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Supercapacitive hybrid materials from the thermolysis of porous coordination nanorods based on a catechol porphyrin

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Synthesis of a series of porous coordination polymers with nanorod morphology constructed from a catechol-substituted porphyrin [meso-tetrakis(3,4-dihydroxyphenyl)porphyrin] is reported. While the coordination polymers had moderate surface areas (100 – 400 m² g⁻¹), their thermolysis in an inert atmosphere led to carboniferous materials with large surface areas (up to 800 m² g⁻¹), containing metal oxide nanoparticles. Capacitance measurements (by electrochemical charge-discharge and cyclic voltammetry) of the resulting hybrid materials revealed that these hybrid nanomaterials exhibit high (super) capacitances (up to 380 F g⁻¹ at 1 A g⁻¹) with good cycling properties. The results demonstrate the utility of using porphyrin coordination polymers for the preparation of hybrid supercapacitor materials and also indicate that these carbon-metal oxide nanoparticle materials are promising for energy storage applications.

Introduction

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Hybrid carbon materials containing different metal oxides are promising as electrochemically-active materials and have been widely explored for their use in high performance supercapacitors,¹⁻¹³ and also for applications involving the oxygen reduction reaction (ORR).¹⁴⁻¹⁶ Of these materials, hybrid materials of carboniferous materials (i.e. graphene, carbon nanotubes or nanoporous carbons) and metal oxides have been intensively studied.¹⁻¹⁸ These hybrid chemical systems, which rely on the synergetic effect of combining two or more materials, are highly anticipated to be used in supercapacitors for battery replacement applications including electric vehicles, artificial muscles and renewable energy storage devices.^{19,20} On the other hand, coordination polymers have been demonstrated as being useful for the preparation of highly porous carbons and other materials by the use of metal clusters or complexes as sacrificial moieties, which can subsequently be removed by acid treatment.²¹ Also, thermolytic treatment of coordination polymers (PCPs), including porous and densely-packed crystalline materials,²² has been found to be an effective method for the preparation of nanoporous carbon materials. In addition, PCPs can also be transformed to metal/metal oxides-containing nanoporous carbon hybrid materials without the removal of metal sites.²³ Although nanoporous carbon/metal oxide hybrids have been reported, it has only recently been reported that such hybrid materials might be applied as effective electrode materials in supercapacitors with several metal oxides having been reported as useful including MnO₂,²⁴ RuO₂,²⁵ SnO₂,²⁶ cobalt oxides²⁷ and iron oxides.²⁸ Porphyrins are well known for their use as building blocks for the synthesis of porous coordination

polymers, or MOFs,²⁹ and these materials have also been investigated for energy-related applications including hydrogen storage and catalysis.³⁰



Scheme 1. Schematic illustration of the preparation of metal oxide/nanoporous carbon hybrid materials from porphyrin coordination polymers. Purple sphere: metal cation; green sphere: metal oxide nanoparticle.

In this work, we report the synthesis of a series of new porous coordination polymers based on a catechol-substituted porphyrin. Catechol-type ligands have only rarely been used in the synthesis of PCPs³¹ despite their known coordination capabilities for transition metal cations. Also, given the lower symmetry of the porphyrin catechol ligand due to free rotation about the macrocycle-phenyl C-C bond, we did not expect to obtain highly crystalline materials although, in some cases, we could prepare micrometer-scale needle-like crystals in reasonable yield. Thus, our PCPs were mostly obtained as



Figure 1. (A) Scanning electron microscopy image and (B) HR-TEM image of CuCP-PCP; (C) model structure of MCP-PCPs; (D) nitrogen sorption curve and (E) pore size distribution of CuCP-PCP; (F) typical powder X-ray diffraction pattern of CuCP-PCP.

amorphous or low crystallinity materials whose fine structures were difficult to analyze by single crystal techniques. Moreover, the catechol-porphyrin-based PCPs prepared here were further processed by thermolysis in an inert atmosphere providing metal oxide/nanoporous carbon hybrid materials in one step (Scheme 1). Thermolytic methods involving catecholsubstituted polymers have been previously applied in the synthesis of metal oxide/carbon hybrid materials. For instance, polydopamine has successfully been applied for this purpose.³² The advantages of our method lie in the intimate contact of metal cations in the carbon-containing ligand framework of PCP, which we believed would promote the formation of pyrolytic materials with metal ions or their oxide nanoparticles in turn intimately mixed within the resulting carbon materials. Also, in this case, metal cations are coordinated in a different geometries and, potentially, with different oxidation states. The resulting materials were characterized by various methods including powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) confirming the formation of metal oxide nanocrystals. Raman spectra indicate the formation of graphitic materials, and their morphologies were observed by FE-SEM and HR-TEM imaging. Porosities of the materials were also measured by using nitrogen sorption measurements, which indicate that thermolysis significantly increases the surface areas of the materials. The potential use of these hybrid materials in energy storage applications was explored. Electrochemical measurements demonstrate that the materials have high specific capacitances and good cycling stabilities indicating that these new nanorod like materials are suitable for energy storage application.

