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"One-for-All" Strategy to Design Oxygen-Deficient Triple-Shelled MnO₂ and Hollow Fe₂O₃ Microcubes for High Energy Density Asymmetric Supercapacitors Henan Jia^{†1}, Haoyan Liang^{†1}, Zhaoyue Wang¹, Chun Li¹, Xiaohang Zheng², Yifei Cai¹, Junlei Qi^{*1}, Jian Cao¹, Jicai Feng¹, Weidong Fei²

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Abstract

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Intrinsically poor conductivity, sluggish ion transfer kinetics and limited specific area are the three main obstacles that confine the electrochemical performance of metal oxide for supercapacitors. Engineering hollow metal oxide nanostructures are effectively to satisfy the increasing process of modern electronics. In this work, both triple-shelled MnO₂ and hollow Fe₂O₃ microcubes synthesize from the single MnCO₃ templates. And the oxygen vacancies are introduced in both positive and negative electrodes through a facile method. The oxygen vacancies can not only improve the conductivity and facilitate the ions diffusion, but also increase the electrodes/electrolyte interfaces and electrochemical active sites. Consequently, both oxygen-deficient tripleshelled MnO_2 and hollow Fe₂O₃ exhibit the larger capacitance and rate capability than samples without oxygen vacancies. Moreover, due to the matchable specific capacitance and potential window between the positive and negative electrodes, the asymmetric supercapacitor exhibits the high specific capacitance (240 F g⁻¹), excellent energy density of 133 Wh kg⁻¹ at 1176 W kg⁻¹, excellent power density (23529 W kg⁻¹ at 73 Wh kg⁻¹) and high cycling stability (90.9 % after 5000 cycles). This strategy is highly reproducible in oxide-based electrodes, which has the potential to meet the requirement of practical application.

Keywords: Pseudocapacitors, Oxygen vacancy, "One for All", Multi-shell structure, Large-scale

1. Introduction

Due to global warming and the fast depletion of fossil fuels, the clean energy technologies have become an urgent need to replace the traditional fuel cells or lithiumion batteries. In order to satisfy the need for the next-generation consumer electronics, supercapacitors, also known as energy storage device, have recently attracted tremendous research attention because of their high power density $(1-10 \text{ KW kg}^{-1})$, fast charge/discharge rates (seconds), and excellent cycling stability (>10000 cycles).[1-5] Among supercapacitors, metal oxide based pseudocapacitors with faradic reactions can exhibit much higher energy density than electrochemical double-layer capacitors [6,7] And the engineering of electrodes materials with different structures can further enhance the performance to satisfy the increasing demands for energy storage and conversion.[8,9] Among them, hollow nanomaterials, in particular those with functional shells and inner voids are promising for supercapacitor electrodes because of their unique architecture, such as well-defined walls, high surface area and permeability. [10-12] Recently, a variety of synthetic strategies have been reported to create hollow metal oxides nanomaterials, which outperform the solid counterparts and may contribute the sustainable development.[13,14] Among different methodologies, self-templating methods are most popular in controlled fabrication of hollow metal oxides due to the availability of involved sacrificial templates.[15-20] However, most of these metal oxides have poor conductivity, which restricts the ionic diffusion and electron transport and thus sluggish the performance and rate capability.

Fortunately, ion doping is a potential way to ameliorate the inferior of metal oxides.[21] The doping ions could form a local built-in electric field around doping sites to change the state of charge distribution and accelerate the transport of ions and electrons.[22,23] However, when doping ions which are different with phase elements,

the crystal structure often becomes instability due to the mismatch of lattice dimensions.[24] Therefore, oxygen vacancies which do not introduce other elements are competitive candidates. Wang et al. developed a convenient and effective plasma surface engineering method to introduce the oxygen vacancies in electrodes, which can modulate the electronic and physical interactions and further result in the enhanced electrochemical performance. [25] Yang et al. developed the MnO hexagonal sheets possessing abundant oxygen vacancies through the reduction process, and further density function theory calculations demonstrate that the incorporation of oxygen vacancies significantly improves the performance. [26] And as previously reported, the introduction of oxygen vacancies in metal oxides shows several advantages: 1) oxygen vacancies which act as shallow donors can act as the electron carrier to improve the conductivity, which facilitates the electron transport and thus enhance the electrochemical performance; [27] 2) it can be believed that oxygen vacancies can contribute to the formation of built-in electric field around themselves at atomic level, resulting the acceleration of the transport of ions and electrons; [26] 3) oxygen vacancies with negative charges act as active sites to attract more positive particles, which can increases the ion diffusion coefficients in electrolyte; [28] 4) oxygen vacancies in active materials can change the contact interface between electrode and electrolyte while maintain the crystal stability due to the insignificant lattice mismatch between them. [28] However, traditional strategy to introduce oxygen vacancies, such as annealing method, is low efficiency because of the complicated, costly, and time-consuming reduction process.[29] Therefore, it is still crucial to design a facile and effective method to introduce oxygen vacancies to accelerate the transport of ions and electrons.

