Hierarchically Structured Co$_3$O$_4$@Pt@MnO$_2$ Nanowire Arrays for High-Performance Supercapacitors

Hui Xia$^{1,2}$, Dongdong Zhu$^{1,2}$, Zhentao Luo$^3$, Yue Yu$^3$, Xiaojin Shi$^1$, Guoliang Yuan$^1$ & Jianping Xie$^3$

$^1$School of Materials Science and Engineering, Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing 210094, China, $^2$Herbert Gleiter Institute of Nanoscience, Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing 210094, China, $^3$Department of Chemical & Biomolecular Engineering, Faculty of Engineering, National University of Singapore, Singapore, 117576.

Here we proposed a novel architectural design of a ternary MnO$_2$-based electrode – a hierarchical Co$_3$O$_4$@Pt@MnO$_2$ core-shell-shell structure, where the complemental features of the three key components (a well-defined Co$_3$O$_4$ nanowire array on the conductive Ti substrate, an ultrathin layer of small Pt nanoparticles, and a thin layer of MnO$_2$ nanoflakes) are strategically combined into a single entity to synergize and construct a high-performance electrode for supercapacitors. Owing to the high conductivity of the well-defined Co$_3$O$_4$ nanowire arrays, in which the conductivity was further enhanced by a thin metal (Pt) coating layer, in combination with the large surface area provided by the small MnO$_2$ nanoflakes, the as-fabricated Co$_3$O$_4$@Pt@MnO$_2$ nanowire arrays have exhibited high specific capacitances, good rate capability, and excellent cycling stability. The architectural design demonstrated in this study provides a new approach to fabricate high-performance MnO$_2$-based nanowire arrays for constructing next-generation supercapacitors.

Sustainable and renewable energy sources, such as hydropower, solar energy, and wind power, in conjunction with flexible energy storage systems, such as rechargeable batteries and supercapacitors, are one of the key solutions to release the heavy burden on the current energy infrastructure and the environment$^{1-6}$. Recently, supercapacitors have emerged as a new class of promising energy storage devices because of their higher power density, faster charge-discharge rate, and longer cycle lifetime than those of rechargeable batteries$^{7,8}$. Supercapacitors can also store more energy than conventional dielectric capacitors$^{9,10}$. The central issues in the development of practical supercapacitors are the selection and fabrication of high-performance electrode materials. Among the emerging electrode materials for supercapacitors, redox-active transition-metal oxides such as RuO$_2$, NiO, Fe$_2$O$_3$, SnO$_2$ and MnO$_2$, are the most attractive materials due to their high specific capacitances$^{11-15}$. In particular, MnO$_2$ has drawn recent interest as a potential electrode material for supercapacitors because of its high specific capacitance (theoretical value of $\sim$1370 F/g), low cost, natural abundance, and environmental benignity$^{16,17}$. However, the practical use of MnO$_2$ as electrode materials is largely weight-down due to its poor electrical conductivity ($10^{-5}$–$10^{-6}$ S/cm)$^{16-20}$, which limits the charge-discharge rate of the supercapacitors; as well as a relatively small surface area of bulk MnO$_2$, which constraints the energy that can be stored in a particular electrode. An effective way to improve the utilization of MnO$_2$ (thus increasing the energy density) is to reduce the MnO$_2$ particles to the nanometer range, in which small particles have a characteristic high surface to volume ratio. For instance, ultrathin (<100 nm in thickness) films of MnO$_2$ have shown high specific capacitances$^{21,22}$. The major strategy to improve the electrical conductivity of the MnO$_2$ electrodes is to combine conductive materials (e.g., carbon-based materials, metals, and oxides) to MnO$_2$, forming MnO$_2$ composite electrodes with improved conductivities$^{23,24}$. Taken together, new designs of high-performance MnO$_2$-based electrodes must feature with a desired combination of small-sized MnO$_2$ nanoparticles and a good electrical conductivity with the help from the conductive additives$^{25-28}$.

