Hierarchical porous PANI/MIL-101 nanocomposites based solid-state flexible supercapacitor

Qian Wang  
_Shaanxi University of Science and Technology, qw97@uow.edu.au_

Liang Shao  
_Shaanxi University of Science and Technology, Shaanxi Research Institute of Agricultural Products Processing Technology, lshao@uow.edu.au_

Zhonglei Ma  
_Shaanxi University of Science and Technology_

Juanjuan Xu  
_Shaanxi University of Science and Technology_

Ying Li  
_Shaanxi University of Science and Technology_

See next page for additional authors
Hierarchical porous PANI/MIL-101 nanocomposites based solid-state flexible supercapacitor

Abstract
Metal-Organic Frameworks (MOFs) have attracted increasing attention in the field of energy storage owing to their high porosity, high specific surface area, high charge storage. However, the poor conductivity in most MOFs largely hinders their electrical properties. In this work, we developed an effective strategy to grow the conductive polyaniline (PANI) inside the pores of MIL-101 (labeled as PANI/MIL-101) to form a fixed interpenetrating network structure. The electron-rich imine group in PANI is chelated with the coordinatively unsaturated metal sites (CUS) in MIL-101 to form a relatively strong bonded complex and through other synergistic effects to enhance the conductivity and electrochemical properties. The resultant PANI/MIL-101 exhibited a superior high capacitance of 1197 F g⁻¹ (i.e., 957.6 C g⁻¹) at 1 A g⁻¹ in constant current charge and discharge test. The assembled flexible solid-state supercapacitor showed a favorable specific capacitance, power density and good cycling stability (a 81% capacitance retention rate over 10,000 cycles). It also demonstrates a good flexibility, as evidenced by a small capacitance loss of 10% after being subject to 1000 bending cycles at 180°. The PANI/MIL-101 nanocomposite showed great potential in energy storage device.

Disciplines
Engineering | Physical Sciences and Mathematics

Publication Details

Authors
Qian Wang, Liang Shao, Zhonglei Ma, Juanjuan Xu, Ying Li, and Caiyun Wang

This journal article is available at Research Online: https://ro.uow.edu.au/aiimpapers/3155
Hierarchical porous PANI/MIL-101 Nanocomposites based Solid-state Flexible Supercapacitor

Qian Wang, a Liang Shao, a, b Zhonglei Ma, a Juanjuan Xu, a Ying Li a, Caiyun Wang c

a College of Chemistry and Chemical Engineering, Shaanxi University of Science and Technology, Xi’an 710021, China.
b Shaanxi Research Institute of Agricultural Products Processing Technology, Xi’an 710021, China.
c Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, AIIM Facility, Innovation Campus, University of Wollongong, Wollongong, NSW 2522, Australia.

* Corresponding author.
E-mail addresses: shaoliang@sust.edu.cn

ABSTRACT: Metal-Organic Frameworks (MOFs) have attracted increasing attention in the field of energy storage owing to their high porosity, high specific surface area, high charge storage. However, the poor conductivity in most MOFs largely hinders their electrical properties. In this work, we developed an effective strategy to grow the conductive polyaniline (PANI) inside the pores of MIL-101 (labeled as PANI/MIL-101) to form a fixed interpenetrating network structure. The electron-rich imine group in PANI is chelated with the coordinatively unsaturated metal sites (CUS) in MIL-101 to form a relatively strong bonded complex and through other synergistic effects to enhance the conductivity and electrochemical properties. The resultant PANI/MIL-101 exhibited a superior high capacitance of 1197 F g⁻¹ (specific capacity, 957.6 C g⁻¹) at 1 A g⁻¹ in constant current charge and discharge test. The assembled flexible solid-state supercapacitor showed a favorable specific capacitance, power density and good cycling stability (a 81% capacitance retention rate over 10,000 cycles). It also
demonstrates a good flexibility, as evidenced by a small capacitance loss of 10% after being subject to 1000 bending cycles at 180°. The PANI/MIL-101 nanocomposite showed great potential in energy storage device.

**KEYWORDS:** metal-organic frameworks; polyaniline; electrochemical; flexible; supercapacitor

1. **Introduction**

At the present information age, the surge demand for flexible electronic devices such as wearable electronic products drives the development of miniaturized, lightweight, and flexible energy storage systems yet with high-performance [1-5]. Being an important type of energy storage devices, the supercapacitor possesses the advantages of fast charge-charge rate, high power density, and very long cycle life [6]. Flexible SCs, with liquid electrolyte may suffer from the problem of electrolyte leakage when integrated into flexible electronics [7, 8]. All-solid-state flexible SCs with solid-state electrolytes are preferred in terms of the compactness, reliability, small size, and free of electrolyte leakage [9].

