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In situ synthesis of Ag/NiO derived from hetero-metallic MOF for supercapacitor application

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Abstract

Nanocomposite metal oxides have been attracted great attention in the electrode material of supercapacitor. Herein, a novel Ag/Ni hetero-metallic complex with the hamburger-like structure was prepared, which was then calcined to form Ag/NiO nanocomposite via in-situ preparation. The in-situ formed Ag/NiO exhibits a very high capacitance of 1480 F g⁻¹ at a current density of 0.6 A g⁻¹ in 1 M KOH solution, and the cycling stability was retained about 85% after 3000 cycles with the current of 5 A g⁻¹. The results showed that the in-situ formed Ag/NiO derived from hetero-metallic MOF possess high specific capacitance, which could provide a new effective strategy to improve the conductivity of metal oxides nanocomposite.

Keywords Supercapacitor · Metal-organic frameworks · Nickel oxide · Ag doped · Specific capacitance

Introduction

The ever-increasing energy needs issues have grown up an urgent need for the development of renewable, sustainable, clean, and highly efficient energy storage devices. Among various energy storage devices, supercapacitor have attracted more eye-catching due to the good circulation performance, fast charge and discharge ability, high power density, and the advantages of environmental friendly, which are subject to the attention of the researchers in many areas (Shu et al. 2019; Zheng et al. 2015; Zhang et al. 2020). According to the charge-storage mechanism and structure of capacitors, supercapacitor can be divided into electrical double-layer capacitors (EDLCs) and pseudo-capacitors. The charge

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² Chemistry Institute for Synthesis and Green Application, School of Material Science and Chemical Engineering, Ningbo University, Ningbo 315211, People's Republic of China separation of EDLCs originates from the electrode/electrolyte interface, which is similar to that of the traditional capacitor (Aldama et al. 2017; Chen et al. 2017a, b). The characteristic of EDLCs is the different carbon materials such as carbon nanotubes, graphene, and carbon nanomesh clusters, which are often used as EDLCs to obtain high surface area and capacitance (Zhang et al. 2017; Kierzek et al. 2004; Chen et al. 2020). However, the relatively low specific capacitance of carbon material electrodes have severely limited in advanced research of the EDLCs.

For pseudo-capacitors, it demonstrated that the charge is stored by rapid and reversible Faradic redox reaction at the electrode surface and possessed higher energy density than EDLCs. Among various pseudo-capacitive electrodes, transition metal-oxide electrode materials (Co_3O_4 , Mn_3O_4 , CuO, NiO) have attracted widely attention due to the benefits of their relative low cost, natural abundance, low toxicity, higher energy density, easily operation, and so on (Liu et al. 2017a, b; Tian et al. 2017; Mohammad et al. 2017; Ehasani et al. 2017). The most important of factor is the capacitance, which often exceed the double-layer capacitors of carbon materials, exhibiting a high theoretical capacitance.

In particular, nickel oxides, as an important p-type wide-band-gap electrode material, are regard as a promising pseudo-capacitor materials owing to its rapid reversible oxidation reduction reaction of Ni^{2+} and Ni^{3+} and high theoretical specific capacitance (2584 F g⁻¹) (Li et al. 2015; Feng et al. 2016; Meng et al. 2016; Peng et al. 2016;

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Lee et al. 2017). However, the practical specific capacitances are much lower than its theoretical specific capacitance, which results from the relatively low surface are and the weak conductivity. Hence, to improve the capacitance of NiO, the most common strategies have been used to synthesize diverse nanostructures with large surface area, such as nanowires, nanotubes, nanoflower, nanofibers, and so on. Other effective approaches are assembly of nanocomposite materials such as introduction of carbon material, metal, and metal oxides (Hu et al. 2017; Lamiel et al. 2017; Sheng et al. 2016; Jiang et al. 2017).

