

# Facile Synthesis of Porous NiO Nanofibers for High-Performance Supercapacitors

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The porous NiO nanofibers have been successfully synthesized by a simple process of hydrothermal treatment with subsequent calcination. The as-prepared porous NiO nanofibers, when applied as supercapacitor electrode exhibited a higher specific capacitance of 884 F/g with enhanced rate capability and good cycle stability. The excellent capacitive behaviors are mainly attributed to their unique configurations, which can not only provide high specific surface area but also greatly enhance the effective utilization of active materials as well as rapid ion/electron transportation. It is expected that such intriguing NiO porous nanofibers can serve as promising electrode materials for high-performance supercapacitors.

**Keywords** electrochemical properties, nickel oxide, porous nano-structures, supercapacitors

## 1. Introduction

Climate change and the decreasing availability of fossil fuels require society to move toward sustainable and renewable resources (Ref 1, 2). With the development of new energy resources, energy storage attracts great interests. Supercapacitors, also called electrochemical capacitors, have recently attracted intense attention because they can instantaneously provide higher power density than batteries and higher energy density than conventional dielectric capacitors, which make them probably the most promising candidates for next generation energy storage device, such as electric vehicles or hybrid electric vehicles with low CO<sub>2</sub> emissions (Ref 1-3). Thus far, many materials have been developed as the electrode materials in supercapacitors, mainly including transition metal oxides (Ref 4, 5), carbonaceous materials (Ref 6, 7) and conducting polymers (Ref 8, 9). Among them, NiO has been considered as one of the most promising electrode materials due to its excellent pseudo-capacitive behavior, low cost, environmental benignity, and practical availability (Ref 10-12). However, like other transition metal oxide materials, the poor conductivity has greatly limited its practical applications in high-performance supercapacitors.

It is noteworthy that the high rate capability of an electrode material is controlled by the ion diffusion

resistance within the crystal structure, which can be mitigated by shortening the diffusion path (Ref 13). One-dimensional nanostructure materials possess the advantages of fast redox reactions, high specific surface areas, and short diffusion paths for electrons and ions, which are expected to play a crucial role in electrochemical fields, and hence have been intensely investigated as electrode materials for supercapacitors (Ref 14, 15). On the other hand, porous nanostructures have been proposed to have the advantages of effectively alleviating the strain generated during the ion insertion/desertion process and resulting in an enhanced cycling stability. It is well-known that pseudo-capacitors store charges only in a thin layer from the surface of electrode materials. As a result, decreasing the particle size could increase the utilization of active materials. For example, Li and coworkers (Ref 11) have synthesized ultrathin Ni(OH)<sub>2</sub> nano-flakes by a simple hydrothermal route, exhibiting an excellent electrochemical performance. Subsequently, the synthesis of hierarchical ultrathin MnO<sub>2</sub> nanostructures (Ref 16) and ultrafine MnO<sub>2</sub> nanowires (Ref 14) has been realized by Li et al.'s group, respectively, also showing a high specific capacitance and good cycling stability. These reports indicated that ultrathin nanostructures with sizes of less than 10 nm are good for the improvement of supercapacitive performances. So far, although one-dimensional nanostructured NiO, in the form of nanowires, nanorods, and nanobelts, have been synthesized by some methods, there are few reports on the synthesis of porous NiO nanofiber composed of ultrathin nanoparticles.

In the present work, porous NiO nanofibers consisting of ultrathin nanoparticles have been successfully synthesized and investigated as electrochemical pseudo-capacitor materials for potential energy storage applications. The porous NiO nanofibers exhibit a high specific capacitance of 884 F/g at a current density of 0.5 A/g with high rate capability and good cycling stability compared with that of other NiO nanostructures reported in the literature. It is expected that the porous NiO nanofibers would be a promising electrode materials or a building block to construct other composites for supercapacitors.