Conductive polymers (CPs) are widely studied as electrode materials for flexible supercapacitors because of their high charge storage, low cost, easy processability, lightweight, and mechanical flexibility [10-13]. Polyaniline (PANI), one type of CPs, has attracted attention as a promising material for supercapacitor due to its advantages of high doping ability, high specific capacitance, good conductivity, ease of synthesis and good environmental stability [2, 14]. However, its molecular chains are easily accumulated affecting the charge transport conductivity. Moreover, the swelling and contraction of PANI chain during the charge/discharge reduce its electrochemical performance (e.g. cyclic stability) [15]. The electrochemical performance of PANI can be improved by creating new compositions with other materials, such as metal oxides.
[16, 17], graphene [17-21], carbon black [22, 23], carbon nanotubes [24, 25] and other organic matter [11, 26-28]. They demonstrate a capacitance in a range of 200F/g and 800F/g, and there is still room to raise the value.

Nanoporous MOFs have demonstrated the use in a wide variety of applications such as gas adsorption, catalytic application and energy storage [29]. However, the conductivity of most MOFs are very poor, since the insulating nature of organic-ligands along with d-orbital participation of metal-ions in coordination bonds does not allow efficient delocalization of electrons across the framework [30]. The carbonized MOFs or their incorporation with conductive carbon-based materials have been used for energy storage application [15, 31]. Recently, MOFs have shown great potential for use in gas adsorption and decontamination [32-34]. However, the application of MOFs in the field of electrochemistry remain scarce [35]. MIL-101, one type of MOFs, is made from terephthalic acid (H₂BDC) as a ligand and a triad metal cluster Cr₃O(CO₂)₆ super tetrahedra (ST) secondary structure unit by hydrothermal synthesis with a three-dimensional pore structure. If the MIL-101 is integrated with conductive polymer PANI, the charge transfer between them can not only allow efficient delocalization of electrons across the framework, but also improve the electrochemical performance of the system. In addition, MIL-101 exhibits a high porosity, excellent water stability and acid resistance. The unsaturated Cr(III) sites in MIL-101 offers an intrinsic chelating property with electron-rich functional groups in PANI chains to form the composite.

Here, we have developed a PANI/MIL-101 nanocomposite via chemical synthesis and PANI was grown in the internal channels and on the surface of MIL-101 as well. This well-designed composite demonstrated a novel hierarchical porous structure. Where the MOFs and PANI showed specific properties through donor-receptor interactions, which overcome the low conductivity of MOF but still retain the porosity.
for efficient charge storage. In this paper, the structure and properties of flexible solid-state SCs based on PANI/MIL-101 were systematically studied.

2. Experimental section

2.1. Materials

Aniline (Ani), ammonium persulfate (APS), N,N′-dimethylformamide (DMF), ethanol and methanol were purchased from Tianjin Tianli Chemical Reagent Co., Ltd. Sulfuric acid (H₂SO₄) and Hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,4-benzenedicarboxylic acid (H₂BDC), Cr(NO₃)₃•9H₂O and paminodiphenylamine (AD) were purchased from Aladdin Reagent Co. Ltd. Carbon cloth (CC) was purchased from CeTech Co. Ltd. Aniline was distilled under reduced pressure prior to use. Other chemicals and solvents were used as received without any further purification.

2.2. Preparation of MIL-101

The synthesis of Cr-MOF (MIL-101) was based on a previously reported procedure with some minor modifications [35, 36]. First, Cr(NO₃)₃•9H₂O (1.92 g, 4.8 mmol) was dissolved into deionized water (30 mL) under ultrasonication, followed by addition of H₂BDC (0.80 g, 4.8 mmol), followed by a sonication process for 5 minutes, then HF (0.24 g, 4.8 mmol) was dissolved in the above solution. The resultant mixture was introduced into three 50 mL teflon-lined autoclaves which were put in an electric blast oven at 220°C for 8 h. After cooling to room temperature, the resulted green solid powders were collected via centrifugation, rinsed with DMF and methanol (3 times), and dried at 120°C overnight.
2.3. Preparation of PANI/MIL-101 Nanocomposites

MIL-101 was degassed overnight at 120 °C under a reduced pressure. Then aniline monomers (0.93 g) were mixed with the activated MIL-101; and a reduced pressure and ultrasonication was applied for 15 minutes allowing aniline to permeate into the MIL-101 channels. AD (0.0047 g) was added into this mixture, followed by continuous ultrasonication under a reduced pressure for 20 minutes. The HCl solution (1.0 mol L⁻¹, 30 mL) was added into the above mixture under ultrasonication for 10 minutes (remove the decompression device at this time) to form solution A. APS (2.28 g) was dissolved into a fresh HCl solution (1.0 mol L⁻¹, 20 mL) to form solution B. Solution A and B were pre-cooled at 0-4 °C for 20 minutes. Then solution B was added into solution A and stirred at room temperature. The polymerization proceeded for 0.5 h. The resulting deep green product (PANI/MIL-101) was centrifuged and rinsed with large amount of ethanol and water and dried at 60°C overnight. The PANI/MIL-101 composites with various PANI contents and MIL-101 contents were prepared by adjusting the aniline concentrations (0.05, 0.1, 0.2, 0.3, 0.4, 0.5 mol L⁻¹) and the mass fraction of MIL-101. (The mass percentage of MIL-101 to aniline was used to represent the dosage of MIL-101, for example MIL-101(10) represents a 10 wt% of MIL-101 relative to aniline) in the original mixed solution. The parameters of PANI/MIL-101 preparation as shown in Table S1, and for comparison, (0.2 M)PANI/MIL-101(30) was also prepared without reduced pressure.