It is well known that silver has excellent electrical conductivity, and some researchers have introduced silver to assemble supercapacitor with enhanced the electrical conductivity of the electrode materials (Dhibar et al. 2017; Kim et al. 2014; Lee et al. 2014; Pawar et al. 2017), such as silver/polypyrrole/graphene, silver/MnO₂/polyaniline, silver/carbon nanotubes, Ag/Co₃O₄, and so on. Judging from the result of the properties, it was surely that introduction of silver could greatly enhance the super-capacitance performance in comparison with the materials itself. However, the method of loading Ag was usually direct mixing, which could be not conducive to increasing the specific capacitances. In fact, the uniformity of load silver will affect the electric conductivity, and the more uniform the load, the better super-capacitance performance of the nanocomposite. Ideas derived from the literature, the controllable synthesis of the nanocomposite materials with Ag uniformity of loaded NiO will be greatly improve the pseudo-capacitance performance. Recently, the MOFs are considered to be pioneers in preparing various metal oxides with promising performance in supercapacitor (Jiang et al. 2016; Liu et al. 2019; Zhou et al. 2020; Xuan et al. 2018; Iqbal et al. 2020). Actually, MOFs have been controllable by metal salt and organic ligands to from a periodic network structure, which can prepare metal-oxide with uniformity lattice component. Thus, we have prepared the material of supercapacitor with uniform distribution of silver by in-situ synthesis method. In this work, a novel Ag/Ni mixed-metallic complex was obtained through a facile one-pot hydrothermal method. Then, the Ag/Ni mixed-metallic complex was regarded as a precursor to prepare nanocomposite materials with Ag-loaded NiO via solid-stated pyrolysis. The Ag/NiO material exhibits a specific capacitance of 1480 F g $^{-1}$ at a current density of 0.6 A g^{-1} and the specific capacitance decreased from 665 F g^{-1} to 555 F g^{-1} after 1000 cycles of charge-discharge at the current density of 5.0 A g^{-1} . In addition, the supercapacitor test of simple Ag/NiO mixture (Ag/NiO-SM) and pure NiO were also conducted. The results show that the MOF-derived material exhibits prominent capacitance at the same current density.

Experimental

Synthesis of the Ag/Ni complex

A reaction mixture of AgNO₃ (170 mg, 1 mmol), pyridazine (pyz) (40 mg, 0.5 mmol), Ni(CH₃COO)₂·4H₂O (124 mg, 0.5 mmol), and 2,6-pyridine-dicarboxylic acid (H₂PDC) (167 mg, 1 mmol) and H₂O (7 mL) was stirred for 30 min, then transferred, and sealed in a 25 mL Teflon-lined stainless steel autoclave, which was heated to 160 °C for 120 h. After cooling to room temperature, the resulting purple prism crystals were washed with distilled water and dried in air. The powder XRD pattern of the Ag/Ni complex is shown in Fig.S1, which was match well with the corresponding single crystal data based on simulated, and the FT-IR spectra were recorded in Fig.S2. Yield based on silver is 68.72%. Elemental analysis: Anal. calc. (found) for C₅₄H₃₀Ag₆Ni₃N₁₂O₂₄: C, 31.53 (31.51); H, 1.46 (1.45); N, 8.18 (8.18) %. IR (KBr, cm⁻¹) data: 3375 (m), 3083 (w), 1622 (vs), 1427 (m), 1379 (s), 1278 (m), 1186 (m), 1076 (w), 914 (w), 732 (m), and 675 (m).

Preparation of Ag/NiO

According to the TG curve of the Ag/Ni complex (Fig.S3), the Ag/Ni complex was heated to 350 °C with a rate of 10 °C min⁻¹ at a flowing air atmosphere. Then, the product was maintained for 2 h at 350 °C to obtain black solid silver/ nickel oxide material (Ag/NiO).

Preparations of the simple mixed Ag/NiO (Ag/ NiO-SM) and pure NiO

A mixture of $AgNO_3$ (169 mg, 2 mmol) and $Ni(CH_3COO)_2 \cdot 4H_2O$ (248 mg, 1 mmol) was dissolved in H_2O (15 mL), the resulted solution was treated by excess KOH to give the precipitate completely. The precipitate was washed with distilled water several times and dried in air, which was heated to 350 °C with a rate 10 °C min⁻¹, and the temperature was kept for 2 h to get the black sample of Ag/NiO-SM. The synthesis of the pure NiO was performed by using the similar method to the Ag/NiO except that AgNO₃ was absent.

Materials characterization

Powder X-ray diffraction patterns were collected at the Bruker D8 Focus X-ray diffractometer with Cu K α 1 radiation (λ = 1.54012 Å). The thermal stability of complex was measured by Seiko Exstar 6000 TG/DTA 6300 apparatus from room temperature to 900 °C in air with rate of

10 °C min⁻¹. The Rigaku R-Axis Rapid X-ray diffractometer was selected to collect the diffraction data with the graphitemonochromated Mo target by $\lambda = 0.071073$ nm. The elemental of C, N, and H analysis were conducted by Perkin Elmer 2400II elemental analyzer. The Shimadzu FT-IR-8900 spectrometer was used to record the FT-IR spectra at room temperature. The specific surface area and pore-size distribution were obtained by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods (Ommishop 100 CX). The scanning electron microscopy and transmission electron microscopy were recorded on FEI Quanta FEG 250 and JEOL, 2010F, respectively. The surface composition of the samples was measured by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD spectrometer).

