

**Fast synthesis of  $\text{Co}_{1.8}\text{V}_{1.2}\text{O}_4/\text{rGO}$  as a high-rate anode material for  
lithium-ion batteries**

Dan Zhang <sup>a</sup>, Guangshe Li <sup>a</sup>, Baoyun Li <sup>a</sup>, Jianming Fan <sup>b</sup>, Dandan Chen <sup>a</sup>, Xiaoqing Liu <sup>a</sup>, and Liping Li <sup>a, \*</sup>

<sup>a</sup> State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China

<sup>b</sup> College of Chemistry and Materials, Longyan University, Longyan, 364012, PR China.

E-mail: [lipingli@fjirsm.ac.cn](mailto:lipingli@fjirsm.ac.cn); Fax: +86-0431-85168358

## Experimental details

All the reactants and solvents were of analytical grade and used without any further purification. Graphene oxide (GO) was purchased from Chengdu Organic Chemicals Co. Ltd. of Chinese Academy of Sciences.

### 2.1 Synthesis of CoVO/rGO composite

CoVO/rGO composite was synthesized in the following steps. Firstly, 0.06 g of GO and 0.374g  $\text{NH}_4\text{VO}_3$  were firstly dispersed in 64 mL of deionized water by ultrasonication for 30 min. Then the above suspension was kept stirring in a water bath at 80 °C and added 0.08g of  $\text{LiOH}\cdot\text{H}_2\text{O}$  and 0.152g of  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ . After stirring for 10 min, the mixed suspension was transferred into a 100 mL Teflonlined stainless steel autoclave and heated in an oil bath under stirring at 180 °C for 10 min. After cooling down to room temperature quickly with cool water, the precipitate was harvested by centrifugation and washed with deionized obtained water and absolute ethanol several times. Finally, the resultant material was dried and annealed at 400 °C for 1 h under inert atmosphere. Sample CoVO was similarly prepared without GO. Sample rGO was similarly obtained without  $\text{NH}_4\text{VO}_3$ ,  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ .

### 2.2 Materials Characterization

The powder X-ray diffraction (XRD) data were collected on a Rigaku D/max-2550 diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Inductively coupled plasma (ICP) analyses were performed on a Perkin-Elmer Optima 3300Dv spectrometer. The transmission electron microscopy (TEM) images and the energy dispersive spectra (EDS) were collected using a Philips-FEI Tecnai G2S-Twin. The thermogravimetric analysis (TG) was measured under air flowing on a STA 449 analyzer with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  from room temperature to 800 °C. Raman spectrum was obtained using a Renishaw INVIA Confocal Raman spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was performed using an ESCALAB 250Xi electron spectrometer from Thermo-VG Scientific using 150W  $\text{AlK}\alpha$  radiation. XANES measurements were carried out using beamline U19 of national synchrotron radiation laboratory (NSRL, Hefei).

### **2.3 Electrochemical measurements**

The electrochemical performance of the samples was tested using CR2025-type coin cell. The test electrodes were prepared by mixing the samples, carbon black, and binder (polyvinylidene fluoride (PVDF)) at a weight ratio of 7:2:1 in N-methyl-2-pyrrolidinone (NMP). The resulting slurries were coated onto a copper foil and then dried under vacuum at 80 °C for 12 h. Coin cells were assembled in an argon-filled glovebox ( $\text{H}_2\text{O}$  and  $\text{O}_2 < 0.1$  ppm) using lithium foil as the counter and reference electrode, a polymer separator (Celgard 2500), and 1 M  $\text{LiPF}_6$  in EC:DMC (1:1 in volume) as the electrolyte. The cells were tested using a Neware Battery Test System in the potential range between 0.01 and 3 V at room temperature. Cyclic voltammetry (CV) was measured using an electrochemical workstation (CHI660C). Electrochemical impedance spectra (EIS) were characterized by the same instrument over a frequency range of 100 kHz to 0.01 Hz.