Recently, assembling asymmetric supercapacitors (ASCs) has served as the potential strategy to improve the energy storage performance of conventional

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supercapacitors. Traditionally, ASCs are always assembled with a positive electrode (metal oxide) with high capacitance and negative electrode (carbon materials) with high rate performance, which aim to narrow the performance gap between supercapacitors and lithium-ion batteries. According to the following equal: $1/C_T=1/C_p+1/C_n$, the total capacitance (C_T) for an ASC can be calculated from the specific capacitance of positive (C_p) and negative (C_n).[30] In order to give full play to the performance of ASCs, researchers have paid tremendous efforts in matching positive and negative materials well with each other. However, in some reports, attentions were paid to design high performance positive materials, while the corresponding negative materials often used commercial active carbon (AC), resulting in limited overall device performance.[31,32] Therefore, designing proper method to achieve high performance of both electrodes for ASCs at the same time is still of great important.

Herein, inspired by the work of Liu et al. and Salunkhe et al.,[32, 33] both positive and negative electrodes of the ASCs were synthesized through "One for All" strategy from one same template. Furthermore, we present a facile and effective oxygen vacancies engineering method to significant enhance the electrochemical performance. Specifically, we managed to synthesis triple-shelled MnO₂ microcubes and hollow Fe₂O₃ microcubes from MnCO₃ template, and introducing oxygen vacancies through NaBH₄ treatment which could facilitate the electrons/ions diffusion at the interface. Significantly, due to the enhanced electrode kinetics, the oxygen-deficient MnO₂ and Fe₂O₃ electrodes revealed significant improvement in both specific capacitance and rate capability. Moreover, an ASC was constructed using the oxygen-deficient MnO₂ as the positive electrode and oxygen-deficient Fe₂O₃ as negative electrode, which achieve high specific capacitance (240 F g⁻¹), high energy density (133 Wh kg⁻¹) and excellent cycling stability (90.9% after 5000 cycles) as expected.

2. Results and discussions

Figure 1 shows the representative synthesis process of the oxygen vacancies introduced triple-shelled MnO₂ microcubes (ov-MnO₂) and hollow Fe₂O₃ microcubes (ov-Fe₂O₃). In our One for All strategy, the MnCO₃ microcubes as the basic frame for all products are firstly synthesized through a simple precipitation step as previously reports (details in experiment process). In terms of triple-shelled MnO₂ microcubes, a controlled redox reaction process is followed to form the MnO₂(shell)@MnCO₃(core) microcube using KMnO₄ as an oxidizer. The unreacted MnCO₃ core can be removed through HCl solution, and the shell structure can be controlled by repeating the reaction and dissolution process, resulting the triple-shelled MnO₂ microcubes. On the other hand, the fabrication of hollow Fe₂O₃ microcubes mainly involves a simple hydrothermal process followed by a calcination process in air. First, FeOOH precursor microcube (XRD proved) is fabricated with well-maintained morphology by a redox reaction between Fe²⁺, O₂ and MnCO₃ under low temperature hydrothermal process, which may be illustrated in the following formula:

 $4FeSO_4 + 4MnCO_3 + O_2 + 2H_2O \rightarrow 4FeOOH + 4CO_2 + 4MnSO_4$

Second, in order to transform FeOOH to Fe_2O_3 while maintaining the microcube morphology, the FeOOH precursor are thermally annealed at 350 °C in air. Moreover, in order to fabricate the oxygen vacancies in both MnO_2 and Fe_2O_3 , a facile and effective NaBH₄ treatment method is introduced and finally obtained triple-shelled ov-MnO₂ and hollow ov-Fe₂O₃.