Experimental section

Synthetic procedures of CP-PCPs

The catechol porphyrin ligand $(CP)^{33}$ was synthesized according to a literature method (see Supplementary Information and Fig. S1). **CP-PCPs** were then synthesized by using a solvothermal method in a 25 mL autoclave. In a typical procedure, **CP** (0.02 mmol) was mixed with a metal salt precursor (0.06 mmol) in 5.5 mL H₂O/NMP (v/v = 10:1). The mixture was sonicated for 5 minutes to disperse the starting materials uniformly. The suspension was maintained at 85 °C for 24 hours then cooled to room temperature by standing under ambient conditions. The resulting precipitate was collected by filtration and washed thoroughly with deionized water then acetone yielding a dark powder. The powder was then sequentially triturated in aliquots of acetone for 24 hours until the supernatant acetone was clear.

Synthesis of metal oxides and nanoporous carbon composites

The CP-PCPs were converted to the corresponding composites by thermolysis of the CP-PCPs at 800 $^{\circ}$ C under an inert atmosphere (flowing nitrogen gas). The temperature was gradually increased from room temperature to 800 $^{\circ}$ C during a 2 h period and then maintained at that temperature for 3 hours before cooling to room temperature.

Characterization of materials

Scanning electron microscopy (SEM) of the materials was performed using an Hitachi S-4800 field effect SEM operating at



 Figure 2. FE-SEM images of MCP-PCP@800 and HR-TEM images of MCP-PCP@800. FE-SEM images of (A) FeCP-PCP@800; (B) CoCP-PCP@800; (C) NiCP-PCP@800; (D)

 CuCP-PCP@800. HR-TEM images of (E) FeCP-PCP@800; (F) CoCP-PCP@800; (G) NiCP-PCP@800; (H) CuCP-PCP@800. Insets in (E) - (H) show TEM images of individual oxide

 nanoparticles
 contained
 in
 the
 respective
 materials.

5 kV. High resolution transmission electron microscopy (HR-TEM) was carried out using a JEOL JEM-2100F operated at 200kV. Samples for HR-TEM were prepared by dropping a suspension onto standard carbon-coated copper grids followed by drying overnight under reduced pressure. Powder X-ray diffraction patterns were measured using a Rigaku Ultima III diffractometer using Cu K α radiation ($\lambda = 1.5406$ Å). Porosities of the materials were determined by measuring nitrogen adsorption-desorption isotherms using a Quantachrome Instruments Autosorb iQ2 automated gas analyzer at 77K after pretreatment at 100 °C for 20 hours.X-ray photoelectron spectroscopy (XPS) was performed on a Theta Probe spectrometer (ThermoElectron Со., Germany) using monochromated Al K_{α} radiation (photon energy 15 KeV, maximum energy resolution ≤ 0.47 eV, maximum space resolution $\leq 15 \,\mu$ m). High resolution high signal to noise ratio spectra: C 1s, Cu 2p, Ni 2p, Co 2p, and Fe 2p were recorded in 0.05 eV steps. A built-in electronic charge neutralizing electron flood gun was used to prevent sample charging. Wide scan spectra in the 1350 - 0 eV binding energy range were recorded. After a linear baseline subtraction, curve fittings were performed assuming Gaussian peak shape to determine the atomic percentages of bonding states of carbon atoms.

Electrochemical measurements

Electrochemical measurements of the electrode materials were conducted by using a three-electrode system, with Pt counterelectrode and Ag/AgCl reference electrode. The materials were prepared as a suspension in deionized water then deposited on a glassy carbon electrode. The loading masses were calculated using a quartz crystal microbalance (QCM). Glassy carbon electrodes with materials deposited were then dried in the oven at 60 $^{\circ}$ C for 2 hours. A drop of binder