Electrochemical measurement

Three-electrode cell was used to perform the electrochemical measurements with 1.0 M KOH aqueous solution at CHI660E station (Chenhua, Shanghai, China). The platinum sheet was used as the counter electrode and the Hg/HgO electrode was the reference electrode. The working electrodes were prepared by mixing 75 wt% Ag/NiO, 15 wt% acetylene black, and 10 wt% polytetrafluoroethylene (PTFE) with a little isopropyl alcohol to form aslurry-like solution. The slurry was smeared on nickel foam with $1 \text{ cm} \times 1 \text{ cm}$ and then further dried over night. After that, the nickel foam was pressed at 10 MPa and dried under vacuum at 60 °C for 12 h. The mass loading of active material on the nickel foam is about 10.0 mg. The electrochemical properties of supercapacitor electrodes were tested by cyclic voltammetry (CV) measurements with a potential range of -0.2 to 0.6 V at the potential scan rate of 1, 3, 5, and 7 mV s⁻¹. The galvanic charge-discharge (GCD) with current densities of 0.6, 1.0, 2.0, 3.0, 5.0, and 7.0 A g^{-1} in the potential range of 0-0.5 V. The electrochemical impedance spectroscopy (EIS) measurement was performed with an AC signal of 5 mV in a frequency range between 0.1 Hz and 0.1 MHz.

Results and discussion

Single-crystal X-ray diffraction analysis revealed that complex crystallized in the orthorhombic space group F_{222} (Table 1), which presented a very complicated complex, and the complex molecule formulated as $[Ag_4Ni_2(pyz)$ PDC₄][Ag₂Ni(pyz)₂PDC₂]. The asymmetric unit contained one and a half Ag (I) ions, one half and one quarter Ni (II) ions, one and a half 2,6-pyridine-dicarboxylic acid, and one half and one quarter pyrazine (pyz) ligands (pyz containing N2 named pyz1, pyz containing N4 named pyz2). As depicted in Fig. 1, two crystallographically independent Ag are occupied the Wyckoff 16k (Ag1) and

 Table 1
 Summary of crystal data, data collection, structure solution, and refinement details for complex 1

Compounds	$[Ag_4Ni_2(pyz)PDC_4] \\ [Ag_2Ni(pyz)_2PDC_2]$	
Empirical formula	C ₅₄ H ₃₀ Ag ₆ Ni ₃ N ₁₂ O ₂₄	
Formula weight	2054.19	
Description	Green, block	
Crystal size (mm)	$0.47 \times 0.40 \times 0.30$	
Temperature (K)	293(2)	
Crystal system	orthorhombic	
Space group	F 222	
<i>a/</i> (Å)	16.052(3)	
<i>b/</i> (Å)	25.774(5)	
<i>c/</i> (Å)	13.860(3)	
α/(°)	90.00	
β/(°)	90.00	
γ/(°)	90.00	
Volume (Å ³)	5734(2)	
Ζ	4	
$D_{\text{calc}}/(\text{g}\cdot\text{cm}^{-3})$	2.380	
<i>F</i> (000)	3984	
$\mu (\mathrm{mm}^{-1})$	3.064	
θ range (°)	3.07-27.44	
Reflections collected	14,122	
Unique reflections (R_{int})	$3288(R_{\rm int}=0.048)$	
Data, restraints, parameters	3169, 0, 227	
Goodness of fit on F^2	1.033	
$R_1, wR_2 [I \ 2\sigma(I)]^a$	0.0440, 0.1039	
R_1, wR_2 (all data) ^a	a) ^a 0.0455, 0.1049	
A, B values in w) ^b 0.0402, 75.2		
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min} / ({\rm e} \cdot {\rm \AA}^{-3})$	1.063, - 1.377	

 $L = PDC^{2-}$

^a $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ^b $w = [S^2(F_o^2) + (AP)^2 + BP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$