2.1. Characterization and Electrochemical Performance of ov-MnO₂ Electrode

The morphologies of all products are studied by field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Figure S1a shows the typical morphology of MnCO₃ microcubes with the uniform cube morphology. As

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shown in Figure S1b, further observation confirms that MnCO₃ microcubes have the rough surfaces and the average diameter is ~600 nm. Figure 2a shows the SEM image of triple-shelled MnO_2 microcubes, it is obviously that the microcubes are still maintained after oxidizing $MnCO_3$ to MnO_2 . Compared with pure $MnCO_3$, the surface of triple-shelled MnO₂ microcubes is laminar which composed of interwoven nanosheets. Moreover, as shown in Figure S2, observation of broken triple-shelled MnO₂ microcubes unambiguously exhibits the multishelled structure and nanosheetsassembled each shell, which strongly indicate the formation of triple-shelled MnO₂ microcubes. The structure of them are further examined by TEM, as shown in Figure 2b. In agreement with SEM results, microcube with interwoven uniform nanosheets (inset in Figure 2b) are observed, whereas the triple-shelled structures were elucidated by the sharp contrast between the MnO₂ shells and hollow interiors and the gap between each shell is about 100 nm. A HRTEM image exhibits the interplanar spacing of 0.25 nm, which is consistent with the (200) plane of MnO₂.[34] MnO₂ microcubes with shells large than 3 are difficult to fabricated in our experiment, which mainly because that the small $MnCO_3$ core in step III (experiment section) can be quickly dissolved in HCl solution and has no chance to react with KMnO₄ to form new shell. In order to introduce oxygen vacancies, we employ NaBH₄ treatment method and the morphology of ov-MnO₂ is examined by SEM analysis. As shown in Figure 2d, after reacting with NaBH₄, it can be obviously conducted that the morphology of microcubes remained intact. Further TEM result in Figure 2e clearly reveals that the multi-shelled hollow structures are unchanged with the gap ~ 100 nm, similar to that of triple-shelled MnO₂ microcubes. However, as shown inset in Figure 2e, it is remarkable that after NaBH₄ treatment, the uniform nanosheets of triple-shelled MnO2 microcubes transfer to homogeneous nanoparticles assembled nanosheets, and plentiful voids can be observed between nanoparticles. This structural transformation can increase the electrochemically active surface area and active sites for increasing electrochemical reaction kinetics. Figure 2f exhibits a HRTEM image of the shell of ov-MnO₂, the lattice fringes of 0.5 nm and 0.25nm can be indexed into (101) plane of Mn_3O_4 and (200) plane of MnO_2 , respectively, which may cause by the formation of oxygen vacancies.[34] Moreover, the edge of MnO_2 nanoparticles shows the amorphous feature with the thickness of ~1nm, further demonstrating the strong reducing ability of NaBH₄ to benefit for forming oxygen vacancies at room temperature.

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The phase purity of as-fabricated samples was investigated through X-ray powder diffraction (XRD), and the results are exhibited in Figure 3a. All the diffraction peaks of MnCO₃ microcubes located at 24.3° , 31.3° , 37.5° , 41.4° , 45.1° and 51.7° can be ascribed to the (012), (104), (110), (113), (202) and (116) planes of MnCO₃, which can be well indexed to standard rhodochrosite-type $MnCO_3$ (JCPDS no. 44-1472). For the XRD result of triple-shelled MnO₂ microcubes and ov-MnO₂, the diffraction peaks at 2θ angles of 12.5, 25.2, 37.3 and 65.6° (marked by *) can be indexed as the (001), (002), (111), and (020) planes of birnessite-phase MnO₂ (JCPDS no. 42-1317), and no peaks from $MnCO_3$ can be detected, suggesting the purity of the obtained MnO_2 . The Raman spectrum of triple-shelled MnO_2 microcubes and ov- MnO_2 are shown in Figure 3b. Both of them exhibit the characteristic peak at around 645 cm⁻¹, corresponding to MnO_6 octahedra symmetric stretching vibrations.[35] The peak of ov-MnO₂ redshifts compared to that of triple-shelled MnO_2 microcubes, demonstrating that MnO_2 acts as the electron-acceptor to lower the symmetric stretching vibrations energy.[36] Moreover, the formation of oxygen vacancies was also confirmed by X-ray photoelectron spectroscopy (XPS). Figure 3c and d show the high-resolution O 1s spectra of triple-shelled MnO₂ microcubes and ov-MnO₂, and two peaks located at

