Electronic Supplementary Information (ESI)

Stabilization of binder-free vanadium oxide-based oxygen electrode using Pd clusters for Li-O₂ battery

Jiade Li,[a] Senchuan Huang,[a] Guangyao Zhang,[b] Zhi Li,[b] Shengfu Tong,*[a] Jue Wang,*[b] Mingmei Wu*[a]

[a.] MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry/School of Marine Sciences, Sun Yat-Sen University, Guangzhou 510275/Zhuhai 519082, China. E-mail: tongshf@mail.sysu.edu.cn; ceswmm@mail.sysu.edu.cn.

[b.] Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province, Yancheng Institute of Technology, Yancheng 224051, China. E-mail: wangjue@ycit.edu.cn.

Experimental

Preparation of CC@VO electrode: In a typical synthesis, 5 mmol NH_4VO_3 and 10 mmol $H_2C_2O_2$ were dissolved in 50 mL of deionized water at 80°C and stirred for 3 hours. Carbon cloths (CC) were dipped directly into a Teflon-lined stainless-steel autoclave filled with the prepared mixture solution, heated at 200°C for 20 h, then cooling down to room temperature naturally. The modified CC were taken out, and followed by washing with water and alcohol for several times. After that, the samples were annealed in air at 350°C for 2 hours to achieve CC@VO.

Preparation of CC@VO-Pd electrode: The Pd clusters were prepared by a magnetron plasma gas aggregation cluster source, and the details of the method can be found in previous papers.[1, 2] Briefly, a stable pressure of ～75 Pa was maintained in the aggregation tube by introducing 120 sccm argon. The Pd was deposited on the substrates with the deposition rate of 1.5 Å·s^{-1} for a certain time (typically 5, 10, and 15 min), and the Pd atomic clusters firmly adhered to the surface directly.

Material Characterization: X-ray diffraction (XRD) patterns were recorded with a Rigaku D/MAX 2200 VPC diffractometer using Cu Kα radiation (λ=0.15045 Å). The microstructural properties were characterized by a scanning electron microscopy (SEM, FEI Quanta 400F) and transmission electron microscopy (TEM, FEI Tecnai G2 F30). The states of the surface elements were estimated by X-ray photoelectron spectroscopy (XPS) (ESCALab250). The specific surface area and pore size distribution were calculated by the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) method respectively, based on the N_2 adsorption-desorption isotherms obtained on a Micromeritics ASAP 2020m instrument at 77.4 K under vacuum. Raman measurement was carried out on a Laser Micro-Raman spectrometer (RenishawinVia, France) with a laser excitation at 633 nm.

Electrochemical measurements: The CR2032 coin-type LOB, assembled in an ultra-pure argon-filled glove-box (the concentrations of O_2 and moisture were both controlled below 0.1 ppm), was utilized for all the electrochemical measurements. The system was similar as that reported in our pervious works [3, 4] with a lithium foil or $LiFePO_4$ as anode, a glass fiber (glass microfiber filters, d=16 mm, Whatman) as separator, and an as-prepared binder-free CC@VO or CC@VO-Pd as oxygen cathode (cut into square, 1 cm × 1 cm). The loaded VO (VO-Pd) was 0.4-0.6 mg cm^{-2}, and the specific energy density was normalized based on the mass of VO (VO-Pd). The electrolyte was composed of $LiCF_3SO_3$ and TEGDME with a molar ratio of 1:4. The galvanostatic discharge-

recharge was performed within the potential range of 2.0-4.5 V using a NEWARE battery tester (Shenzhen, China).
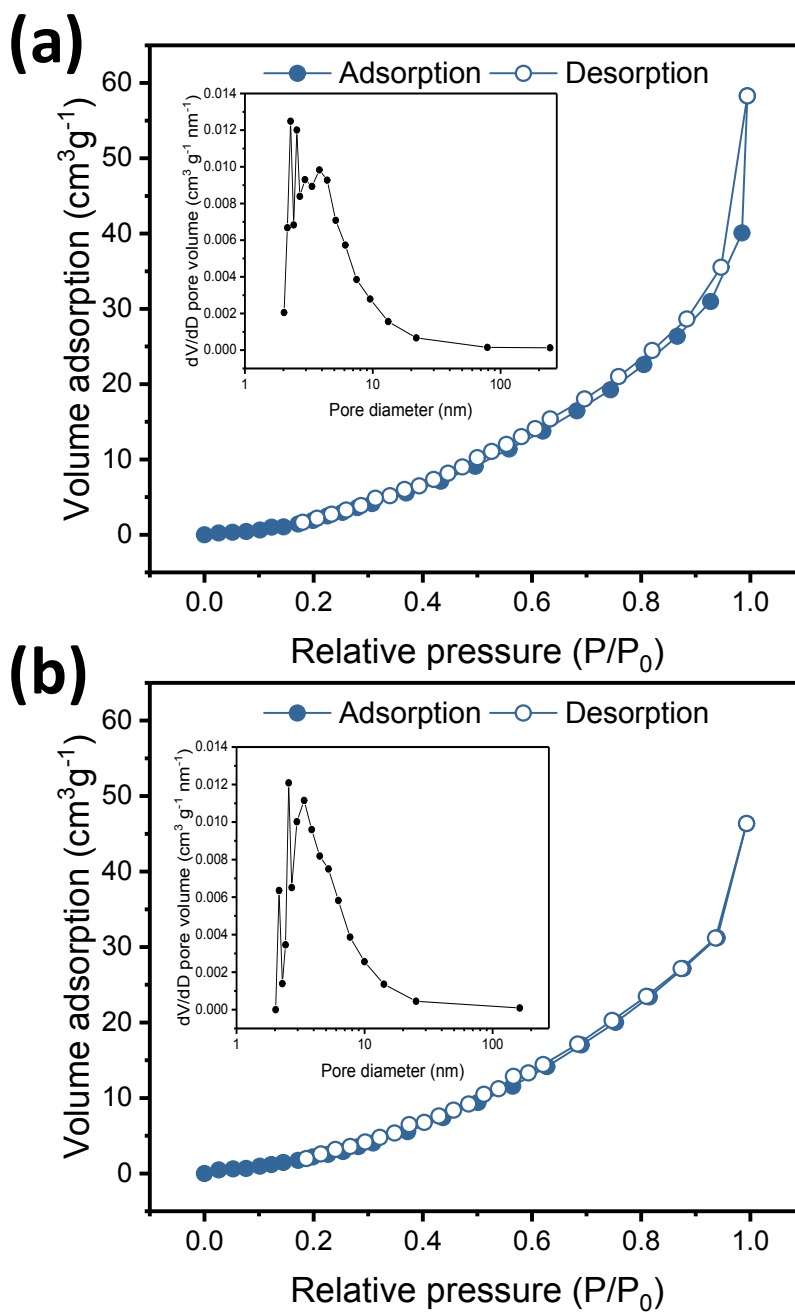
Figure S1 Nitrogen adsorption and desorption isotherms of (a) CC@VO and (b) CC. Insets are the pore size distributions.

