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Introduction

Metal-organic frameworks (MOFs) are a class of crystalline porous materials that are constructed by organic linkers and inorganic metal nodes. Because of their high degree of chemical and structural tunability at a molecular level, MOFs have attracted significant attention as versatile materials for a plethora of applications such as gas storage/separation, sensor, catalysis and energy devices. Furthermore, MOFs have recently emerged as new precursors/sacrificial templates for preparation of functional porous carbon and carbon based metal/metal oxide composites that may not be easily synthesized by conventional synthesis routes.

To meet the ever-growing demand of MOFs in a myriad of potential applications, considerable research efforts have been devoted to controlling the size and morphology of MOFs in a nanosize regime, which can tailor the physical/chemical properties without changing chemical compositions. Structuring MOFs at the nano- and mesoscopic scale has been accomplished by various methodologies such as microwave assisted synthesis, mechanochemical synthesis, interfacial assembly, emulsion templating, and coordination modulation. However, these approaches usually require specific reactors and equipment, or additional additives and modulators that sometimes work in a narrow synthesis parameter window. In addition, less attention has been paid to control framework topology (i.e., polymorphism), although it can potentially provide new opportunities for controlling the intrinsic properties and morphologies of MOF. In this regard, development of a simple strategy that simultaneously enables control over size, morphology, and framework topology of MOF under ambient synthetic condition is highly relevant.

The solvent is one of the critical parameters in MOF synthesis, as its properties such as polarity and solubility of the building blocks greatly influences the nucleation and growth of MOFs.

Solvent Mediated Morphology Control of Zn MOFs as Carbon Templates for Application in Supercapacitors

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While downscaling metal-organic frameworks (MOFs) into a nanosize regime is highly relevant to meet their growing demand in various potential applications, a simple synthesis of nano-MOF under ambient conditions still remains a difficult task. Here we report a room temperature synthesis of 3D MOF, [Zn(bdc,dabco)], (ZBD) (bdc = benzene-1,4-dicarboxylic acid and dabco = 1,4-diazabicyclo[2.2.2]octane) with controlled polymorphism, size, and morphology by changing the kind and composition of the solvents. Solvent functions as both a template and a crystal modulator. Dimethylformamide (DMF) preferably forms hexagonal rod MOF (ZBDH) while methanol (MeOH) leads to tetragonal plate MOF (ZBDP) via a solvent template effect (i.e., polymorph control). The size and morphology can be further controlled by using a cosolvent of DMF and MeOH with various volume ratios. DMF and MeOH work competitively, and the solvent with weaker template effect at the given condition acts as a crystal modulator that lowers the rate of nucleation and increases the size of crystals. With an increase of MeOH amount, morphology changes from 1D rods to 2D plates. Proton MeOH reduces the reactivity of nucleophilic dabco and suppresses the crystal growth along Zn-dabco [001], thereby leading to formation of 2D ZBDP plates. To help understanding fundamental morphology-volumetric capacitance relations in energy storage devices, the resulting ZBDs are conformally pyrolyzed to hexagonal rod- and tetragonal plate-nanoporous carbons and used as electrodes for supercapacitors. Thanks to a 2D morphology and a relatively high packing density, tetragonal plate carbon delivers two times higher volumetric capacitance than hexagonal rod carbon, despite of their similar gravimetric capacitance.
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Thus, solvent can act as not only a reaction medium but also a structure directing agent that affects the structures and topologies of final MOFs by a solvent template effect.\(^{21,22}\) Considering the fact that the pores of as-made MOF are generally filled with the solvents as guest molecules, the solvent template effect can become an effective means for preparing MOFs with desired framework topology. To date, a few systematic studies about solvent effect on MOF formation have been reported,\(^{22,26}\) however, most of works are usually MOF specific and limited to polymorph control only, and therefore considerably lack ability to adjust particle size and morphology (e.g., aspect ratio). While a simple solvent mediated strategy toward designable nano-MOF is highly desirable, it still remains largely unexplored due to the lack of efficient solvent systems and incomplete understanding of the associated MOF formation mechanisms.