(Nafion® 0.5% wt in ethanol) was added followed by drying at 60 $^{\circ}$ C overnight. Cyclic voltammograms (CV) were measured using an electrochemistry workstation (ALS CH Instruments Electrochemical Analyzer Model 850D) in the potential range from -0.5 V to 0.5 V. Supercapacitance was measured by cyclic voltammogram and chromopotentional charge-discharge methods. The specific capacitance was calculated according to the following equation:

$$C = \frac{I \times \Delta t}{m \times \Delta V}$$

Results and Discussion

Porphyrin building blocks containing carboxylic acid groups have previously been widely exploited to synthesize PCPs (and MOFs).³⁴ In this work, a catechol-substituted porphyrin (CP) has been used for the first time to synthesize porous coordination nanorods. Catechol is known to coordinate many metal ions so that molecules substituted with several catechol ligands ought to be polymerizable by their reaction with a variety of metal precursors such as iron (III) chloride, cobalt (II) acetate, nickel (II) acetate or copper (II) acetate. MCP-PCPs were synthesized under solvothermal conditions, and were obtained in 79% (Fe), 70%(Co), 78%(Ni) and 81%(Cu) yields respectively.

The structures of MCP-PCPs were studied by using powder X-ray diffraction (pXRD) with CuCP-PCP presenting the highest crystallinity of this series (see Figure 1). NiCP-PCP and CoCP-PCP exhibited similar diffraction patterns to that of CuCP-PCP (Figure S2). In contrast, FeCP-PCP gave no diffraction peaks suggesting an amorphous structure (Figure S2). The lack of crystallinity for FeCP-PCP may reflect the variable coordination geometry/multiplicity of iron cations with



Figure 3. (A) pXRD profiles of carbonized samples MCP-PCP@800: (i) FeCP-PCP@800; (ii) CoCP-PCP@800; (iii) NiCP-PCP@800; (iv) CuCP-PCP@800. (B) Raman spectra of CP-coordination polymers after thermolysis. (C) XPS survey scans for MCP-coordination polymers. (D,E) Representative XPS spectra of MCP-PCP@800 for NiCP-PCP@800 (carbon 1s region) and FeCP-PCP@800 (Fe 2p region).

catechol, which leads to an irregular crosslinked structure. Porosities of MCP-PCPs were studied by nitrogen sorption measurements at 77 K. The isotherms did not exhibit a saturation limit (Figure 1D and S3-S5) and are probably representative of Type II behaviour. Pore sizes of MCP-PCPs were calculated by a non-local density functional theory method revealing that CuCP-PCP, CoCP-PCP and NiCP-PCP have similar pore size distributions indicating that they have the same or very similar lattice structures, as anticipated from the geometries coordination expected for those metal catecholates.35,36 The pore size distribution curves showed wider pore size distributions (Figure 1E and S3B-S5B). The average pore sizes of CuCP-PCP, CoCP-PCP and NiCP-PCP were found to be ~ 2.8 nm, whereas FeCP-PCP has a slightly larger pore size around 3.2 nm. NiCP-PCP exhibited the highest BET surface area of 354 m² g⁻¹. BET surface areas of the other PCPs, FeCP-PCP, CoCP-PCP, and CuCP-PCP, were found to be 120, 135 and 221 m²g⁻¹, respectively. Total pore volumes of 0.267, 0.269, 0.422 and 0.315 cm³ g⁻¹ were respectively found for FeCP-PCP, CoCP-PCP, NiCP-PCP and CuCP-PCP.

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Morphologies of the MCP-PCPs were observed by FE-SEM and HR-TEM. Interestingly, the MCP-PCPs have a nanorodlike morphology (Figure S6,S7) regardless of the central metal MCP-PCP materials contain transition metal cations in different

This journal is © The Royal Society of Chemistry 2013 013, **00**, 1-3 | **4** environments (i.e. porphyrinate and catecholate) suggesting their application as catalysts for concurrent transformations. However, in this case, we were interested to determine the products of thermolysis of these materials since we have previously found that the crystalline form of some transition metal complexes can have a substantial effect on the morphologies of the resulting thermolysis products and other resulting (carboniferous) materials.^{22b} Although here we did not expect any special templating effects, we were interested to assess the fate of the metal cations upon thermolysis. After several trials, it was found that a thermolysis temperature of 800 °C for 3 hours duration is appropriate to obtain consistent products for MCP-PCPs with the resulting materials referred to as MCP-PCP@800. After thermolysis, the nanorod like morphology could still be observed although random structures also emerged (Figure 2A-D). As mentioned earlier, MCP-PCPs exhibit rod-like crystalline morphologies, and even amorphous FeCP-PCP tended to have a fibre-like morphology (Figure 1 and Figure S6A). After thermolysis at 800 °C, the morphologies of the materials were to some extent retained but with the appearance of some obviously amorphous features formed probably due to the disruption of the crystals during heating. From HR-TEM we could clearly observe that formation of crystalline metal oxide particles had also occurred

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during thermolysis leading to hybrid metal/metal oxide/porous carbon materials (Figure 2E-H).