Table S1 Surface areas of CC@VO and CC

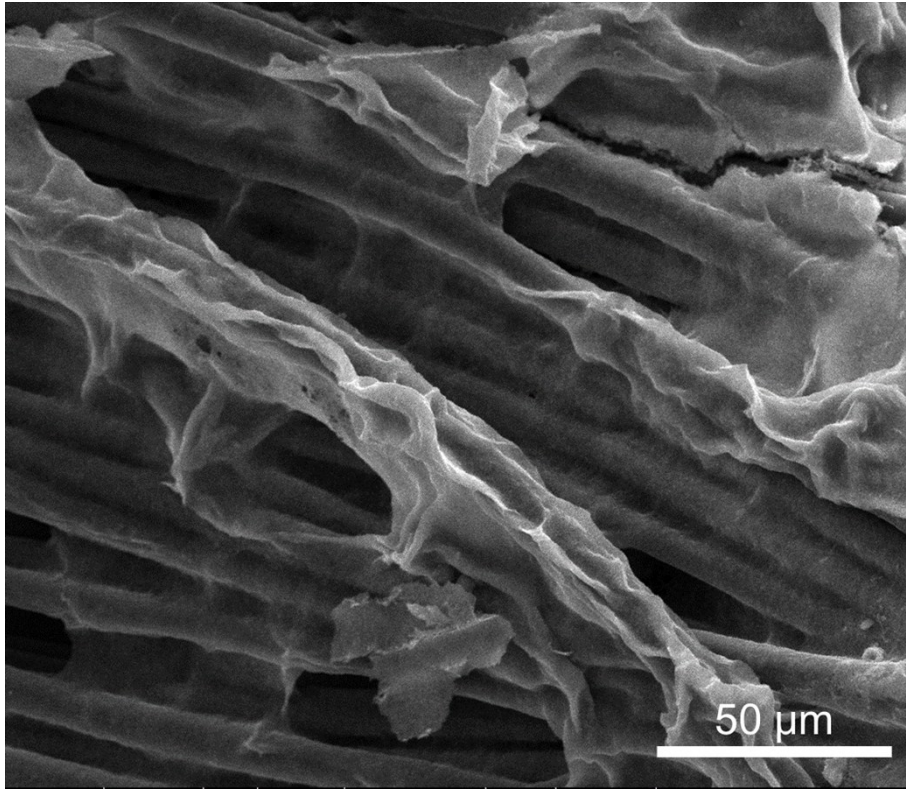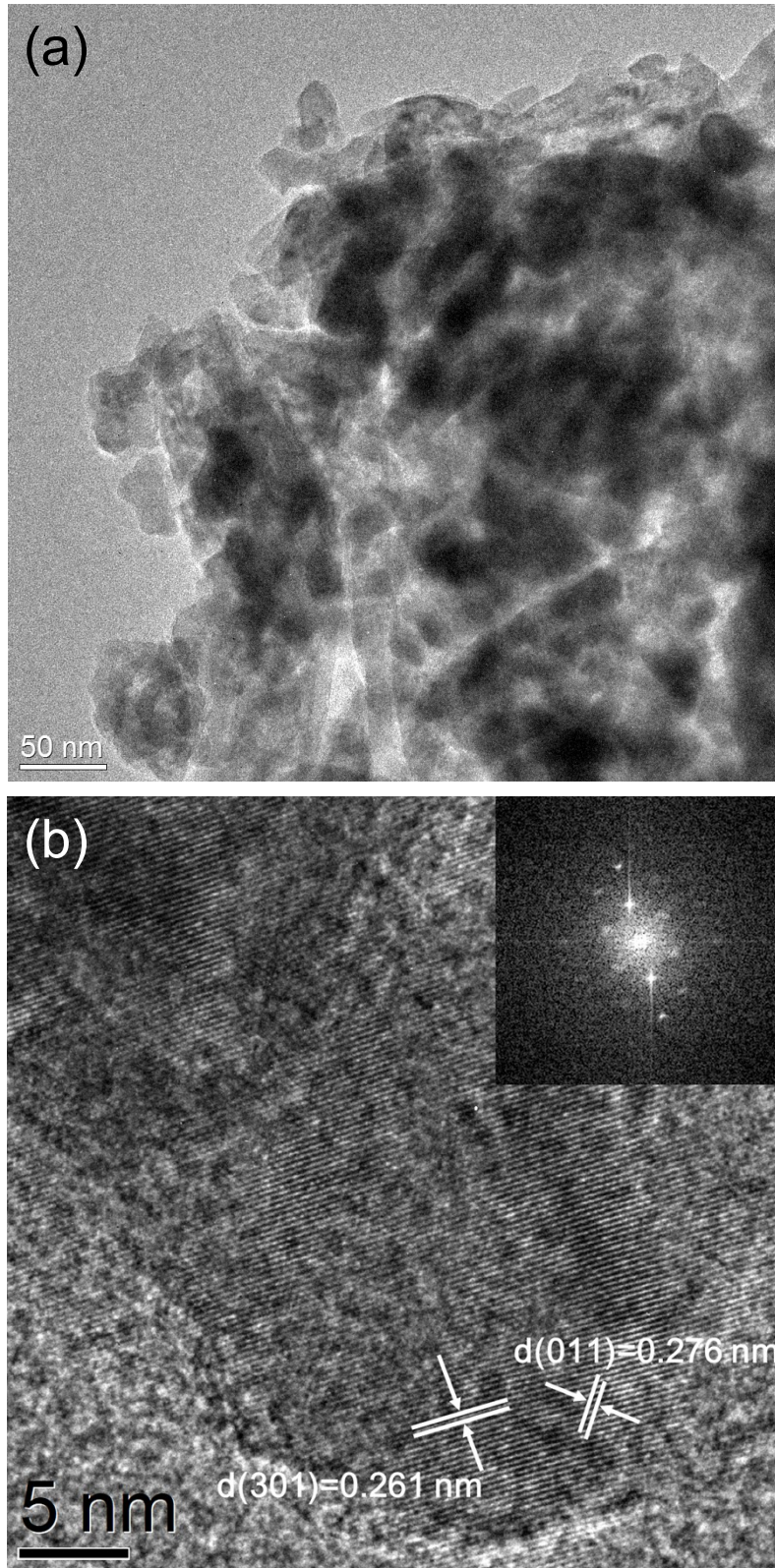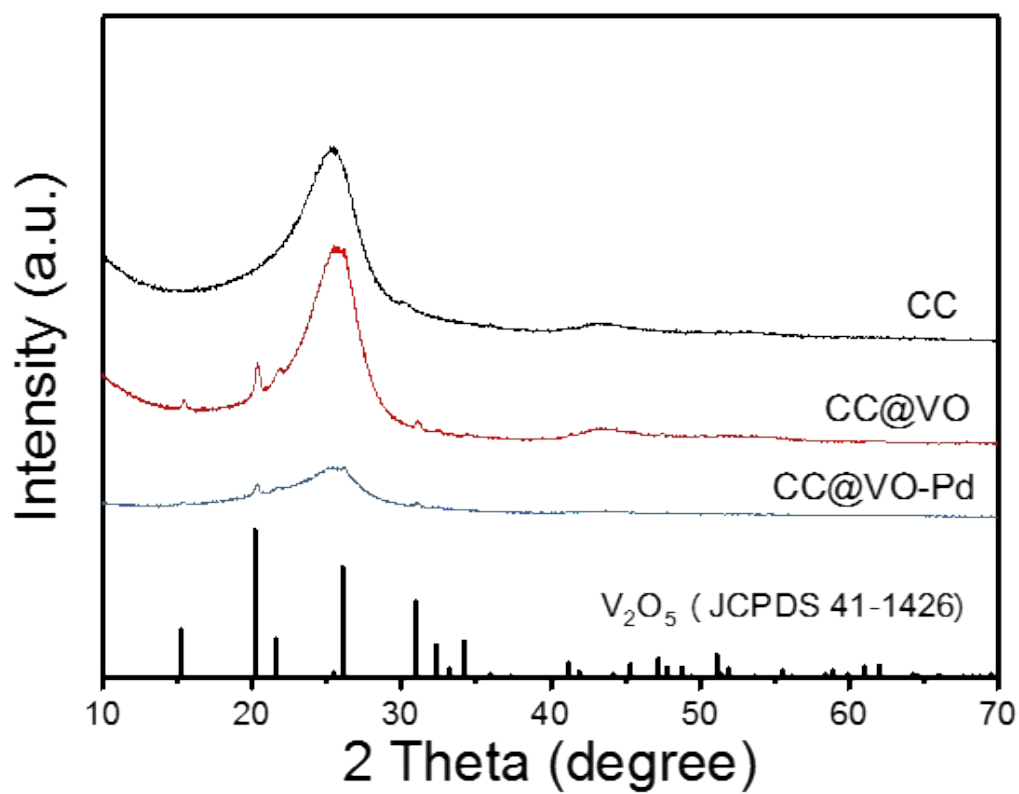| Sample	Surface area ($m^2 \ g^{-1}$)
CC@VO	7.719
CC	6.686

Figure S2 The low magnification SEM image of CC@VO

(a)

50 nm

(b)

d(011)=0.276 nm

d(301)=0.261 nm

5 nm

Figure S3 TEM and HR-TEM images of VO.

