the as-synthesized $NiWO_4$ or $CoWO_4$ powders (80 wt%) with acetylene black (15 wt%), and poly(tetrafluoroethylene) (5 wt%). Then, the mixture was transferred into a bottle with a few drops of ethanol and was stirred by magnetic over 8 hours to form slurry uniformly. After that, the slurry was pressed onto cleaned Ni foam substrate and dried at 100 °C in vacuum oven overnight to remove the solvent. The electrodes were pressed under 10 MPa to enhance contact with the Ni foam. The testing of the electrochemical performance are the same as their binder-free electrodes testing.

Calculation of the weight of active materials

The weight of the active materials were calculated as follows: First, a piece of Ni foam was dried in a vacuum oven at 60 ^{o}C for 6 h after washing with 6 M hydrochloric acid and DI water. Then, the mass of such dried Ni foam was weighed by XS analytical balance (Mettler Toledo; δ = +/- 0.01 mg), which was noted as m_a. Second, the Ni foam was put into the autoclaves for reaction; after that, the Ni foam with active materials were washed with DI water and ethanol and dried in a vacuum oven at 60 ^{o}C overnight. The mass was weighed by analytical balance and noted as m_b. Finally, the weight of the active materials for binder-free electrodes were calculated according to the equation: $m_{\text{binder-free materials}} = m_b - m_a$. As the Ni foam for testing is 2 cm^2 and the total area of it is 4 cm^2. So the mass for calculation is $m_{test} = 0.5 \times m_{\text{binder-free materials}}$.

The weight of the powder samples were calculated as follows: First, a piece of Ni foam was cleaned, dried and weighed m_c. Second, after the slurry was dried and pressed on the Ni foam, the mass was noted as m_d. Finally, the mass of the powdery active materials were calculated according to the equation: $m_{powder\ materials} = 0.8\times(m_d-m_c)$.

Optimizing the reaction time

As can be noticed from XRD patterns, 4 h samples and 10 h samples showed almost no obvious difference for both $NiWO_4$ and $CoWO_4$ nanostructures, which demonstrated the $NiWO_4$ and $CoWO_4$ phase were formed at the early stage of the synthesis and maintained unchanged with longer hours. From SEM images of different reaction time samples, the ions and precursors in the solutions were absorbed on the Ni foam substrates and formed layer by layer self-assembly structures. The final morphologies depend on the reaction time as expected. The 4 h and 6 h samples show limited layers of nanoparticles on the Ni foam and the expected morphologies are not totally formed. While, for 10 h and 12 h samples, the nanostructures are either too large to be peeled off or aggregated, which limited the active materials contact with electrolyte.

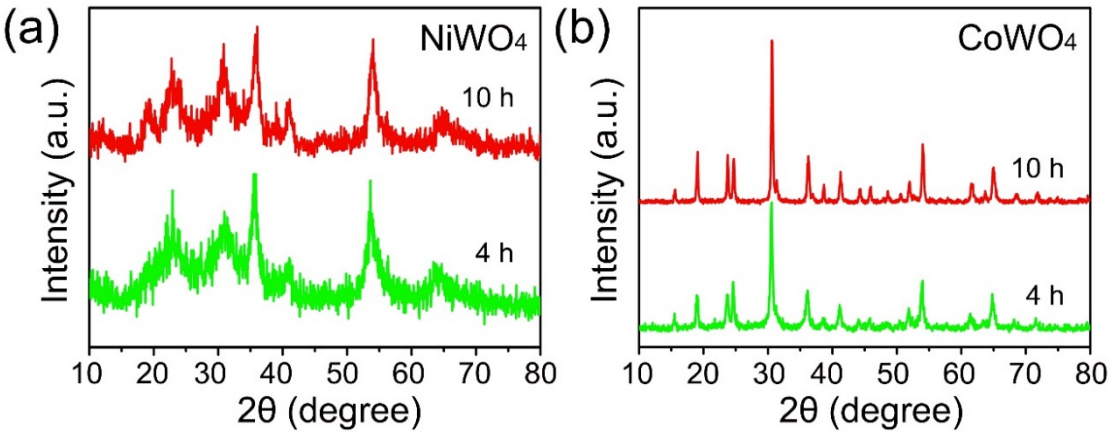


Figure S1 (a), (b) XRD patterns of $NiWO_4$, $CoWO_4$ samples with different reaction times (green line: 4 h; red line: 10 h).