MCP-PCP@800 materials were also characterized using pXRD (Figure 3A), Raman spectroscopy (Figure 3B) and X-ray photoelectron spectroscopy both after and prior to thermolysis (Figures 3C-3E). Powder XRD patterns also confirm the formation of metal-oxides contained within the carbonized matrix.³⁷ For FeCP-PCP@800, y-Fe₂O₃ was formed while CuCP-PCP@800 contains Cu2O, CoCP-PCP@800 contains CoO/Co and NiCP-PCP@800 contains NiO/Ni. FeCP-PCP@800 contains XRD peaks at 26.04°, 30.22°, 35.6°, 43.3°, 53.8°, 57.3° and 62.9°, with that at 26.04° attributed to amorphous carbon, and other peaks originate from the (220), (311), (400), (422), (511), (440) facets of y-Fe₂O₃. In particular, the (400) reflection at 43.3° can be used to differentiate maghemite y-Fe₂O₃ from magnetite Fe₃O₄ where this peak appears at 43.05°.38 This assignment was confirmed by considering the XPS profile of this material (Figure 3E), which also indicates the presence of y-Fe₂O₃ rather than Fe₃O₄ because of broad peaks at 720 eV and between 730 and 735 eV.39 The presence of small quantities of Fe₃O₄ cannot be discounted although we assign the major oxide phase here as being Fe₂O₃. In CoCP-PCP@800, peaks at 36.51° (111), 42.39° (200), 61.50° (220) are assignable to CoO with other peaks at 44.29° (111), 51.61° (200) and 75.99° (220) assignable to cobalt metal. XRD peaks of 37.18°, 43.19°, 62.74° and 75.24° are assignable to (111), (200), (220) and (311) facets of NiO respectively and 44.39°, 51.73° and 76.18° are assignable to (111), (200) and (220) facets of nickel metal in NiCP-PCP@800. XRD peaks for CuCP-PCP@800 at 29.62°, 36.49°, 42.39°, 61.50°, 73.67° and 77.54° are attributed to (110), (200), (220), (311) and (222) facets of Cu₂O. The presence of obvious Raman peaks at 1337 and 1589 cm⁻¹ (see Figure 3B) can be respectively attributed to D and G bands of the amorphous graphitic carbon in the samples. XPS also reveals the formation of the hybrid materials in these systems (Figure 3C MCP-PCPs prior to thermolysis; Figure 3D,E and Figure S8,9 MCP-PCP@800). MCP-PCP@800 were found to contain the metals mostly in oxide states although the presence also of metals in the case of NiCP-PCP@800 and CoCP-PCP@800 is not surprising given the reducing conditions of the carbonization process. Metals were likely not detected by XPS due to formation of an oxide coating. Also, with regard to this subject, metal content of the MCP-PCP@800 materials is an important parameter affecting their properties. First, we must note a disadvantage of the preparation method applied here due to the metal content of the starting MCP-PCP compounds being largely invariant since the quantity of metal consumed in the preparation is fixed by coordination at the porphyrin and the coordination geometry of the catechol units. We used XPS data to estimate the effect of thermolysis on the metal contents of MCP-PCP and MCP-PCP@800 samples. The main trend not surprisingly involves increases in carbon contents from ~65 wt% to up to 80 wt% with concurrent decreases in oxygen contents. Metal contents of the MCPC-PCP are similar at 4-5wt% for Fe, Co, and Ni with Cu somewhat higher at 8 wt%.

Thermolysis leads to increases in metal content corresponding to oxide contents of 6 wt% for Fe_2O_3 and NiO, and around 12 wt% for CoO and Cu₂O. Of course, these values are subject to the inhomogeneities in the samples.



Figure 4. Nitrogen sorption isotherm and pore size distribution of MCP-PCP@800. Nitrogen sorption isotherm curves of (A) FeCP-PCP@800; (C) CoCP-PCP@800; (E) NiCP-PCP@800; (G) CuCP-PCP@800 and pore size distribution of B) FeCP-PCP@800; (D) CoCP-PCP@800; (F) NiCP-PCP@800; (H) CuCP-PCP@800.

