Electronic Supplementary Material (ESI) for Nanoscale

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

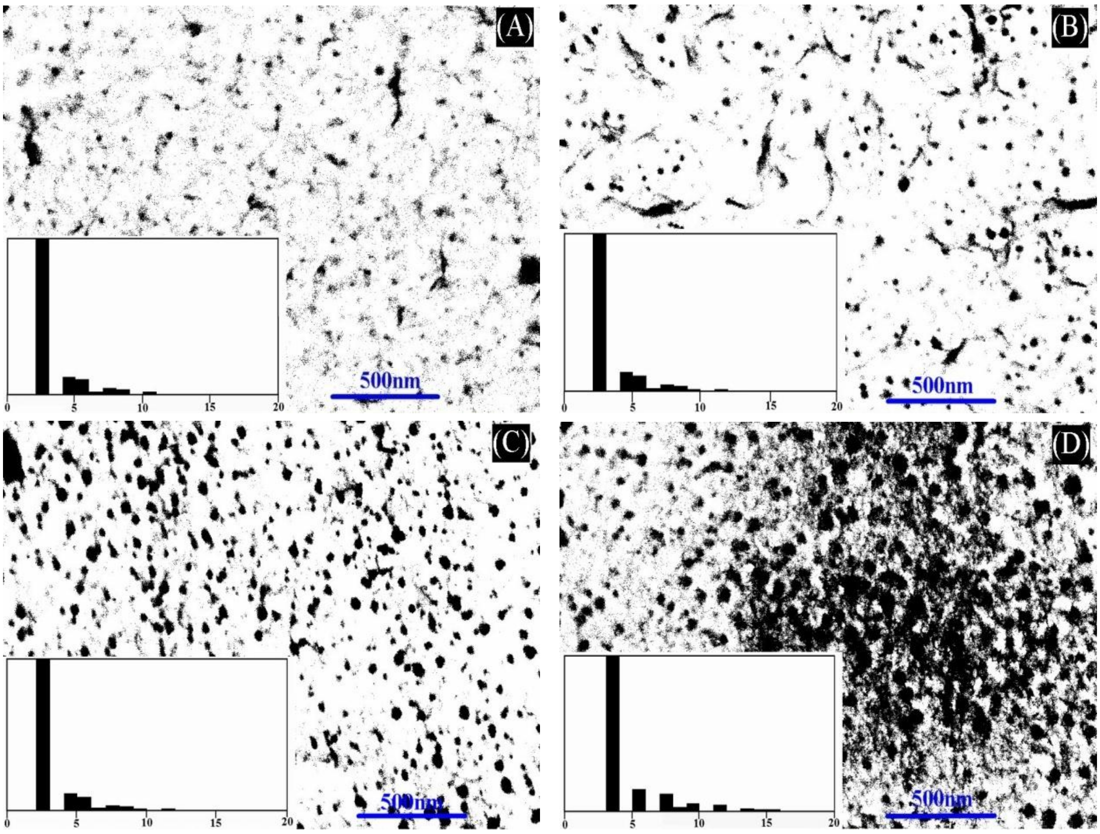


Fig. S1 Corresponding binary images of Pt/NF-30s (A), Pt/NF-150s (B), Pt/NF-210s (C) and Pt/NF-270s (D) electrodes after processing the imaging using an automated threshold for background subtraction and nanoparticle selection (the Pt particles size distribution is shown in the inset).