2.4. Preparation of PANI Nanofibers

PANI nanofibers were synthesized as previously reported with some slight
modification [37, 38]. The process was the same as PANI/MIL-101 Nanocomposites without MIL-101.

2.5. Preparation of Electrodes

Carbon cloth (0.3 mm thick) was used as current collector. Carbon cloth was treated by being immersed in 6 mol L⁻¹ HNO₃ at room temperature for 12 h, and rinsed with acetone, ethanol and water, and dried in a vacuum oven at 80°C for 3 h. An uniform slurry composed of active materials (PANI/MIL-101 or PANI), acetylene black and polyvinylidene difluoride at a weight ratio of 8:1:1 in NMP was coated onto carbon cloth. The formed electrode was dried in a vacuum oven at 80°C for 3 h. Its mass loading was in the range of 0.25-4 mg cm⁻².

2.6. Preparation of Flexible Solid-State Supercapacitors

Flexible solid-state supercapacitor was fabricated with a gel electrolyte H₂SO₄/PVA. It was prepared by dissolving PVA powder (6 g) and concentrated H₂SO₄ (6 g) into DI water (60 mL), and then stirred at 85°C until the solution became clear. Two pieces of CC supported electrodes and a piece of hydrophilic polypropylene film (used as separator) were immersed into H₂SO₄/PVA gel solution for 60 min and taken out. The electrodes were dried in air at room temperature to vaporize excessive water. Afterwards, two electrodes and one polypropylene film filled with gel electrolyte were stacked together face-to-face to assemble the flexible solid-state supercapacitors (SCs). Finally, it was encapsulated by flexible polyethylene terephthalate (PET) film to form a symmetric supercapacitor device.

The characterization tests of structure and performance are in electronic support
3. Results and discussion

3.1. Structure, morphology and properties of electrode materials

PANI is normally synthesized under acidic conditions and, the selected MOF must be stable under acidic conditions. The MIL-101 was stable under acidic conditions as demonstrated by Fig. S1.

Fig. 1 showed a schematic diagram of the experimental method and technical route, which the aniline monomer was adsorbed into the pores of MIL-101 under reduced pressure and then polymerized. The chemical structures of the prepared samples were examined by FT-IR. Fig. 2(a) and Fig. S2 shows the FT-IR spectra of pure PANI, MIL-101, and a series of samples PANI/MIL-101. The main characteristic bands of PANI appeared at 1561, 1484, 1299, 1109, and 801 cm\(^{-1}\), which are in agreement with the emeraldine form of PANI. The bands at 1561 and 1484 cm\(^{-1}\) are assigned to the C=C stretching vibration of quinoid rings and benzene rings, while the peaks at 1299, 1109 and 801 cm\(^{-1}\) correspond to C=N and C=N\(^+\) stretching vibration mode or C−H bending mode of benzene ring, C−H bending mode of quinoid ring, and C−H out-of plane bending vibration of 1,4-disubstituted aromatic rings, respectively.[39, 40] For MIL-101, clearly showed the vibrational bands around 1622, 1553 and 1400 cm\(^{-1}\), characteristic of the framework −(O−C−O)− groups confirming the presence of dicarboxylate; the characteristic band at 1018 cm\(^{-1}\) is assigned to the Cr−O vibration [41, 42]. For the PANI/MIL-101 nanocomposites, characteristic peaks of PANI and MIL-101 can be found in the FT-IR spectra, verifying the successful polymerization of
aniline in the presence of MIL-101. Moreover, the C=C stretching vibrations of the quinoid and benzenoid units of PANI shifted from lower wavenumber to higher wavenumber (Fig. 2a), which can be related to a variety of interactions including π–π/N–H–π interactions, or charge transfer (CT) between MIL-101 and partial PANI [30, 33]. The CT can also be demonstrated by another interaction; the amine functional groups on the polyaniline molecule are rich in electrons and the presence of unsaturated Cr(III) sites in MIL-101 provides an intrinsic chelating property with electron-rich functional groups, these imino groups could interact with the presence of Cr(III) coordinatively unsaturated metal sites (CUS) via Lewis acid-base interaction [34, 43, 44]. Compared to PANI, the composite materials demonstrated new absorption peaks around 1399 cm\(^{-1}\) and around 747 cm\(^{-1}\), corresponding to vibration of –(O–C–O)– and C–H. In addition, the red shift of other vibration peaks of polyaniline may be related to the coordination of CUS in MIL-101 molecules. These results clearly demonstrate that PANI was grafted onto the CUS in MIL-101 cages. These interactions may enhance the delocalization of π-electrons of PANI. Moreover, the hydrogen bond may be present in the oxygen atom of MIL-101 and PANI molecular chain. These interactions between PANI and MIL-101 may influence the morphology of PANI and enhance the electrochemical performance.