Figure S4 XRD spectra of CC, CC@VO and CC@VO-Pd, respectively.
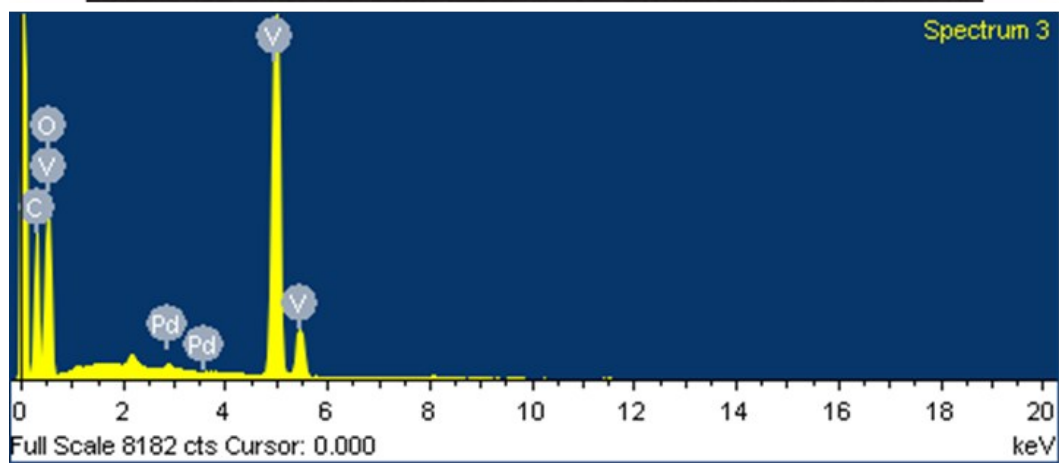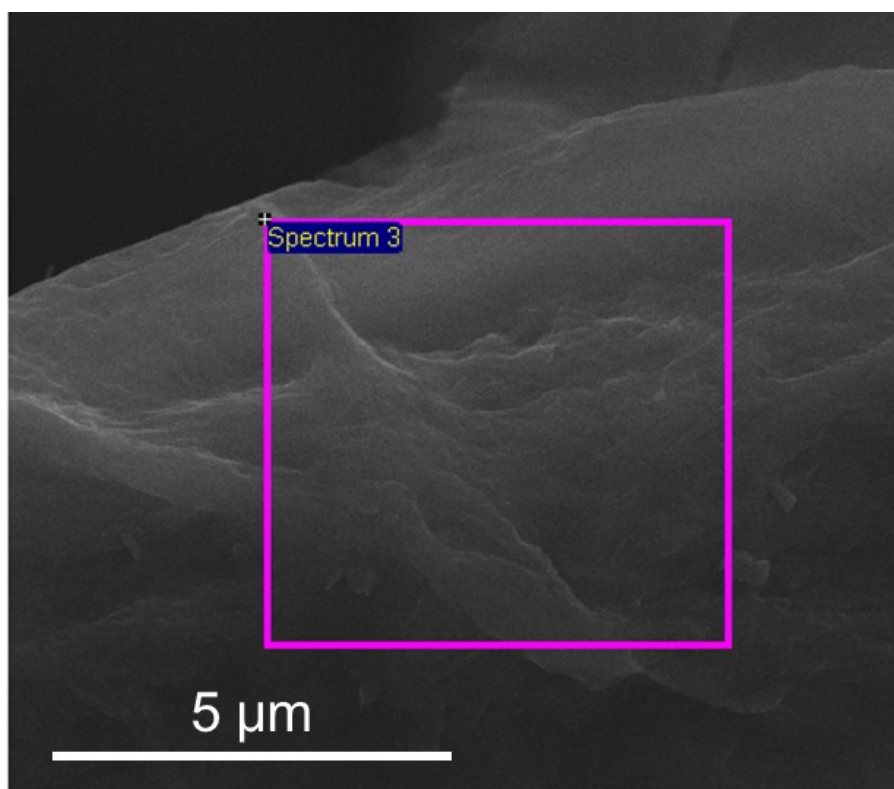
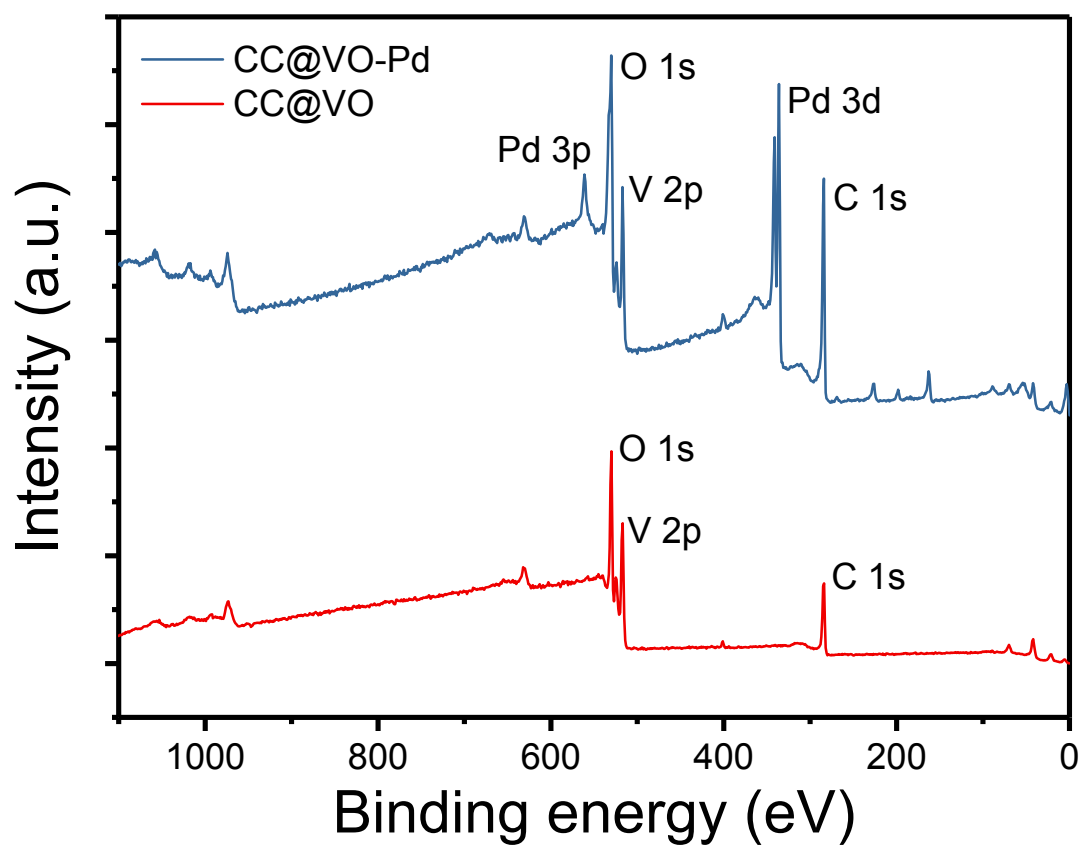**Figure S5** The SEM image (top) and EDS (bottom) spectra of CC@VO-Pd.