Electric double-layer capacitors (EDLCs) have aroused tremendous research interest for decades because of their fast charging capabilities, long cycle life, high stability and safe operation.\(^{27-30}\) One of the most important components in such devices are the carbonaceous electrode materials as their ability for electro sorption of electrolyte ions is crucial for the specific capacitance and thus the energy density.\(^{31,32}\) A wide variety of novel carbonaceous materials such as activated carbon,\(^{33}\) carbide-derived carbon,\(^{34}\) zeolite-templated carbon,\(^{35}\) carbon nanotubes,\(^{36}\) and graphene\(^{37}\) have been extensively investigated as electrodes in EDLCs. The capacitance of carbon-based electrode materials and supercapacitors in general has been effectively enhanced by i) increasing the specific surface area and tailoring pore size and distributions,\(^{32,38,39}\) ii) producing composites with pseudocapacitive materials (e.g., metal oxides and conductive polymers),\(^{40}\) and iii) doping with heteroatoms or incorporating functional moieties.\(^{41}\)

Recently, volumetric performance has become more and more important criterion that gives a realistic picture of the charge-storage capacity in the limited space of energy devices, particularly in next generation portable electronic devices and electric vehicles.\(^{38,42,43}\) Although nanoporous carbons provide a stable and reliable performance, they show relatively low volumetric performance due to their inherent low density. This in turn leads to the presence of significant “dead volume” in EDLC electrodes, that is, electrode volume that has to be filled with electrolyte but is not used for energy storage. One promising strategy to overcome this limitation is preparation of carbon particles with controlled size and morphology that can maximize the materials’ packing density.\(^{44}\) In this respect, MOF-derived carbons (MDCs) are highly advantageous because a wide variety of inherent crystal morphologies of MOF can be transferred through pseudomorphic transformation.\(^{45-51}\) Moreover, MDCs can have high surface area, adjustable porosity, and can be doped with heteroatoms without post-treatments. These properties are highly attractive for development of high performance EDLC electrodes. Therefore, morphology controlled MDCs are highly relevant to understanding fundamental morphology-performance relations in electrochemical energy storage, which in turn potentially enables targeted development of electrodes with high volumetric efficiency.

Herein, we report solvent mediated room temperature synthesis of 3D MOF, \(\left[\text{Zn}_2(\text{bdc})_2\text{dabco}\right]_n\) \((\text{ZBD})\) \((\text{bdc} = \text{benzene-1,4-dicarboxylic acid and dabco} = 1,4\text{-diazabicyclo}[2.2.2]\text{octane}) with controlled size, morphology and polymorph by changing the kind and composition of the solvents used (Scheme 1). ZBD is a prototypical dabco MOF having unique guest-dependent framework flexibility and continuous 1D nanochannels,\(^{44,45}\) which are suitable for broad range of applications such as gas storage, adsorption, separation and controlled polymerization.\(^{46-51}\) Dimethylformamide (DMF) and methanol (MeOH) induce selective formation of hexagonal rod MOF with Kagome nets \((\text{ZBDh})\) and tetragonal plate MOF with square-grid nets \((\text{ZBDt})\), respectively. The size and morphology can be further controlled by using DMF and MeOH with different ratios as a cosolvent, which can tailor polarity and solubility of reactants and thus nucleation and growth of MOF. Conformal transformation of MOF precursors via carbonization at 900 °C leads to preparation of hexagonal rod- and tetragonal plate-nanoporous carbon, which are subsequently employed as electrodes for EDLCs. Benefiting from a 2D morphology and a high packing density, tetragonal plate MDC delivers two times higher volumetric capacitance than hexagonal rod MDC, despite of their similar gravimetric capacitance. The result highlights the importance of particle morphology for fabrication of high volumetric capacitance EDLC electrodes.

**Experimental**

**Materials**

Benzene-1,4-dicarboxylic acid (bdc, > 99%, Sigma-Aldrich), 1,4-diazabicyclo[2.2.2]octane (dabco > 99%, Sigma-Aldrich), \(N,N\)-dimethylformamide (DMF, analytical grade, VWR), methanol (MeOH analytical grade, VWR), and zinc nitrate hexahydrate (\(\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}, 98\%, \text{Acros}\)) were used as received.