PANI displayed two characteristic peaks at about 223 and 467 nm in the UV-Vis absorption spectra (Fig. 2b, Fig. S3), attributing to π–π* and polaron–π* transitions in quinoid and benzenoid units, respectively. The peak at 467 nm is related to the doping level and the formation of polaron, indicating that the obtained PANI is in an emeraldine
A gradual red shift in the benzenoid unit peak at about 223 nm occurred for all PANI/MIL-101 nanocomposites, indicative of the increased conjugate length of PANI main chains that was resulted from the increased range of $\pi$ electrons, since the electron cloud tend to average owing to strong interaction between PANI and MIL-101 (Fig. 1) [37]. Similarly, a red shift of the peak at 467 nm to 471, 475, 464, 469, and 480 nm was evidenced for (0.05 M)PANI/MIL-101, (0.2M)PANI/MIL-101(30), (0.5M)PANI/MIL-101, PANI/MIL-101(10) and PANI/MIL-101(50), respectively. Compared to PANI (2.65 eV), the lower band gap of (0.2M)PANI/MIL-101(20)(2.61 eV) suggested that the charge transfer chelating mechanism between PANI and CUS in MIL-101 enabled an even distribution of polaron on the PANI molecular chain [33]. The increase in degree of its conjugate delocalization is caused by the interaction as shown in Fig. 1. Therefore, the electron transition is easier and the electrochemical performance will be better for PANI/MIL-101 nanocomposites compare with those of PANI.

In Fig. 2(c), MIL-101 showed the characteristic Raman peaks at 866, 1146, 1341,1447, and 1609 cm$^{-1}$. After addition of PANI, the intensity of these peaks decreased. Those peaks corresponding to the PANI are clearly observed in (0.2 M)PANI/MIL-101(20), and the peak at 1450 cm$^{-1}$ corresponds to $\text{C=\text{N}}$ stretching of quinoid rings. In addition, two distinct peaks at 1354 and 1585 cm$^{-1}$ can be assigned to the stretching vibrations of $\text{C−N}^+$ fragments and $\text{C−C}$ stretching of benzenoid rings, respectively, suggesting that PANI was in a highly electrical conductive form (emeraldine salt). Furthermore, with the incorporation with MIL-101, the peak at 1337
cm\(^{-1}\) corresponding to C–N\(^{+}\)’ stretching vibration shifted to the higher wavenumber of 1354 cm\(^{-1}\) due to the strong interaction of the C–N\(^{+}\)’ species of PANI with negative species of MIL-101 (COO\(^{-}\)). Thus the peak shifting is the result of the combined contribution of MIL-101 peaks and PANI peaks [15], which promotes the charge transfer. Raman analysis indicates that PANI/MIL-101 composites were formed.

Fig. 2(d) and Fig. S4 showed the PXRD patterns of PANI, and MIL-101 a series of PANI/ MIL-101. PANI displayed three broad peaks centered at \(2\theta = 15.6^\circ, 20.3^\circ\) and \(25.4^\circ\), suggesting a partially crystalline structure and a highly doped emeraldine salt form [46]. All the XRD peaks for MIL-101 match well with the previously reported results by G. Férey et al, evidencing that MIL-101 was successfully synthesized [35, 36, 42, 47, 48]. However, it can be seen that the peak between 4 and 8° of MIL-101 almost disappeared after loading PANI. This is due to the filling of PANI insied the MIL-101 pore [32, 49]. Furthermore, from the PXRD patterns, it can be seen that the intensity of the characteristic peaks of MIL-101 from PANI/ MIL-101(10) to PANI/MIL-101(50) gradually increased with the increasing content of MIL-101, and intensity gradually increased from (0.05 M)PANI/MIL-101 to (0.5 M)PANI/MIL-101 with the increase of PANI, as well as some new peaks appeared. That can be attributed to the PANI moieties inside the channels of MIL-101, leading to an extended conjugated network, which is believed to induce higher conductivity and mobility.

