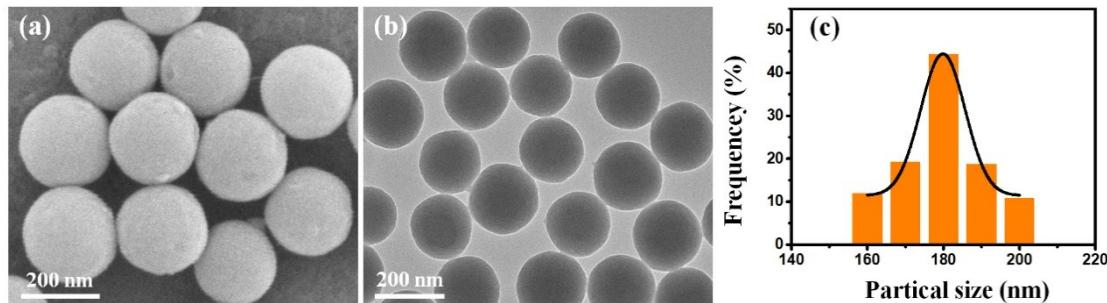
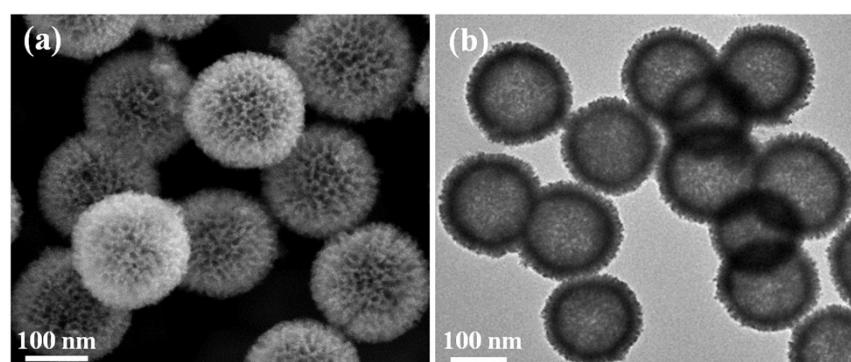


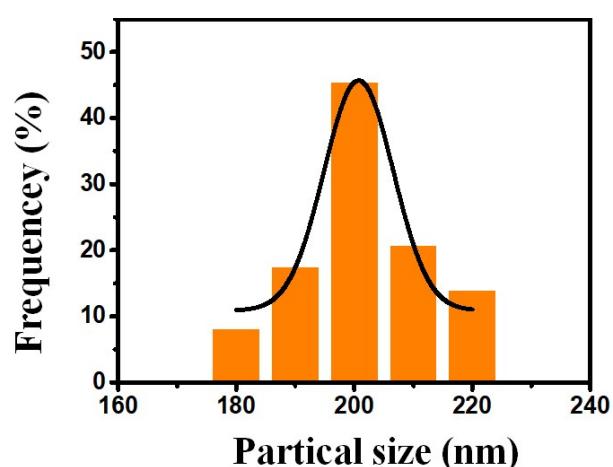
## Electronic Supplementary Information



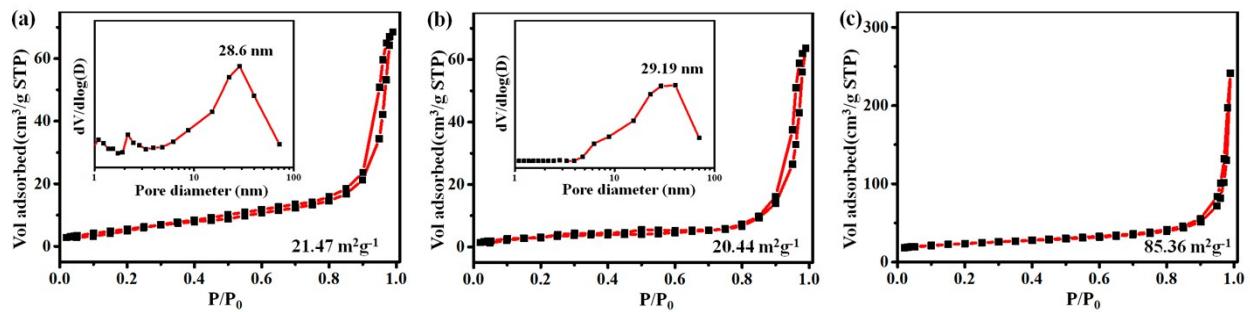
**Fig. S1** (a) SEM image, (b) TEM image and (c) particle-size distribution histogram of the  $\text{SiO}_2$  spheres.