In this context the recent developments on the conductive metal oxide nanowire arrays (NAs, e.g., SnO$_2$ and Co$_3$O$_4$) look very promising$^{22,29}$. Metal oxide NAs can be easily fabricated on the conductive substrates (e.g., Ti foil). The well-defined NAs have good conductivity and can work as current collectors, providing effective pathways for ion and electron transport throughout the entire electrode. Moreover, the three-dimensional
Na$_2$SO$_4$ solution). The key to fabricate the well-defined ternary material is to develop a method to fabricate Co$_3$O$_4$@MnO$_2$ NAs, which can improve the capacitive performance of Co$_3$O$_4$. Co$_3$O$_4$ is a typical electrode material used in the alkali aqueous electrolyte. However, the practical use of the alkali solution as the electrolyte is limited by its corrosive nature to the metal substrate. There is therefore strong interest in developing high-performance MnO$_2$-based electrodes that could be operated in a neutral aqueous electrolyte to fully realize its potential for supercapacitors. In addition, since Co$_3$O$_4$ is still a semiconductor material, the relatively poor conductivity of the Co$_3$O$_4$@MnO$_2$ NAs may further affect the capacitive performance of MnO$_2$ in the neutral aqueous electrolyte.

Herein we report a facile approach to fabricate a novel hierarchical Co$_3$O$_4$@Pt@MnO$_2$ nanostructure. The as-fabricated Co$_3$O$_4$@Pt@MnO$_2$ NAs electrode showed high electrochemical performance for supercapacitors operated in a neutral aqueous electrolyte (1 M Na$_2$SO$_4$ solution). The key to fabricate the well-defined ternary Co$_3$O$_4$@Pt@MnO$_2$ NAs was to use an ultrathin layer of Pt nanoparticles on the Co$_3$O$_4$ nanowire surface, which not only enhanced the conductivity of the NAs, but also induced a perfect coating of small MnO$_2$ nanoflakes on the NAs. The as-fabricated Co$_3$O$_4$@Pt@MnO$_2$ electrode showed several desirable electrochemical features for supercapacitors: a high specific capacitance (497 F/g on the basis of MnO$_2$ mass by cyclic voltammetry and 539 F/g by galvanostatic charge-discharge at 1 A/g), good rate performance (39.6 Wh/kg at 40 A/g), and excellent cycling performance (no capacity loss over 5000 cycles).

### Results

As illustrated in Figure 1, the fabrication of Co$_3$O$_4$@Pt@MnO$_2$ NAs on the Ti foil involved three steps. In the first step, Co$_3$O$_4$ NAs were grown on the Ti foil according to published hydrothermal procedures. The second step was the coating of small Pt nanoparticles (10–20 nm) on the Co$_3$O$_4$ nanowire surface by using a common sputter-coater. The final step was the deposition of a thin layer of MnO$_2$ on the Pt-coated Co$_3$O$_4$ NAs via a chemical bath deposition method, forming Co$_3$O$_4$@Pt@MnO$_2$ NAs as the final product.

The successful fabrication of Co$_3$O$_4$@Pt@MnO$_2$ NAs on the Ti foil was first confirmed by powder X-ray diffraction (XRD). As shown in Figure 2 (black line), the diffraction patterns of the bare Co$_3$O$_4$ NAs in the 2θ range of 10–80° could be indexed to the cubic phase Co$_3$O$_4$ (JCPDS Card No. 42-1467). The three peaks marked by "a" belong to the Ti substrate. In contrast, besides the peaks from Co$_3$O$_4$ and Ti, the XRD patterns of the Co$_3$O$_4$@Pt@MnO$_2$ NAs (blue line) showed three additional diffraction peaks (marked by "b") in the 2θ range of 10–80°, indexable to the (111), (200), and (220) reflections of face-centered cubic (fcc) Pt (JCPDS, Card No. 4-0802). This data supports the successful coating of Pt nanoparticles on the Co$_3$O$_4$ NAs. It should be mentioned that no peaks pertaining to MnO$_2$ crystals were observed in the XRD patterns of the Co$_3$O$_4$@Pt@MnO$_2$ NAs, which suggests that the deposited MnO$_2$ thin film on the NA surface is most likely amorphous or poorly crystallized, similar to two earlier observations in the MnO$_2$ deposition.

