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Hierarchical heterostructures of Ag nanoparticles decorated MnO₂ nanowires as promising electrodes for supercapacitors

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Coating the redox-active transition-metal oxides (e.g., MnO₂) with a conductive metal layer is one efficient approach to improve the electrical conductivity of the oxide-based electrodes, which could largely boost the energy density and power density of supercapacitors. Here, we report a facile yet efficient method to uniformly decorate conductive silver (Ag) nanoparticles (~10 nm) on MnO₂ nanowires (width of ~10-20 nm), which leads to a remarkable improvement of the electrical conductivity and the supercapacitive performance of MnO₂-based electrodes. For instance, at a low scan rate of 10 mV s⁻¹, the as-designed Ag/MnO₂ hybrid electrode delivers a specific capacitance of 293 F g⁻¹, which is twofold higher than that of the bare MnO₂ electrode (~130 F g⁻¹). In addition, the highly conductive Ag nanoparticle layer can also improve the rate capability of the Ag/MnO₂ nanowire electrode, delivering a high specific energy density and power density of 17.8 Wh kg⁻¹ and 5000 W kg⁻¹, respectively, at a current density of 10 A g⁻¹.

Introduction

In recent years, supercapacitors have been a topic of strong and sustained interest for the development of next-generation power devices.¹ As one of the energy storage systems, supercapacitors feature with high energy density (better than traditional electrostatic capacitors) and high power density (higher than rechargeable batteries). Due to its high power density, supercapacitors are ideal complementary power devices to rechargeable batteries in applications in diverse fields such as hybrid electric vehicles, mass rapid transit, and power tools. Such power systems typically require high or peak power pulses for a time-dependent usage.² In the past few years, the technology of supercapacitors has progressed enormously owing to the development of several new high-performance electrode materials, including the redox-active transition-metal oxides such as RuO₂, NiO, Fe₂O₃, Co₃O₄, SnO₂ and MnO₂. Such oxides are promising as electrode materials due to their high specific capacitances from the fast and reversible redox reactions on the electrode surface.³-⁸

One good example is RuO₂. RuO₂ exhibits good supercapacitive performance due to its large specific capacitance and excellent rate capability. However, the relatively high cost and toxic feature of RuO₂ may severely limit its commercial utility.⁹ To address this issue, MnO₂ has been recently surfaced in the community due to its high or peak power pulses for a time-dependent usage.² In the past rapid transit, and power tools. Such power systems typically require applications in diverse fields such as hybrid electric vehicles, mass complementary power devices to rechargeable batteries (better than traditional electrostatic devices).¹ As one of the energy storage systems, supercapacitors supercapacitors are ideal complementary power devices to rechargeable batteries in applications in diverse fields such as hybrid electric vehicles, mass rapid transit, and power tools. Such power systems typically require applications in diverse fields such as hybrid electric vehicles, mass rapid transit, and power tools. Such power systems typically require high or peak power pulses for a time-dependent usage.² In the past few years, the technology of supercapacitors has progressed enormously owing to the development of several new high-performance electrode materials, including the redox-active transition-metal oxides such as RuO₂, NiO, Fe₂O₃, Co₃O₄, SnO₂ and MnO₂. Such oxides are promising as electrode materials due to their high specific capacitances from the fast and reversible redox reactions on the electrode surface.³-⁸

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Among the newly explored conductive materials, Ag is very attractive due to its good conductivity and low cost. Recently, Ag nanoparticles (AgNPs) have been used as conductive dopants in electrode materials for lithium-ion batteries and supercapacitors. For example, AgNPs have been coated on RuO₂, and the resulting Ag-doped RuO₂ exhibited much higher specific capacitance than the pure RuO₂.⁵ Similarly, Ag-doped MnO₂ thin films and AgNPs-loaded MnO₂ nanosheets also delivered larger specific capacitances than their bare MnO₂ counterparts.⁶-⁷ Although there are some successful attempts in developing Ag-coated MnO₂-based electrodes, efficient strategies for doping or coating of uniform AgNPs on nanostructured MnO₂ are presently lacking. Here, we report a simple and efficient strategy to fabricate a hierarchical heterostructure of AgNPs-decorated MnO₂ nanowires (or Ag/MnO₂ nanowires). Our strategy is a simple one-pot method to prepare one dimensional hierarchical Ag/MnO₂ nanowires by simply immersing an Ag foil into a mixed solution of KMnO₄ and H₂SO₄. The simplicity of the fabrication can be readily transferred to good scalability of our protocol for practical applications. The as-fabricated Ag/MnO₂ nanowires showed much larger specific capacitances compared to the bare MnO₂ nanowires with similar size. Furthermore, the Ag/MnO₂ nanowires also showed good rate capability and cycle performance, making them promising electrodes for high-performance supercapacitors.
Experimental