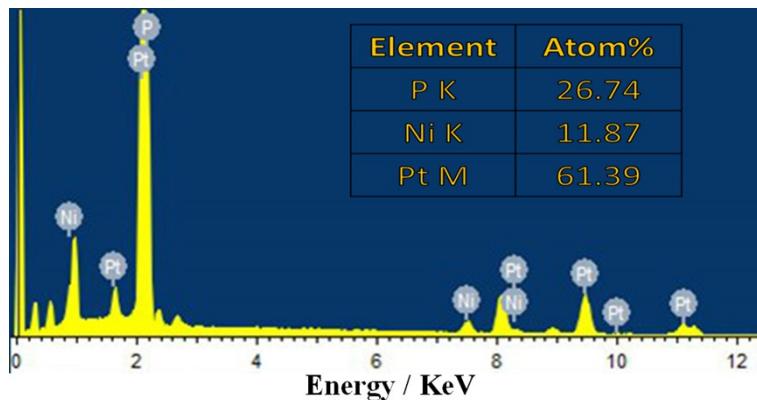
**Fig. S2** (a) SEM and (b) TEM images of the Pt MNCs.



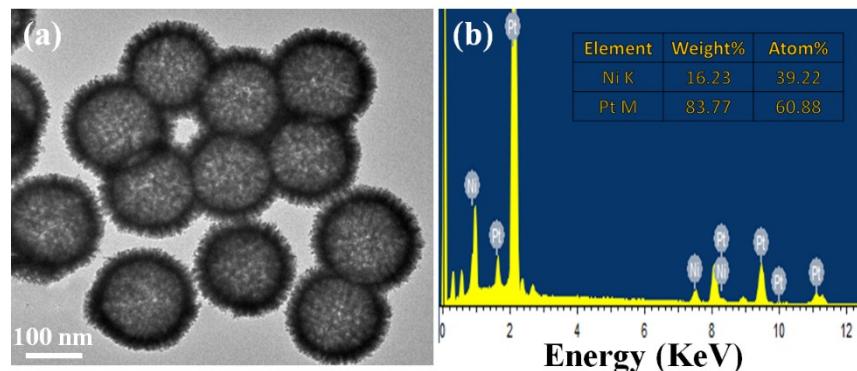
**Fig. S3** Particle-size distribution histogram of the Pt-Ni-P MNCs.



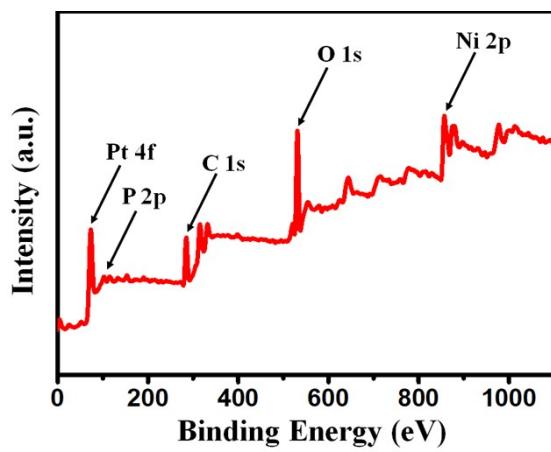
**Fig. S4** N<sub>2</sub> adsorption-desorption isotherms for (a) Pt-Ni-P MNCs , (b)Pt-Ni MNCs , and (c) Pt/C. The insets in (a) and (b) are the BJH pore-size distribution curves.