(a)

20 nm

(b)

100 nm
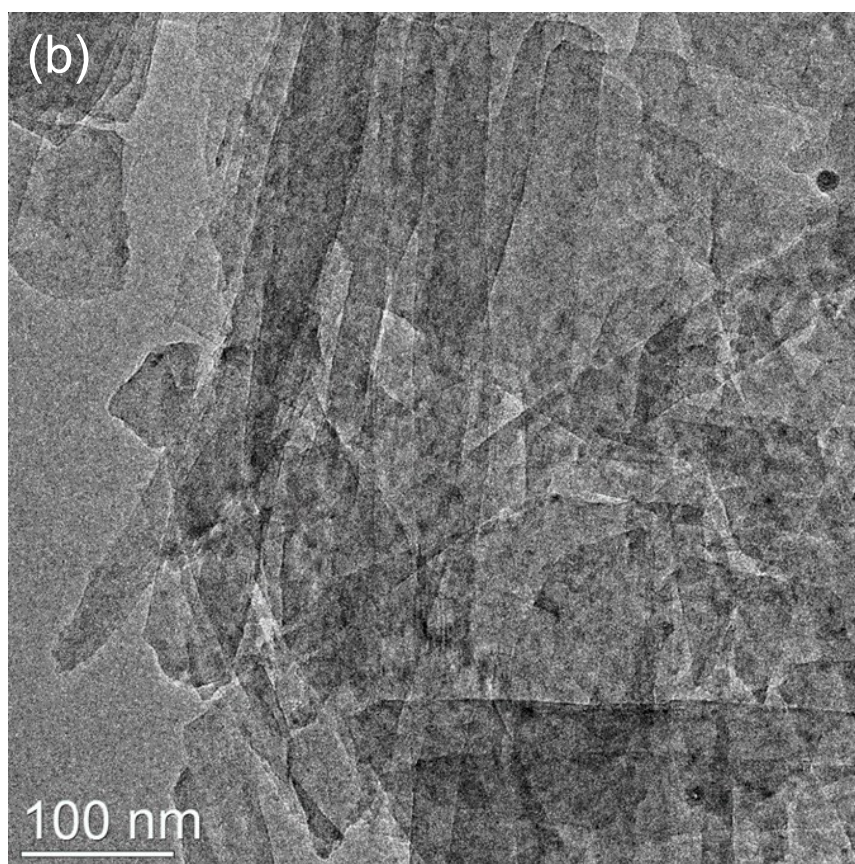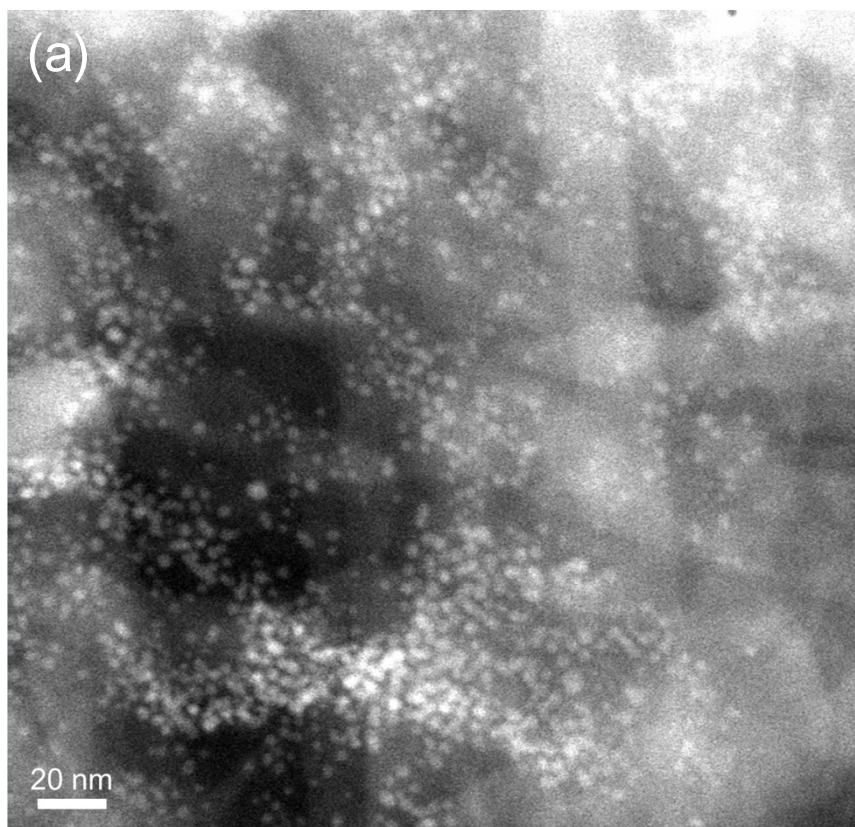
Figure S6 The (a) HAADF-STEM and (b) TEM images of VO-Pd.
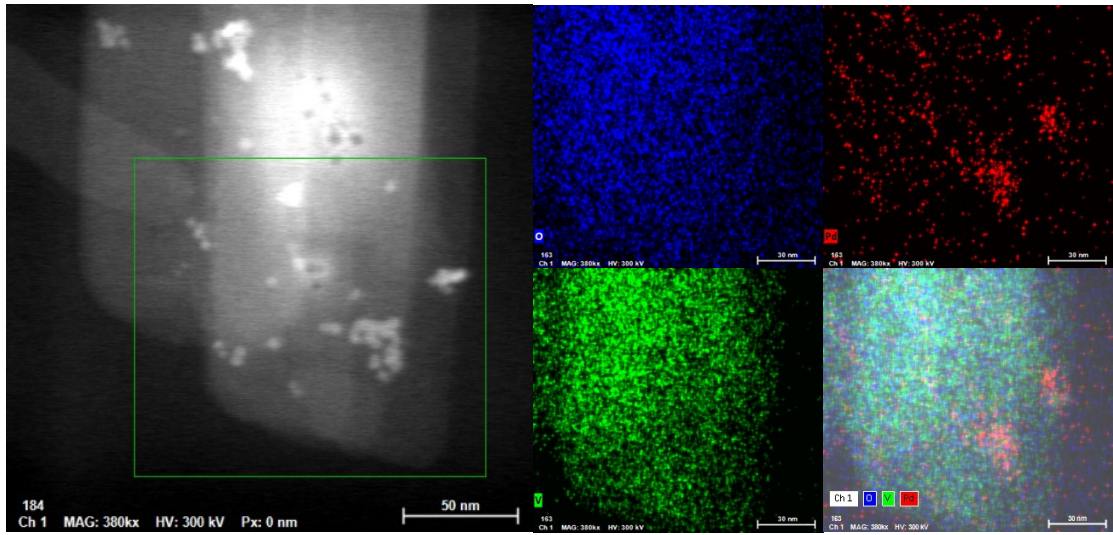
Figure S7 The element mapping of VO-Pd.