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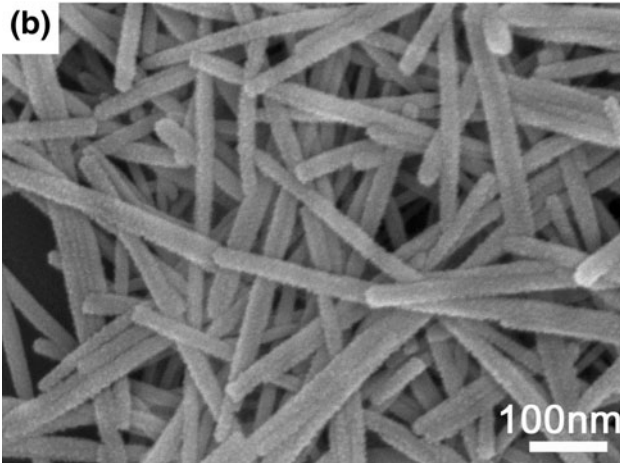
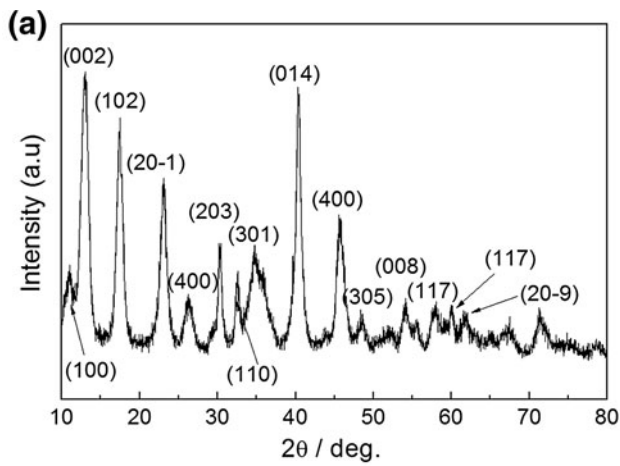


Fig. 1 XRD pattern and SEM image of the Ni(OH)<sub>2</sub> nanofibers

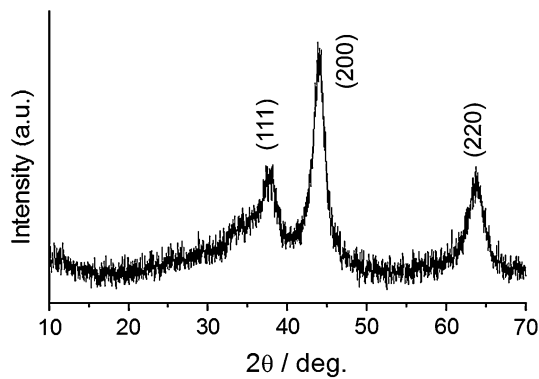


Fig. 2 XRD patterns of the porous NiO nanofibers

## 2. Experimental

### 2.1 Synthesis of NiO Nanofibers

All the reagents were analytical grade (Sigma-Aldrich) and used without further purification. In a typical synthesis, an aqueous solution (40 mL) containing NiSO<sub>4</sub>·7H<sub>2</sub>O (9.8 mmol), NaOH (4.9 mmol), and P123 (200 mg) was sealed into a 50 mL capacity Teflon-lined autoclave and heated at 120 °C for