binding energies of 529.7 and 531.1 eV can be assigned to Mn-O-Mn and Mn-O-H, respectively.[37] It can be clearly deduced from Figure 3c and d that there is an obvious decrease about the content of Mn-O-Mn after NaBH₄ treatment (61% to 55%), which can be deduced to the formation of oxygen vacancies. From the Mn 2p spectrum of both samples, as shown in Figure S3, the spin-energy separation is about 11.8 eV, which agree with the previous reports about MnO₂.[37] As previous report, the spin-energy of Mn 3s shows the linear relationship with the chemical state of Mn, and that of MnO₂ and Mn₃O₄ are 4.78 and 5.41 eV respectively.[38,39] Figure 3e and f show the Mn 3s spectrum of triple-shelled MnO₂ microcubes and ov-MnO₂. The spin-energy of triple-shelled MnO₂ microcubes is 4.9 eV, which is closely to standard MnO₂. And that of ov-MnO₂ is 5.1 eV, which is between MnO₂ and Mn₃O₄, demonstrating the formation of oxygen vacancies.

To explore the electrochemical performance of both electrodes, a series of electrochemical measurements were investigated employing a three-electrode system with the working potential window of 0 to 1 V, as shown in Figure 4. Figure S4 illustrates the CV curves of MnO₂ microcubes with different shell numbers of 1, 2 and 3. It is obvious that all CV curves show the symmetric rectangular shape, indicating the high reversibility and ideal electrochemical behavior. And triple-shelled MnO₂ microcubes show the largest area compared with others, demonstrating both the yolk and shell of MnO₂ microcubes can increase the active sites and specific area for redox reactions. Figure 4a illustrates the typical comparison of CV curves of triple-shelled MnO₂ microcubes and ov-MnO₂ electrodes at a scan rate of 20 mV s⁻¹. Moreover, the ov-MnO₂ presents a larger current signal and integral area in comparison to triple-shelled MnO₂ microcubes, indicating ov-MnO₂ possesses the enhanced capacitance, which can also be proved from the longer discharge time in galvanostatic charge–

discharge (GCD) curves of ov-MnO₂ in Figure 4b (2 A g^{-1}). In addition, benefitting from the enhanced conductivity caused by oxygen vacancies, the internal resistance (IR) drop of ov-MnO₂ (0.019 V) is also smaller than that of triple-shelled MnO₂ microcubes (0.038 V), which is beneficial to reducing charge transfer resistance and enhancing the energy storage properties. Figure 4c displays the CV profiles of ov-MnO₂ at the scan rate range from 5 to 100 mV s⁻¹. Even at high scan rate, the CV curve shows the rapid current-voltage response and maintain the symmetrical rectangular shape, revealing excellent charge-transfer kinetics and rate capability. Figure S5 illustrate the typical GCD curves of ov-MnO₂ electrode at the current densities ranging from 1 to 20 A g^{-1} . Note that the symmetric feature of all curves indicates the high coulombic efficiency and conductivity during continuous charge/discharge process. Through GCD curves, the specific of triple-shelled MnO_2 microcubes and ov- MnO_2 can be calculated, and the results are shown in Figure 4d. The ov-MnO₂ can deliver an improved electrochemical performance with the maximum specific capacitance reaching as high as 608 F g⁻¹ at 1 A g^{-1} which is higher than triple-shelled MnO₂ microcubes (501 F g^{-1}). Most importantly, when the current density reached 20 A g⁻¹, the ov-MnO₂ can still retain 57 % of initial capacitance, which is higher than that of triple-shelled MnO_2 microcubes (28.3%), demonstrating the superior rate performance of ov-MnO₂. Furthermore, as shown in Figure 4e, electrochemical impedance spectroscopy (EIS) analyses are tested to further investigate the electrochemical behavior of both electrodes. in the highfrequency region, the intercept of curves and semicircular arc on the real axis are related to internal resistance (R_s) and charge transfer resistance (R_{ct}), respectively.[40] It can be obviously seen that the Rs and R_{ct} of the ov-MnO₂ (R_s=1.38 Ω , R_{ct}=3.15 Ω) are smaller than triple-shelled MnO_2 microcubes, which is in common with its enhanced performance. In the low frequency region, the slope of the straight line stands for the