Presence of a large number of mesopores in the thermolyzed materials is indicated by Type IV isotherms with hysteresis loop (Figure 4A,C,E,G), which suggests a cage like structure. The pore size distribution curves (Figure 4B,D,F,H) showed the existence of mesopores of about 3.6, 3.2, 5.2, and 5.2 nm in diameter for FeCP-PCP@800, CoCP-PCP@800, NiCP-PCP@800 and CuCP-PCP@800, respectively. Note that the average pore size of thermolyzed materials are relatively

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bigger than MCP-PCPs. Because of the increased porosity following their heat treatment, the BET surface areas also increased significantly relative to the pristine porphyrincatecholate complexes. BET surface areas of FeCP-PCP@800 CoCP-PCP@800, NiCP-PCP@800 and CuCP-PCP@800 were found to be 550 m² g⁻¹, 417 m² g⁻¹, 815 m² g⁻¹ and 453 m² g⁻¹, respectively. The highest BET surface area was found for NiCP-PCP@800 at 815 m² g⁻¹; a nearly twofold increase over that prior to thermolysis and carbonization. The total pore volumes of FeCP-PCP@800 CoCP-PCP@800, NiCP-PCP@800 and CuCP-PCP@800 were found to be 0.82, 0.68, 0.86, and 0.51 cm³ g⁻¹, respectively.

Because of the higher surface area and large pore volumes of MCP-PCP@800, we have attempted to demonstrate the utility of our materials for capacitive applications. For this purpose, we studied the electrocapacitive properties of MCP-PCP@800 and the results are presented in Figure 5. Cyclic voltammograms (CV) of different metal samples measured at different scanning rates from 10 mV/s to 20 mV/s, 50 mV/s, 100 mV/s, and to 200 mV/s (Figure 5) give different shapes due to their different redox properties. FeCP-PCP@800 and NiCP-PCP@800 samples mostly demonstrate as rectangular shape, which indicate the electric double layer capacitor contribute the most of the capacitance (Figure 5 B and F). Whereas the CoCP-PCP and CuCP-PCP gave obvious redox peaks as observed from the CV curves, indicating the existence of significant pseudocapacacitance (Figure 5 D and H). Specific supercapacitances were calculated by measuring chargedischarge curves at different current densities (Figure 5). These data reveal that the different metal species have a large impact capacitance. Notably, the initially amorphous FeCPon PCP@800 gave the highest specific capacitance with a value of 380 F g⁻¹ at a current density of 1 A g⁻¹ and it retained about 52% of this value when current density was increased to 10 A g⁻¹ (see Figure S10). NiCP-PCP@800 also exhibited a large specific capacitance of 330 F g⁻¹ at 1 A g⁻¹ with capacitance retention of about 49% at 10 A g⁻¹. CoCP-PCP@800 and CuCP-PCP@800 had relatively lower capacitances of 100 F g⁻¹ and 104 F g⁻¹, respectively. The lower capacitance may be attributed to the smaller BET surface area of CoCP- PCP@800 and CuCP-PCP@800 as compared to the NiCP- PCP@800 and FeCP-PCP@800 in terms of the diffusion efficiency. The capacitance of FeCP-PCP@800 and NiCP-PCP@800 is also quite high and comparable to their reported counterparts,⁴⁰ and thus showing great potential for energy storage applications.

The stability of the electrode materials is important for supercapacitance applications, thus we have also investigated the cyclic stability of MCP-PCP@800 materials by recording charge-discharge curves up to 1000 cycles. Overall, MCP-PCP@800 materials showed good cyclic stability over 1000 cycles (Figure S11). FeCP-PCP@800 (99%) and NiCP-PCP@800 (98%) gave the best cyclic stability in the series.



Figure 5. Charge-discharge curves of A) FeCP-PCP@800, (C) CoCP-PCP@800, (E) NiCP-PCP@800, (G) CuCP-PCP@800 at different current density; cyclic voltammetry of B) FeCP-PCP@800, (D) CoCP-PCP@800, (F) NiCP-PCP@800, (H) CuCP-PCP@800.

Conclusions

In summary, we report the synthesis of a series of new porous coordination polymers based on a catechol porphyrin ligand. These MCP-PCPs exhibit a crystalline nanorod-like morphology. The porous coordination nanorods were treated thermolytically for their conversion into nanoporous carbon/metal oxide hybrid materials and applied as electrode materials for energy storage. Although this method has as a disadvantage a paucity of control over materials' composition, the application of the hybrids as anode materials for supercapacitors was investigated by electrochemical (cyclic voltammetry and chronopotentiometry) measurements revealing good performance for supercapacitance with excellent 20 cyclic stability of 99% after 1000 cycles. These results demonstrate that the synthesis of new porous coordination 21 nanofiber materials is promising for high performance energy storage application.