X-ray photoelectron spectroscopy (XPS) was then used to confirm the chemical composition and metal oxidation states of the Co$_3$O$_4$@Pt@MnO$_2$ NAs. Six elements (Mn, Co, Ti, Pt, O, and C) were identified from the full-survey scan spectrum of the NAs (Figure S1). Panels A, B, C, and D of Figure 3 show the Mn 2p, Co 2p, O 1s, and Pt 4f core level spectra of the Co$_3$O$_4$@Pt@MnO$_2$ NAs, respectively. Two distinct peaks at binding energies of 642.1 and 653.5 eV with the spin-orbital splitting of 11.4 eV were observed in the Mn 2p core level spectrum (Figure 3a), which correspond well to the Mn 2p$_{1/2}$ and Mn 2p$_{3/2}$ in MnO$_2$, respectively. Two distinct peaks at binding energies of 642.1 and 653.5 eV with the spin-orbital splitting of 11.4 eV were observed in the Mn 2p core level spectrum (Figure 3a), which correspond well to the Mn 2p$_{1/2}$ and Mn 2p$_{3/2}$ in MnO$_2$, respectively. In particular, two distinct peaks at 779.9 and 795.1 eV could be assigned to Co 2p$_{3/2}$ and Co 2p$_{1/2}$ in Co$_3$O$_4$ and CoO, respectively; whereas two small peaks at 788.9 and 803.5 eV could be attributed to 2p$_{3/2}$ and 2p$_{1/2}$ of Co$^{2+}$, respectively. This data provide direct evidence for the presence of Co$_3$O$_4$ phase in the as-fabricated NAs. The O 1s core level spectrum (Figure 3c) had three distinct components. Besides the O 1s peaks at 531 and 532.8 eV due to oxygen atoms in the hydroxyl groups and absorbed water, the strong peak at 529.6 eV could be assigned to oxygen atoms in the oxides of MnO$_2$ and Co$_3$O$_4$. The Pt 4f core level spectrum (Figure 3d) showed two distinct peaks at 70.9 and 74.3 eV, which could be attributed to Pt 4f$_{5/2}$ and Pt 4f$_{7/2}$, respectively, confirming the presence of metallic Pt in the as-fabricated NAs.

Scanning electron microscopy (SEM) was used to examine the structure of the bare Co$_3$O$_4$ NAs, and the as-fabricated Co$_3$O$_4$@Pt and Co$_3$O$_4$@Pt@MnO$_2$ NAs. Freestanding and well-aligned Co$_3$O$_4$ nanowires on the Ti substrate were observed for the bare Co$_3$O$_4$ NAs, as shown in Figure 4a. The nanowires had a uniform diameter of ~100 nm (Figure 4b). After the Pt coating (forming Co$_3$O$_4$@Pt NAs), the diameter of the nanowires did not change much (Figure 4c and 4d). However, a rough surface of the Co$_3$O$_4$@Pt nanowires can be seen in the SEM images (Figure 4c and 4d) as small Pt nanoparticles covered on the nanowire surface. Further deposition
of MnO₂ on the surface of Co₃O₄@Pt NAs formed Co₃O₄@Pt@MnO₂ NAs (Figure 4e), and the diameter of the nanowires increased to ~200 nm (Figure 4f). In addition, a thin layer of MnO₂ consisting of small nanoflakes can be seen in the SEM image (Figure 4f). It is worth mentioning that the loading amount of MnO₂ or the thickness of the thin layer of MnO₂ on the Co₃O₄@Pt@MnO₂ NAs can be tailored by varying the deposition time of MnO₂ (Figure S2). In particular, Figure 4e and 3f are representative SEM images of the Co₃O₄@Pt@MnO₂ NAs prepared by 6 h MnO₂ deposition.

More detailed structural information of the Co₃O₄@Pt@MnO₂ NAs was provided by transmission electron microscopy (TEM). The TEM samples were prepared by scratching the Co₃O₄@Pt@MnO₂ NAs from the Ti substrate, followed by dispersing them in ethanol and casting them on the TEM copper grids. Figure 5a and 5b show the typical TEM images of the Co₃O₄@Pt@MnO₂ NAs taken at different magnifications, indicating that porous Co₃O₄ nanowires were uniformly covered with small MnO₂ nanoflakes. Figure 5c and 5d are enlarged TEM images of the square area 1 and 2 in Figure 5b, respectively. A core-shell-shell structure was observed for a typical Co₃O₄@Pt@MnO₂ nanowire (Figure 5c). The thickness of the deposited Pt nanoparticles and MnO₂ nanoflakes was in the range of 10–20 and 50–100 nm, respectively. The primary MnO₂

![Figure 3](https://www.nature.com/scientificreports)  XPS Mn 2p (a), Co 2p (b), O 1s (c), and Pt 4f (d) core-level spectra of the as-fabricated Co₃O₄@Pt@MnO₂ NAs.