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Warburg resistance (R_w) , which corresponding to the electrolyte diffusion resistance into the interior of the electrodes. Through comparison, the ov-MnO₂ shows a shorter straight line with a more vertical shape, revealing the lower R_w for faster charge-transfer kinetics. It is mainly attributed to the introducing of oxygen vacancies, which are desirable for fast charge/discharge kinetics.[41] To further thorough comprehension the pseudocapacitive contribution in all electrochemical performance, the total charge can be derived from the surface capacitive contribution $(k_1 v)$ and diffusion controlled contribution $(k_2v^{1/2})$, where k_1 and k_2 are constants and v is the scan rate.[42] The shaded region in the inset in Figure 4f shows the surface capacitive contribution at 5 mV s⁻¹. The ratio of capacitive contribution is shown in Figure 4f, at all scan rates, it can be found that the capacitive contribution of ov-MnO₂ is higher than that of tripleshelled MnO₂ microcubes. This result demonstrates the rapid transfer kinetics and short ions diffusion path, which can also imply the high rate performance of ov-MnO₂.[43] Based on above mentioned results, it can be deduced that multishelled structure can increase the electrochemical active electrode/electrolyte interface area, shorten the ions and electrons diffusion path, and the introduction of oxygen vacancies can improve the conductivity and rate capacity. The as-fabricated ov- MnO_2 is competitive positive electrode with outstanding electrochemical performances.

2.2. Characterization and Electrochemical Performance of ov-Fe₂O₃ Electrode

For purpose of high performance ASCs, the ov-Fe₂O₃ electrodes have been synthesized as the negative electrode, and the morphology are also studied by SEM and TEM. The as-prepared Fe₂O₃ maintains the microcube morphology, with numerous nanoribbons and nanosheets on the surface, were observed by SEM and TEM (Figure 5a and b). And the hollow structure of the microcubes were also confirmed by the different contrast of the shell and the hollow interior in the TEM image, which can be also proved from the SEM image of the cracked Fe_2O_3 microcube (Figure S6). TEM image of Fe_2O_3 shows the ultrathin and smooth geometrical feature of the nanoribbon, as shown in Figure 5c. HRTEM image (Figure 5d) of a nanoribbon exhibits the lattice spacing of 0.251 and 0.269 nm, corresponding to the (110) and (104) planes of Fe₂O₃.[29] After NaBH₄ treatment, the ov-Fe₂O₃ hollow microcubes were obtained, which still maintain the hollow structure with nanoribbons and nanosheets interpenetrating on the surface, as shown in Figure 5e and f. However, the TEM image of $ov-Fe_2O_3$ in Figure 5f clearly shows that nanoribbon still maintains the ultrathin feature, while numerous mesopores generated on the surface of nanoribbon. The nanoribbons feature a thin and porous structure, which may be favorable for improving the performance. As previously report, the mesoporous structure is particularly important to accelerate the ions transport for fast reaction kinetics and increase the electrode/electrolyte interface, thus increasing electrochemical performance.[44] For HRTEM image of ov-Fe₂O₃, as shown in Figure 5h, except numerous mesopores, an expanded interplanar spacing of 0.253 nm can also be observed, which can be assigned to (110) planes of Fe_2O_3 (discussion in XRD result). Compared with order lattice, the expanded lattice could expand the channels for ions diffusion and further enhance the electrochemical performance.[29]

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XRD and Raman spectroscopy were measured to explore the structure and phase features of all samples. Before the annealing treatment, the XRD result of FeOOH can be indexed to FeOOH phase (JCPDS card 29-0713), and no impurity phase, especially MnCO₃, can be found in FeOOH samples, as shown in Figure S7. Figure 6a shows the XRD results of Fe₂O₃ hollow microcubes and ov-Fe₂O₃ hollow microcubes, and all diffraction peaks accord with the hematite phase (JCPDS card 33-0664). Moreover, in comparison with Fe₂O₃ hollow microcubes, the XRD peaks of ov-Fe₂O₃ shift to the