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Notes and references

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Electronic Supplementary Information (ESI) available: details of synthesis, additional analytical data including XPS data, nitrogen sorption data, additional electron microscopy images, cyclic stability test data. See DOI: 10.1039/b000000x/

- 1 G. Wang, L. Zhang and J. Zhang, Chem. Soc. Rev., 2012, 41, 797.
- 2 G. Yu, X. Xie, L. Pan, Z. Bao and Y. Cui, *Nano Energy*, 2013, **2**, 213.
- 3 M. Zhi, C. Xiang, J. Li, M. Li and N. Wu, Nanoscale, 2013, 5, 72.
- 4 Q. Qu, S. Yang and X. Feng, Adv. Mater., 2011, 23, 5574.
- 5 C. Nethravathi, C. Rajamathi, M. Rajamathi, X. Wang, U. K. Gautam, D. Golberg and Y. Bando, *ACS Nano*, 2014, **8**, 2755.
- 6 Z. J. Han, D. H. Seo, S. Yick, J. H. Chen and K. Ostrikov, NPG Asia Mater., 2014, 6, 140.
- 7 M. Mazloumi, S. Shadmehr, Y. Rangom, L. F. Nazar and X. Tang, ACS Nano, 2013, 7, 4281.
- 8 G. Lota, K. Fic, and E. Frackowiak, *Energy Environ. Sci.*, 2011, **4**, 1592.
- 9 S. Bose, T. Kuila, A. Mishra, K. Ananta, R. Rajasekar, N. H. Kim and J. H. Lee, *J. Mater. Chem.*, 2012, 22, 767.
- 10 M. Zhi, C. Xiang, J. Li, M. Li and N. Wu, Nanoscale, 2013, 5, 72.
- 11 M. G. Bakker, R. M. Frazier, S. Burkett, J. E. Bara, N. Chopra, S. Spear, S. Pan and C. Xu, *Nanomaterials and Energy*, 2012, 1, 136.
- 12 T. Kuila, P. Khanra, N. H. Kim and J. H. Lee in *Handbook of Carbon Nanomaterials*, Eds.: F. D'Souza, K. M. Kadish, World Scientific, Singapore, 2014, 6, 1–49.
- S. Faraji and F. N. Ani, *Renewable Sustainable Energy Rev.*, 2015, 29 42, 823.
- 14 H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang and Y. Wang, J. Am. Chem. Soc., 2015, 137, 2688.
- 15 Y. Liang, H. Wang, J. Zhou, Y. Li, J. Wang, T. Regier and H. Dai, J. Am. Chem. Soc., 2012, 134, 3517.
- 16 Y. Liang, H. Wang, P. Diao, W. Chang, G. Hong, Y. Li, M. Gong, L. Xie, J. Zhou and J. Wang, J. Am. Chem. Soc., 2012, 134, 15849.
- 17 H. Jiang, J. Ma and C. Li, Adv. Mater., 2012, 24, 4197.
- 18 J. Jiang, Y. Li, J. Liu, X. Huang, C. Yuan and X. W. Lou, Adv. Mater., 2012, 24, 5166.
- 19 D. Yu, Q. Qian, L. Wei, W. Jiang, K. Goh, J. Wei, J. Zhang and Y. Chen, *Chem. Soc. Rev.*, 2015, 44, 647.