8h (Ag2) sites, respectively, and exhibit different coordination behaviors. Each Ag1 center is four coordinated by one pyz1 nitrogen atom and three oxygen atoms from three PDC ligands with Ag-O/N distances ranging from 2.225(4) to 2.693(7) Å. The Ag2 is located in distorted tetrahedron geometry and coordinated by two N4 atoms from pyz2 ligand and two O5 atoms from two different PDC ligands. Besides, the Ni1 and Ni2 ions are each centered at the Wyckoff 8i and 4a sites, respectively. Each Ni atom exhibits the same coordination mode with interlinked by four carboxylate oxygen atoms and two pyridyl nitrogen atoms from two PDC ligands to form the octahedron NiO₄N₂ geometry. The distance of Ni–N bond is obviously smaller than Ni-O distance, indicating that it is dressed octahedron geometry. The PDC1 ligand (PDC containing N1 named PDC1) chelated one Ni1 ion through the



Fig. 1 The coordination environment of Ag(I) and Ni(II) ions, and PDC and pyz ligands in **1** with the thermal ellipsoids at 30% probability level (symmetry codes:#1 = x, -y + 1/2, -z + 1/2; #2 = x + 1/2,

pyridyl N1 atom and two oxygen atoms (O1 and O3) from 2- and 6-position carboxylate group, and simultaneously coordinating three Ag1 atoms through the carboxylate O1, O2, and O4 atoms. The PDC2 ligand, which contained N3 atoms, also chelated one Ni2 atom via N3 atom and its two -y, -z+1/2; #3 = -x+3/2, y, -z+1/2; #4 = 1/2 - x, y, -z+1/2; #5 = -x+1/2, -y+1/2, z; #6 = -x, -y, z; #7 = -x, y, -z; #8 = x, -y, -z; #9 = -x+1, y, -z, #10 = x - 1/2, -y, 1/2 - z.)

neighboring carboxylate O6 atoms, and at the same time, linking two Ag2 atoms through two neighboring carboxylate O5 atoms.

As shown in Fig. 2a, two PDC1 ligands chelate to one Ni1 ion to form a $Ni(PDC1)_2$ unit, and the resulted $Ni(PDC1)_2$



Fig. 2 a Ball-and-stick view of 2D sheet containing PDC1 in the *ac*-plane. b Ball-and-stick view of the 2D sheet containing PDC2. All H atoms are omitted for clarity

units are further interlinked by the interaction of Ag1-O bond to form 2D layer structure. Interestingly, the pyz ligands fill in the voil of the 2D layer with coordination between the Ag1 atoms and oxygen atoms. It is obviously that the coordination of pyz ligands with μ_4 - η^4 modes makes a contribution to the stabilization of the 2D layer. Topologically, the pyz ligand acted as bridging ligand, the Ni(PDC1)₂ unit can be considered as a four-connected node, while the two Ag1 atoms can be considered as a six-connected node. Consequently, on the basis of this simplification, the 2D [Ag₄Ni₂(pyz)PDC₄] layer presents topological net with the point symbol of {3;4³;5²}{3²;4⁴;5²;6²} (Fig. S4).

Furthermore, the pyz ligands are bridged the Ag2 atoms with the μ_2 -N: N' coordination mode to form 1D infinite chains along to [001] direction and two PDC2 ligands also coordinated one Ni2 ion to form a Ni(PDC2)₂ unit. The resulting 1D chains are further interlinked to the Ni(PDC2)₂ units into 2D layers parallel to (010) plane via the interaction of Ag2-O5 bond (Fig. 2b). The Ni(PDC2)₂ unit can be considered as a four-connected node, the one Ag2 atom can be considered as a four-connected node, and the pyz ligand can act as bridging ligand. Thus, the 2D [Ag₂Ni(pyz)₂PDC₂] sheet can be simplified to a {3²;6²;7²} topological net (Fig. S4). The two different layers are stacked together by the π - π interactions between the parallel pyridine rings of interlayer PDC²⁻ ligands with a centroid-to-centroid distance of 3.773 Å (Fig. 3), which are interaction on each other to build the three-dimensional metal organic framework similar to hamburger structure. The distances and bond angles are given in Table S1.