**Synthesis of [Zn\(_2\)(bdc)\(_2\)dabco]\(_n\) and its derived carbon**

\(\left[\text{Zn}_2(\text{bdc})_2\text{dabco}\right]_n\) MOFs with either hexagonal \((\text{ZBDh})\) or tetragonal \((\text{ZBDt})\) framework topology were selectively prepared by using DMF, MeOH or their mixture as a solvent. \(\text{ZBDh-DxMy}\) denotes \(\left[\text{Zn}_2(\text{bdc})_2\text{dabco}\right]_n\) with hexagonal topology prepared in a cosolvent of DMF x: MeOH y, wherein x and y represent a volume ratio of each solvent (x + y = 10). In a typical synthesis of \(\text{ZBDh-D10}\), three solutions of bdc (1.20 mmol, 200 mg in 250 mL DMF), \(\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\) (1.20 mmol, 227 mg in DMF 25 mL), and dabco (0.60 mmol, 67.3 mg in DMF 25 mL) were prepared separately. The Zn and dabco solutions were added to bdc solution in sequence under stirring for 10 min. The mixture remained for 48 h without stirring. The solid was collected by centrifugation,
washed with DMF for 3 times, and dried under vacuum at 85 °C. For synthesis of ZBDt-M10, MeOH was solely used instead of DMF. For synthesis of ZBDh(t)-DxMy, the cosolvent of DMF and MeOH with various volume ratios was used, while the concentration of the reactants was kept constant. The other procedures were the same with those described in ZBDh-D10 synthesis. The resulting MOFs were carbonized at 900 °C for 2 h under Ar flow in a horizontal tubular furnace with a heating rate of 5 °C min⁻¹, and used as electrodes in EDLCs without further treatment.

Materials characterization.

The crystal structure was confirmed by powder X-ray diffractometer (PXRD) using Cu-Kα radiation (λ = 0.154 nm) and a scintillation counter (KeveX Detector). Nitrogen adsorption and desorption experiments were performed using Quantachrome Quadrasorb apparatus at 77 K. The samples were degassed at 150 °C for 20 h before measurements. Isotherms were analyzed with the QuadraWin software (version 5.05). The surface area was determined by Brunauer–Emmett–Teller (NLDFT) equilibrium model for N₂ adsorbed on silica. Pore size distribution of MDC was calculated by using a slit/cylindrical pore quenched solid density functional theory (QSDFT) equilibrium model (adsorption branch kernel) for N₂ adsorbed on carbon. Scanning electron microscopy (SEM) (LEO 1550-Gemini microscope) and transmission electron microscopy (TEM) (EM 912 Omega/Carl-Zeiss Oberkochen) operating at 120 kV were used to observe particle morphologies and pore structures. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was conducted using a PerkinElmer Optima 8000 instrument, calibrated with standard solutions. Raman spectra were recorded using a Witec Raman microscope operating at an excitation wavelength of 532 nm with a power of 4.0 mW. Thermogravimetric analysis (TGA) was conducted with a Netzsch TG 209 F1 device under constant artificial air flow in platinum pans at a heating rate of 10 °C min⁻¹ to 1000 °C. Elemental analysis was performed with a vario MICRO cube CHNOS Elemental Analyzer in the CHNS mode. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific K-Alpha® X-ray Photoelectron Spectrometer.

Fabrication of EDLCs and electrochemical measurements.

To prepare free-standing electrodes for EDLCs, carbonized MOFs and polytetrafluoroethylene (PTFE, 60 wt% solution in H₂O) from Sigma Aldrich) were mixed with various volume ratios was used, while the concentration of the reactants was kept constant. The other procedures were the same with those described in ZBDh-D10 synthesis. The resulting MOFs were carbonized at 900 °C for 2 h under Ar flow in a horizontal tubular furnace with a heating rate of 5 °C min⁻¹, and used as electrodes in EDLCs without further treatment.