- a) F. El-Kady Maher and R. B. Kaner, *Nature Commun.*, 2013, 4, 1475; b) P. Simon and Y. Gogotsi, *Nature Mater.*, 2008, 7, 845.
- 21 a) W. Chaikittisilp, K. Ariga and Y. Yamauchi, *J. Mater. Chem. A*, 2013, **1**, 14; b) S. J. Yang, T. Kim, J. H. Im, Y. S. Kim, K. Lee, H. Jung and C. R. Park, *Chem. Mater.*, 2012, **24**, 464.
- a) W. Schmitt, J. P. Hill, M. P. Juanico, A. Caneschi, F. Costantino, C. E. Anson and A. K. Powell, *Angew. Chem., Int. Ed.*, 2005, 44, 4187; b) W. Schmitt, J. P. Hill, S. Malik, C. E. Anson and A. K. Powell, *Angew. Chem., Int. Ed.*, 2005, 44, 7048.
- a) W. Bak, H. S. Kim, H. Chun and W. C. Yoo, *Chem. Commun.*, 2015, **51**, 7238; b) W. Chaikittisilp, N. L. Torad, C. Li, M. Imura, N. Suzuki, S. Ishihara, K. Ariga and Y. Yamauchi, *Chem.– Eur. J.*, 2014, **20**, 4217; c) F. Meng, Z. Fang, Z. Li, W. Xu, M. Wang, Y. Liu, J. Zhang, W. Wang, D. Zhao and X. Guo, *J. Mater. Chem. A*, 2013, **1**, 7235; d) B. Liu, H. Shioyama, T. Akita and Q. Xu, *J. Am. Chem. Soc.*, 2008, **130**, 5390.
- 24 a) M. Lu, K. Zhang, H. S. Chan and J. Wu, *J. Mater. Chem. A*, 2012,
 22, 1845; b) J. Tao, N. Liu, W. Ma, L. Ding, L. Li, J. Su and Y. Gao, *Scientific Reports*, 2013, 3, 2286; c) G. Yu, L. Hu, N. Liu, H. Wang, M. Vosgueritchian, Y. Yang, Y. Cui and Z. Bao, *Nano Lett.*, 2011, 11, 4438.
- a) Z. S. Wu, D. W. Wang, W. Ren, J. Zhao, G. Zhou, F. Li and H. M. Cheng, *Adv. Mater.*, 2010, **20**, 3595; b) R. Bi, X. L. Wu, F. F. Cao, L. Y. Jiang, Y. G. Guo, and L. J. Wan, *J. Phy. Chem. C*, 2010, **114**, 2448; c) S. C. Hong, S. Kim, W. J. Jang, T. H. Han, J. P. Hong, J. S. Oh, T. Hwang, Y. Lee, J. H. Lee and J. D. Nam, *RSC. Adv.*, 2014, **4**, 48276.
- a) J. Zhu, D. Lei, G. Zhang, Q. Li, B. Lu and T. Wang, *Nanoscale*, 2013, 5, 5499; b) Y. Huang, D. Wu, J. Wang, S. Han, L. Lv, F. Zhang and X. Feng, *Small*, 2014, 10, 2226; c) Y. Zhang, Z. Hu, Y. Liang, Y. Yang, N. An, Z. Li and H. Wu, *J. Mater. Chem. A*, 2015, 3, 15057.
- 27 a) R. Madhu, V. Veeramani, S. M. Chen, A. Manikandan, A. Y. Lo and Y. L. Chueh, *ACS Appl. Mater. & Inter.*, 2015, **174**, 1104; b) Q. Liao, N. Li, S. Jin, G. Yang and C. Wang, *ACS Nano*, 2015, **9**, 5310-5317.
- a) J. Mu, B. Chen, Z. Guo, M. Zhang, Z. Zhang, P. Zhang, C. Shao and Y. Liu, *Nanoscale*, 2011, 3, 5034; b) D. Liu, X. Wang, X. Wang, W. Tian, J. Liu, C. Zhi, D. He, Y. Bando and D. Golberg, *J. Mater. Chem. A.*, 2013, 1, 1952; c) B. Sethuraman, K. Purushothaman and G. Muralidharan, *RSC Adv.*, 2014, 4, 4631; d) C. Guan, J. Liu, Y. Wang, L. Mao, Z. Fan, Z. Shen, H. Zhang and J. Wang, *ACS Nano*, 2015, 9, 5198.
- 29 a) D. Sun, S. F. Tham, A. C. Reed and D. W. Boyd, *Proc. Natl. Acad. Sci.*, 2002, **99**, 5088; b) O. Tetsushi, U. Arimitsu, F. Kenzo, O. Takashi, I. Mikinao and T. Kazuyuki, *Inorg. Chem.*, 2006, **45**, 7988.
- a) A. M. Shultz, O. K. Farha, J. T. Hupp and S. T. Nguyen, J. Am. Chem. Soc., 2009, 131, 4204; b) Y. C. Lee, O. K. Farha, B. J. Hong, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, J. Am. Chem. Soc., 2011, 133, 15858; c) X. S. Wang, L. Meng, Q. Cheng, C. Kim, L. Wojtas, M. Chrzanowski, Y. S. Chen, X. P. Zhang and S. Ma, J. Am. Chem. Soc., 2011, 133, 16322; d) X. L. Yang, M. H. Xie, C. Zou, Y. He, B. Chen, M. O'Keeffe and C. D. Wu, J. Am. Chem. Soc., 2012, 134, 10638; e) A. Fateeva, P. A. Chater, C. P. Ireland, A. A. Tahir, Y. Z. Khimyak, P. V. Wiper, J. R. Darwent and M. J. Rosseinsky, Angew. Chem., Int. Ed., 2012, 51, 7440; f) D. Feng, W. C. Chung, Z. Wei, Z. Y. Gu, H. L. Jiang, Y. P. Chen, D. J. Darensbourg and H. C.