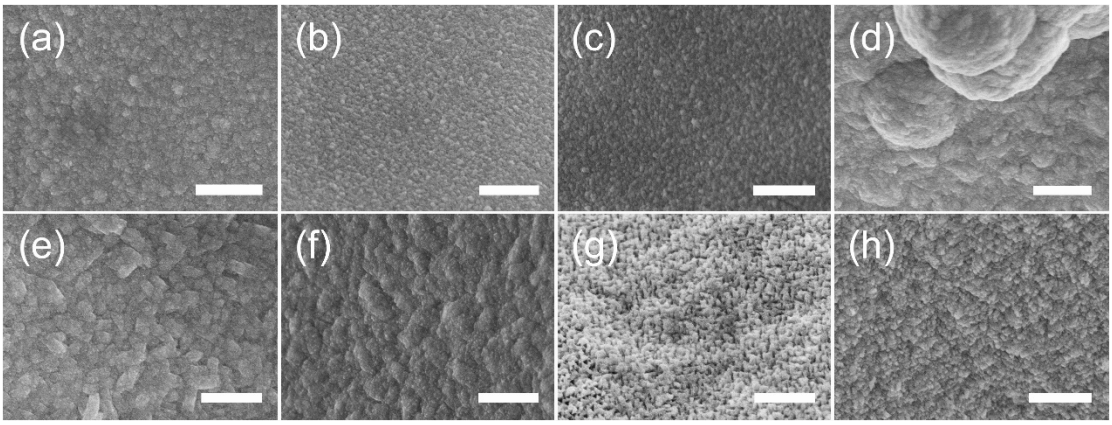


Figure S2 (a-d) SEM image of $NiWO_4$/Ni foam with different reaction time: (a) 4 h, (b) 6 h, (c) 10 h, (d) 12 h; (e-h) SEM image of $CoWO_4$/Ni foam with different reaction time: (e) 4 h, (f) 6 h, (g) 10 h, (h) 12 h (Scale bar: 500 nm).