Synthesis of $\beta$-MnO$_2$ nanowires and Ag/MnO$_2$ composite

The synthesis of AgNPs-decorated MnO$_2$ nanowires is very simple. In the first step, the Ag foils (99.95% purity, 0.25 mm thickness, Alfa Aesar) were cut into small pieces (2 x 2 cm) and sonicated in acetone, ethanol, and deionized water for 10 min. After that, one piece of Ag foil was immersed into a 100 mL of 0.1 M KMnO$_4$ solution under continuous stirring. Two drops of 98 wt% H$_2$SO$_4$ were then introduced into the solution. The reaction mixture with a small piece of Ag foil was continuously stirred at room temperature for 24 h till the solution changed to transparent. The mixed solution was then rested for about one week to obtain the final products. After one week, the precipitates in the solution were collected by centrifugation, followed by washing with copious deionized water. The final products were dried in a vacuum oven at 50 °C for 12 h. For comparison purpose, $\beta$-MnO$_2$ nanowires were prepared by a similar method as the reported protocol.\textsuperscript{21}

Characterization

The microstructure, surface morphology, and chemical composition of the samples were characterized by powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and high resolution transmission electron microscopy (HRTEM). The powder XRD measurements were performed on a Bruker D8 advanced diffractometer with a Cu K$\alpha$ radiation in the 2θ range of 20–80°. XPS spectra were recorded on a PHI Quantera spectrometer using a Mg K$\alpha$ X-ray as the excitation source. FESEM and TEM images were taken on a Hitachi S-4800 microscope and a JEOL JEM2100 microscope, respectively, both equipped with EDS. N$_2$ adsorption-desorption isotherms were measured at the liquid nitrogen temperature using a Micromeritics ASAP 2010 instrument.

Electrochemical measurements

Electrochemical measurements were carried out on the three-electrode cells using a CHI 660D electrochemical workstation. To prepare the working electrode, the active materials (80 wt%, Ag/MnO$_2$ or MnO$_2$ nanowires), carbon black (10 wt%) and polyvinylidene difluoride (PVDF, 10 wt%, dissolved in N-methylpyrrolidone (NMP)), were mixed to form a slurry. The slurry was pasted onto a Ti foil and dried for 12 h in a vacuum oven. The loading of the working electrode was typically in the range of ~2-3 mg cm$^{-2}$. A platinum foil, an Ag/AgCl (saturated KCl) electrode, and a 1.0 M Na$_2$SO$_4$ solution, were used as the counter electrode, reference electrode, and electrolyte, respectively. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to evaluate the electrochemical behaviors of different composite electrodes. CV measurements were carried out between 0 and 1.0 V (vs. Ag/AgCl) at different scan rates of 10-100 mV s$^{-1}$. EIS measurements were carried out at a frequency from 10 kHz to 0.01 Hz with an AC amplitude of 10 mV.

Results and discussion

The as-synthesized MnO$_2$ and Ag/MnO$_2$ nanowires were first characterized by XRD. As shown in Fig. 1a, all diffraction peaks of MnO$_2$ nanowires can be indexed to the tetragonal phase of MnO$_2$ (JCPDS no. 24-0735). No other peaks were observed in the spectrum. As for the XRD spectrum of Ag/MnO$_2$ nanowires (Fig. 1b), besides the diffraction peaks from the $\beta$-MnO$_2$, four peaks at 38.1, 44.2, 64.5, and 77.4° were observed, which correspond to the (111), (200), (220), and (311) reflections of metallic Ag, respectively (JCPDS no. 65-2871). No phase of silver oxide was observed in the Ag/MnO$_2$ nanowires. This data provides supportive evidence for the successful synthesis of the AgNPs/MnO$_2$ nanowires via our simple chemical route.