According to the thermal analysis curve (Fig. S3), the as-prepared Ag/Ni-MOF complex is very stable up to 200 °C and decomposes about 300 °C in air atmosphere. The resultant product was identified by PXRD pattern measurement. According to the diffraction peaks of PXRD pattern in Fig. 4, the diffraction peaks located at 38.1, 44.3, 64.5, and 77.4 correspond to the (111), (200), (220), and (311) planes of cubic-structured Ag (JCPDS 87-0717). The other peaks at 43.4 and 63.0 could be indexed to the (200) (220) crystal planes of cubic-structured NiO (JCPDS 75-0197). Beyond that, there is no impurity diffraction peaks in Fig. 4. Thus, the residual solid product can be assigned to contain NiO and Ag, and the product is indicated a high purity. Besides, the simple Ag/NiO mixture and pure NiO were also characterized by PXRD, which are consistent

Fig. 3 3D framework of complex 1





Fig.4 The experimental and simulated PXRD patterns of Ag/NiO, Ag/NiO-SM, and NiO

with the literature reports and no other peaks of impurities can be found (Jiang et al. 2017; Pawar et al. 2017).

To confirm the chemical and electronic state of the asmade Ag/NiO, the full X-ray photoelectron spectroscopy (XPS) elemental survey scans of Ag/NiO are shown in Fig. 5a, and all of the binding energies of Ni 2p, Ag 3d, and O 1 s were corrected by the C1s peak. As seen in the Ni 2p spectrum (Fig. 5c), the binding energies located at 853.7 and 855.5 eV corresponding to the Ni 2p_{3/2}, which could be ascribed to the surface effect (Zuo et al. 2016). The peak appears at 860.8 eV corresponding to the satellite peak of Ni 2p_{3/2}. Besides, the peaks centered at 879.4 eV and 872.6 eV can be assigned to Ni $2p_{1/2}$ and its satellite peak, respectively (Wang and Li et al. 2017). The main binding energy peaks of Ag $3d_{3/2}$ (372.7 eV) and Ag $3d_{5/2}$ (366.6 eV) are separated by 6 eV (Fig. 5b), which proves the existence of Ag (Sekhar et al. 2017). The O 1 s core-level spectrum exist three peaks (529.2 eV, 530.8 eV, and 532.7 eV), as illustrated in Fig. 5d, ascribed to a typical Ni–O bond (Zhang and Su et al. 2017), oxygen in the lattice (Xiang et al. 2017), and H-O-H bond of residual water on the surface, respectively. The results of XPS are further demonstrated the well combination of Ag and NiO.

The detailed microstructure of the Ag/Ni-MOF and Ag/NiO was characterized by scanning electron microscopy (SEM). Figure 6a shows the SEM image of the granular MOF with a smooth surface, and the size of the particles are with a diameter of $2-8 \mu m$. After calcinations of the Ag/Ni-MOF at 350 °C under air atmosphere, the organic ligands



Fig. 5 XPS spectra of Ag/NiO a survey spectrum; b Ag₃d region; c Ni 2p region, and d O 1s region



Fig. 6 a, b SEM images of Ag/Ni complex before and after calcinations. c-f EDS elemental mapping images of Ag/NiO sample d nickel, e silver, and f oxygen

in the Ag/Ni-MOF were removed by decomposition, and the elements of Ag and Ni were converted into uniformly Ag/ NiO micro-particles. Figure 6b further shows a typical SEM of the Ag/NiO, which keeps the similar nanometer-sized as the Ag/Ni-MOF except with roughened surface. Furthermore, the corresponding EDS elemental mapping figures are presented in Fig. 6c–f, indicating that Ag, Ni, and O elements are homogenously distributed within the entire asprepared Ag/NiO material, and the information for the EDS agrees well with the PXRD and XPS analysis.

The morphology and microstructure of the Ag/NiO were characterized by the TEM and HRTEM, as shown in Fig. 7a and Fig. 7b. From the TEM image of Fig. 6a, it can be observed that Ag and NiO dispersed throughout in the sample. The observed lattice fringes in HRTEM image are 0.241 nm and 0.209 nm, which matches the (111) and (200) planes of NiO. Besides, the other lattice spacing is 0.235 and 0.204 nm, consistent with the spacing of the (111) and (200) planes of the Ag. In addition, TEM and HRTEM of the Ag/NiO-SM were also tested (Fig. S10), and the results show that lattice spacing corresponds to Ag and NiO, respectively.