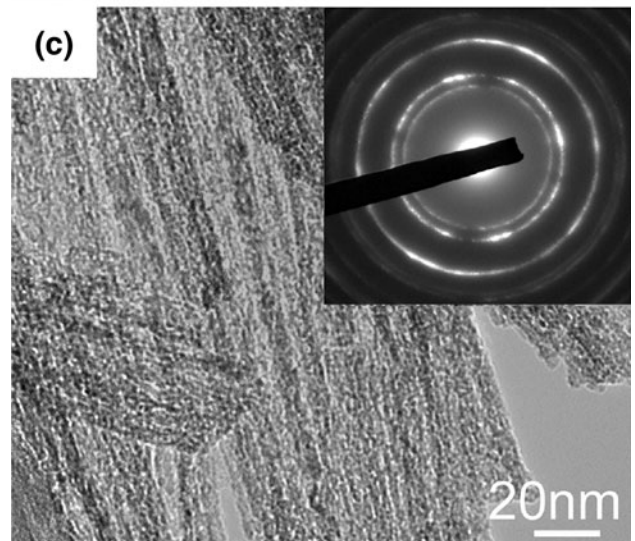
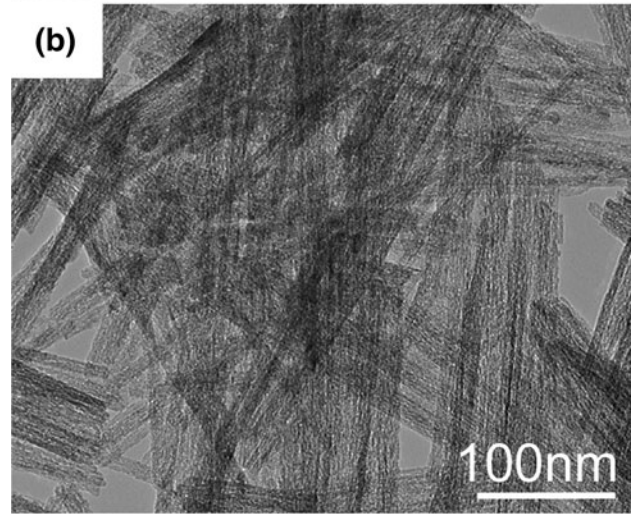
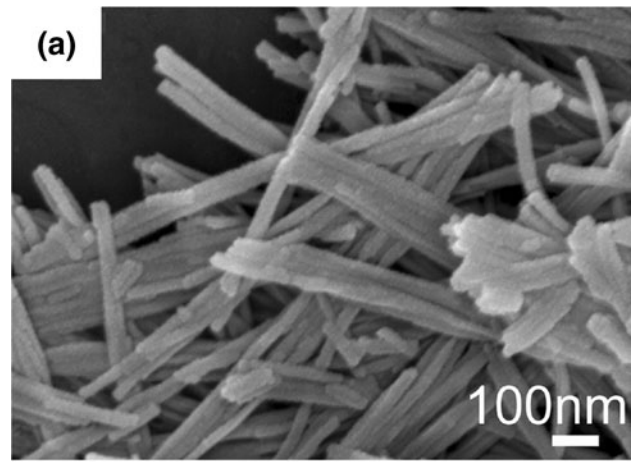
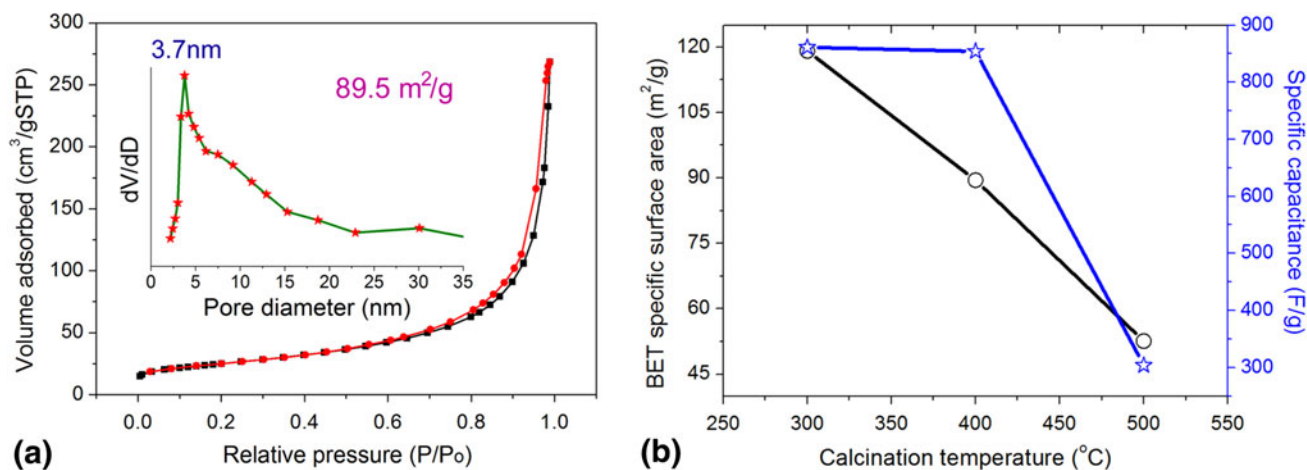


Fig. 3 (a) SEM, (b) low-, and (c) high-magnification TEM images of the porous NiO nanofibers, inset in (c) showing the corresponding SAED pattern

24 h. After that, the precipitates, i.e., Ni(OH)<sub>2</sub> nanofibers, were collected by filtration, washed for several times with absolute ethanol and dried at 60 °C for 6 h. Finally, the resulting products were calcined at 400 °C for 2 h in a muffle furnace.