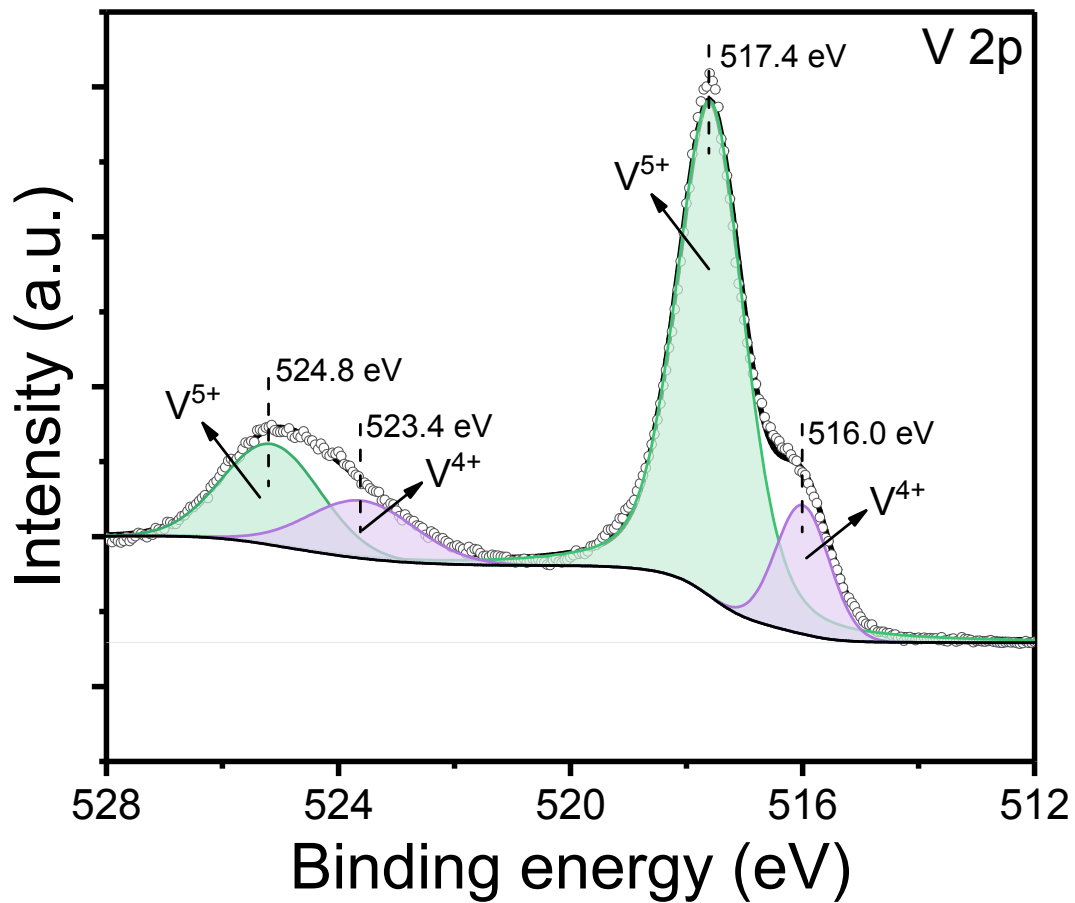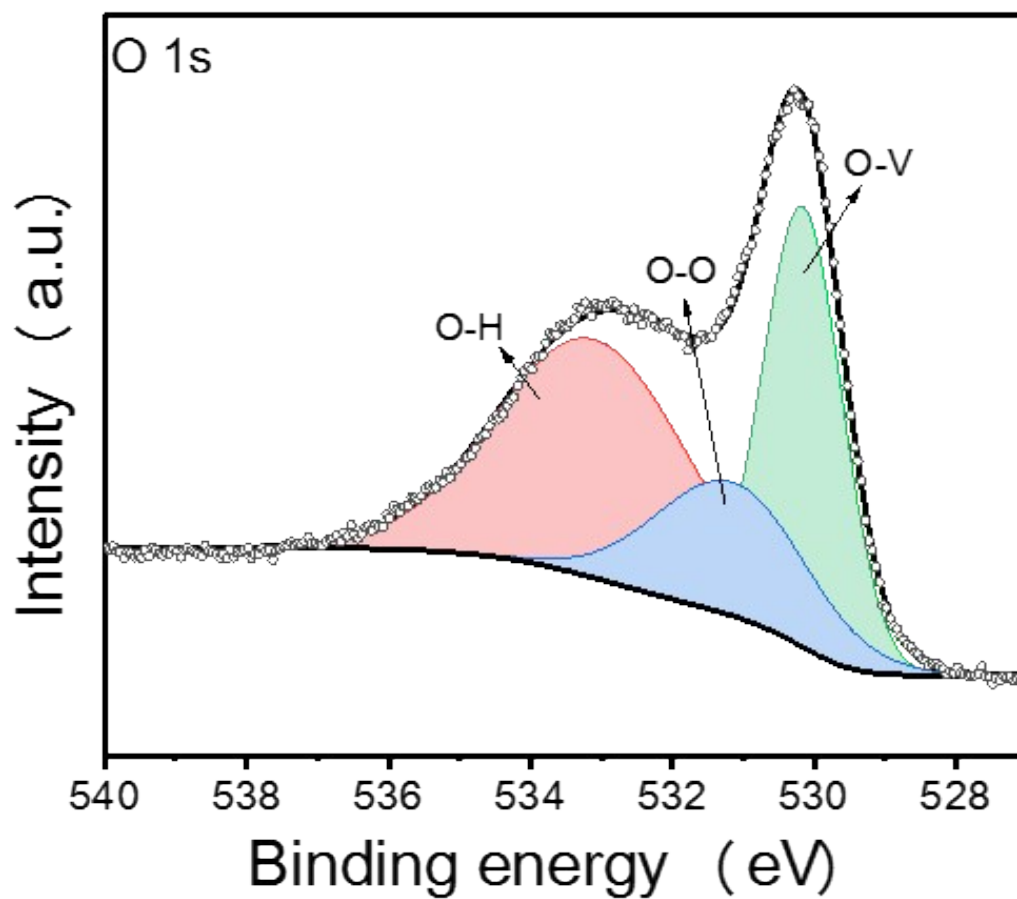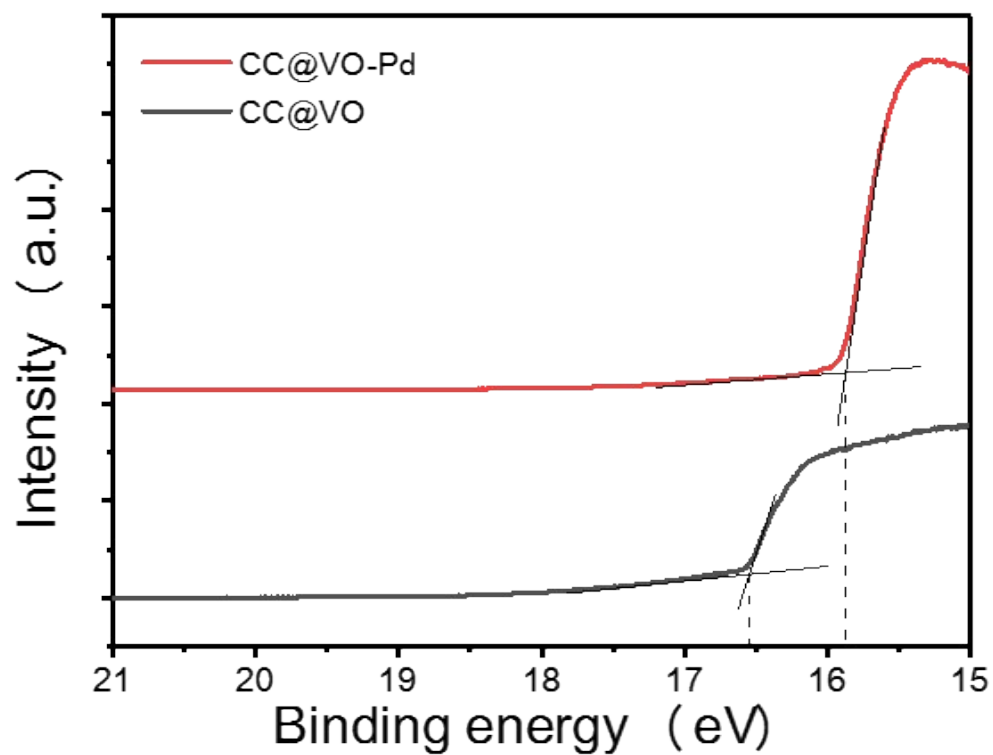**Figure S8** XPS spectra survey of CC@VO and CC@VO-Pd