To obtain the specific surface area and pore textures of asprepared sample, the nitrogen adsorption–desorption analysis was performed using Brunauer–Emmett–Teller (BET) gas adsorption–desorption measurements. As presented in Fig. 8, the isotherms can be classified as type V, implying the existence of porous structure in the Ag/NiO sample, and the BET-specific surface area of the synthesized Ag/NiO sample is $14.32 \text{ m}^2 \text{ g}^{-1}$. The pores of Ag/NiO fall into the size are mainly centered in the range of 8–46 nm determined by the Barrett–Joyner–Halenda (BJH) method (inset in Fig. 8). As shown in Fig. S5, the specific surface area of the simple Ag/NiO mixture (Ag/NiO-SM) is $2.52 \text{ m}^2 \text{ g}^{-1}$, which is obviously smaller than Ag/NiO.

The electrochemical performances of the Ag/NiO architecture were evaluated using three-electrode system in 1 M KOH. Figure 9a shows the CV curves of various electrode materials in the potential range of -0.2 to 0.6 V with a scan rate of 2 mV s⁻¹ in a 1 M KOH aqueous solution. From the CV plots, the oxidation peak between NiO with NiOOH can be observed within the range 0.2–0.3 V, indicating the pseudo-capacitance of NiO. In comparison with the pure NiO, the interconnected Ag elements make a significant contribution to the capacitance. Compared with the simple mixture Ag/NiO-SM, the Ag was introduced into with more uniform better in Ag/NiO electrode, which has enhanced the electrical conductivity to a greater extent and promotes the entire capacitance of the electrode. CV plots of the Ag/NiO,



Fig. 7 TEM and HRTEM images of Ag/NiO



Fig. 8 Nitrogen adsorption-desorption isotherms and the corresponding pore-size distribution curves (inset) of Ag/NiO

Ag/NiO-SM, and pure NiO are shown in Fig. 9b, Figure S6, and Figure S7 with a scan rate of 2, 3, 5, and 7 mV s⁻¹. It was clear from the curves that the shape of the CV curves is unaffected by the increasing scan rate, indicating that the electrodes have good reversibility. As the scanning speed increases, the anode peak is shifted to the high-voltage direction and the cathode peak is shifted to the low-voltage direction, which is attributed to the electrode polarization and irreversible reaction. At the lower scan rate, the diffusion ions can easily penetrate into the activity site of the electrode under electrolyte, but the higher scan rate can reduce the electrolyte utilization of the inner active of electrode material, which could led to the resistance increases (Yao et al. 2015).

The galvanic charge/discharge (GCD) measurement of Ag/NiO, Ag/NiO-SM, and pure NiO was performed with the same current densities (0.6 A g^{-1}) in the range of 0–0.5 V, as shown in Fig. 9c. The shape of hat-like discharge plots were confirmed the pseudo-capacitance characteristic. The massspecific capacitance $[C_{\rm m} (F g^{-1})]$ is calculated based on the following equations: $C_{\rm m} = (I_{\rm d} \times \Delta_{\rm t})/(\Delta V \times m)$. Where $I_{\rm d}$ (A) is the charging/discharging current, Δ_t (s) is represented as the discharging time, $\Delta V(V)$ is defined as the potential window, and *m* (mg) is the mass loading of active materials. The mass-specific capacitance of Ag/NiO-SM is 712 F g^{-1} , and the value of the specific capacitance is obviously higher than the pure NiO with 72 F g^{-1} , indicating that the introduction of Ag element can remarkably enhance the electric conductivity and prove the energy storage ability. Comparison with the Ag/NiO-SM, the specific capacitance of Ag/ NiO can be calculated to be 1480 F g^{-1} , which is more than twice as much as Ag/NiO-SM, exhibiting superior capacitive performance. Because of the existence of Ag substance, all of the specific capacitances of the Ag/NiO-SM and Ag/ NiO electrode have largely enhanced in relation to the pure NiO. For Ag/NiO electrode, the more superior capacitive performance may be due to that the Ag/NiO is obtained by in-situ modification with MOF as precursor, in which the Ag may take place uniformly with NiO to facilitate the electric conductivity. Furthermore, it was easy for the shape of GCD plot to find that both Ag/NiO and Ag/NiO-SM have plateaus around voltage 0.25 V in charge/discharge curve except for pure NiO. According to the literature (Usman et al. 2017), the plateaus in charge/discharge curve should be contributed to the redox couple Ag/Ag^{+1} .