D10-900 and ZBDt-M10-900 was determined to be 5.6 and 10.4 mg cm⁻², respectively. The electrodes were dried at 60 °C for 12 h under air. EDLCs were tested in a symmetrical two-electrode configuration employing the common organic electrolyte 1 M tetraethylammonium tetrafluoroborate/acetonitrile (TEABF₄/AN). A Swagelok cell was assembled using a pair of circular electrodes sandwiching a 25 µm trilayer polypyrrole-polyethylene-polypropylene membrane (Celgard 2325, 13 mm in diameter), with 60 µL electrolyte and two platinum foils as current collectors. The EDLCs were assembled in an Ar filled glove box (H₂O < 0.1 ppm, O₂ < 0.1 ppm). A Biologic MPG-2 galvanostat/potentiostat was used for electrochemical characterization. All measurements were performed at room temperature. The electrochemical impedance spectroscopy was performed at open circuit potential with a sinusoidal signal over a frequency range from 20 kHz to 10⁻² Hz at an amplitude of 10 mV.

Cyclic voltammetry (CV) tests were performed at a cell voltage of 0-2.5 V and at scan rates of 10-500 mV s⁻¹. The carbon integral volumetric capacitance, C (F cm⁻³), were calculated according to the following equations:

\[ C = \left( \frac{\int U(1 - \int U) dI}{\int U(1 - U) dU} \right) \cdot \gamma \cdot (U_2 - U_1) \]

where \( I \) is the current (A), \( U \) (V) is differential cell voltage, \( \gamma \) is the scan rate (V s⁻¹), and \( V \) is the volume of a single carbon electrode (cm³).

Galvanostatic charge/discharge with potential limitation (GCPL) was applied at specific currents between 0.1 and 10 A g⁻¹ in a voltage range from 0 to 2.5 V.

For long-term stability tests, the voltage of the cell was kept at 2.5 V for 100 h, and the specific capacity was measured every 10 h by galvanostatic cycling at 1 A g⁻¹.

Results and discussion

Conventional Synthesis of ZBD

Because of the flexible nature of bdc ligand, ZBD has two polymorphs either hexagonal framework with 2D Zn-bdc Kagome layers (ZBDh),32 or tetragonal framework with 2D Zn-bdc square-grid layers (ZBDt),44 which are connected by dabco pillars to form 3D structure (Scheme 1; Figure S1). Previous researches reveal that ZBDt is the metastable kinetic phase and ZBDh is the thermodynamically stable phase.20, 53, 54 In a typical solvothermal synthesis in DMF at 120 °C, ZBDh is firstly formed at the early stage of reaction but subsequently undergoes dissolution and recrystallization to thermodynamic ZBDt upon prolonged reaction.53 Thus, ZBDt single crystal can be obtained only after solvothermal reaction for 48 h.44 Because of this complex crystallization process, synthesis of nano-ZBDt with controlled size has ever been achieved yet. Likewise, although ZBDh is relatively easy to access via solvothermal- and mechanochemical methods,15, 52, 54 its size and morphology are difficult to control because of inherent metastability. Taken together, selective
synthesis of nano-ZBDh and -ZBDt with adjustable size and morphology is yet to be realized.

**Selective and controllable synthesis of ZBD at room temperature**

The solvent effect was studied by using DMF, MeOH and their mixture with various DMF:MeOH volume ratios (Figure 1). The resulting products are labelled as ZBDh(t)-DxMy, wherein x and y represent a volume ratio of each solvent (x + y = 10). The reactants (Zn(NO$_3$)$_2$·6H$_2$O, bdc, dabco) were separately dissolved in a targeted solvent, and mixed together under stirring. The solution became turbid right after the mixing, and remained under static condition for 48 h. The white precipitates were collected, washed and dried under vacuum at 85 °C.