II：EDS of MnPtNF-210s

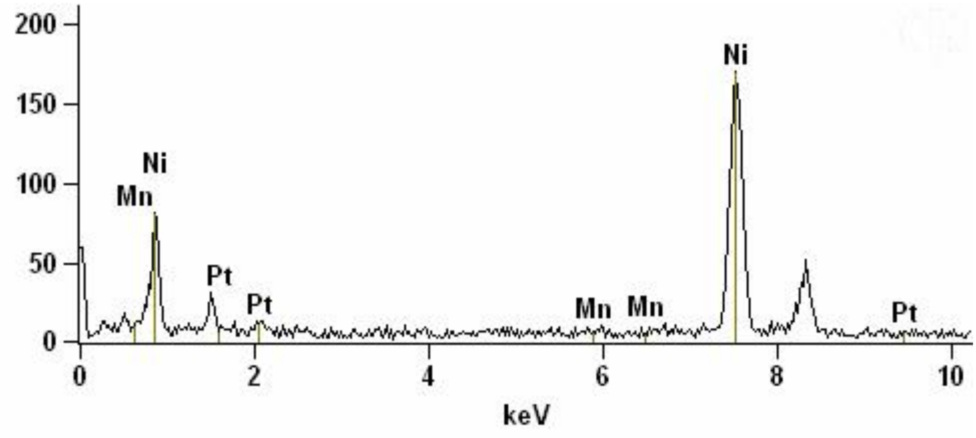
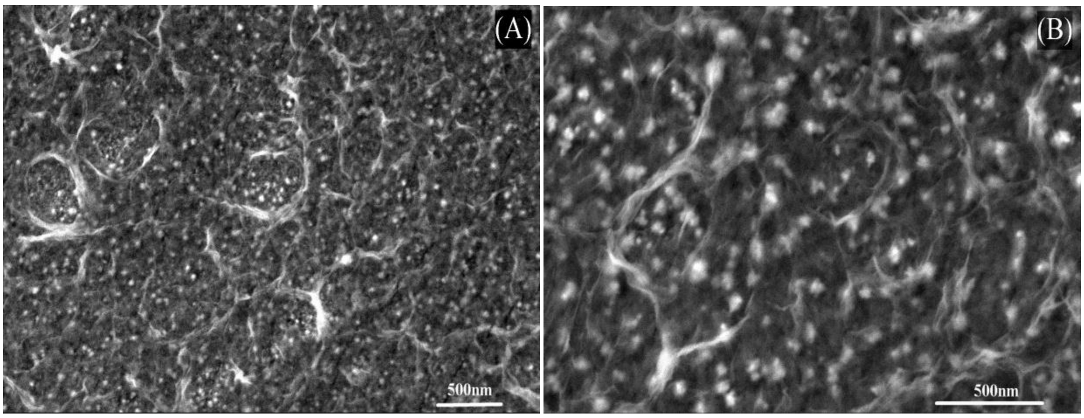


Fig. S2 EDS pattern of MnPtNF-210s electrodes.

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_2AuCl_4 with 0.1 M NaCl or 4.3 mM $PdCl_2$ with 0.25 M H_3BO_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.