The GCD curves of Ag/NiO with different current densities are shown in Fig. 9d. The specific capacitance of Ag/



Fig.9 a CV curves of Ag/NiO, Ag/NiO-SM, and NiO electrodes between -0.2 and 0.6 V with a scan rate of 2 mV s⁻¹; **b** CV curves of Ag/NiO electrode between -0.2 and 0.6 V with a scan rate of 2, 3, 5, and 7 mV s⁻¹; **c** galvanostatic charge–discharge curves of Ag/NiO,

NiO was 1480, 1454, 828, 744, 665, and 364 F g⁻¹ at 0.6, 1, 2, 3, 5, and 7 A g⁻¹, respectively. The specific capacitance tendency of Ag/NiO-SM and pure NiO is shown in Fig. S8-S9, and the specific capacitance was calculated to vary from 712 F g⁻¹ at 0.6 A g⁻¹ to 168 F g⁻¹ at 7 A g⁻¹ for Ag/NiO-SM, and from 89 F g⁻¹ at 0.6 A g⁻¹ to 23 F g⁻¹ at 5 A g⁻¹ for NiO. To evaluate the stability of the electrodes, the charge–discharge cycling performance was performed with a higher current density of 5 A g⁻¹. As shown in Fig. 10, the Ag/NiO-doped electrodes exhibit good capacitance retention of 85% at 5 A g⁻¹ after 1000-cycle charge–discharge test. In summary, the in-situ metal oxides derived from MOFs are potential of supercapacitor electrode materials, which provide a new strategy for the modification of metal oxides.

EIS measurements were carried out to investigate the detailed electrochemical characteristics of the Ag/NiO, Ag/NiO-SM, and NiO. All electrodes were measured in the frequency range of $0.01-10^5$ Hz at 0.3 V with an AC perturbation of 5 mV. The resultant Nyquist plots are shown in Fig. 11. All the impedance spectra of the as-prepared



Ag/NiO-SM, and NiO electrodes at current density of 0.6 A g^{-1} ; **d** galvanostatic charge–discharge curves of Ag/NiO electrode at current density of 0.6–7 A g^{-1}



Fig. 10 Charge/discharge cycling test of Ag/NiO as electrode at constant current density of 5 A $\rm g^{-1}$

samples are composed of two parts, one semicircle in the high-frequency range and a straight line in the low-frequency region, which are related to the charge-transfer resistance



Fig. 11 Nyquist plots of Ag/NiO, Ag/NiO-SM, NiO electrodes at room temperature. The insets show the electrochemical impedance spectrums in the high-frequency range and corresponding equivalent circuit

 $(R_{\rm ct})$ and Warburg impedance $(Z_{\rm w})$, respectively. The Warburg impedance is deviated from 45 degrees in the low-frequency range, which may be attributed to many reasons such as the surface roughness of electrode, the dispersion effect of ion, and so on. It is quite obvious that the Ag/NiO and Ag/NiO-SM electrodes have a smaller $R_{\rm ct}$ than the pure NiO electrodes due to the introduction of Ag element, showing a fast electron transfer process. In addition, according to the fitting result of the equivalent circuit model, the calculated value of charge-transfer resistance $R_{\rm ct}$ of Ag/NiO is 0.27 Ω ,

Table 2 The comparison ofthe supercapacitance electrodematerials containing NiO

which is obviously smaller than the Ag/NiO-SM (0.37 Ω) and NiO (0.43 Ω), implying that the in-situ introduction of Ag by MOF can provide a path for fast electron transport and further improve its capacitive performance.

According to many previous reports, several studies have been carried out to prepare various unique morphologies of NiO with larger surface area or nanocomposite NiO materials for the application of the supercapacitor. Table 2 summarizes the capacitance of NiO and other substance modification of NiO (Li et al. 2015; Jiang et al. 2017; Xiang et al. 2017; Atalay et al. 2014; Cao et al. 2014; Fan et al. 2014; Li et al. 2016; Liu et al. 2016; Wang et al. 2014, 2016; Xu et al. 2014; Yang et al. 2014; Yu et al. 2015; Zang et al. 2014; Zhang et al. 2015; Han et al. 2017; Liu et al. 2017; Zhao et al. 2017; Li et al. 2012). It can be seen from Table 2 that the in-situ formed Ag/ NiO nanocomposite via hetero-metallic MOF possesses a high specific capacitance of 1454 F g⁻¹ at 1 M KOH solution and good cycling stability. In addition, compared to the in-situ formed Ag/NiO nanocomposite, the nano-NiO electrode materials with nanowires and nanosheets exhibit a large capacitance value and excellent cycling stability, which can be assigned to its high specific surface area. We speculate that the unique morphology characteristic can provide larger surfaces in liquid electrolyte, which could guarantee exposure of more active sites at the pseudocapacitive reactions. Thus, it is apparent that the preparation of diverse morphologies of NiO with larger surface area is an effective way to enlarge the capacitance. Furthermore, the greatly improvement of the electrochemical