The morphologies of as-synthesized ZBDh(t)-DxMy were investigated by electron microscopy (Figure 1). ZBDh-D10 has anisotropic hexagonal 1D rod-like morphology with hundreds of nanometers in length (Figure 1a). As the volume ratio of MeOH increased from D10 to D9M1 to D7M3 to D6M4, the particle size increased from 0.58 to 1.2 to 13 to 75 μm (Figure 1a-d), accompanied with morphology changes from nanorods to microplates. Hexagonal faces along [001] direction were clearly observable in SEM. An intermediate mixture of both morphologies was observed in a narrow window of reaction condition, e.g., D5.5M4.5 (Figure S2). Further increase in MeOH fraction ≥ 50 vol% (i.e., 66 mole%) led to crystal phase transition from hexagonal to tetragonal framework topology. With an increase of MeOH ratio from D5M5 to D3M7 to D1M9 to M10, the particle size decreased from 3.4 to 0.72 to 0.65 to 0.43 μm (Figure 1e-h), and the morphology changed from cubic microparticles to 2D-like cubic nanoparticles. The changes in particle size and aspect ratio of ZBDh(t)-DxMy are summarized in Table S1 and Figure S3.

Selective formation of ZBDh and ZBDt was further supported by PXRD and N$_2$ physisorption analysis (Figure 2). PXRD patterns revealed that synthesized ZBD can be assigned to one of three polymorph, size and morphology by simply adjusting the kind and composition of solvent used for MOF synthesis. It should be mentioned that synthesis of nanoZBDt with controlled size is reported - to the best of our knowledge - for the first time in the present work.

**Solvent effect on ZBD formation**

To better present the relations between solvent composition and ZBD structures, the graph of surface area change (i.e., morphology and topology change) with respect to MeOH mole fraction is illustrated in Figure 2d, which highlights the abrupt change in morphology with solvent composition.

The slight change in the size of the solvent template (guest molecule) can lead to formation of ZBD with different framework topologies, i.e., bulkier solvent molecule has bigger steric hindrance and may thus induce the formation of MOF polymorph with larger pore size. As expected from the bulk density (ZBDh 0.730 vs. ZBDt 0.870 g cm$^{-3}$) and pore size (ZBDh 1.5 vs. ZBDt 0.75 nm), bulkier DMF prefers ZBDh while MeOH prefers ZBDt, respectively. As confirmed in Figure 2d and Figure S3, formation of ZBDh dominates over ZBDt in a broad range of MeOH mole fractions (0-0.6). ZBDt can be obtained when MeOH mole fraction > 0.66 was employed. Thus, it can be inferred that DMF has stronger template effect than MeOH. DMF and MeOH work competitively rather than cooperatively. One overwhelms the other and preferentially induces formation of one particular crystal phase.

The competitive relation between DMF and MeOH further enables the control over size of resulting ZBD crystals. For instance, in the case of ZBDh synthesis in DMF/MeOH system, MeOH hinders the formation of ZBDh nuclei, decreases the rate of nucleation and therefore fewer nuclei grow to larger crystals with increasing amount of MeOH (Figure 2d). Likewise, the size of ZBDt increases with increasing amount of DMF. This phenomenon was experimentally further supported by time dependent observation of crystal growth of ZBDh-D10 and ZBDt-D6M4. In a pure DMF system (ZBDh-D10) most of ZBDh nuclei rapidly generated and grew/saturated to a few hundreds nanometer-sized crystals after reaction for 5 h, which suggests the fast and homogeneous
nucleation at the early stage of reaction (Figure S6). In contrast, in ZBDh-D6M4, the nucleation was largely retarded, and continuously proceeded (Figure S7). The newly generated nuclei/small nanocrystals and large crystals existed together even after reaction for 32 h (Figure S7a-f). With increasing reaction time, the initially formed nuclei grew to large crystals at the expense of small nanocrystals via Ostwald ripening, leading to formation of pure hexagonal microplates after reaction for > 48 h (Figure S7g, h).