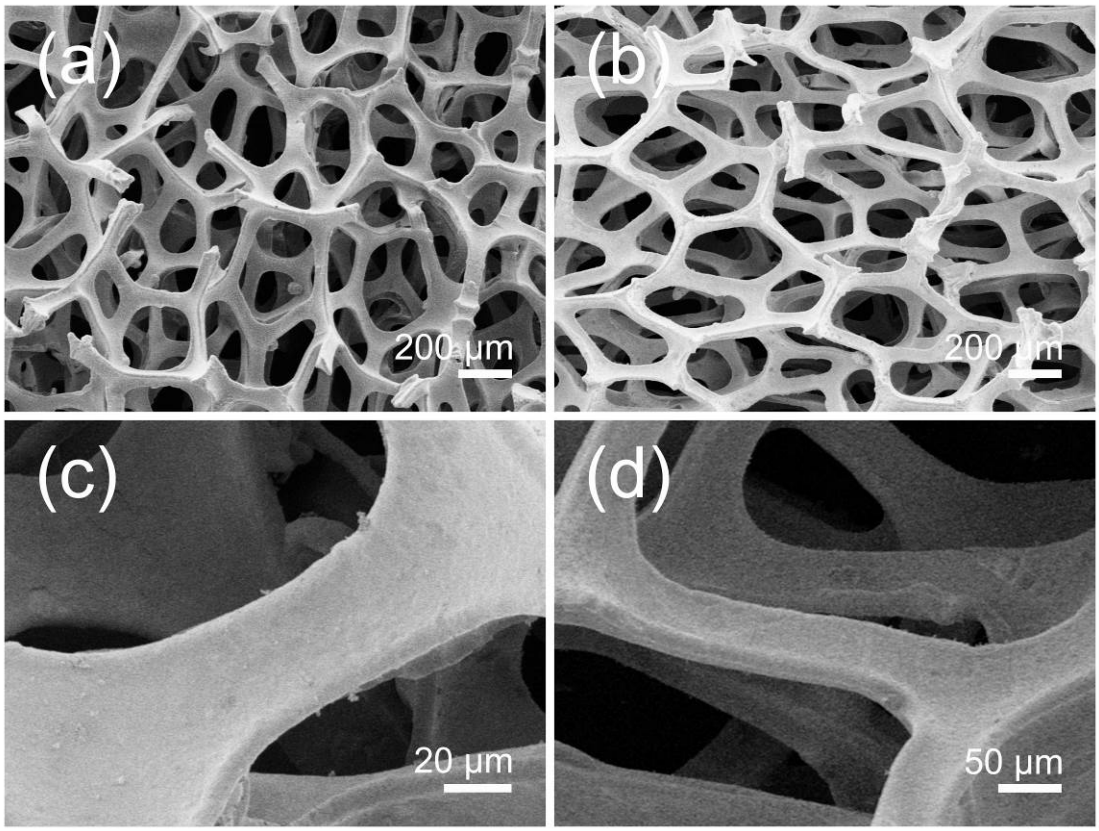
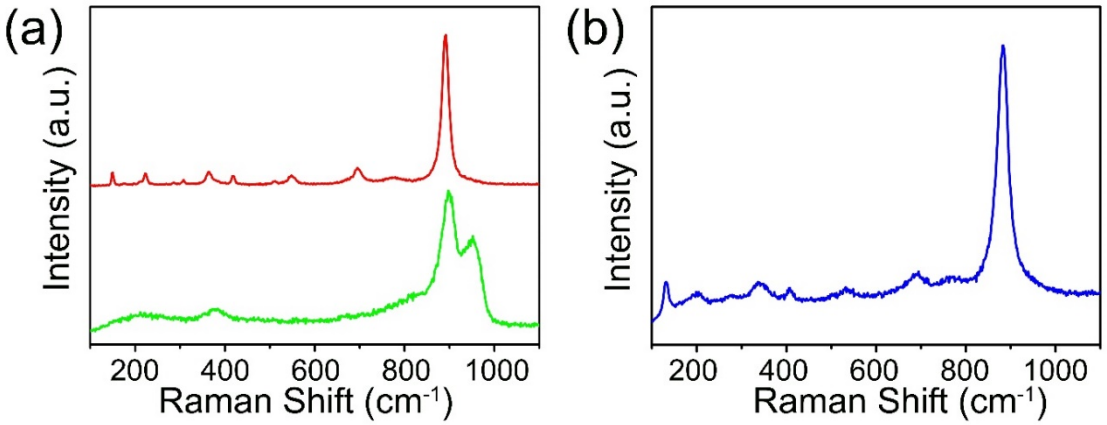


Figure S3 (a), (b) Lower-magnification SEM image of $NiWO_4$/Ni foam and $CoWO_4$/Ni foam, respectively; (c), (d) Low-magnification SEM image of NiWO4/Ni foam and $CoWO_4$/Ni foam, respectively.

Figure S4 (a) Raman spectrum of $NiWO_4$ nanostructures, before (green line) and



after (red line) annealing; (b) Raman spectrum of $CoWO_4$ nanostructures.