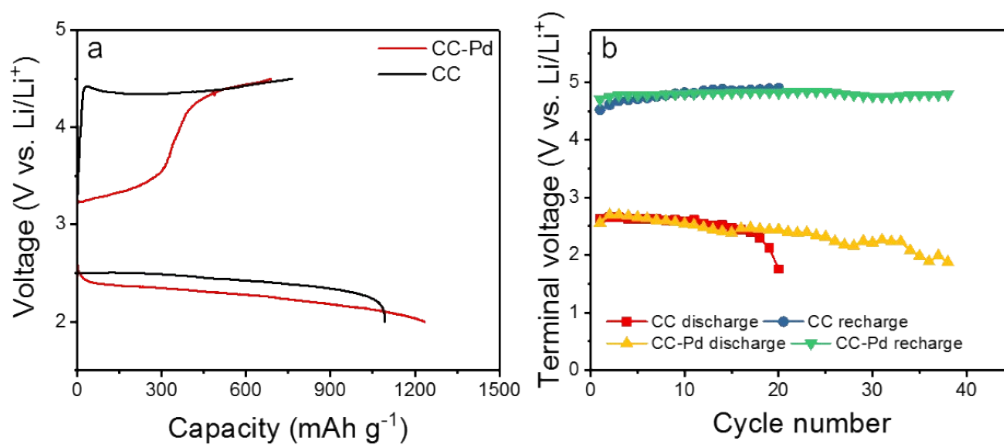**Figure S9** XPS spectra of V 2p for VO

Figure S10 The XPS spectra of O 1s for VO-Pd.

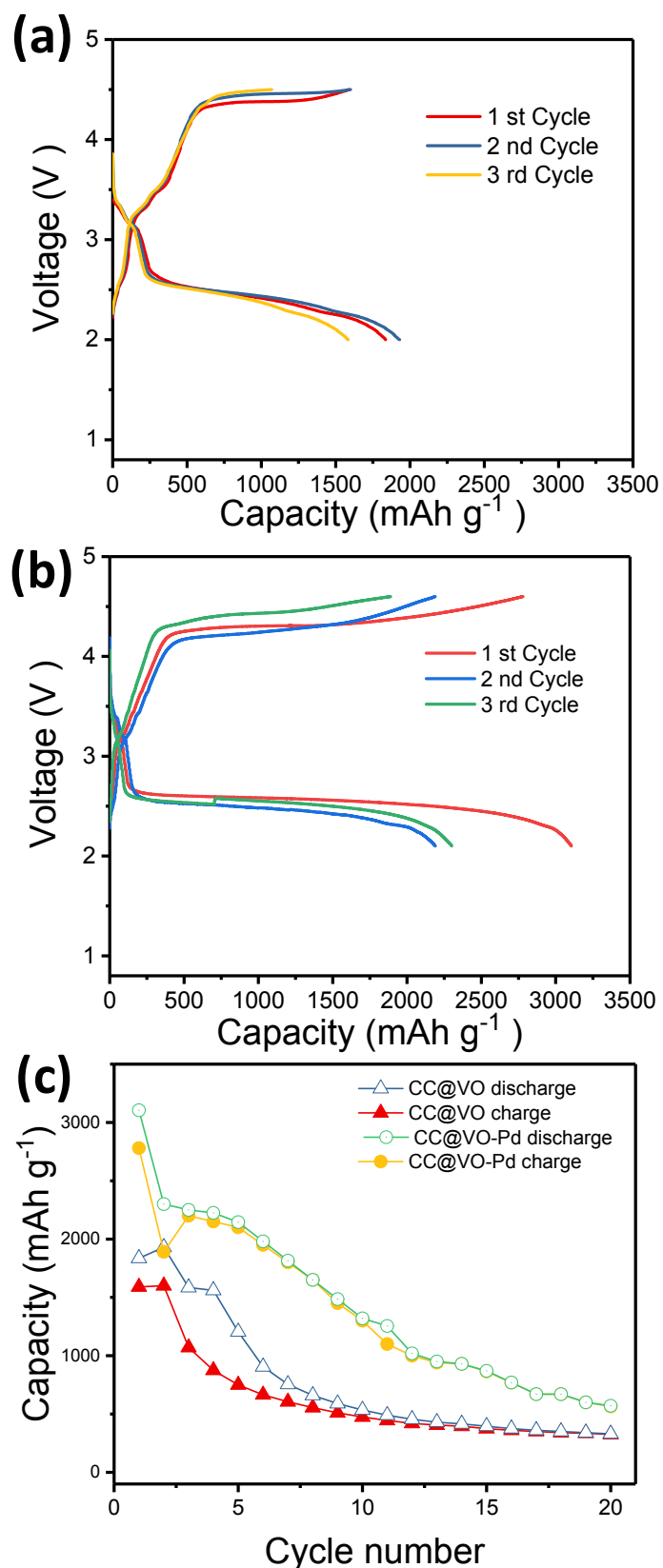**Figure S11** The UPS spectra of CC@VO and CC@VO-Pd.

Table S2 The work function of CC@VO and CC@VO-Pd

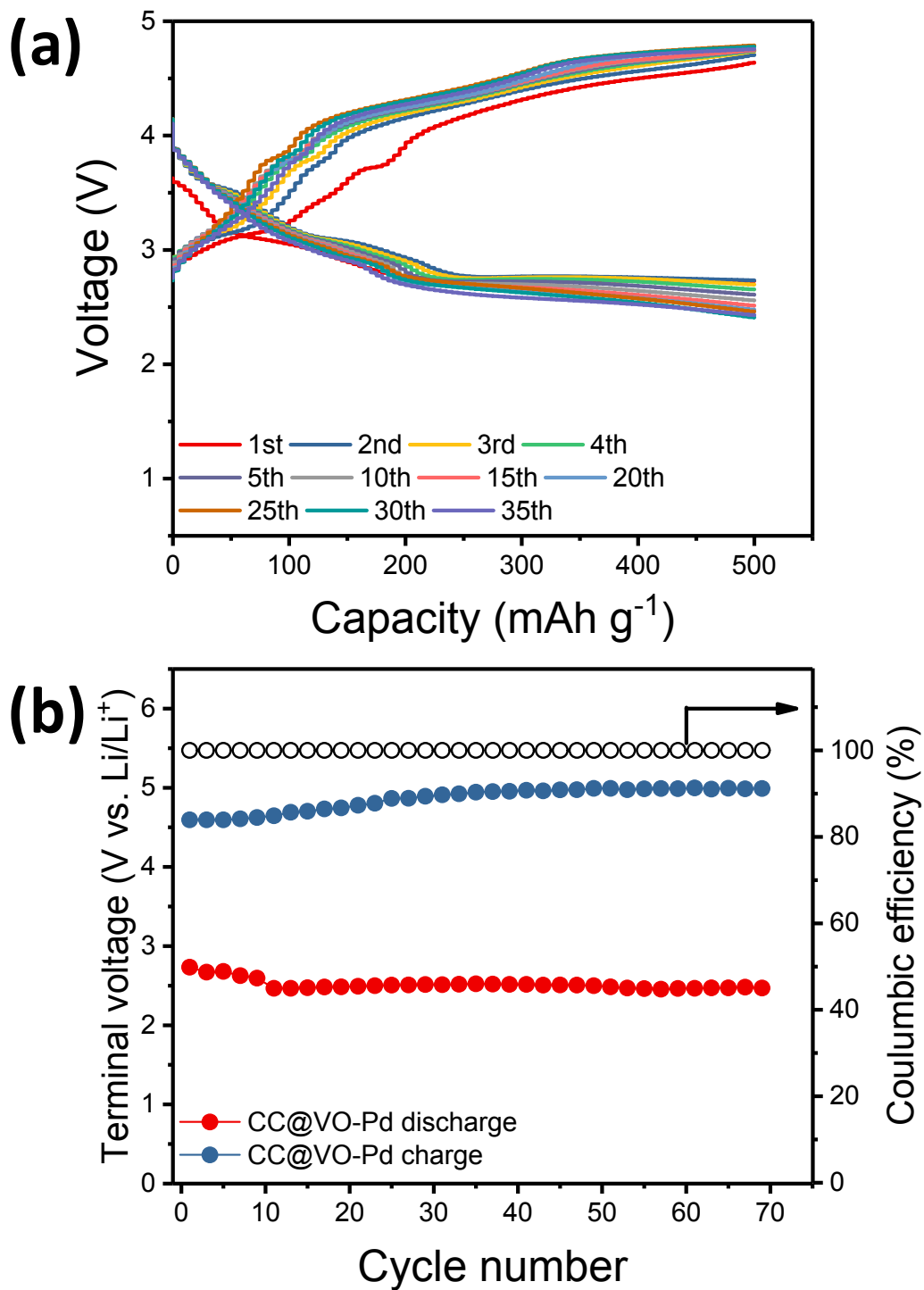| Sample	Work function
CC@VO	4.54 eV
CC@VO-Pd	5.29 eV