lower diffraction angels, as shown in inset in Figure 6a. Based on the shift of (110) peak, according to Bragg formula, the interlayer spacing of (110) plane can be calculated to be 0.253 nm for ov-Fe₂O₃, and this phenomenon can also be found in previously reports.[29] Raman spectrum is investigated and shown in Figure 6b. And there are conspicuous peaks at 215, 278, 391, 495, and 592 cm⁻¹ are assigned to the Fe-O symmetric stretching vibration (A_{1g}) and Fe-O symmetric bending vibration $(E_g$ mode) of Fe₂O₃, confirming the successful preparation of Fe₂O₃ and no impurity phase in all samples.[45] XPS was performed to probe the compositional informational of different samples. As shown in Figure 6c and d, the O 1s core-level spectra of Fe_2O_3 hollow microcubes and ov-Fe₂O₃ display two distinct peaks at 530.3 eV (denoted as O_1) and 531.8 eV (denoted as O_{II}), respectively. And O_1 corresponds to the lattice oxygen and O_{II} corresponds to the oxygen vacancy.[46] The different O_I and O_{II} contents in two samples indicate the different level of oxygen vacancies. Evidently, compared with that of Fe₂O₃ hollow microcubes, the O_{II} of ov-Fe₂O₃ exhibits higher intensity, indicating more oxygen vacancies than Fe₂O₃ hollow microcubes. Moreover, these results can also be proved by Fe 2p spectrum of two samples, as shown in Figure S8. In composition to Fe_2O_3 hollow microcubes, the Fe 2p spectrum of ov-Fe₂O₃ exhibits an additional peak located at 710 eV, which is caused by the existence of Fe^{2+} [47] This result illustrates that, due to the reducing property of NaBH₄, the Fe³⁺ species of Fe_2O_3 were partially reduced to Fe^{2+} to generate the oxygen vacancies.

Figure 7 shows the electrochemical performance behaviors of Fe_2O_3 hollow microcubes and ov- Fe_2O_3 in 1 M Na₂SO₄ electrolyte. As shown in Figure 7a, comparison of the CV curves of Fe_2O_3 hollow microcubes and ov- Fe_2O_3 at the scan rate of 100 mV s⁻¹ shows larger integral area of the ov- Fe_2O_3 than Fe_2O_3 hollow microcubes. According to the CV shapes, it can be indicated that the high specific capacitance of

ov-Fe₂O₃ can be attributed to the surface absorption of the ions and the redox reactions between Fe^{3+}/Fe^{2+} that leads to pseudocapacitance[48]. The large capacitive current density of ov-Fe₂O₃ suggests that the oxygen vacancies can provide more active sites for both ion absorption and redox reactions to consequently increase the specific capacitance. As illustrate in Figure 7b, the CV curves still maintain the rectangular shape when increasing the scan rate without obvious polarization, suggesting the good rate capacity and excellent reversibility. Figure 7c shows the typical GCD curves of ov-Fe₂O₃ at different current densities from 1 to 20 A g⁻¹. All curves exhibit the symmetric characteristics, implying the high coulombic efficiency of ov-Fe₂O₃ during charge/discharge reaction. Besides, the GCD curves of Fe₂O₃ hollow microcubes is shown in Figure S9. Based on the GCD curves, the specific capacitance of Fe_2O_3 hollow microcubes and ov-Fe₂O₃ can be calculated and plotted in Figure 7d. It can be seen that the ov-Fe₂O₃ delivers the higher capacitance of 495 F g^{-1} at 1 A g^{-1} , which only 236 F g⁻¹ is obtained for Fe₂O₃ hollow microcubes. Even at a high current density of 20 A g⁻¹, the ov-Fe₂O₃ can still retain the large capacitance of 312 F g^{-1} , which shows much higher rate capacity than Fe₂O₃ hollow microcubes (122 F g⁻¹). The Nyquist plot of all samples were also achieved to prove the enhancement of electrical conductivity after the NaBH₄ treatment. As shown in Figure 7e, between the two kinds of electrodes, the ov-Fe₂O₃ electrode presents the smaller R_s of 0.68 Ω and the R_{ct} of 2.51 Ω , which could help the electron and ion transport and enable a high rate performance. As shown in Figure 7f, the capacitive ratio of ov-Fe₂O₃ is almost constant (> 80%) during a wide range of the scan rates, from 5 to 100 mV s⁻¹. In contrast, the capacitive ratio Fe_2O_3 hollow microcubes shows the smaller portion of the total capacitance compared with ov-Fe₂O₃, contributing less than 60% at 5 mV s⁻¹. This collective result illustrates excellent rate capacity of ov-Fe₂O₃, which is ascribed to the introduction of oxygen

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vacancies for fast ions and electrons transfer kinetics.[49] Accordingly, based on above mentioned results, the ov-Fe₂O₃ electrode is a kind of perfect negative materials due to its exceptional electrochemical performances.