Fig. 3 showed the morphologies and microstructures of PANI, MIL-101 and PANI/MIL-101 at different aniline concentrations. Pristine PANI exhibited a continuous network of interconnected 1D nanofibers with diameters around 50 nm and
length on the order of several micrometers (Fig. 3a). MIL-101 exhibited an octahedron shape with a size range of 150 nm to 1 µm (Fig. 3b). As shown in Fig. 3(c-h) and Fig. S5, the morphology of MIL-101 remains nearly intact in the composite, proving the stability of MIL-101 under the formation condition as shown in Fig. S1. Thus, maintaining the crystallinity and morphology ensures efficient use of the void space in MIL-101 for accommodating the PANI portion without loss of structural integrity. Moreover, Fig. 3(c-h) showed the aniline concentration dependent morphological changes and Fig. S5(a-e) showed the MIL-101 content dependent morphological changes. By increasing the concentration of aniline or reducing the MIL-101 content, the polyaniline particles increased progressively. This may be due to part of the polyaniline was initially incorporated into the MIL-101 framework when the aniline concentration was low or the MIL-101 content was high. With the progress of polymerization, the molecular weight of polyaniline was increasing and could not be completely entered into the pores of MIL-101 framework. Moreover, assuming that PANI can be polymerized from inside may induce uniform coverage of PANI on the MOF surface. This was confirmed in Fig. 3(d,e), which show that polyaniline particles were grown uniformly on the surface of MIL-101 and exhibit a rice ball, which could be described as hierarchical structure. This may be due to the large number of nucleation sites provided by CUS in MIL-101, which was grafted onto CUS and then grown vertically as a nucleus. The fabrication process was shown in Fig. 1.

In order to verify that PANI entered the MIL-101 pores, (0.2 M)PANI/MIL-101(20) was milled for 10 h and worn off the surface PANI, and the morphology of the MIL-
101 is destroyed as shown Fig. S6(a). In contrast, PANI was still present and coated on the MIL-101 surface after 10 hours of ball milling Fig. S6(d). This may be due to the lack of decompression during the synthesis of (0.2M)PANI/MIL-101(20), PANI was coated on the surface of MIL-101 and not no infiltrated into the MIL-101 channel. In addition, the incorporation of PANI inside the framework of MIL-101 was confirmed by the distribution of elements, as shown in Fig. S6(b,e). Because MIL-101 was destroyed by the milling process. It can be clearly seen that the N element content in Fig. S6 (b,c) is higher than the N element content in Fig. S6 (e,f), because the N element from PANI is interior concentrate in the Cr element area beside that attached on the surface of MIL-101, indicating that PANI was entered into the MIL-101 pore under reduced pressure.

The Brunauer–Emmett–Teller (BET) analysis was used to illustrate the specific surface area of PANI, MIL-101 and (0.2M)PANI/MIL-101(20). The corresponding nitrogen adsorption/desorption isotherm curves and the pore size distribution plots are shown in Fig. 4, and the detailed data are listed in Table S2. PANI, MIL-101 and PANI/MIL-101 are typical of III, I and IV isotherm characteristics and adsorption lines and desorption lines coincide [50]. Fig. 4(a) indicates that the specific surface area of PANI is significantly improved after the incorporation with of MIL-101. Based on the pore size distribution calculated by BJH (Fig. 4(b)) and Table S2), PANI mainly contains mesopores mainly, and some macroporous, while MIL-101 contains mesopores mainly and some micropores. Most of (0.2M)PANI/MIL-101(20) was mesopores in addition to a small amount of microporous and macroporous.
Interestingly, it can be seen from Fig. 4(b) that (0.2M)PANI/MIL-101(20) displayed a much smaller surface area and pore volume than MIL-101, with only 318.95 m² g⁻¹ and 0.08 m³ g⁻¹, indicating that most of the framework pores of MIL-101 were filled with PANI [32]. Compared to that of PANI, the specific surface area of PANI/MIL-101 increased obviously, while the pore size and pore volume were smaller than PANI. The smaller pore size is due to the introduction of MIL-101, which reduces the self-accumulation of polyaniline molecular chains. Moreover, the smaller pore volume can be attributed to polyaniline molecular chains into the MIL-101 frame, occupying a certain volume, so that the pore volume of PANI/MIL-101 was smaller than those of PANI and MIL-101. This result is in agreement with the results form PXRD, SEM and TEM analysis. Thus it can be concluded that PANI does enter into the MIL-101 pores. Moreover, the interaction between these two components has been demonstrated by the combining the FT-IR, UV–Vis, Raman and PXRD analysis. These results show that addition of MIL-101 increases the conjugate delocalization length of PANI and enhances the charge-carrier transport, which may lead to an enhance electrochemical performance. The Schematic illustration of interaction and carrier conduction between PANI and MIL-101 is shown in Fig. 1.