Figure S12 (a) The potential cut off (2.0 V~4.5 V) galvanostatic discharge/charge voltage curves of CC and CC-Pd; (b) the terminal discharge/charge voltages of CC and CC-Pd at the current density of 200 mA g-1.
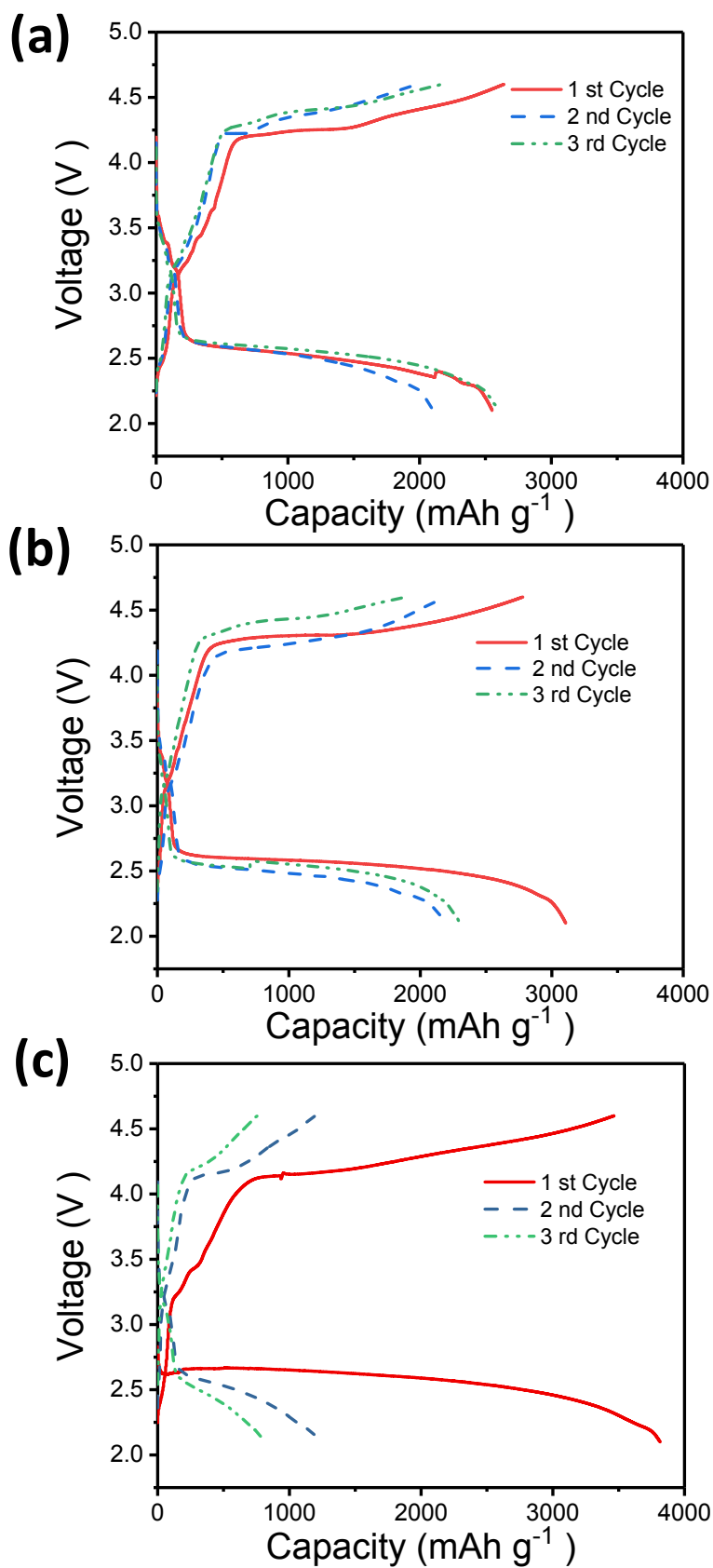
Figure S13 The potential cut off (2.0 V~4.5 V) galvanostatic discharge-charge voltage curves of (a) CC@VO and (b) CC@VO-Pd. (c) A cycle number dependent capacity obtained on CC@VO and CC@VO-Pd (as indexed in the figure) at a current density of 200 mA g^{-1}.
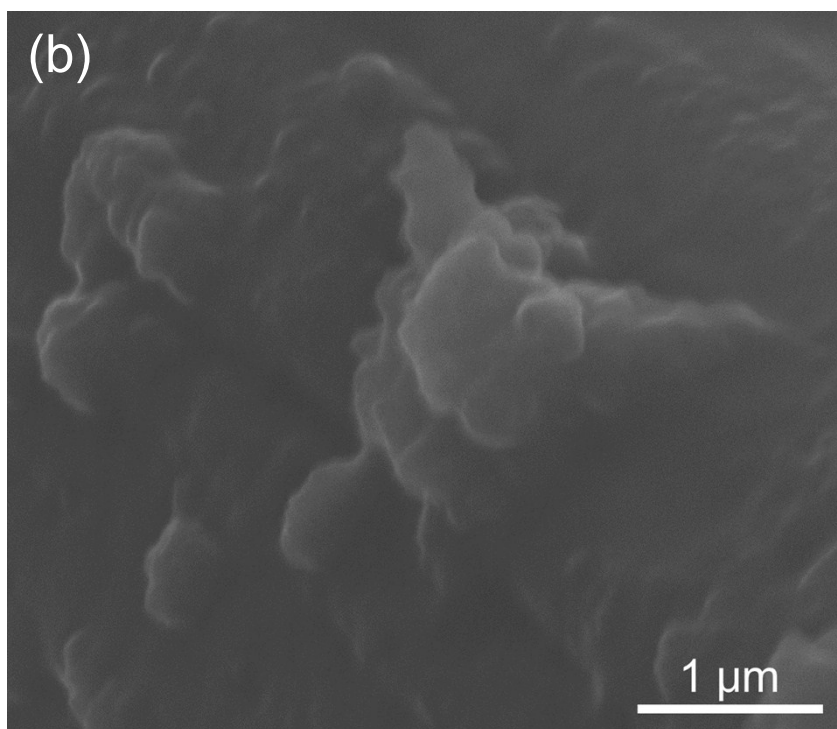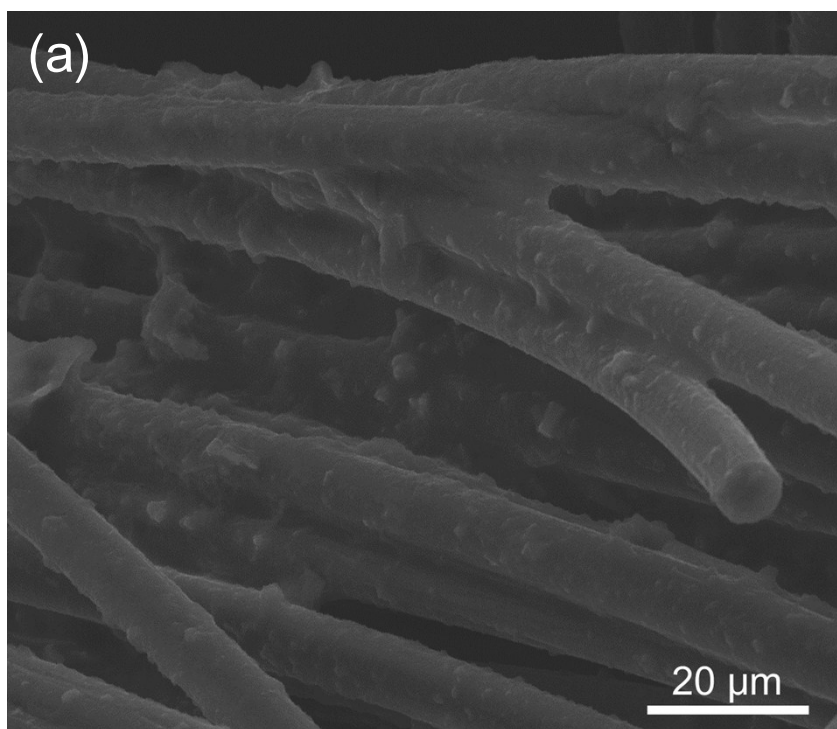
Figure S14 (a) The cycle performance and (b) the terminal discharge-charge voltages of CC@VO-Pd at the current density of 400 mA g⁻¹.