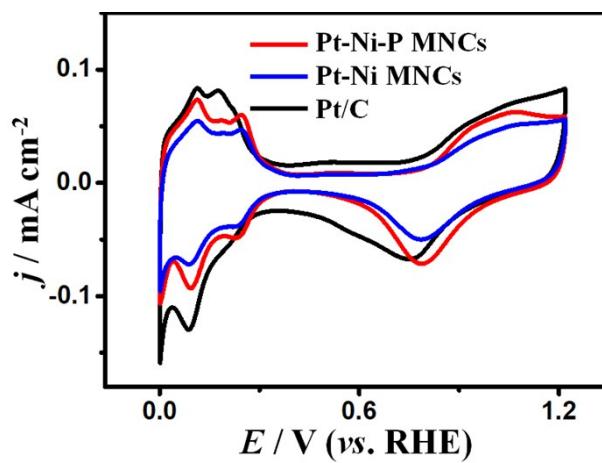
**Fig. S5** EDX spectrum of the Pt-Ni-P MNCs.



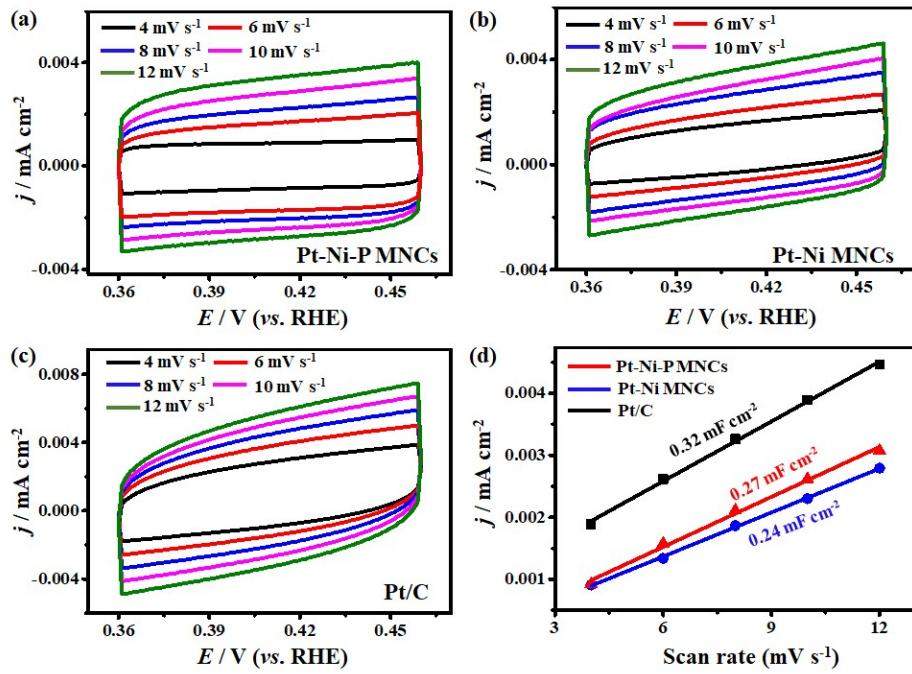
**Fig. S6** (a) TEM image and (b) EDX spectrum of the Pt-Ni MNCs.



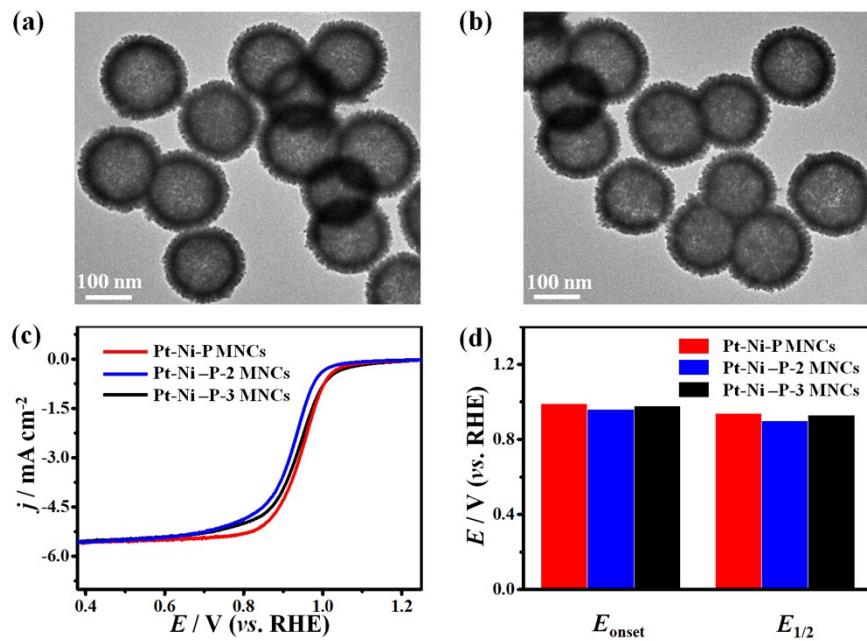
**Fig. S7** XPS survey spectrum for the Pt-Ni-P MNCS.