2.3. Electrochemical Performance of ov-MnO₂//ov-Fe₂O₃ ASC Device

To estimate the possibility of the as fabricated materials for energy storage, an asymmetric supercapacitor (ASC) was built, in which the ov-MnO₂ and ov-Fe₂O₃ act as the positive and negative electrode, respectively, as shown in Figure 8a. As shown in Figure S10, due to the exactly complementary potential window ranges of ov- MnO_2 and ov-Fe₂O₃, it can be expected that the voltage window of the ASC can be extended to 2 V. CV tests under various potential windows at 100 mV s⁻¹, as shown in Figure S11, are measured to obtain the operating potential, and the stable voltage window of the ASC can be extended to 2 V. Figure 8b presents typical CV curves for ov-MnO₂//ov-Fe₂O₃ ASC at different scan rates, all CV curves show the rectangular shape that are attributed from the typical pseudocapacitive characteristics of both electrodes. Moreover, no distinct distortion at all scan rates demonstrates the high rate property due to the ions transport kinetics. The GCD curves at all current densities reveal the high coulombic efficiency (Figure 8c). Based on the total mass of active materials, as shown in Figure 8d, the specific capacitance of the ASC can reach as high as 239.6 F g⁻¹ at 1 A g⁻¹, and it can still obtain 132 F g⁻¹ at 20 A g⁻¹, demonstrating the prominent rate performance of the ASC. The durability of the ASC for practical applications was also evaluated at 5 A g⁻¹, as shown in Figure 8e. only 9.1 % capacitance loss is observed after the successive 5000 charge/discharge reactions, demonstrating excellent cycling stability for the ov- $MnO_2//ov-Fe_2O_3$ ASC Device. In addition, for the sake of the practice application of the ASC, we connected two ASCs devices in series after charging them, which can light up 3 light-emitting diodes (LED) in in parallel (in set in

Figure 8e). Based on the experimental results, the Ragone plot of the constructed ASC device is shown in Figure 8f.[34,50-57] The ov-MnO₂//ov-Fe₂O₃ ASC can deliver the maximum energy density of 133 Wh kg⁻¹ at the power density of 1176 W kg⁻¹, and at high power density of 23529 W kg⁻¹ it still retains 73 Wh kg⁻¹. Our ov-MnO₂//ov-Fe₂O₃ ASC demonstrates the superior performance and therefore possesses substantial promise for high-energy-density devices.

The superior energy storage properties of ov-MnO₂ and ov-Fe₂O₃ electrodes reported in this work are due to the following practical reasons: 1) both the ov- MnO_2 and ov- Fe_2O_3 electrodes show the unique hollow structure, which can enlarge the surface area and enhanced surface to volume ratio per unit mass, thus substantially decrease the "dead volume" in electrode and increase the electrode/electrolyte interface to provide more faradic redox reaction sites. 2) The porous shells of ov-MnO₂ and ov-Fe₂O₃ can not only increase the specific surface area, but also accelerate the electrolyte to access the surface of the oxide with remarkably improved conductivity and shortened transport path for both ions and electrons. 3) The oxygen vacancies on the surface of electrodes can greatly improve the conductivity and facilitate the fast ions diffusion. Importantly, it is well known that the oxygen vacancies in the electrodes can effectively regulate and tune the surface physical and electronic structure, which may offer stable and active sites to attract more positive particles for the increased ion diffusion coefficients; 4) From the perspective of ASC, according to the calculation formula of ASC, $1/C_{T}=1/C_{p}+1/C_{n}$, the matchable specific capacitance and potential window between the positive and negative electrodes guarantee the full use of both advantages and enlarge the energy density of the ASC. Therefore, the synergistic effect from the unique structure and oxygen vacancy doping together with the perfect match with both electrodes makes the ASC device an outstanding performance for energy storage.