**Fig. 4** (a) Nitrogen adsorption and desorption isotherm and its corresponding pore size distribution curves of the porous NiO nanofibers, (b) plots of BET specific area and specific capacitance vs. the calcination temperature for the porous NiO nanofibers

## 2.2 Characterization

The as-prepared products were characterized with x-ray powder diffractometer (XRD; Shimadzu XRD-6000, Cu K $\alpha$  radiation) at a scan rate of 1 °C/min, scanning electron microscopy (FESEM; JEOL, JSM-7600F) equipped with an energy dispersive x-ray spectrometer (EDS), and transmission electron microscopy (TEM; JEOL, JEM-2100F) operated at 200 kV. N<sub>2</sub> adsorption/desorption was determined by Brunauer-Emmett-Teller (BET) measurements using a Tristar-3000 surface area analyzer.

## 2.3 Electrochemical Measurements

The electrochemical measurements (Autolab PGSTAT30 potentiostat) were conducted using a three-electrode mode in a 1 M KOH aqueous solution. The working electrodes were prepared by mixing the active materials (80 wt.%), acetylene black (15 wt.%), and polyvinylidene fluoride (PVDF, 5 wt.%) in NMP (*N*-methyl-2-pyrrolidone). A small amount of absolute ethanol was then added to the mixture to promote homogeneity. After that, the mixture was coated onto the graphite paper (1 cm<sup>2</sup>) to form the electrode layer by drying at 120 °C for around 2 h. The reference electrode and counter electrode were Ag/AgCl electrode and platinum foil, respectively.

## 3. Results and Discussion

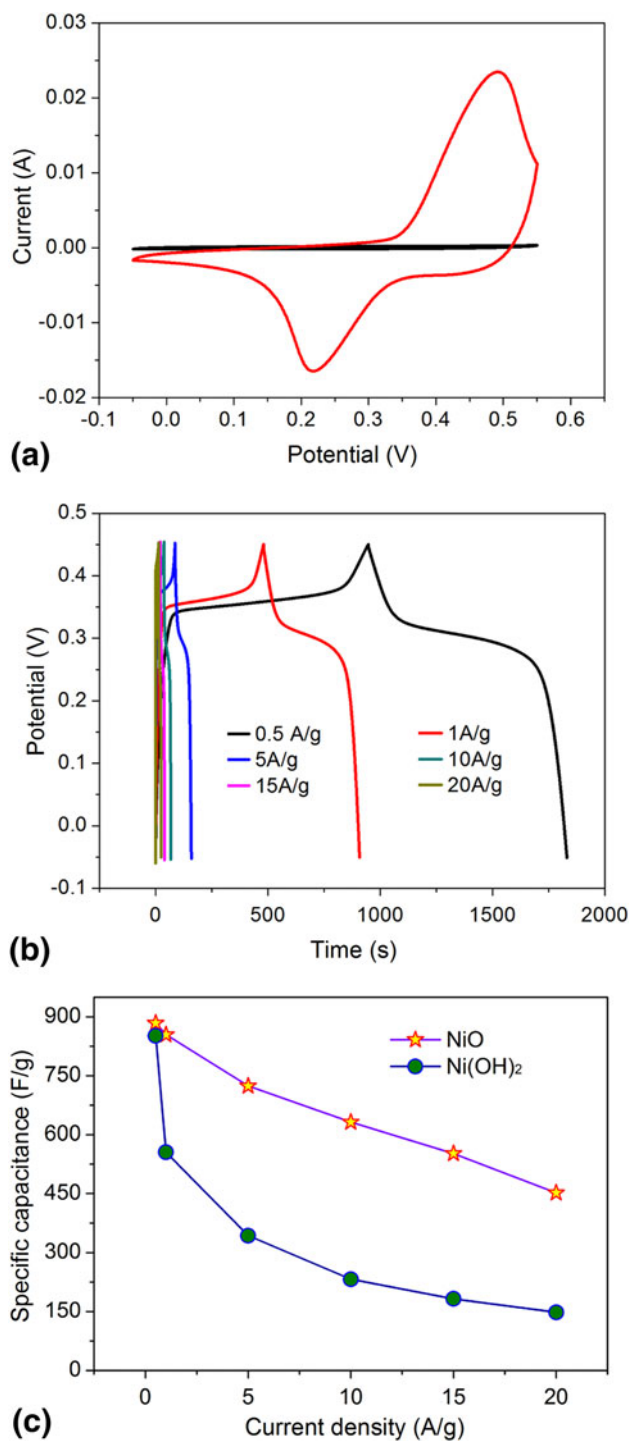
Figure 1(a) shows the XRD pattern of the Ni(OH)<sub>2</sub> nanofibers. All of the diffraction peaks could be indexed to the monoclinic phase  $\alpha$ -Ni(OH)<sub>2</sub> with lattice constants of  $a = 0.79$  nm,  $b = 0.30$  nm,  $c = 1.67$  nm, and  $\beta = 91.1^\circ$  in accordance with the standard card PDF No. 41-1424. Figure 1(b) shows representative SEM image of the Ni(OH)<sub>2</sub> nanofibers, indicating the large quantity and good uniform width over their entire lengths with a diameter typically in the range of 25–45 nm.