![Figure 1](image)

Fig. 1 XRD spectra of (a) the bare MnO$_2$ nanowires and (b) the Ag/MnO$_2$ hybrid nanowires.

XPS was used to investigate the oxidation states of the Ag/MnO$_2$ nanowires. Four elements (Mn, Ag, O, and C) were identified from the full-survey-scan spectrum of the Ag/MnO$_2$ nanowires (Fig. S1, ESI†). In particular, Fig. 2a shows the Ag 3d core level spectrum, where two distinct peaks at 374.2 and 368.2 eV can be attributed to Ag 3d$_{x^2}$ and Ag 3d$_{yz}$, respectively. These values and the 6.0 eV splitting of the 3d doublet signal suggest the presence of metallic Ag, which also agree well with the previous report.\textsuperscript{22} As shown in Fig. 2b, two distinct peaks with binding energies of 642.1 and 653.5 eV, and a spin-orbital splitting of 11.4 eV were observed in the Mn 2p core level spectrum. Such values correspond well to the Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ in MnO$_2$.\textsuperscript{22} Fig. 2c shows the deconvoluted O 1s core-level spectrum, where one sharp peak at 530.1 eV and one small peak at 531.7 eV were observed. The peak at 530.1 eV is a typical state of O$^2-$ species in MnO$_2$, while the small peak could be attributed to the physisorbed, chemisorbed, or dissociated oxygen or hydroxyl species on the surface of the sample, similar to the data reported in a previous study.\textsuperscript{24} The XPS spectra, together with the XRD data, strongly support the successful preparation of Ag/MnO$_2$ composite in our samples.

FESEM and TEM were then used to investigate the morphology of the as-prepared Ag/MnO$_2$ nanowires. As shown in Fig. 3a, well-dispersed nanowires with high aspect ratios were clearly seen from the FESEM image of the Ag/MnO$_2$ composite. The nanowires are very thin with a diameter of ~10–20 nm (Fig. 3b). Similarly, the bare $\beta$-MnO$_2$ nanowires synthesized by the hydrothermal method also feature with the same morphology (Fig. S2, ESI†). However, an agglomeration of nanowires was observed in the bare MnO$_2$ sample, where bundles comprising of several nanowires were clearly seen. Fig. 3b is the representative TEM image of the Ag/MnO$_2$ nanowires at a low magnification. Some small black dots on the nanowires were observed, and such dots are well-distributed on the surface of nanowires. The high magnification TEM image (Fig. 3c) suggests...
that the small black dots are monodisperse AgNPs with particle sizes of ~10 nm, and such NPs are closely attached to the surface of MnO₂ nanowires, most likely via the strong bonding between the surface atoms of the AgNPs and the surrounding oxygen of the MnO₂ nanowires. Fig. 3d is a HRTEM image of a single Ag/MnO₂ nanowire, where the lattice fringe with an interplanar spacing of 0.31 nm can be assigned to the (311) planes of β-MnO₂. For the attached AgNPs on the MnO₂ nanowires, an interplanar spacing is determined to be 0.23 (Fig. S3, ESI†), which corresponds well to the (111) planes of the metallic Ag.

Fig. 2 XPS core-level spectra of (a) Ag 3d, (b) Mn 2p, and (c) O 1s of the as-prepared Ag/MnO₂ hybrid nanowires.

Fig. 3 (a) FESEM image of the Ag/MnO₂ hybrid nanowires. (b) – (d) TEM images of the Ag/MnO₂ hybrid nanowires with different magnifications. Inset in (a) is an enlarged FESEM image of the Ag/MnO₂ hybrid nanowires.

Fig. 4 (a) TEM image of the Ag/MnO₂ hybrid nanowires and EDS element maps of (b) Ag, (c) Mn, and (d) O.