Zhou, J. Am. Chem. Soc., 2013, **135**, 17105; g) D. Feng, Z. Y. Gu, Y. P. Chen, J. Park, Z. Wei, Y. Sun, M. Bosch, S. Yuan and H. C. Zhou, J. Am. Chem. Soc., 2014, **136**, 17714.

- 31 a) M. Hmadeh, Z. Lu, Z. Liu, F. Gandara, H. Furukawa, S. Wan, V. Augustyn, R. Chang, L. Liao, F. Zhou, E. Perre, V. Ozolins, K. Suenaga, X. Duan, B. Dunn, Y. Yamamoto, O. Terasaki and O. M. Yaghi, *Chem. Mater.*, 2012, 24, 3511; b) N. T. Nguyen, H. Furukawa, F. Gandara, C. A. Trickett, H. M. Jeong, K. E. Cordova and O. M. Yaghi, *J. Am. Chem. Soc.*, 2015, 137, 15394.
- 32 a) L. Guo, Q. Liu, G. Li, J. Shi, J. Liu, T. Wang and G. Jiang, *Nanoscale*, 2012, 4, 5864; b) L. Huang, L. Ao, X. Xie, G. Gao, M. F. Foda and W. Su, *Nanoscale*, 2015, 7, 806; c) H. Shen, Y. Long, X. Yang, N. Zhao and J. Xu, *Polymer International*, 2015, 64, 986.
- 33 a) G. Richards and S. Swavey, *Eur. J. Inorg. Chem.*, 2009, 5367; b) R.
 P. Bonar-Law, *J. Org. Chem.*, 1996, 61, 3623.
- 34 a) N. Kornienko, Y. Zhao, C. S. Kley, C. Zhu, D. Kim, S. Lin, C. J. Chang, O. M. Yaghi and P. Yang, *J. Am. Chem. Soc.*, 2015, 137, 14129; b) I. Hod, M. D. Sampson, P. Deria, C. P. Kubiak, O. K. Farha and J. T. Hupp, *ACS Catalysis*, 2015, 5, 6302; c) S. Motoyama, R. Makiura, O. Sakata and H. Kitagawa, *J. Am. Chem. Soc.*, 2011, 133, 5640.
- 35 a) C. W. Lange and C. G. Pierpont, *Inorg. Chim. Acta*, 1997, 263, 219; b) C. Benelli, A. Die, D. Gatteschi and L. Pardi, *Inorg. Chem.*, 1988, 27, 2831.
- 36 a) C. G. Pierpont, *Inorg. Chem.*, 2011, **50**, 9766; b) C. G. Pierpont, *Coord. Chem. Rev.*, 2001, **219-221**, 415.
- X-ray diffraction references of γ-Fe₂O₃: PDF 01-089-5892 (ICDD, 2012); CoO: PDF 01-078-5806 (ICDD, 2012) , Cobalt: PDF 01-077-7456 (ICDD, 2012); NiO: PDF 00-047-1049 (ICDD, 2012), Ni₂O₃: PDF 00-014-0481 (ICDD, 2012) and Cu₂O: PDF 00-005-0667 (ICDD, 2012).
- 38 J. A. R. Guivar, A. I. Martínez, A. O. Anaya, L. D. L. S. Valladares, L. L. Félix and A. B. Dominguez, *Adv. Nanopart.* 2014, 3, 114.
- 39 T. Fujii, F. M. F. de Groot, G. A. Sawatzky, F. C. Voogt, T. Hibma and K. Okada, *Phys. Rev. B.*, 1999, **59**, 3195.
- a) Y. Lin, X. Wang, G. Qian and J. J. Watkins, *Chem. Mater.*, 2014,
 26, 2128; b) C. Guan, J. Liu, Y. Wang, L. Mao, Z. Fan, Z. Shen, H. Zhang and J. Wang, *ACS Nano*, 2015, 5, 5198; c) S. Yang, X. Song,
 P. Zhang and L. Gao, *ACS Appl. Mater. & Inter.*, 2015, 7, 75; d) H. Wang and H. Dai, *Chem. Soc. Rev.*, 2013, 42, 3088.

Supercapacitive hybrid materials from the thermolysis of porous coordination nanorods based on a catechol porphyrin



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Synthesis of a series of porous coordination polymers with nanorod morphology constructed from a catechol-substituted porphyrin [meso-tetrakis(3,4-dihydroxyphenyl)porphyrin] is reported. Thermolysis of these materials yields supercapacitive materials with high capacitances and excellent cycling properties.