The particle morphology (e.g., aspect ratio) is also greatly affected by solvent composition (Table S1; Figure S3). As the amount of MeOH increased, the anisotropic hexagonal nanorods (ZBDh-D10) transformed to hexagonal microplates (ZBDh-D6M4) to tetragonal microcubes (ZBDt-DSM5) to 2D-like tetragonal nanoplates (ZBDt-M10) (Figure 1; Figure 2d). This unique morphology evolution can be understood by the intrinsic crystal growth modes of ZBD and the polar protic nature of MeOH. ZBD has two growth modes (Zn-bdc and Zn-dabco) (Figure S1). Zn-bdc forms 2D hexagonal or tetragonal layers which are three dimensionally extended by dabco pillars. As a result, ZBDh consists of two hexagonal (001) faces terminated by Zn-dabco bonds and the other six faces terminated by Zn-bdc bonds (Scheme 2). The relatively high energy Zn-dabco (001) surfaces disappear through preferential anisotropic growth along [001] direction in ZBDh-D10. However, such Zn-dabco growth can be largely suppressed by addition of polar protic MeOH, which can form hydrogen bonding with the nucleophilic dabco ligand, creating a shell of MeOH molecules around dabco (Scheme 2). The lone pair electrons of dabco possibly interact with the electron-poor hydrogen atoms of MeOH. As a result, polar protic MeOH can decrease the reactivity of dabco and hinder the growth of Zn-dabco (001) surfaces - whereas polar aprotic DMF cannot - thereby resulting in formation of 2D-like nanoplates of ZBDt-M10.

The present solvent mediated approach enables the selective isolation of pure crystalline ZBD phase with desired structures by simply choosing appropriate solvent composition. In addition, it is more energy efficient and environmentally friendly and requires less demanding synthesis equipment than the conventional synthesis methods. In terms of framework stability and pore activation, the solvent template is highly preferred over typical organic template (additive). Solvent generally has no direct interaction with the framework and is relatively easy to remove by volatile solvent exchange and thermal activation, thereby generating permanent porosity. In contrast, organic templates such as amines and polymers usually induce strong host-guest interactions and thus are often difficult to remove which might result in structural collapse.56-58

ZBD derived carbon and its application in EDLCs

The size and morphology of nanoMOFs and many other nanomaterials are inherently relevant to the type of targeted applications. As one example, EDLCs need a high packing density of electrode materials to achieve high volumetric capacitance desired in practical uses. As a proof of concept to demonstrate the morphology effect on volumetric capacitance, here we transformed two representative ZBDs with distinct morphologies and particle aspect ratio but similar particle size (1D hexagonal nanorods of ZBDt-D10 and 2D tetragonal nanoplates of ZBDt-M10) (Table S1) to MDCs via carbonization at 900 °C. The carbonized samples were denoted as ZBDt-D10-900 and ZBDt-M10-900, respectively.

The morphologies of parent ZBDs were well preserved after carbonization. Randomly yet homogeneously distributed mesopores were generated throughout the particles (Figure 3a, b). ZBDt-D10-900 and ZBDt-M10-900 show type IV N2 sorption isotherms and an obvious hysteresis loop between P/P0 0.4-0.9, suggesting the presence of substantial amount of mesopores (Figure 3c). ZBDt-D10-900 has higher BET surface area and larger porosity than ZBDt-M10-900 (1490 vs. 1230 m2g−1), which is a similar trend as in the parent ZBD precursors (Figure 3d).

All Raman spectra have two broad peaks at 1342 and 1600 cm−1 that correspond to the D and G band, respectively (Figure S8). The G-band arises from stretching of any pair of sp2 sites whether in rings or chains. The D-band originates from the breathing mode of sp2 sites in rings of defects and disorder. Both carbons have almost identical I/D/IG intensity ratio near 0.97 and a broad G line width of 110 cm−1, suggesting the presence of graphitic cluster sizes in amorphous carbon smaller than 10 Å.59, 60 The results reveal that both carbons have amorphous characteristic with similar degree of aromatization and thus similar electric conductivity. In addition, they have comparable nitrogen content of 4.2 wt% originated from dabco ligands, as determined by CHN elemental analysis (Table S3). The N1S XPS spectra can be deconvoluted into pyridinic-N (398.2 eV), pyrrolic-N (399.5 eV), and graphitic-N (401.2 eV). The relative proportion of nitrogen species in both carbons are almost identical to each other (Figure S9). ICP-OES confirmed that most of Zn (residual amount < 0.03wt%) was removed during carbonization at 900 °C by carbothermal reduction and evaporation (Table S3).