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3. Conclusion

In summary, rationally designed oxygen-vacancies-introduced triple-shelled MnO₂ and hollow Fe₂O₃ microcubes have been successfully prepared via a facile "One-for-All" design strategy from a single template following a facile NaBH₄ treatment process. Due to the unique hollow structure, both positive/negative electrodes exhibit the large specific surface area and porous shell structures. Importantly, in this unique oxygen-deficient structure in both electrodes, enhanced electrons and ions transport can be simultaneously achieved due to the improved electronic conductivity and diffusion kinetics. Benefitting from these advantages, both electrodes exhibit superior pseudocapacitive performance and rate capacity. Moreover, with both high performance of positive and negative electrode, the ov-MnO₂//ov-Fe₂O₃ ASC presents high specific capacitance and outstanding high energy density, and demonstrates the practical application potential as power source for LED. This study develops a new research direction for developing advanced electrode materials for energy storage devices for next-generation applications.

Supporting Information

Electronic supplementary information (ESI) available. See DOI:

Conflicts of interest

There are no conflicts to declare.

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Figure captions:

Figure 1. Schematic illustration for the fabrication procedures of the ov- MnO_2 positive electrodes and ov- Fe_2O_3 negative electrodes from the same $MnCO_3$ template.

Figure 2. a) SEM image, b) TEM image and c) HRTEM image of triple-shelled MnO₂ microcubes; d) SEM image, e) TEM image and f) HRTEM image of ov-MnO₂ microcubes.

Figure 3. a) XRD patterns of triple-shelled MnO_2 microcubes and ov- MnO_2 microcubes; b) Raman spectrum of triple-shelled MnO_2 microcubes and ov- MnO_2 microcubes; High-resolution XPS spectrum of O 1s and Mn 3s in triple-shelled MnO_2 microcubes (c and e) and ov- MnO_2 microcubes (d and f).

Figure 4. a) CV curves of triple-shelled MnO_2 and $ov-MnO_2$ microcubes at the scan rate of 20 mV s⁻¹. b) Galvanostatic charge/discharge curves of triple-shelled MnO_2 and $ov-MnO_2$ microcubes at 1 A g⁻¹. c) CV curves of $ov-MnO_2$ at different scan rates. d) specific capacitances of triple-shelled MnO_2 and $ov-MnO_2$ microcubes at different current densities. e) Nyquist plots in a frequency range from 0.1 Hz to 100 kHz for all samples. f) Deconvolution of the charge contribution as a function of scan rates for triple-shelled MnO_2 and $ov-MnO_2$ microcubes, inset: separation of the capacitive (shaded region) and diffusion currents in $ov-MnO_2$ at a scan rate of 5 mV s⁻¹.

Figure 5. a) SEM image, b) and c) TEM image, d) HRTEM image of hollow Fe₂O₃

microcubes; e) SEM image, f) and g) TEM image, h) HRTEM image of ov-Fe₂O₃ microcubes.

Figure 6. a) XRD patterns of hollow Fe₂O₃ microcubes and ov-Fe₂O₃ microcubes; b) Raman spectrum of hollow Fe₂O₃ microcubes and ov-Fe₂O₃ microcubes; Highresolution XPS spectrum of O 1s in c) hollow Fe₂O₃ microcubes and d) ov-Fe₂O₃ microcubes.

Figure 7. a) CV curves of hollow Fe_2O_3 and ov- Fe_2O_3 microcubes at the scan rate of 50 mV s⁻¹. b) CV curves of ov- Fe_2O_3 microcubes at different scan rates. c) Galvanostatic charge/discharge curves of ov- Fe_2O_3 microcubes at different current densities. d) specific capacitances of hollow Fe_2O_3 and ov- Fe_2O_3 microcubes at different current densities. e) Nyquist plots in a frequency range from 0.1 Hz to 100 kHz for all samples. f) Deconvolution of the charge contribution as a function of scan rates for hollow Fe_2O_3 and ov- Fe_2O_3 microcubes.

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Figure 8. a) Schematic structure of the ov- $MnO_2//ov-Fe_2O_3$ ASC. b) CV curves of the ov- $MnO_2//ov-Fe_2O_3$ ASC at different scan rates. c) GCD curves of the ASC at different current densities. d) specific capacitances of the ASC. e) cycling stability of the ov- $MnO_2//ov-Fe_2O_3$ ASC, and the inset in (e) presenting the two ASC configurations connected in series to power LEDs. f) The Ragone plot related to energy and power densities of the ov- $MnO_2//ov-Fe_2O_3$ ASC.

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Figure 1



Figure 2



Figure 3



Figure 4



Figure 5



Figure 6



Figure 7



Figure 8