Figure S15 The potential cut off (2.0 V~4.5 V) galvanostatic discharge-charge voltage curves of CC@VO-Pd with Pd gas-phase-cluster beam deposition for (a) 5 min, (b) 10 min, and (c) 15 min.

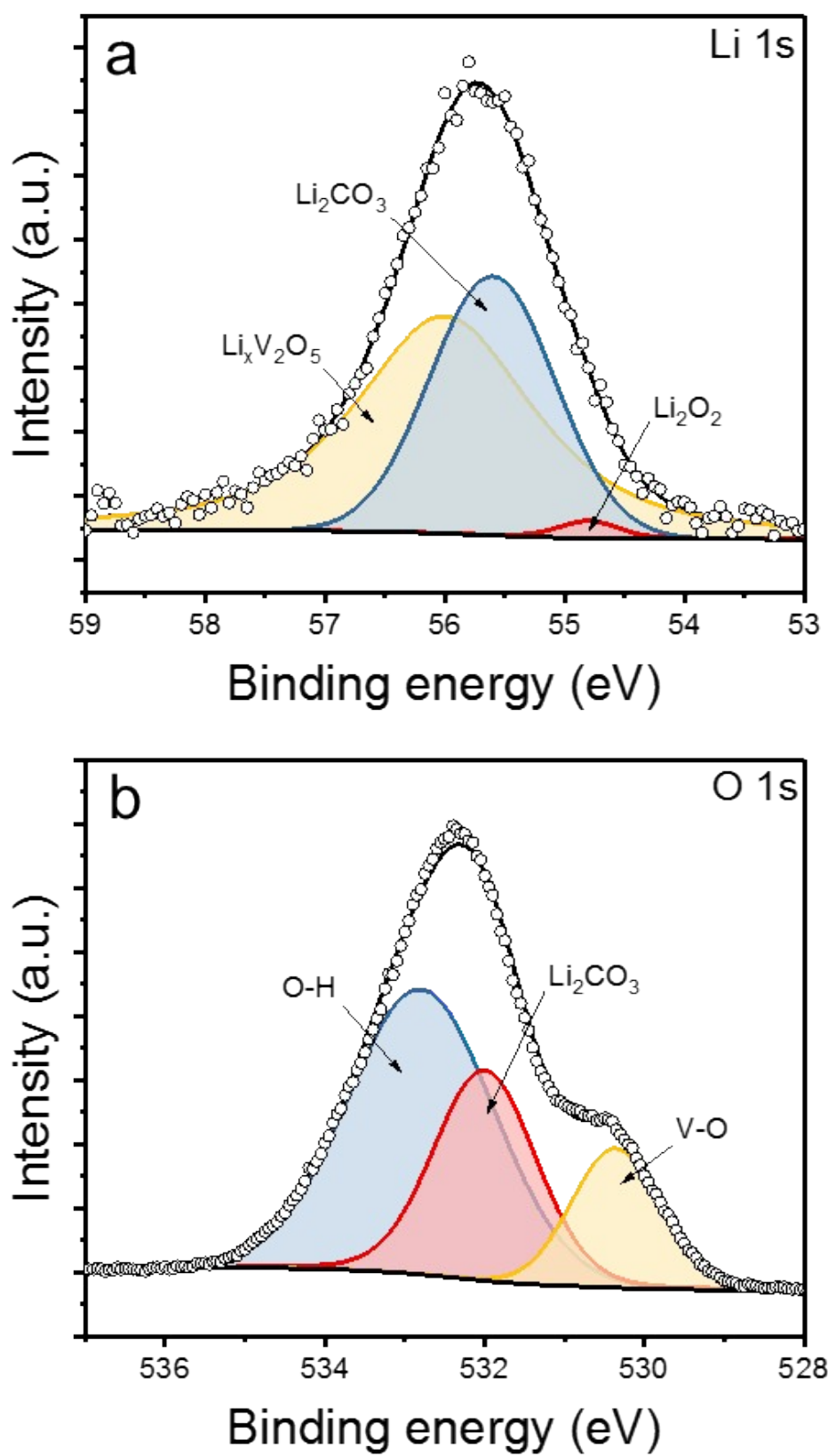**Figure S16** The SEM images of CC@VO-Pd after 120 cycles.

Figure S17 The XPS spectra of CC@VO-Pd after 120 cycles.

References

1   J. Wang, H. Y. Pan, Y. Y. Ding, Y. C. Li, C. Liu, F. Liu, Q. F. Zhang, G. H. Wang and M. Han, *Electrochim. Acta*, **2017**, 251, 631-637.

2   M. Han, C. Xu, D. Zhu, L. Yang, J. Zhang, Y. Chen, K. Ding, F. Song and G. Wang, *Adv. Mater.*, **2007**, 19, 2979-2983.

3   S. Tong, M. Zheng, Y. Lu, Z. Lin, X. Zhang, P. He and H. Zhou, *Chem. Commun.*, **2015**, 51, 7302-7304.

4   C. Luo, J. Li, S. Tong, S. He, J. Li, X. Yang, X. Li, Y. Meng and M. Wu, *Chem. Commun.*, **2018**, 54, 2858-2861.