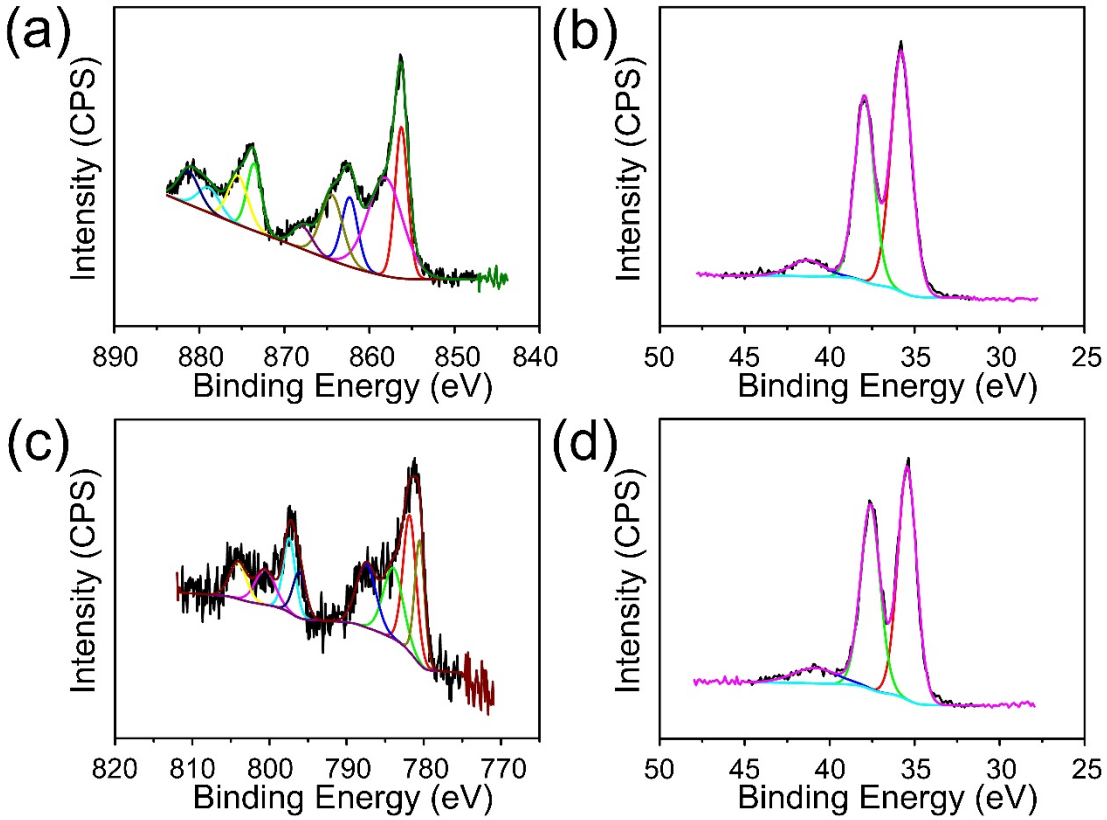


Figure S5 (a) Ni2p XPS spectrum and (b) W4f XPS spectrum of $NiWO_4$ nanostructures; (c) Co2p XPS spectrum and (d) W4f XPS spectrum of $CoWO_4$

nanostructures.