After annealed at 400 °C for 2 h in air, the Ni(OH)<sub>2</sub> products were converted into porous NiO nanofibers. The corresponding XRD pattern is shown in Fig. 2. All of the diffraction peaks are in good accordance with the standard

spectrum (PDF, card no 44-1159). No other characteristic peaks form impurities are detected in the spectrum. The corresponding SEM image is shown in Fig. 3(a). It is clearly seen that the products are composed of NiO nanowires bundles. To obtain more detailed structural information, the sample was dispersed in ethanol by prolonged sonication for TEM observation. As shown in Fig. 3(b) and (c), the porous nanofibers have an average diameters of  $\sim 9.3$  nm, demonstrating an obvious porous feature. The corresponding ED pattern (inset in Fig. 3c) shows diffuse rings, indicating the NiO nanofiber is polycrystalline. These characteristics are anticipated to be very beneficial for electrochemical properties.

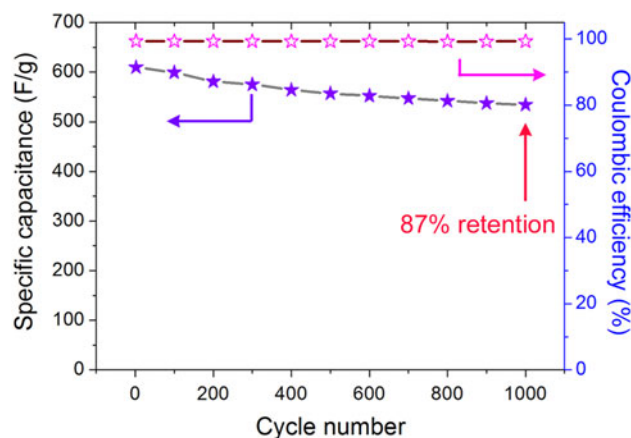
The NiO nanofibers also possess a higher BET surface area of 89.5 m<sup>2</sup>/g with a pore volume of 0.42 m<sup>3</sup>/g. Nitrogen adsorption and desorption isotherm and the pore size distribution curves are shown in Fig. 4(a). The isotherm exhibits the type IV characteristics. The profile of the hysteresis loop indicates an adsorption-desorption of the porous materials (Ref 17). The pore size distribution, calculated from desorption data using the BJH modal, was evaluated to have an average of  $\sim 3.7$  nm. It is reckoned that the porous NiO nanofibers, with the unique structures of high BET surface area and uniform size distribution, will provide the possibility of efficient transport of electrons and ions in electrode, hence leading to high electrochemical performance. We also investigated the relationship among annealing temperature, BET specific surface area and specific capacitance, as shown in Fig. 4(b). The specific surface area of porous NiO nanofibers is 118 and 52 m<sup>2</sup>/g when the calcinated temperature is 300 and 500 °C, respectively. It is noted that the specific capacitance exhibits almost the same value when the products calcinated at 300 and 400 °C. Considering that the high crystallinity of the products will lead to long cycle life, we chose the products calcinated at 400 °C as a research objective in this study.