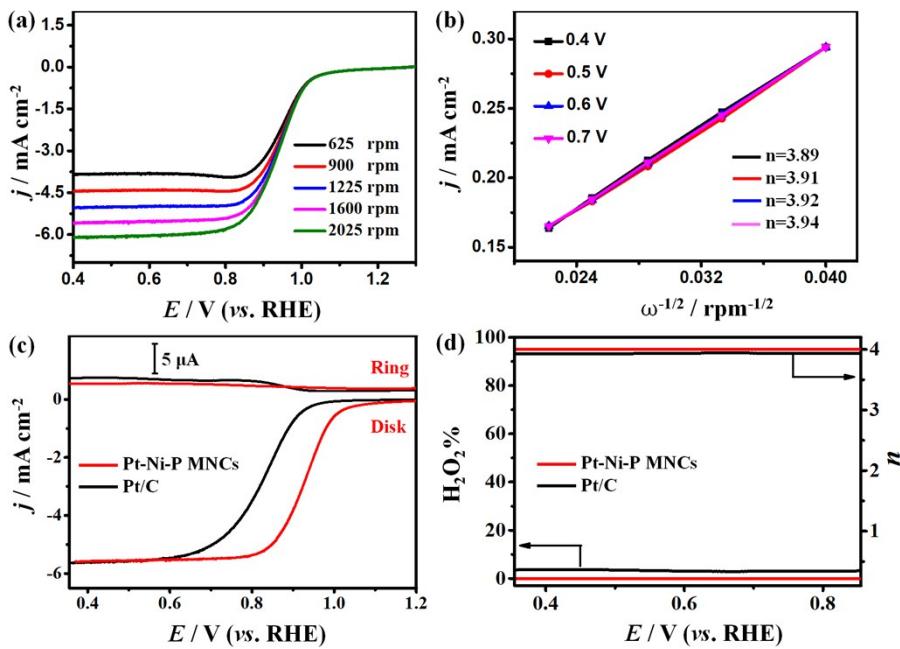
**Fig. S8** Cyclic voltammogram curves of the electrocatalysts recorded in a  $\text{N}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  solution at a scan rate of 50 mV s<sup>-1</sup>.



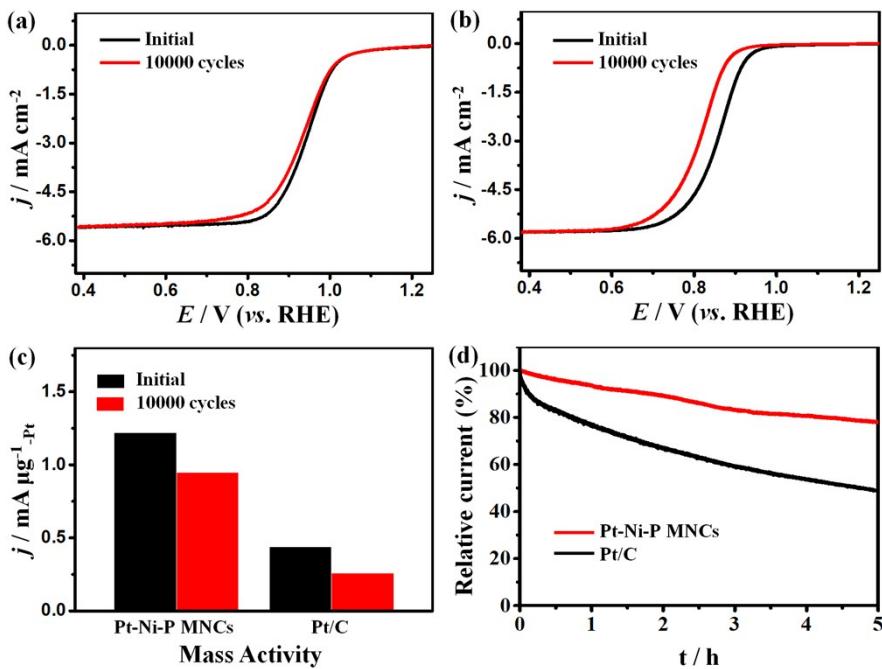
**Fig. S9** Electrochemical double-layer capacitance measurements of various catalyst-modified electrodes: (a) Pt-Ni-P MNCs; (b) Pt-Ni MNCs; and (c) Pt/C. (d) Current density at 0.40 V as a function of the scan rate for the different electrodes.