Fig. S7 and Table 1 show the effect of the interaction between PANI and MIL-101 on the electrical and semiconductor properties. It can be seen from Fig. S7(a) that the conductivity of pure PANI is low, and its conductivity gradually increased with the increase of MIL-101 content when it formed the compound with MIL-101. The conductivity reached a maximum of 0.55 S cm⁻¹ when the content of MIL-101 reached
20%, and it decreased with further increased content. This may be due to the fact that MIL-101 provided a rich CUS when PANI was incorporated into MIL-101, thus polyaniline was adsorbed inside the pores of MIL-101 and increased its charge transport path resulting in an improved conductivity. When the conductivity reached a maximum (MIL-101 content of 20%), the conductivity does not increase but decreased with the increased amount of MOFs. This is because the addition of too many insulators (MIL-101) reduces the utilization of pores. Polyaniline was self-accumulating and grows heavily on the surface of MIL-101, hindering charge transfer. So its conductivity curve shows the trend of increasing first and then decreasing. In comparison with Fig. S7(a), when the content of MIL-101 was kept constant, the conductivity increased with increasing aniline concentration as shown in Fig. S7(b). This may be due to the excessive amount of polyaniline acting as a conductive agent, and the cumulative effect of increased conductivity. The electronic and semiconducting properties of PANI, MIL-101 and (0.2M)PANI/MIL-101(20) were further evaluated by temperature change Hall-effect measurement (Table 1). The results showed that MIL-101 belongs to insulator and no data was available. The coefficient of (0.2M)PANI/MIL-101(20) was found to be -55.4 cm$^3$ C$^{-1}$ and thus it was clearly an n-type semiconductor material with extremely high-carrier density of $1.25 \times 10^{18}$ cm$^{-3}$, and the carrier type was a hole. The carrier mobility and conductivity were observed to be 8.98 cm$^2$ V$^{-1}$ s$^{-1}$ and 0.43 S cm$^{-1}$, respectively, higher than PANI. The discrepancy in the conductivity values of PANI and PANI/MIL-101 from the four-probe and the Hall-effect measurements could be related to the probe-contact issue.
All the above analysis results indicate that the addition of MIL-101 plays an important role in the electrical properties of PANI/MIL-101. First, polyaniline was incorporated into the MIL-101 through the interaction with CUS in MIL-101, which reduced the accumulation of PANI molecular chains and increased the charge transport path. The charge transfer interaction between PANI and MIL-101 allowed PANI/MIL-101 to form an exciplex type of species. Moreover, through these synergistic interactions, the conjugate delocalization length of PANI and the electronic and semiconducting properties of PANI/MIL-101 were improved.

3.2. Electrochemical properties of PANI/MIL-101 electrodes

The capacitive behaviours of the PANI/MIL-101 composites as electrode materials were investigated using GCD in a three-electrode configuration. There was no significant voltage drop (IR drop) during the initial stage of the discharge process, indicating that the internal resistance of the electrode was relatively small, as shown in Fig. S8(a,c). Fig. S8(a) presents comparative GCD curves of the materials prepared under same concentration of aniline with changed content of MIL-101 content. It can be seen from the Fig. S8(b) that the specific capacity is basically increased and then decreased with the increased content of MIL-101, which is consistent with the trend of the conductivity. These results show that the PANI molecular chain grew into the pores through the interaction with MIL-101, which improved the charge transfer performance and electrochemical performance of PANI/MIL-101. However, too much insulator (MIL-101) in the system can affect electrochemical performance, resulting in a decrease in specific capacitance. In addition, when the MIL-101 content remained
constant, it is found that when the aniline content reached 0.2 mol L\(^{-1}\), the specific capacitance was no longer increased with the increased content of aniline as shown in Fig. S8(d). This may be ascribed to the aggregated PANI molecular chains hinder the charge transfer, thus affecting the energy storage. Excessive polyaniline weakens the synergistic effect between polyaniline and MIL-101, and mainly shows the property of single polyaniline. The result is in conformity with the SEM and Conductivity analysis.

All the above results showed that the composite material (0.2M)PANI/MIL-101(20) had the highest specific capacitance of 633 F g\(^{-1}\) when the MIL-101 content was 20% and the aniline concentration was 0.2 mol L\(^{-1}\). It’s specific capacity was also calculated as 506.4 C g\(^{-1}\), since the Faradaic characteristics was involed. As a control, the carbon cloth and MIL-101 electrodes were tested by GCD and CV, which showed a negligible specific capacitance and areal capacitance in comparison with that of the PANI and (0.2M)PANI/MIL-101(20) electrodes (Fig. 5). After determining the composite material, in order to explore the scope of PANI/MIL-101 loading, the areal loading of (0.2M)PANI/ MIL-101(20) was varied from 0.25 mg cm\(^{-2}\) to 4 mg cm\(^{-2}\). The obtained (0.2M)PANI/MIL-101(20) electrodes were examined by using GCD method at a current density of 1 A g\(^{-1}\), as shown in Fig. S9(a). The highest specific capacitance was obtained with a mass loading of 0.5 mg cm\(^{-2}\) (0.2M)PANI/MIL-101(20), reaching 1197 F g\(^{-1}\) (i.e., 957.6 C g\(^{-1}\)), which is much higher than the previously reported conductive polymer based electrodes (Table S3). In addition, as shown in Fig. S9(b), the highest areal capacitance was obtained with a mass loading of 4 mg cm\(^{-2}\) PANI loading, reaching 178 mF cm\(^{-2}\). When the (0.2M)PANI/MIL-101(20) loading increased, the
specific capacitance of electrode gradually decreased, while the areal capacitance gradually increased (Fig. S9(c)). At a mass loading of 2 mg cm\(^{-2}\) for (0.2M)PANI/MIL-101(20), the specific capacitance and areal capacitance was balanced. Thus, the (0.2M)PANI/MIL-101(20) loading of the electrode was fixed at 2 mg cm\(^{-1}\) for the following test.