To demonstrate the morphology-volumetric capacitance relations of ZBD derived carbons for EDLCs, ZBDt-D10-900 and ZBDt-M10-900 were fabricated into electrodes and characterized with cyclic voltammetry (CV) tests, in 1 M solution of tetryraethylammonium tetrafluoroborate/acetonitrile (1 M TEABF4/AN), which is a common organic electrolyte.

Both ZBD-derived carbons present rectangle-like CV curves (0-2.5 V) without an obvious distortion even at a scan rate as high as 500 mV s−1, indicating typical capacitive behavior with an excellent rate capability (Figure 4a-b). This is further underlined by the galvanostatic charging/discharging curve of ZBDt-M10-900 showing symmetric triangle shape at 0.1 A g−1 and 10 A g−1 indicates the typical capacitor behavior (Figure S10). The small voltage drop even at 10 A g−1 reveals low resistance of the EDLC. A voltage floating stability test performed for the EDLC cell with ZBDt-M10-900 as the electrodes for 100 h at 2.5 V shows sufficient
stability of the device (Figure S11). From the gravimetric perspective, due to the comparable surface area, conductivity and surface chemistry, the performance of the two carbons is similar to each other, exhibiting the similar specific capacitance and rate capability (around 80 F g\(^{-1}\) at 10 mV s\(^{-1}\), 50 F g\(^{-1}\) at 500 mV s\(^{-1}\)) (Figure 4c). However, the volumetric performance shows a significant difference. At the scan rate of 20 mV s\(^{-1}\) and 500 mV s\(^{-1}\), the differential current density of ZBdT-M10-900 is almost twice as high as that of the ZBdh-D10-900 (Figure 4a-b). This is further confirmed by the integral volumetric capacitance (Figure 4d), where the volumetric capacitance of ZBdT-M10-900 is pronouncedly higher than that of the ZBdh-D10-900 at all scan rates. This is attributed to the different pore structures and particle morphology. The meso- and macro-porosity of ZBdT-M10-900 are much lower compared with those of ZBdh-D10-900, leading to a higher density of the carbon materials in the electrodes. In addition, 2D plate morphology of ZBdT-M10-900 can facilitate preferential and uniform alignment along basal plane with relatively high packing density, as demonstrated by high volumetric capacitance of various 2D materials.\(^{37, 61, 62}\) Simulation studies also show that the particle elongation can lead to decrease in packing density because of the increase in the orientationally excluded volume.\(^{63}\) Therefore, despite of the similar gravimetric specific capacitance, ZBdT-M10-900 can provide higher volumetric capacitance. On the other hand, the lower meso-macroporosity of ZBdT-M10-900 results in the faster decay of capacitance at higher rates (Figure 4c), as the meso/macropores tend to facilitate the ion transport inside carbon electrodes. Note that the ZBdT-M10-900 still provides higher volumetric capacitance over the entire range of scan rates investigated (Figure 4d).

The general importance of the particle morphology and porosity on the volumetric efficiency of supercapacitor electrode materials is further shown by using commercial mesoporous carbon CMK-3 as additional reference materials.\(^{64}\) CMK-3 typically shows hexagonal rod-like shape and particles with sizes in the range of 1-3 μm.\(^{30}\) Its typical mesoporous structure is shown by the nitrogen physisorption isotherm (Figure S12a) with the pore volume 1.23 cm g\(^{-1}\). The gravimetric capacitance is ~80 F g\(^{-1}\), thus comparable to that of the two ZBD-derived carbons (Figure S12b). However, due to the mesoporous feature and different particle texture leading to moderate packing density, its volumetric capacitance is lower than that of the ZBdT-M10-900 with the highest packing density, and higher than that of the ZBdh-D10-900 with the lowest packing density (Figure S12c). Hence, the packing density generally plays a vital role for the volumetric capacitance. It has to be pointed out that in comparison to other recently reported supercapacitor electrode materials, ZBdT-M10-900 does not show a particularly impressive volumetric or gravimetric capacitance but the MOF-derived carbons are a suitable model system to evaluate the importance of the morphology of the electrode material particles for the volumetric capacitance of supercapacitors (Table S4).