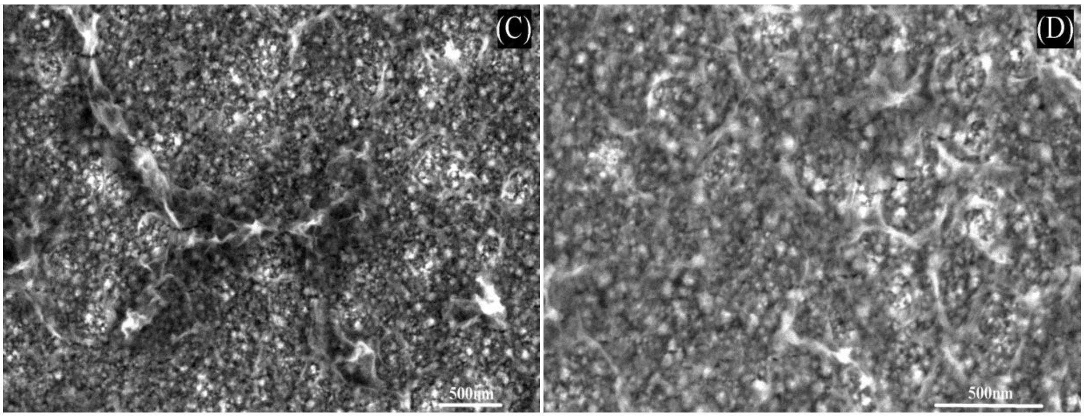
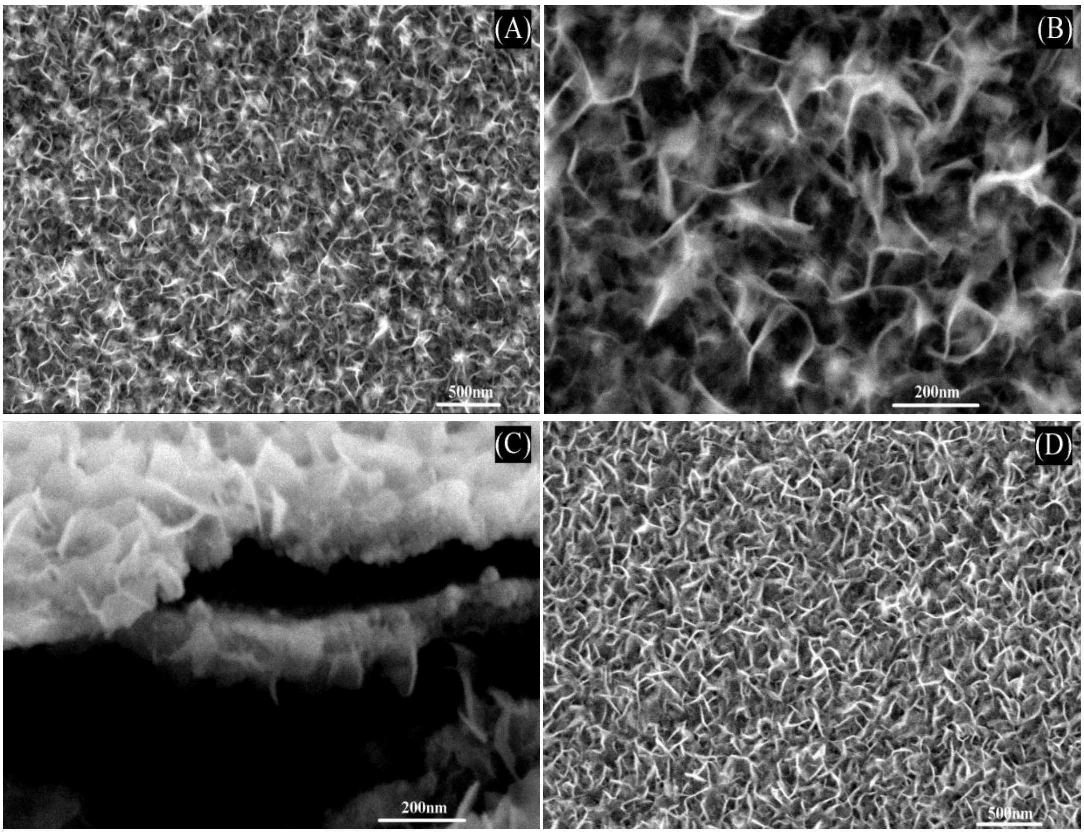


Fig. S3 FESEM images of AuNF (A, B) and PdNF (C, D) electrodes.

As shown in Fig. S3A 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).