Electrode materials	Current density	Specific capacitance (F g ⁻¹)	Electrolyte	References
NiO	1 A g^{-1}	515	6 M KOH	Li et al. (2015)
NiO nanowire	1 A g^{-1}	1589	6 M KOH	Usman et al. 2017
Roselike NiO nanosheets	1 A g^{-1}	1860	6 M KOH	Han et al. 2017
NiO nanostructures	$0.2 \ { m A g^{-1}}$	329	6 M KOH	Li and Liu et al. 2016
flowerlike NiO	5 mA cm^{-2}	619	6 M KOH	Wang et al. 2014
NiO nanotubes	1 A g^{-1}	919	2 M KOH	Xu et al. 2014
NiO ball-flower	1 A g^{-1}	734	6 M KOH	Yang et al. 2014
NiO	$0.5 \ { m A g^{-1}}$	1201	_	Yu et al. 2015
NiO nanospheres	1 A g^{-1}	982	6 M KOH	Zhao et al. 2017
NiO nanofibers	2 A g^{-1}	700	6 M KOH	Li et al. 2012
MOF-derived NiO Nanoparticle	1 A g^{-1}	324	6 M KOH	Atalay et al. 2014
NiO@Co ₃ O ₄ nanofibres	1 A g^{-1}	437	6 M KOH	Jiang et al. 2017
Co ₃ O ₄ /NiO nanofilms	2 A g^{-1}	710	6 M KOH	Liu et al 2017
ACNF/PANI/NiO composite	1 A g^{-1}	1157	6 M KOH	Xiang et al 2017
NiO/ZnO	1.3 A g^{-1}	497	3 M KOH	Wang et al. 2014
C@NiO hollow microsphere	1 A g^{-1}	211	6 M KOH	Zang et al. 2014
Ag/NiO-MOF derived	1 A g^{-1}	1454	1 M KOH	This work

performance of the modification NiO is attributed to the structure feature. First, the modification nanocomposite can provide a high-speed channel for electron delivery, which can ensure effectively increasing interface area in the charge-discharge processes. Thus, compared with the pure NiO itself, the modification NiO composite possesses a better electrical conductivity and more rapidly diffusion kinetics. Second, other substance was load on the NiO to form nanocomposite, which could prevent the aggregation of NiO itself during the oxidation/reduction reaction process, guaranteeing the cycling stability of the supercapacitor. However, it is important to note that the best methods of the modification is uniformity loaded on the NiO, rather than by directly mixed at random, which will greatly influence the capacitance performance of the nanocomposite. Therefore, the capacitance of the in-situ formed Ag/NiO via hetero-metallic MOF is much greater than the directly mixed Ag/NiO-SM.

Conclusions

In conclusion, we have successfully synthesized a new Ag/Ni hetero-metallic complex [Ag₄Ni₂(pyz)PDC₄] [Ag₂Ni(pyz)₂PDC₂], which was converted to form an insitu Ag/NiO nanocomposite via calcinations. The resulted Ag/NiO exhibits a specific capacitance of 1480 F g^{-1} at a current density of 0.6 A g^{-1} and presents an exceptional cycling stability with 15% decrease after 1000 cycles. The supercapacitor performance of Ag/NiO derived from MOF is obvious better than directly mixed Ag/NiO-SM and pure NiO, which is mainly attributed to the uniformity of Ag loaded on NiO. These strategies provide a new direction for improvement the specific capacitance performance of supercapacitor in the future. It is also attractive us that the preparation of transition-metal-oxide nanocomposite with controlled morphologies and diverse structures will be readily extended to other materials.

Supporting Information Available

Crystallographic data for compound **1** deposited with the Cambridge Crystallographic Data Center, 1566257. [CCDC, 12 Union Road, Cambridge CB2 1EZ, United Kingdom. Fax: (44)1223–336-033. E-mail: deposit@ccdc.cam.ac.uk. Website: http://www.ccdc.cam.ac.uk]. Experimental and simulated PXRD patternof **1**; IR spectra and TG curves of **1**; Selected inter-atomic distances and bond angles for **1**; The 3D framework and 2D topological net of complex **1**.

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Compliance with ethical standards

Conflict of interest No potential conflict of interest was reported by the authors.

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