Fig. 4a is a representative TEM image of the Ag/MnO₂ nanowires, with a corresponding energy-dispersive X-ray spectroscopy (EDS) elemental mapping for Ag (Fig. 4b), Mn (Fig. 4c), and O (Fig. 4d). The Mn and O distributions are continuous and well-matched with each other, resembling the morphology of the MnO₂ nanowires. In comparison, the Ag distribution is not...
continuous, although it also resembles the nanowire morphology, indicating a hierarchical heterostructure of AgNPs well-dispersed on the MnO2 nanowires. The atomic ratio of Ag to Mn is 1:3, as determined from its EDS spectrum (Fig. S4, ESI†). The EDS line-scanning across one nanowire with two AgNPs (Fig. S5, ESI†) clearly shows that the profile of O overlaps with that of Mn, but not Ag, further suggesting the formation of AgNPs rather than Ag2O in our composite. The specific surface area of the Ag/MnO2 hybrid nanowires (101.8 m2 g⁻¹) was obtained from analysis of the desorption branch of N2 gas isotherm (Fig. S6, ESI†).

Fig. 5 Schematic illustration of the formation of the hierarchical heterostructures of AgNPs-decorated MnO2 nanowires.

The chemical route to prepare Ag/MnO2 nanowires is simple, and it can be schematically illustrated in Fig. 5. When an Ag foil is immersed in the mixed solution of KMnO4 and H2SO4, the following reaction (Equation 1) occurs to form MnO2.

\[
2\text{KMnO}_4 + 6\text{Ag} + 4\text{H}_2\text{SO}_4 \rightarrow 2\text{MnO}_2 + 3\text{Ag}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + 4\text{H}_2\text{O}
\]  

(1)

KMnO4 is a strong oxidant and it is often used to prepare MnO2 by reacting with some reducing agents like carbon and Cu. However, without the Ag foil, the mixture of KMnO4 and H2SO4 is quite stable at room temperature, and only at an elevated temperature or under a hydrothermal treatment, the KMnO4 in the mixture can be decomposed to form MnO2. This is distinctly different from the case with a Ag foil, where at the first stage, the chemical reaction between KMnO4 and Ag could generate a large number of MnO2 nuclei. Such small nuclei possess a large specific surface area and high surface energy, and they intend to aggregate for surface energy reduction. As a result, the concentration of MnO2 decreases, and the subsequent growth of the nuclei is restrained due to the exhaustion of the precursors. The aggregated nuclei therefore form spheres consisting of nanosheets, which are formed from the anisotropic growth of MnO2. However, the as-formed MnO2 spheres are not very stable in the solution in the presence of Ag⁺ ions due to the possible catalytic effect of Ag⁺, which was also observed in previous studies. Such effects may induce the one-dimensional growth of the as-formed MnO2 NPs in the reaction solution, leading to the formation of MnO2 nanowires at room temperature. This process is mild and slow, and it needs about one week to fully convert the MnO2 spheres to nanowires. In this process, the as-formed Ag₂SO₄ in the solution also gradually decomposes to form AgNPs because of its sensitivity to daylight, according to the following reaction (Equation 2), which is also well-documented.

\[
\text{Ag}_2\text{SO}_4 \rightarrow 2\text{Ag} + \text{SO}_2 + \text{O}_2
\]  

(2)

As a result, the decomposition of Ag₂SO₄ leads to the formation of AgNPs, which subsequently attach to the surface of newly-formed MnO2 nanowires. One week incubation can fully transform the colloidal MnO2 spheres to the AgNPs-decorated MnO2 nanowires. In other reports, AgNPs were usually prepared by reduction of AgNO3 using NaBH₄. In the present study, the newly developed method can prepare ultrafine AgNPs decorated on MnO2 nanowires without using such toxic reductant.