Conclusions

We reported a simple yet effective synthetic route toward nano-MOFs with controlled polymorphism, particle size and morphology under ambient conditions. The solvent effect on ZBD synthesis was systematically investigated for the first time by changing the kind and composition of the solvents. Solvent template effect enables selective synthesis of 1D rod-like ZBdh in DMF and 2D plate-like ZBD in MeOH. Since DMF and MeOH work competitively, the use of DMF/MeOH with different ratios as cosolvents further enables the control over the crystal size and aspect ratios. Each solvent can act as a crystal modulator that decreases the rate of nucleation and thus increases the crystal size, e.g., the crystal size of ZBdh increases with increasing the amount of MeOH. The addition of MeOH induces the morphology transition from 1D rods to 2D plates. The polar protic MeOH reduces the reactivity of nucleophilic dabco and hinders the crystal growth along Zn-dabco [001], preferably inducing the formation of 2D plate-like ZBD. As a proof of concept to demonstrate the advantages of morphology controlled MOF, the resulting ZBds are thermally transformed to hexagonal rod- and tetragonal plate-nanoporous carbons for application in EDLCs. Despite of the similar gravimetric capacitance, 2D plate carbon shows two times higher volumetric capacitance than hexagonal rod carbon, highlighting the importance of MOF/MDC morphology for development of EDLC electrodes with a high packing density. The present solvent mediated MOF synthesis is facile yet highly effective in controlling the size and morphology of MOFs, and could be extended to preparation of various nano-MOFs that are desired in a wide variety of potential applications.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


**Scheme 1.** Solvent mediated synthesis of \([\text{Zn}_2(\text{bdc})_2\text{dabco}]_n\) (ZBD) with controlled size, morphology and polymorphism. (a) ZBD with hexagonal framework (ZBD\(_h\)), (b) ZBD with tetragonal framework (ZBD\(_t\)) and their transformation to nanoporous carbon.

**Figure 1.** SEM and TEM images of ZBD\(_h\)-(t)-D\(_x\)M\(_y\), wherein \(h\) and \(t\) represent hexagonal and tetragonal framework, and \(x\) and \(y\) represent a volume ratio of DMF \(x\): MeOH \(y\) (\(x+y = 10\)). (a) ZBD\(_h\)-D\(_10\), (b) ZBD\(_h\)-D\(_9\)M\(_1\), (c) ZBD\(_h\)-D\(_7\)M\(_3\), (d) ZBD\(_h\)-D\(_6\)M\(_4\) (e) ZBD\(_t\)-D\(_5\)M\(_5\), (f) ZBD\(_t\)-D\(_3\)M\(_7\), (g) ZBD\(_t\)-D\(_1\)M\(_9\), and (h) ZBD\(_t\)-M\(_{10}\).
Figure 2. Effect of solvent composition on ZBD\textsubscript{h(t)}-D\textsubscript{x}M\textsubscript{y} formation. (a) PXRD patterns. (b) Representative N\textsubscript{2} sorption isotherms of ZBD\textsubscript{h}-D\textsubscript{10} and ZBD\textsubscript{t}-M\textsubscript{10} and (c) their pore size distributions. (d) Graph of BET surface area change (i.e., morphology and topology change) with respect to MeOH mole fraction.

Scheme 2. Suggested mechanism for morphology change from nanorods to microplates upon MeOH addition.
Figure 3. Morphology conserved carbonization of ZBD. SEM and TEM images of (a) ZBDh-D10-900 and (b) ZB Dt-M10-900, and their (c) N\textsubscript{2} sorption isotherms and (d) pore size distributions.

Figure 4. EDLC performance comparison of ZBDh-D10-900 and ZB Dt-M10-900 tested in 1 M TEABF\textsubscript{4}/AN using a two-electrode configuration: Cyclic voltammograms (normalized to electrode volume) of the ZBDh-D10-900 and ZB Dt-M10-900 at the scan rate of (a) 20 mV s\textsuperscript{-1} and (b) 500 mV s\textsuperscript{-1}, and (c) gravimetric and (d) volumetric capacitance retention with the increase of scan rate.
A simple yet effective solvent mediated synthesis of nano-MOF with controlled polymorphism, size and morphology under ambient condition is presented.