![Figure 4](https://www.nature.com/scientificreports)  SEM images of (a, b) Co₃O₄ NAs, (c, d) Co₃O₄@Pt NAs, and (e, f) Co₃O₄@Pt@MnO₂ NAs.

![Figure 5](https://www.nature.com/scientificreports)  TEM images of the Co₃O₄@Pt@MnO₂ nanowires taken at different magnifications: (a, b) low-magnification images; (c, d) high-magnification images of the square area 1 and 2 in (b), respectively. The inset in (d) shows a HRTEM image of the square area 3.
nanoflakes were ultrathin and had a thickness of ~5 nm, as shown in Figure 5c and 5d. The inset of Figure 5d is the high-resolution TEM image of the square area 3, showing single crystallinity and the <111> direction of Pt nanoparticles. The lattice spacing between the (111) planes, 0.23 nm, is the same as that of bulk Pt.41,42 In contrast, no clear lattice fringes could be observed for the MnO2 nanoflakes (Figure S3), corroborating the amorphous nature of MnO2, which is similar to the observation in its XRD patterns. Elemental mapping by energy-dispersive X-ray spectroscopy (EDS) (Figure 6) confirmed the core-shell hierarchical structure of the Co3O4@Pt@MnO2 nanowires. The EDS spectrum (Figure 6f) also supports the incorporation of Pt between the MnO2 shell and Co3O4 core. Cu and C signals in Figure 6f are from the TEM copper grid.

The electrochemical performance of the Co3O4@Pt@MnO2 NAs was first examined by cyclic voltammetry (CV) by using an aqueous solution of Na2SO4 (1.0 M) as the electrolyte. The CV curves of the Co3O4@Pt@MnO2 NA electrode were recorded at scan rates of 10, 25, 50, and 100 mV/s. As shown in Figure 7a, all CV curves displayed a quasi-rectangular shape with a perfect mirror-image feature, suggesting that the Co3O4@Pt@MnO2 NAs have an ideal capacitive behavior and high rate capability.43 In contrast, the rectangularity of CV curves of the bare MnO2 thin film electrode (Figure 7b) was remarkably distorted, especially at a high scan rate of 100 mV/s. The current densities of the CV curves of the Co3O4@Pt@MnO2 NA electrode were much higher than those of the bare MnO2 thin film electrode. Moreover, the CV curve of the Co3O4@Pt@MnO2 NA electrode at the scan rate of 50 mV/s (Figure 7c) had a much larger integrated area compared to that of the bare MnO2 thin film electrode, which suggests that a much higher specific capacitance was achieved in the Co3O4@Pt@MnO2 NA electrode. Since the capacitance contribution of Co3O4 and Pt was small and can be neglected, the specific capacitance of the Co3O4@Pt@MnO2 NA electrode was calculated on the MnO2 mass basis. As shown in Figure 7d, the Co3O4@Pt@MnO2 NA electrode had a specific capacitance of 497, 435, 393, and 354 F/g at scan rates of 10, 25, 50, and 100 mV/s, respectively, which were about 3-fold of increase than those of the bare MnO2 thin film electrode. For example, at the scan rate of 10 mV/s, the Co3O4@Pt@MnO2 NA electrode delivered a specific capacitance of 497 F/g. By comparison, the bare MnO2 thin film electrode can only provide the specific capacitance of 133 F/g. Among all Co3O4@Pt@MnO2 NAs prepared by different MnO2 deposition times, the one prepared by 6 h MnO2 deposition had the best electrochemical performance (Table S1), combining the merits of both high specific capacitance and good MnO2 loading.

Figure 6 | (a) TEM image of the Co3O4@Pt@MnO2 nanowires and EDS element maps of (b) Co, (c) Pt, (d) Mn, and (e) O. (f) EDS spectrum of the Co3O4@Pt@MnO2 nanowires.