EIS was used to investigate the bulk resistance (equivalent series resistance), charge transfer resistance and diffusion resistance of the device, and its capacitance properties. The Nyquist plot consisted of low frequency and high frequency region (Fig. 6a), the straight line at the low frequency region indicates diffusion resistance (Warburg element). The intercept of the high frequency region at the X axis was 2.6 Ω, indicating a small series resistance. The small semicircle at high frequency indicates a low charge transfer resistance. In low frequency region, the slope was relatively large, indicating a good capacitive behavior [51, 52].

The CV curves of the device are depicted in Fig. 6(b) over the range of 0-0.8 V at scan rates recorded from 5 to 100 mV s\(^{-1}\). The PANI-based electrode obviously demonstrated two pairs of redox peaks ascribed to the transitions of PANI between leucoemeraldine based state to emeraldine state and emeraldine state to pernigraniline state [50, 53]. As the scan rate increased from 5 to 100 mV s\(^{-1}\), the current values of positive and negative peaks all increased gradually. This behavior is attributed to the lack of redox reactions inside the (0.2 M)PANI/MIL-101(20) at fast scan rates. The electrochemical properties of these samples were investigated using galvanostatic charge/discharge at different current density from 0.25 to 20 A g\(^{-1}\) (Fig. 6c,d). The
shoulder platforms in the potential ranging from 0 to 0.8 V may be attributed to the redox reaction of polyaniline. Additionally, the IR drops (the voltage drops due to resistance) on these GCD plots are negligible, owing to the high conductivity of PANI/MIL-101. The calculated specific capacitance versus current density were illustrated in Fig. 6(e), the specific capacitance decreased with the increase of current density. This result can be explained by that at high current densities, the electrolyte ions can not enter all the active surface regions due to the rapid scanning rate, which makes poor interaction between the electrolyte and the ions of the electrode offering a gradually decreases capacitance [54]. The (0.2 M)PANI/MIL-101(20) exhibited a good rate capability, a capacitance retention rate of 61% was obtained at a current density increases to 10 A·g⁻¹ (152 F g⁻¹, 121.6 C g⁻¹) when increased from 1 A·g⁻¹ (248 F g⁻¹, 198.4 C g⁻¹) (a typical rate performance which give 50–60% capacitance retention at a 10-fold higher current density) [50, 55]. In general, because of the swelling and shrinking of molecular chains during charge and discharge processes, the cycle stability of conductive polymers is relatively poor [56, 57]. For example, the specific capacitance retention rate of polyaniline is generally about 70% after cycling for 1000 cycles [58]. However, in this work, (0.2 M)PANI/MIL-101(20) electrode shows an excellent electrochemical stability, with 90% capacitance retention after 10,000 GCD cycles at a current density of 20 A g⁻¹ as shown in Fig. 6(f), superior to the performance of other polyaniline-based flexible supercapacitor electrodes (Table S3). Because of the interaction between PANI and MIL-101, the charge transfer is easy to occur between them, increasing the redox efficiency and reducing the swelling and shrinking of PANI.
3.3. Electrochemical properties of PANI/MIL-101 supercapacitors

Fig. S10 shows the design and flexible supercapacitor was constructed using two identical electrodes (0.2M)PANI/MIL-101(20) and gel electrolyte (PVA/H₂SO₄). The prepared supercapacitor was pretreated in 1 mol L⁻¹ H₂SO₄ solution for 30 minutes before the test. It was firstly investigated in a conventional three-electrode system. The results form a three-electrode system test reflect the theoretical specific capacitance of the prepared supercapacitor, as can be seen from Fig. S11(a), the (0.2M)PANI/MIL-101(20)-based supercapacitor showed typical charge-discharge curves. Fig. S11(b) shows the values of the specific capacitance for PANI/MIL-101 supercapacitor as a function of current densities. It can be seen that the specific capacitance of the device was as high as 371 F g⁻¹ (i.e., 296.8 C g⁻¹) at a current density of 0.5 A g⁻¹, superior to the performance of other PANI-based flexible supercapacitors [59].

