## **Electronic Supplementary Material (ESI)**

## VN hollow spheres assembled from porous nanosheets for highperformance lithium storage and oxygen reduction reaction

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Fig. S1 (a,b) FE-SEM images of the carbon spheres.



Fig. S2 XRD patterns of V<sub>2</sub>O<sub>5</sub> HSs and VN HSs in a narrow range of degrees.



**Fig. S3** (a) Survey XPS spectra of VN HSs,  $V_2O_5$  HSs and bulk VN. (b) XPS spectra of O 1s and V 2p for VN HSs.

Fig. S3a shows typical survey XPS spectra of VN HSs, V<sub>2</sub>O<sub>5</sub> HSs and bulk VN, all of which involve three distinct peaks at 515.3 (V 2p), 286.1 (C 1s), and 531.8 (O 1s) eV, characteristic of vanadium oxide, indicating the presence of an oxide layer on the surface of VN. In addition, it is also clearly observed that VN HSs and bulk VN have principal peak at 397.5 eV compared with that of V<sub>2</sub>O<sub>5</sub> HSs, which indicates the presence of VN.<sup>S1-S3</sup> The peak at 512.3 eV probably belongs to V<sup>0+</sup> in VN structure.<sup>S2</sup> The O1s core level signals in V2p spectra (Fig. S3b) confirm the presence of an oxide layer on the surface of VN. The principal peak (530.4 eV) is assigned to oxygen in a metal oxide.<sup>S3</sup> In addition, the weak peak at the binding energy of 528.7 eV is the crystal lattice oxygen (O<sub>latt</sub>) of vanadium oxide, which plays an important role in catalysis.<sup>S4</sup> The third peak at about 532 eV can be attributed to -OH groups chemisorbed on the surface or carbon-oxygen bond.<sup>S1,S5</sup>

## References

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**Fig. S4** Raman spectra of VN HSs and  $V_2O_5$  HSs. VN HSs exhibit silimar peaks to  $V_2O_5$  HSs, which is consistent with other reported literatures.<sup>S6,S7</sup>

## References

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**Fig. S5** TG curve of  $C@VO_x$  spheres.



Fig. S6 Nitrogen adsorption-desorption isotherms of  $V_2O_5$  HSs and corresponding pore size distribution.



Fig. S7 XRD pattern and FE-SEM image of bulk VN.



**Fig. S8** (a) CV curves of bulk VN in the voltage range of 0.01-3.5 V with a scan rate of 0.5 mV s<sup>-1</sup>. (b) Comparison of CV curves using the same full scale for the y axes.



**Fig. S9** Cycling performance of VN HSs electrode at 0.2 A  $g^{-1}$  (a) and 2.0 A  $g^{-1}$  (b) in the voltage range of 0.01–3.5 V.



**Fig. S10** Cycling performance of VN HSs electrode at 2 A  $g^{-1}$  after activation at 50 mA  $g^{-1}$  for the initial ten cycles.



Fig. S11 Electrochemical ORR catalytic performance of Pt/C: CV curves in  $N_2$ - and  $O_2$ -saturated 0.1 M KOH at a sweep rate of 10 mV s<sup>-1</sup>.



**Fig. S12** (a) Rotating ring-disk electrode (RRDE) voltammograms of VN HSs in  $O_2$ -saturated 0.1 M KOH at 1600 rpm. (b)  $HO_2^-$  yield and the corresponding electron-transfer number (n) of VN HSs based on the corresponding RRDE data.