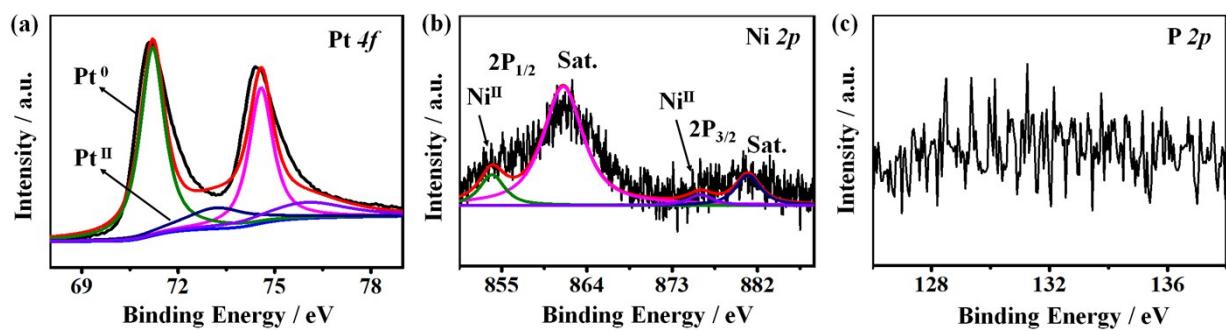
**Fig. S10** TEM images of (a) Pt-Ni-P-2 MNCs (65.59 at% Pt, 5.26 at% Ni, and 29.35 at% P) and (b) Pt-Ni-P-3 MNCs (58.21 at% Pt, 17.28 at% Ni, and 24.51 at% P). (c) ORR polarization curves of the catalysts. (d)  $E_{\text{onset}}$  and  $E_{1/2}$  of the catalysts.



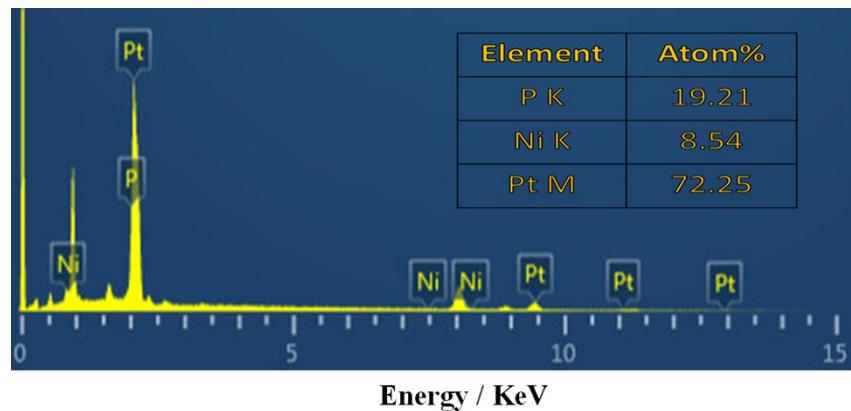
**Fig. S11** (a) Rotation-rate-dependent current-potential curves of the Pt-Ni-P MNCs. (b) The electron transfer number at different potentials. (c) RRDE test in an  $\text{O}_2$ -saturated 0.1 M  $\text{HClO}_4$  solution at a rotation rate of 1600 rpm. (d) Peroxide percentage and electron transfer number measured by using an RRDE test.