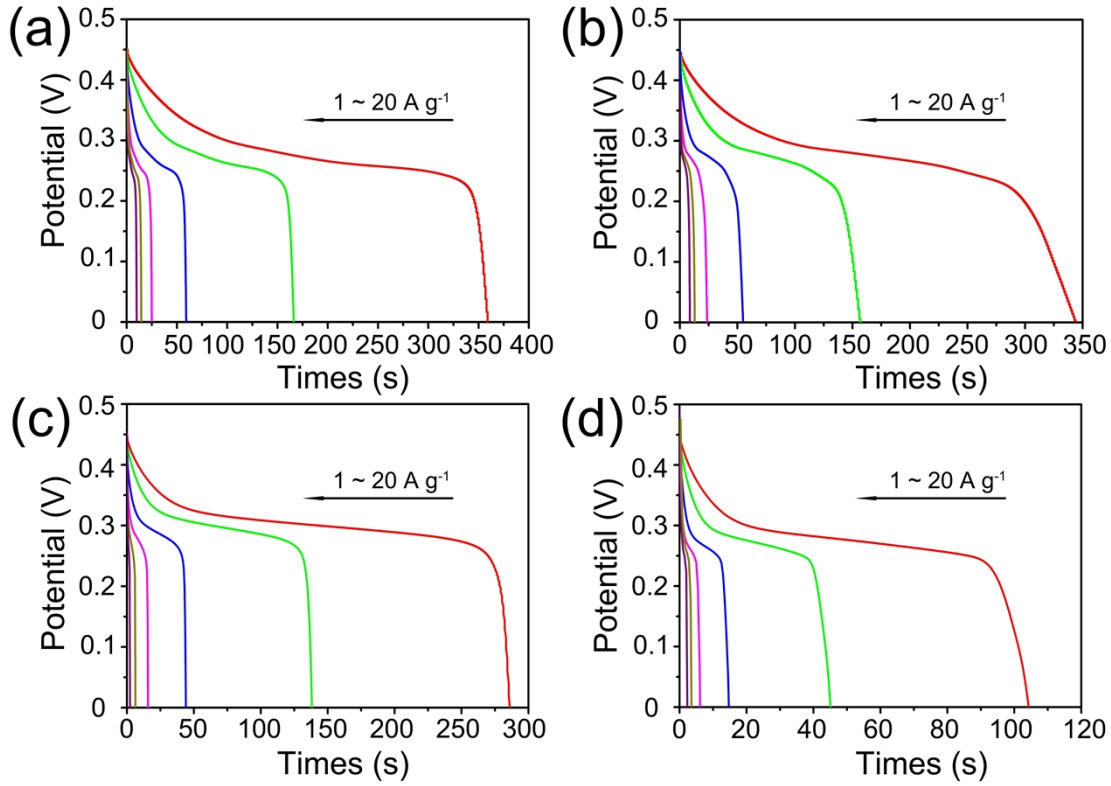


Figure S6 Discharge curves of (a) $NiWO_4$/Ni foam nanostructures, (b) $CoWO_4$/Ni foam nanostructures, (c) $NiWO_4$ powders, (d) $CoWO_4$ powders at the current densities of 1, 2, 5, 10, 15, 20 A g^{-1} respectively.

The specific capacitances of $NiWO_4$ powder samples analogue are 634, 613.3 488.9, 344.4, 200, 88.9 F g^{-1} at current densities of 1, 2, 5, 10, 15, 20 A g^{-1}, respectively, calculated from CD curves; The specific capacitances of $CoWO_4$ powder samples analogue are 231.1, 200, 161.1, 133.3, 110, 88.9 F g^{-1} at current densities of 1, 2, 5, 10, 15, 20 A g^{-1}, respectively. Rate capacitance are 14% and 38.4% of their initial values when the current density increase 20 times.

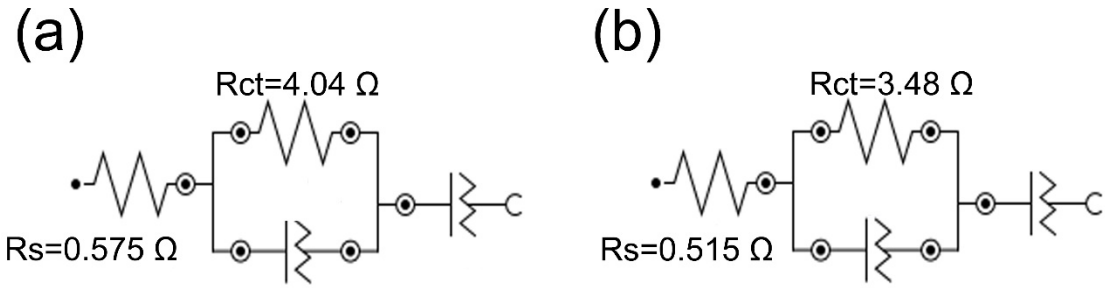


Figure S7 the equivalent fitting circuit of $NiWO_4$/Ni foam and $CoWO_4$/Ni foam.