The as-fabricated hierarchical heterostructures of AgNPs-decorated MnO2 nanowires are attractive electrode materials for supercapacitors. We recorded the CV curves of the Ag/MnO2 and the bare MnO2 nanowire electrodes at various scan rates from 10 to 100 mV s⁻¹, and with a voltage window of 0-1.0 V (vs. Ag/AgCl in 1.0 M Na₂SO₄ electrolyte). As for the Ag/MnO2 nanowire electrode (Fig. 6b), all CV curves displayed a quasi-rectangular shape with a perfect mirror-image feature, which suggests an ideal capacitive behavior and good rate capability of the Ag/MnO2 nanowire electrode. By comparison, the CV curves of the bare MnO2 nanowire electrode (Fig. 6a) showed a distorted rectangularity, especially for the CV curves at a high scan rate of 100 mV s⁻¹. In addition, the Ag/MnO2 nanowire electrode delivered a specific capacitance of 293, 261, 226, and 183 F g⁻¹ at scan rates of 10, 25, 50, and 100 mV s⁻¹, respectively, while the respective values for the bare MnO2 nanowire electrode are 130, 95, 72, and 51 F g⁻¹ (Fig. 6c). The larger specific capacitance of the Ag/MnO2 nanowire electrode suggests that the hybrid nanowires can improve the utilization efficacy of MnO2 for charge storage. In particular, as seen in the FESEM image (Fig. 3a), the Ag-decorated MnO2 nanowires are well-dispersed, which may provide a large surface area with more active surface sites. In comparison, without the AgNP decoration, the bare MnO2 nanowires tend to aggregate to form bundles, which may reduce the surface sites of MnO2 nanowires for charge storage. Moreover, the MnO2 nanowires prepared in the presence of Ag⁺ ions (as a catalyst) at room temperature feature with smaller diameters compared to the MnO2 nanowires obtained via the hydrothermal method. The smaller size of the Ag/MnO2 nanowires further increases their surface area. Fig. 6d shows the cycle performance (5000 cycles) of the Ag/MnO2 and the bare MnO2 nanowire electrodes at a scan rate of 50 mV s⁻¹. Both samples showed good cycle performance. In particular, after 5000 cycles, the Ag/MnO2 nanowire electrode still retained ~96.8% of its initial capacitance, slightly higher than that of the bare MnO2 nanowire electrode (~92.5%).
Fig. 6 CV curves of (a) the bare MnO2 nanowire electrode and (b) the Ag/MnO2 hybrid nanowire electrode at different scan rates in 1 M Na2SO4 electrolyte. (c) Specific capacitances of the Ag/MnO2 hybrid nanowire (red) and the bare MnO2 nanowire electrodes (blue). (d) Cycle performance of the Ag/MnO2 hybrid nanowire (red) and the bare MnO2 nanowire electrodes (blue) at a scan rate of 50 mV s⁻¹ for 5000 cycles.

Fig. 7 Charge-discharge curves of (a) the bare MnO2 nanowire electrode and (b) the Ag/MnO2 hybrid nanowire electrode at different current densities. (c) Ragone plots of the Ag/MnO2 hybrid nanowire (red) and the bare MnO2 nanowire electrodes (blue). (d) Nyquist plots of the Ag/MnO2 hybrid nanowire (red) and the bare MnO2 nanowire electrodes (blue).

**Conclusions**

A hierarchical heterostructure of AgNPs-decorated MnO2 nanowires was successfully prepared in the present study by using a facile yet efficient chemical protocol. The ultrafine AgNPs with particle sizes of ~10 nm not only suppressed the aggregation of MnO2 nanowires, but also improved the electrical conductivity of the MnO2-based electrodes. As a result, the Ag/MnO2 nanowire electrode showed both improved electrical conductivity and increased surface area, which led to its superior supercapacitive performance, such as large specific capacitance (293 F g⁻¹ at a scan rate of 10 mV s⁻¹), good cycle performance (96.8% capacitance retention after 5000 cycles), and excellent rate capability (with a specific energy and power density of 17.8 Wh kg⁻¹ and 5000 W kg⁻¹ at 10 A g⁻¹, respectively). Such values are better than those of the bare MnO2 nanowire electrode. The hierarchical heterostructure design presented in this study may provide an efficient platform to improve the electrochemical performance of MnO2-based electrodes for supercapacitors, and further pave their way towards practical applications.

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**Notes and references**
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Hierarchical heterostructures of AgNPs-decorated MnO\textsubscript{2} nanowires are prepared by a facile yet efficient chemical strategy, and the composite electrode exhibits superior supercapacitive performance compared to the bare MnO\textsubscript{2} electrode.