Support information

Metal Decorated Nickel Foam Inducing Regulatable Manganese Dioxide Nanosheet Arrays Architecture for High-Performance Supercapacitor Application

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**I: SEM images of Pt/NF electrodes after treated with Imagej and the Pt particles size distribution of Pt/NF electrodes**

Fig. S1 Corresponding binary images of Pt/NF-30s (A), Pt/NF-150s (B), Pt/NF-210s (C) and Pt/NF-270s (D)
electrodes after processing the imaging using an automated threshold for background subtraction and nanoparticle selection (the Pt particles size distribution is shown in the inset).

II: EDS of MnPtNF-210s

![EDS pattern of MnPtNF-210s electrodes](image)

Fig. S2 EDS pattern of MnPtNF-210s electrodes.

III: Fabrication of MnO$_2$/metal (Au or Pd)/NF electrodes

Typically, Au or Pd particles were first deposited at a overpotential of -1.3 V to nucleation for 3 s, and then grown at constant potential of -0.2 V for 150 s (Au) or -0.3 V for 180 s (Pd) in the aqueous solution of 1 mM H$_2$AuCl$_4$ with 0.1 M NaCl or 4.3 mM PdCl$_2$ with 0.25 M H$_3$BO$_3$, respectively. Then the as-prepared metal/NF electrodes (donated as AuNF or PdNF electrodes, respectively) were washed with distilled water several times, and severed as working electrode for depositing MnO$_2$, which were carried out by the same method shown in the section 2.1.1. And the obtained hybrid electrodes are donated as MnAuNF and MnPdNF electrodes.
As shown in Fig. S3 A and C, the surface morphology of AuNF and PdNF electrodes is just like salt precipitated from salt pond. While the aggregated big Au or Pd nanoparticles are directly deposited on the top part of NF nanofibers; and the bottom porous structure of NF skeleton is stuffed by many small Au or Pd nanoparticles (Fig. S3B and D).
The MnAuNF electrode (Fig. S4A and B) possess many curved thin MnO$_2$ nanosheets, which surround the big Au nanoparticles to form porous structure. Similarly, MnPdNF electrode (Fig. S4D and E) exhibits a gully-like structure composed by many thick MnO$_2$ nanosheets. Compared to MnAuNF electrode, these thick MnO$_2$ nanosheets thoroughly mask the Pd nanoparticles and exhibit a compact structure. From Fig. S4C and F, it is worth noting that MnAuNF and MnPdNF electrode only possesses nanosheet structure on their top surface.

Fig. S5 EDS pattern of MnAuNF (A) and MnPdNF (B) electrodes.
Furthermore, the EDS measurement confirms the presence of Mn, Ni, Au or Pd elements in MnAuNF or MnPdNF electrodes, whereas no other chemical elements were detected (Fig. S5).

![Fig.S6 Raman spectra of MnAuNF and MnPdNF electrodes.](image)

As shown in the Raman spectra of MnAuNF and MnPdNF electrodes (Fig. S6), a strong band at about 618 cm$^{-1}$ is related to the symmetric stretching vibration M-O of MnO$_6$ groups, which can be assigned to α-MnO$_2$.

![Fig.S7 TEM images of MnAuNF (A and B) and MnPdNF (C and D) electrodes with white arrows (metal species) and red arrows (MnO$_2$ species).](image)

It can be seen from Fig. S7A that the Au nanoparticles is composed of randomly distributed big (diameter: 5-20 nm) and small (diameter: 2-3 nm) nanoparticles. And the thin MnO$_2$ nanosheet with looming edges and corners (as shown in Fig. S7B) could almost not be retained because of
the damage of ultrasonic pretreatment. Compared to MnAuNF electrode, the randomly stacked folds shown in Fig. S7C demonstrates the presence of thick MnO$_2$ nanosheet in MnPdNF electrode. Besides, Fig. S7D reveals that the aggregated big Pd particles (diameter: about 30 nm) is constituted of many small nanoparticles.

![Illustration of the formation process of metal hybrid MnO$_2$ electrodes.](image)

A formation process of these hybrid MnO$_2$ electrodes is proposed in Fig. S8. First, Au, Pt or Pd is double-pulse deposited on the nanofibers of NF. Compared to the deposition of Pt, it has been known that the deposition of Au and Pd usually tends to irregularly dendritic crystal growth, which results in some aggregated nanoparticles $^{[1, 2]}$. Herein, the aggregated big Au or Pd nanoparticles take dominant place on the surface of NF nanofibers and the relative small Au or Pd nanoparticles almost fill up the porous structure of NF skeleton; whereas the uniformly deposited Pt nanoparticles combines with NF nanofibers forming 3D highly conductive structure. Second, the electrochemical growth of MnO$_2$ from an aqueous solution containing Mn$^{2+}$ ions can be expressed as $^{[3]}$:

$$\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{H}^+ + 2\text{e}^-$$

In the case of metal hybrid electrodes, MnO$_2$ seeds initially nucleate on the highly conductive metal particles, which follows an instantaneous nucleation mechanism and are prone to form nanosheets $^{[4]}$. Herein, the 3D highly conductive structure of PtNF electrode provides a large number of fast electron transport routes for MnO$_2$ growing reaction, which make the free-standing MnO$_2$ nanosheets arrays uniformly growing on PtNF electrode. On the contrary, MnO$_2$ nucleation
takes priority on the surface of AuNF and PdNF electrodes because of their uneven distribution of metal particles, which leads to a partial aggregated nanosheet structure surrounding around the big Au or Pd particles.

**IV: CV curves of NF, PtNF-210s and MnNF electrodes**

![CV curves of NF, PtNF-210s and MnNF electrodes at a scan rate of 100 mV s⁻¹.](image)

Fig. S9 CVs of NF, PtNF-210s and MnNF electrodes at a scan rate of 100 mV s⁻¹.

**References:**