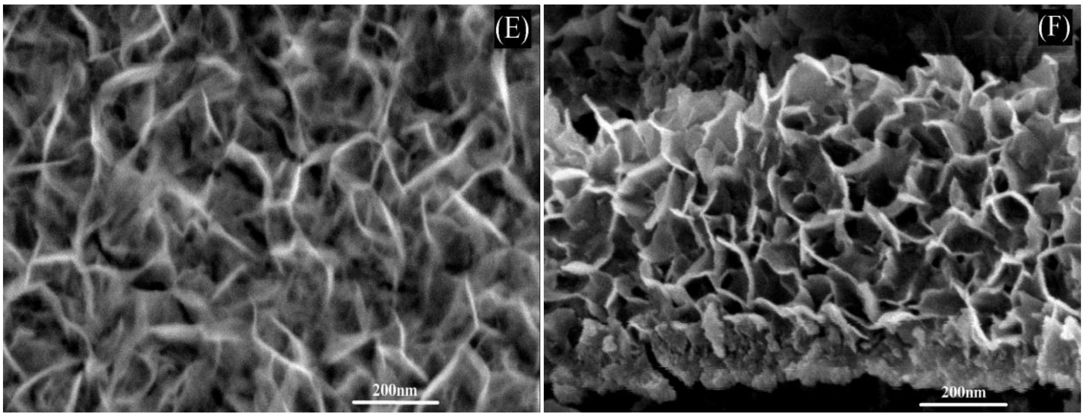


Fig.S4 Top surface and cross-section FESEM images of MnAuNF (A-C) and MnPdNF (D-F).

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.

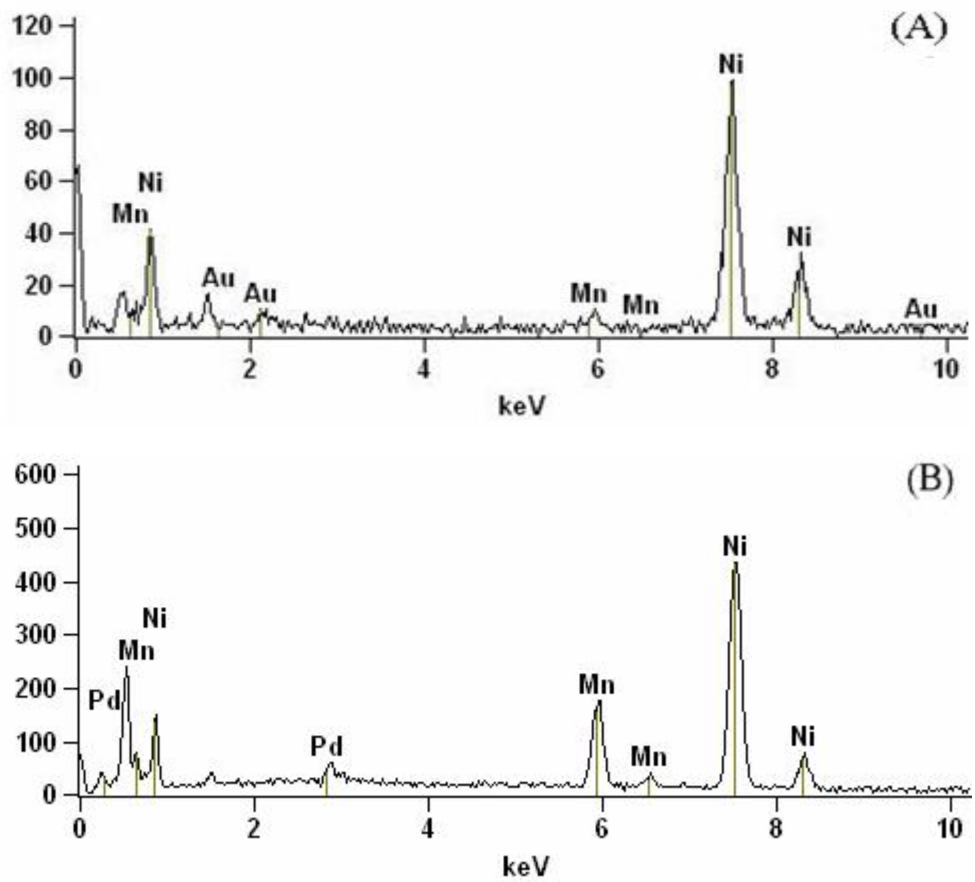


Fig. S5 EDS pattern of MnAuNF (A) and MnPdNF (B) electrodes.