The electrochemical performances of the as-synthesized NiO nanofibers have been evaluated as electrode materials for supercapacitors using cycle voltammogram (CV) and galvanostatic charge-discharge (CD) measurements in 1 M KOH aqueous solution. Figure 5(a) shows the CV curves of the NiO nanofibers and substrate at a scan rate of 10 mV/s, respectively. The shape of CV is very different from that of electric double-layer capacitance in which the shape is normally



**Fig. 5** (a) CV curves at a scan rate of 10 mV/s, (b) charge-discharge curves at 0.5–20 A/g of the porous NiO nanofibers, and (c) the specific capacitance as function of the current densities of the porous NiO nanofibers and the corresponding Ni(OH)<sub>2</sub> nanofibers

close to an ideal rectangular shape. For this electrochemical system, a pair of strong redox peaks can be observed within the potential range of  $-0.05$  to  $0.55$  V, indicating that the capacitance characteristics are mainly governed by Faradaic reactions. In addition, the capacitance contribution from substrate is negligible. The direct evidence is the measured CV curve of the substrate, which exhibits only a straight line



**Fig. 6** Variations of specific capacitance and Coulombic efficiency with cycle number at a scan rate of 20 mV/s of the porous NiO nanofibers

compared with that of the NiO nanofibers, as shown in Fig. 5(a), black line.

It is well accepted that galvanostatic charge/discharge examination is an established method to estimate the supercapacitive performance. The charge-discharge curves of the NiO porous nanofibers at different current densities are shown in Fig. 5(b) within a potential range of  $-0.05$  to  $0.45$  V. The nonlinear discharge curves further verify the pseudo-capacitive behavior. The specific capacitance as a function of current density for the NiO porous nanofibers was illustrated in Fig. 5(c). It can be seen that the specific capacitance can achieve a maximum of 884 F/g at a low current density of 0.5 A/g, which can still retain 452 F/g (about 51.1% capacitance retention) even at a current density as high as 20 A/g. As comparisons, the corresponding Ni(OH)<sub>2</sub> nanofibers exhibit similar capacities of 852 F/g at 0.5 A/g, but with poor rate performance (the capacities of only 148 F/g for Ni(OH)<sub>2</sub> nanofibers at 20 A/g). To the best of our knowledge, such high specific capacitance and good rate capability are comparable or superior to the best results reported for NiO electrode materials in the literature, such as flowerlike NiO hollow nanospheres (770 F/g) (Ref 18), nanoporous NiO pine-cone nanostructures (337 F/g) (Ref 19), and mesoporous NiO nanotubes (405 F/g) (Ref 20). Very recently, Kong and coworkers (Ref 21) reported the synthesis of loose-packed NiO nano-flakes, showing a highest specific capacitance as high as 942 F/g under a low annealing temperature (at 250 °C). However, they showed a low potential window (0.4 V) and a poor stability (18% loss after only 1000 cycles) due to their low crystallinity. In our case, the excellent capacitive performance of our materials is attributed to the intriguing nanostructure. Firstly, the porous feature provides high specific surface area, which can not only ensure the fully contact between active materials and electrolytes but also digest the possible volume changes during the repeated charge-discharge process. Secondly, the building block of the NiO porous nanofibers, i.e., ultrafine nanoparticles, promotes a high distribution of active sites, and thus greatly enhances the effective utilization of electrode materials. Finally, the one-dimensional configurations endow the electrode materials with fast redox reactions and short diffusion paths for electrons and ions, enhancing their power density compared to bulk materials. More importantly, we found that the present porous NiO nanofibers exhibited a higher specific capacitance with excellent rate capability in 1 M KOH aqueous solution.

The long-term cycle stability of electrode materials is another critical requirement for practical applications. Figure 6 depicts the specific capacitance and Coulombic efficiency as a function of cycle number plots at a scan rate of 20 mV/s up to 1000 cycles. After the cycling test, the specific capacitance also remains 87% of the initial capacitance with stable Coulombic efficiencies (~99.3%). The results indicated that the Ni@MPC also possessed outstanding electrochemical stability.

## 4. Conclusion

In conclusion, the porous NiO nanofibers have been successfully synthesized by a simple process of hydrothermal treatment with subsequent calcination. The as-prepared porous NiO nanofibers, when applied as supercapacitor electrode, exhibited an intriguing electrochemical performance, such as high specific capacitance (884 F/g at 0.5 A/g), enhanced rate capability (~51.1% capacitance retention even at 20 A/g), and good cycle stability (only 13% loss after 1000 cycles). Such excellent capacitive behaviors are attributed to their unique configurations, making them a promising electrode material for high-performance supercapacitors.

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