In order to investigate the practical electrochemical performance of the supercapacitor, a two-electrode system was used for the subsequent tests. Nyquist plot in Fig. 7(a) shows that the equivalent series resistance (EIS) extracted from high frequency was around 7.4 Ω, and charge-transfer resistance was relatively small. It is easy to see that the diffusion resistance in the low frequency region was relatively large, indicating that the charge diffusion between the electrode and the electrolyte showed some resistance. Fig. 7(b) shows the CV curves recorded at scan rates of 5-100 mV s⁻¹, it can be seen that the values of oxidation peaks increased significantly with the increasing of scan rate, indicating that the supercapacitor possesses an excellent electrochemical response. As the scanning rate increased, the CV curves does not
always maintain the original shape because that the charging–discharging process of the supercapacitor in the H$_2$SO$_4$ electrolyte was governed by the insertion of H$^+$ from the electrolyte into the device and its release from the supercapacitor to the electrolyte.

The GCD profiles (Fig. 7(c)) of the supercapacitor showed typical charge-discharge curves for PANI/MIL-101-based supercapacitor. Although there was a voltage drop, the specific capacitance of the device remained as high as 80 F g$^{-1}$ (i.e., 64 C g$^{-1}$) at a current density of 0.5 A g$^{-1}$. A Ragone chart that depicts the relationship between power density and energy density was plotted for SSCs, as shown in Fig. 7(d). It can be seen from the Fig. that the device exhibited a relatively high energy density of 7 Wh kg$^{-1}$ and a power density of 2000 W kg$^{-1}$ for a 0.8 V voltage window. The stability of the supercapacitor was tested by GCD measurements at 2.5 A g$^{-1}$ and the obtained results are presented in Fig. 7(e). The supercapacitor exhibited good electrochemical stability and maintained a specific capacitance of about 81% after the 10,000 GCD cycles, superior to the performance of other PANI-based flexible supercapacitors (Table S4).

The flexibility of the device was confirmed by the CV at different bending angles of 0°, 90°, and 180°. It can be seen that the CV curves remained unchanged and stable (Fig. 8(a)), which indicates the high flexibility and good electrochemical stability. Also, the GCD curves of the supercapacitor bent at different angles at a current density of 2.5 A g$^{-1}$, showed that variation of capacitance is small(Fig. 8(b)). In order to further verify its mechanical cycle stability, was subject to a bending angle of 180° for 1000 times. The specific capacitance of this supercapacitor retains 90% of its initial value(Fig. 8(c)), which means that the contact between the different layers of the device remained well
after during bending test, rather than continuing to deteriorate. All of these bending tests were carried out using only one device, indicating that the supercapacitor can be bent for many times and still keep almost the same performance, which suggests that it is suitable for flexible device applications.

In order to demonstrate the practical application of the prepared flexible supercapacitor device, four cells were connected in series and charged to 3.2 V at a constant current of 8 mA. And then connect it to a red light emitting diode (LED) (rated voltage 1.8 V) and observe the successful lighting of the LED for 90 seconds, as shown in Fig. 8(d) and supported video.

4. Conclusions

PANI/MIL-101 nanaocomposites were successfully fabricated via in situ polymerization for use in a flexible solid-state supercapacitor with superior electrochemical performance. It demonstrated that the incorporation of PANI in the MIL-101 pores greatly improved the electrochemical performance of PANI. The non-covalent π–π/N–H–π interaction or charge transfer interaction between the MIL-101 and PANI, increased the conjugate delocalization length of PANI and improved the ability of carrier transfer. The PANI/MIL-101 based electrode showed a specific capacitance up to 1197 F g⁻¹ (i.e., 957.6 C g⁻¹) at 1 A g⁻¹, and specific capacitances retention rate of about 90% after 10,000 cycles. The specific capacitance of the supercapacitor retained 90% of the initial capacitance after being bent at 180° for 1000 cycles. The four devices were connected in series to light a red light emitting diode (LED) (rated voltage 1.8 V) for 90 seconds. Moreover, this work demonstrates that the
A combination of conductive polymer and metal-organic framework compounds has great application prospect in supercapacitors and other electrochemical devices.

Acknowledgements

This work was supported by Natural Science Foundation Research Project of Shaanxi Province (2017JM2024) and Key Scientific Research Group of Shaanxi Province (No:2013KCT-08).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/

References

Cui, Hierarchical nanostructured conducting polymer hydrogel with high electrochemical activity, PNAS. 109 (2012) 9287-9292.


[52] K. Wang, H. Wu, Y. Meng, Y. Zhang, Z. Wei, Integrated energy storage and electrochromic function in one flexible device: an energy storage smart window,


Graphic Abstract
Figure 1

Figure 2

(a) Transmittance/a.u.

(b) Absorbance/a.u.

(c) Intensity/a.u.

(d) Intensity/a.u.
Figure 6
Figure 8

(a) Current (mA) vs. Applied potential difference (V)

(b) Applied potential difference (V) vs. Time (t/s)

(c) Capacitance retention (%) vs. Bend Cycles

(d) Physical setup showing bending angle