Figure 7 | Cyclic voltammograms of (a) Co3O4@Pt@MnO2 NA electrode and (b) MnO2 thin film electrode at different scan rates in an aqueous solution of Na2SO4 (1 M). (c) Comparison of the CV curves of Co3O4@Pt@MnO2 NA electrode (red) and MnO2 thin film electrode (black) at a scan rate of 50 mV/s. (d) Specific capacitances of Co3O4@Pt@MnO2 NA electrode (red) and MnO2 thin film electrode (black) at different scan rates.
For example, further increasing the MnO$_2$ deposition time to 10 h, the specific capacitance per gram of the Co$_3$O$_4$@Pt@MnO$_2$ NA electrode decreased to 210.3 F/g (Figure S5 and Table S1).

The Co$_3$O$_4$@Pt@MnO$_2$ NA electrode showed an impressive rate capability (Figure 8). A good symmetry and fairly linear slopes were observed in the galvanostatic charge-discharge curves of the Co$_3$O$_4$@Pt@MnO$_2$ NA electrode at current densities of 1–40 A/g, indicating a good electrochemical capacitive characteristic and superior reversible redox reaction. Figure 8b compares the charge-discharge curves of the Co$_3$O$_4$@Pt@MnO$_2$ NA and MnO$_2$ thin film electrodes at the current density of 1 A/g. The charge storage capacity of the Co$_3$O$_4$@Pt@MnO$_2$ NA electrode was significantly higher than that of the MnO$_2$ thin film electrode with a 235% increase in the discharge time. In addition, the internal resistance (IR) of the Co$_3$O$_4$@Pt@MnO$_2$ NA electrode (the IR drop is 0.0016 V) was significantly reduced compared to that of the MnO$_2$ thin film electrode (the drop is 0.065 V). Figure 8c compares the specific capacitances of the two electrodes derived from the discharging curves at different current densities. The Co$_3$O$_4$@Pt@MnO$_2$ NA electrode delivered a specific capacitance of 539 F/g at the current density of 1 A/g. This value was much higher than that of the MnO$_2$ thin film electrode (171 F/g). In addition, the specific capacitance of our electrode is comparable to the reported values in the high-performance MnO$_2$-based hybrid electrodes, such as graphene/MnO$_2$ (with a specific capacitance of ~380 F/g) and Zn$_2$SnO$_4$@MnO$_2$ (with a specific capacitance of ~621 F/g) electrodes$^{44,26}$. In addition, at a high current density of 40 A/g, the Co$_3$O$_4$@Pt@MnO$_2$ NA electrode still delivered a high specific capacitance of 298.1 F/g, or ~55.3% of the specific capacitance at 1 A/g, indicating its superior rate capability.

Power density and energy density are two key performance indicators of supercapacitors. Figure 8d compares the Ragone plots of the Co$_3$O$_4$@Pt@MnO$_2$ NA and MnO$_2$ thin film electrodes, showing that the energy density of the Co$_3$O$_4$@Pt@MnO$_2$ NA electrode decreased from 74.6 to 39.6 Wh/kg, and its power density, on the contrary, increased from 0.5 to 19.6 kW/kg.

Cycling stability is another key performance indicator of supercapacitors. Figure 9a compares the cycling performance of the Co$_3$O$_4$@Pt@MnO$_2$ NA and MnO$_2$ thin film electrodes at the current density of 5 A/g over 5000 cycles. The specific capacitance of the Co$_3$O$_4$@Pt@MnO$_2$ NA electrode increased slightly for the initial several hundreds of cycles and was relatively constant from the cycles onwards, indicating an excellent stability for the Co$_3$O$_4$@Pt@MnO$_2$ NA electrode. After 5000 cycles, the specific capacitance was still slightly larger than the value of the first cycle, corresponding to a capacitance retention of ~105.6%. In addition, no obvious dissolution of MnO$_2$ nanoflakes in the electrolyte was observed during cycling, as suggested by the unchanged transparent electrolyte solution during cycling$^{21,22,45}$. A slight increase of the specific capacitance of the Co$_3$O$_4$@Pt@MnO$_2$ NA electrode after the first cycle was due to the activation of the electrode via increasing the contact area between the electrode and the electrolyte during cycling. In contrast, only 89.8% of the initial capacitance was retained for the MnO$_2$ thin film electrode. The current density dependence of the cycling performance of the Co$_3$O$_4$@Pt@MnO$_2$ NA electrode was also evaluated from 5 to 20 A/g. Figure 9b shows a very good cycling behavior of the Co$_3$O$_4$@Pt@MnO$_2$ NA electrode at these current densities. In addition, the specific capacitance was fully recovered at 5 A/g after cycling at those higher rates, and no noticeable decrease was observed after another 300 cycles.