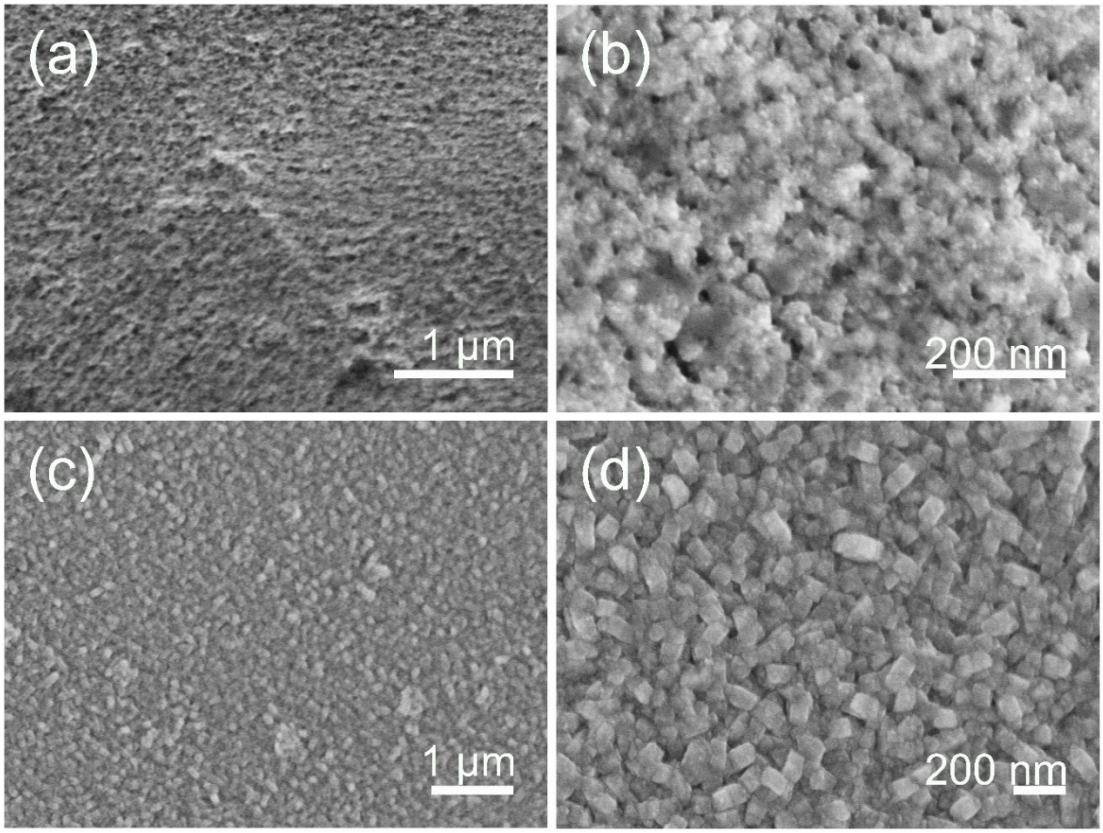


Figure S8 (a), (b) Low- and high-magnification SEM image of $NiWO_4$/Ni foam nanostructures after 6000 cycles at 50 mV s^{-1}, respectively; (c), (d) Low- and high-magnification SEM image of $CoWO_4$/Ni foam nanostructures after 6000 cycles at 50 mV s^{-1}, respectively.

References

1 L. Y. Niu, Z. P. Li, Y. Xu, J. F. Sun, W. Hong, X. H. Liu, J. Q. Wang, S. R. Yang, *ACS Appl. Mater. Interfaces*, 2013, **5**, 8044.

2 X. W. Xu, J. F. Shen, N. Li, M. X. Ye, *Electrochim. Acta*, 2014, **23**, 150.