**Fig. S12** ORR polarization curves of (a) Pt-Ni-P MNCs and (b) Pt/C before and after an accelerated durability test. (c) Comparisons of mass activities before and after an accelerated durability test. (d)  $i$ - $t$  response in an  $\text{O}_2$ -saturated 0.1 M  $\text{HClO}_4$  solution at a rotation rate of 1600 rpm.



**Fig. S13** XPS spectra of the Pt 4f (a), Ni 2p (b) and P 2p (c) for the Pt-Ni-P MNCs after ORR durability test.



**Fig. S14** EDX spectrum of the Pt-Ni-P MNCs after ORR durability test.

**Table S1.** The mass activity comparison of MOR on various Pt-based electrocatalysts.

Catalyst	Condition	Scan rate (mV s <sup>-1</sup> )	Mass activity ( $j / \text{mA } \mu \text{g}^{-1}_{\text{Pt}}$ )	Ref.
Pt-Ni-P MNCS	0.5 M H <sub>2</sub> SO <sub>4</sub> containing 1 M CH <sub>3</sub> OH	50	1.22	This work
Pt Nanoparticles	0.5 M H <sub>2</sub> SO <sub>4</sub> containing 1 M CH <sub>3</sub> OH	50	0.46	[1]
Dendrites PtPdCu	0.5 M H <sub>2</sub> SO <sub>4</sub> containing 1 M CH <sub>3</sub> OH	50	0.69	[2]
Hollow Pt-Pd nanodendrites	0.5 M H <sub>2</sub> SO <sub>4</sub> containing 1 M CH <sub>3</sub> OH	50	0.58	[3]
Pt Nanoparticles	0.5 M H <sub>2</sub> SO <sub>4</sub> containing 1 M CH <sub>3</sub> OH	50	0.87	[4]
Au-Pt nanodendrites	0.5 M H <sub>2</sub> SO <sub>4</sub> containing 1 M CH <sub>3</sub> OH	50	0.45	[5]
Ultrathin Pt nanowire	0.5 M H <sub>2</sub> SO <sub>4</sub> containing 1 M CH <sub>3</sub> OH	50	0.58	[6]
Au@Pd@Pt nanoparticles	0.5 M H <sub>2</sub> SO <sub>4</sub> containing 1 M CH <sub>3</sub> OH	50	0.43	[7]
Pt <sub>1</sub> Ru <sub>3</sub> nanospunge	0.5 M H <sub>2</sub> SO <sub>4</sub> containing 1 M CH <sub>3</sub> OH	50	0.41	[8]

## References

- [1] Meng, H.; Xie, F.; Chen, J.; Sun, S.; Shen, P. K. *Nanoscale* **2011**, *3*, 5041.
- [2] Chang, R.; Zheng, L.; Wang, C.; Yang, D.; Zhang, G.; Sun, S. *Appl. Catal. B: Environ.* **2017**, *211*, 205.
- [3] Wang, L.; Yamauchi, Y. *J. Am. Chem. Soc.* **2013**, *135*, 16762.
- [4] Yan, M.; Jiang, Q.; Zhang, T.; Wang, J.; Yang, L.; Lu, Z.; He, H.; Fu, Y.; Wang, X.; Huang, H. *J. Mater. Chem. A* **2018**, *6*, 18165.
- [5] Li, Y.; Ding, W.; Li, M.; Xia, H.; Wang, D.; Tao, X. *J. Mater. Chem. A* **2015**, *3*, 368.
- [6] Ruan, L.; Zhu, E.; Chen, Y.; Lin, Z.; Huang, X.; Duan, X.; Huang, Y. *Angew. Chem. Int. Ed.* **2013**, *52*, 12577.
- [7] Wang, L.; Yamauchi, Y. *Chem. Mater.* **2011**, *23*, 2457.
- [8] Xiao, M.; Feng, L.; Zhu, J.; Liu, C.; Xing, W. *Nanoscale* **2015**, *7*, 9467.