**Discussion**

It is worth mentioning that the intermediate Pt nanoparticle layer is crucial for the construction of the core-shell-shell Co$_3$O$_4$@Pt@MnO$_2$ nanowires. The Pt nanoparticle layer on the Co$_3$O$_4$ nanowires was used to confine the growth of MnO$_2$ nanoflakes on the nanowire surface during the chemical bath deposition. Without the help from the Pt layer, no MnO$_2$ layer can be deposited on the surface of Co$_3$O$_4$ nanowires, and only agglomerated MnO$_2$ spheres attaching on the top of the Co$_3$O$_4$ nanowires were obtained (Figure S4). A similar
Second, the thin and well-separated MnO2 nanoflakes could shorten MnO2 on the Pt nanoparticle surface compared to the homogeneous MnO2 and the current collector. This constraint has been success-
the findings reported in a previous study43. Moreover, Co3O4 is a p-
nucleation in solution during the chemical bath deposition, similar to metal (e.g., the electrical conductivity of Pt is 106 S/cm)47.
This value is much lower than that of a noble metal (e.g., the electrical conductivity of Pt is \( \sim 10^4 \) S/cm)47. Therefore, although the incorporation of Co3O4 NWs in our hybrid electrode can improve the loading efficiency of the nanostructured MnO2, it may still suffer with the poor conductivity between the MnO2 and the current collector. This constraint has been successfully addressed by the smart incorporation of an intermediate Pt nanoparticle layer in our hybrid electrode, which provides a good electrical conductivity, thus leading to a good electrical performance including a large specific capacitance and a good rate capability.

The high specific capacitance and superior rate capability had much to be credited to the hierarchical architecture and the synergy of the three key components in the Co3O4@Pt@MnO2 NAs. First, a highly porous structure was created by growing small MnO2 nanoflakes on the Co3O4@Pt scaffold, which not only increased the utilization of active MnO2 owing to the small size feature of the MnO2 nanoflakes, but also benefited the penetration of the electrolyte due to the highly porous structure. These two effects are essential to the high specific capacitance of the Co3O4@Pt@MnO2 NAs considering the charge storage of MnO2 is a surface or near-surface process. Second, the thin and well-separated MnO2 nanoflakes could shorten the electron and ion diffusion paths, and make possible fast and reversible redox reactions, thus enhancing the electrochemical kinetics. Third, a thin layer of Pt nanoparticles between the Co3O4 and MnO2 layer could further improve the transport and collection of electrons, leading to a fast charge-discharge rate. Furthermore, the NAs directly grown on the Ti substrate had excellent mechanical adhesion and electrical connection to the current collector, and the polymer binders or conductive additives were not required. In general, the use of the polymer binders or conductive additives might increase the “dead volume” in the electrode materials43-45.

The electrochemical impedance spectra (EIS) of the Co3O4@Pt@MnO2 NAs and MnO2 thin film electrodes were also measured to provide further insights. The Nyquist plots in Figure 10 for the Co3O4@Pt@MnO2 NA and MnO2 thin film electrodes show a straight line in the low frequency region, a depressed semicircle in the high-to-medium frequency region, and a high frequency intercept in the real Z’ axis. Almost the same high frequency intercepts were observed for the two electrodes, indicating that they had the same overall ohmic resistance (the combination of the ionic resist-
ance of the electrolyte, the intrinsic resistance of the active materials, and the contact resistance between the active materials and the current collector). The semicircle in the high-to-medium frequency region represents the parallel combination of the charge-transfer resistance (\( R_c \)) and double-layer capacitance. The size of the semi-
circle, which equals to \( R_c \), was clearly smaller for the Co3O4@Pt@MnO2 NA electrode (\( \sim 3 \) Ω) compared to that of the MnO2 thin film electrode (\( \sim 300 \) Ω). The large surface area and improved electrical conductivity of the Co3O4@Pt@MnO2 NA electrode could be the main reason for the reduction of the charge-transfer resistance. The straight line in the low frequency region corresponds to the diffusion-controlled region, where a finite slope represents the dif-
susive resistance of the electrolyte in the electrode pores and the cation diffusion in the host materials43,48. The slope of the straight line was obviously larger for the Co3O4@Pt@MnO2 NA electrode compared to that of the MnO2 thin film electrode, indicating a lower diffusive resistance for the Co3O4@Pt@MnO2 NA electrode.