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).

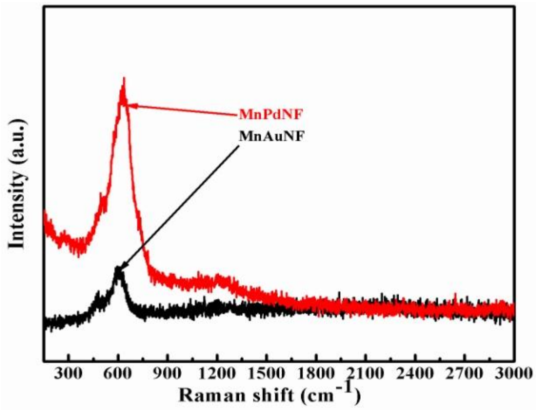


Fig.S6 Raman spectra of MnAuNF and MnPdNF electrodes.

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.

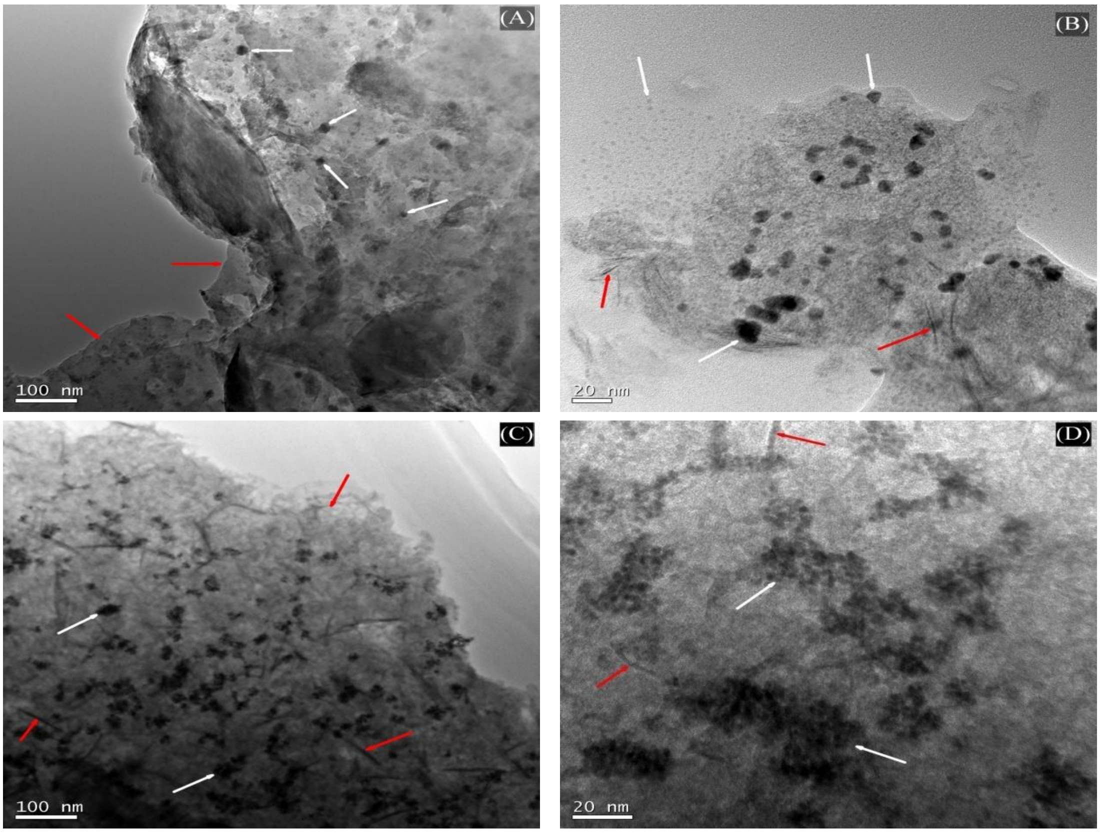


Fig.S7 TEM images of MnAuNF (A and B) and MnPdNF (C and D) electrodes with white arrows (metal species) and red arrows (MnO_2 species).

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.

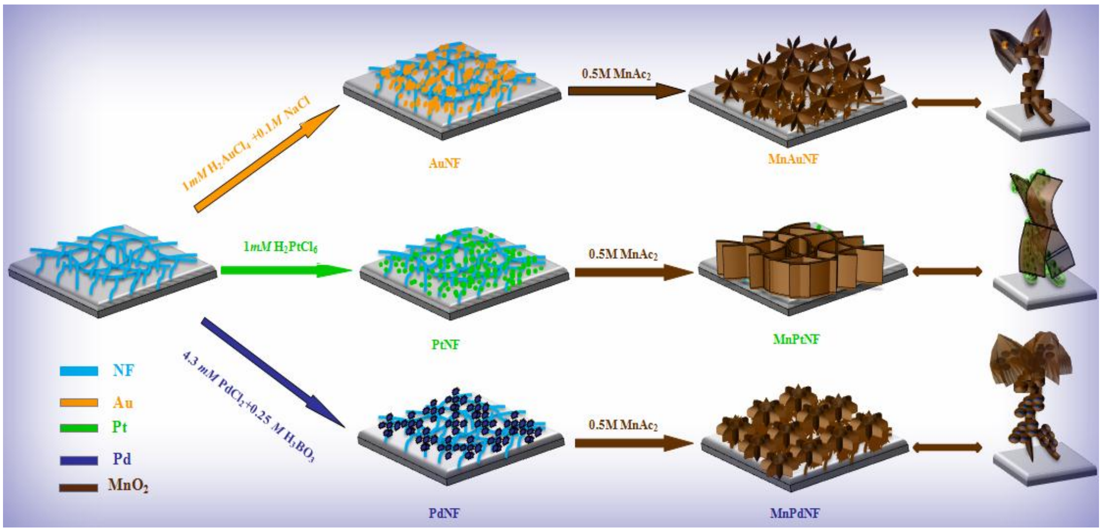


Fig. S8 The illustration of the formation process of metal hybrid MnO_2 electrodes.

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]:

$$Mn^{2+} + 2H_2O \longrightarrow MnO_2 + 4H^+ + 2e^-$$

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

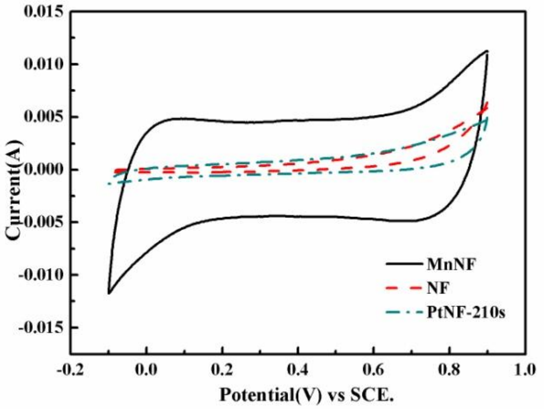


Fig. S9 CVs of NF, PtNF-210s and MnNF electrodes at a scan rate of 100 mV s^{-1}.

References:

[1] Wang, H. J.; Ishihara, S. S.; Ariga, K. S.; Yamauchi, Y. S. J. Am. Chem. Soc., 2012, 134, 10819.

[2] Mohamed, S. E.; Takeo, O. Electrochimica Acta, 2007, 52, 2166.

[3] Kozawa, A. Manganese dioxide. In Batteries; Kordesch, K. V., Ed.; Marcel Dekker: New York, 1974; Vol. 1, pp 385.

[4] Babakhani, B.; Ivey, D. G., J. Power Sources, 2011, 196, 10762.