In summary, a novel hierarchical Co3O4@Pt@MnO2 nanostruc-
ture was fabricated by a facile strategy in this study. The comple-
mental features of the three key components: a well-defined Co3O4 NA on the conductive Ti substrate (good conductivity), an ultrathin layer of small Pt nanoparticles (further enhancing the conductivity), and a thin layer of MnO2 nanoflakes (large surface area), have been combined to construct a high-performance electrode for supercapacitors. Hence high specific capacitances [e.g., 539 F/g at 1 A/g in an aqueous Na2SO4 solution (1 M)], good rate capability (a specific
energy and power density of 39.6 Wh/kg and 19.6 kW/kg at 40 A/g, respectively), and excellent cycling stability (no capacity loss over 5000 cycles) were achieved in the as-fabricated Co$_3$O$_4$@Pt@MnO$_2$ NA electrode. The architectural design developed herein provides an efficient way to improve the electrochemical performance of MnO$_2$-based electrodes for supercapacitors.

**Methods**

**Fabrication of Co$_3$O$_4$@Pt@MnO$_2$ NAs.** Co$_3$O$_4$ NAs were grown on the Ti foil by a common hydrothermal method according to a previous publication. A thin film of Pt nanoparticles was then coated on the Co$_3$O$_4$ NAs using a sputter coater. After that, a thin MnO$_2$ layer was deposited onto the surface of Co$_3$O$_4$@Pt NAs via a facile chemical bath deposition method. In a typical MnO$_2$ deposition process, the Ti foil grown with Co$_3$O$_4$@Pt NAs was submerged into an aqueous solution (30 mL, 25°C) of MnSO$_4$·H$_2$O, (NH$_4$)$_2$SO$_4$, and Na$_2$SO$_4$ (molar ratio of 1:1:1, and the concentration was 0.1 mol/L). The mixture was stirring at room temperature for 2 to 10 h, which led to 0.1 to 0.3 mg MnO$_2$ deposited on the nanowire surface on the Ti foil. The as-fabricated Co$_3$O$_4$@Pt@MnO$_2$ NAs were then washed with copious water and subsequently dried at 60°C in an oven. For comparison, a planar MnO$_2$ thin film was also fabricated on the Ti foil by the anodic deposition according to published procedures.

**Materials characterization.** The microstructure, surface morphology, and chemical composition of the samples were characterized using 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 Kα radiation in the 2θ range of 10°–80°. XPS spectra were recorded on a PHI Quantera spectrometer using Al Kα X-ray radiation as the excitation source. FESEM and TEM images were taken on a Hitachi S-4800 microscope and a JEOL JEM2100 microscope equipped with an Energy Dispersive Spectroscopy (EDS), respectively.

**Electrochemical measurements.** Electrochemical measurements were performed on an electrochemical workstation (CHI 660D, CH Instruments Inc., Shanghai). The three-electrode cell was used as the reference electrode, Pt foil as the counter electrode, and the as-fabricated samples as the working electrode. The electrolyte was used for the electrochemical measurements. 1 M Na$_2$SO$_4$ was used as the electrolyte. CV measurements were carried out between 0 and 1 V at different scan rates of 10, 25, 50, and 100 mV/s. Galvanostatic charge-discharge measurements were used to evaluate the power and energy densities at different current densities of 1, 5, 10, 20, and 40 A/g. Electrochemical impedance spectroscopy (EIS) was performed by applying an AC voltage of 5 mV in a frequency range of 0.01 Hz to 100 kHz at an open circuit potential.

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**Author contributions**

H.X., D.Z. and J.X. designed project, carried out data analyses and co-wrote the manuscript. Z.L. and Y.Y. performed the materials characterization. X.S. and G.Y. prepared figures 8–10.

**Additional information**

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