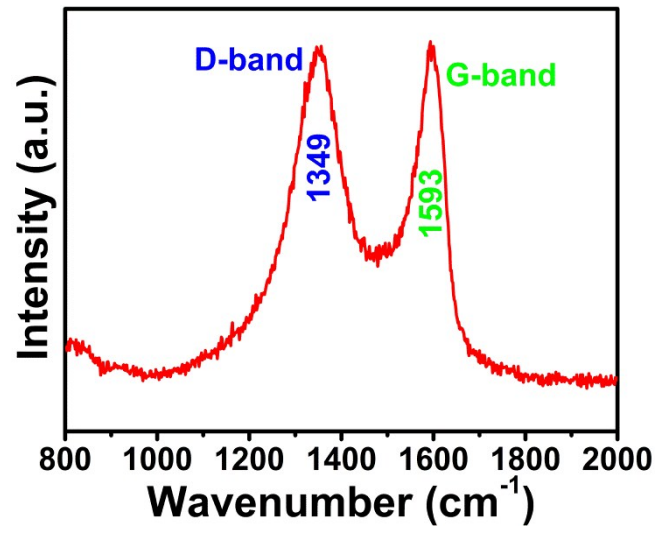
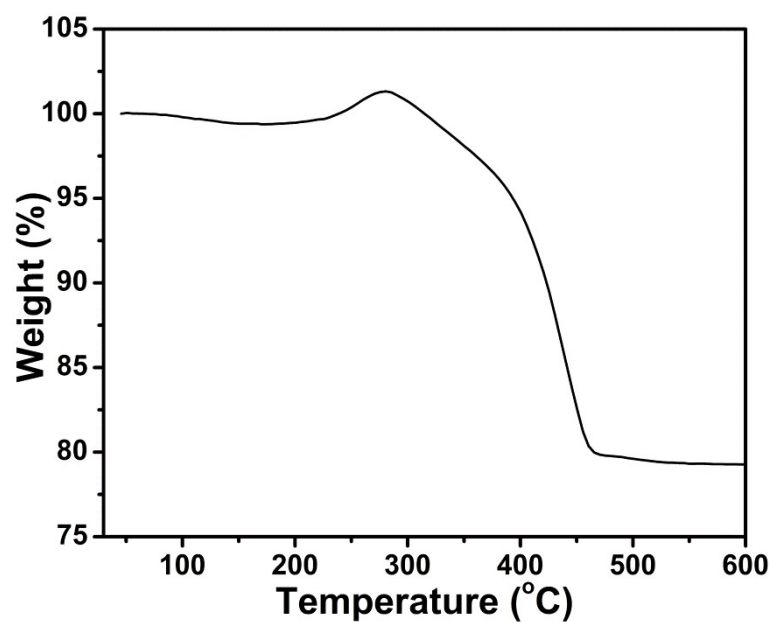
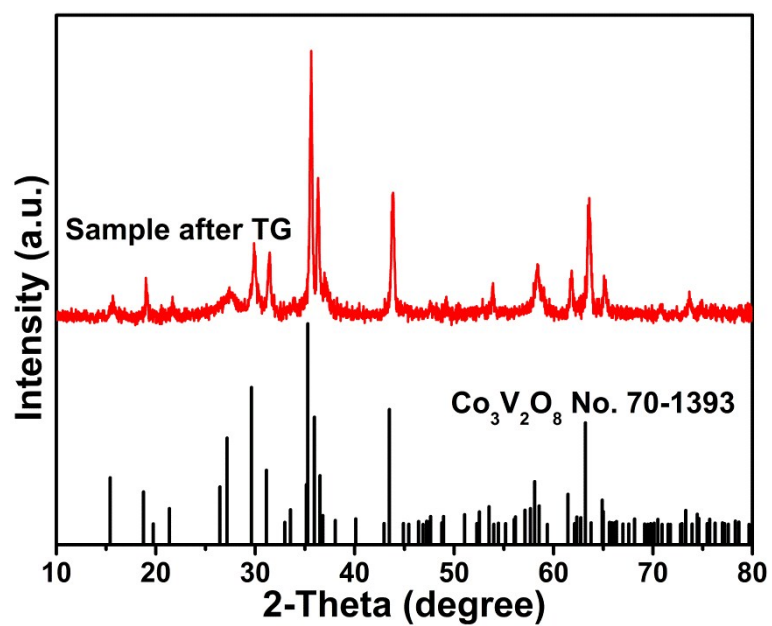


Fig. S1 Raman spectra of CoVO/rGO composite.

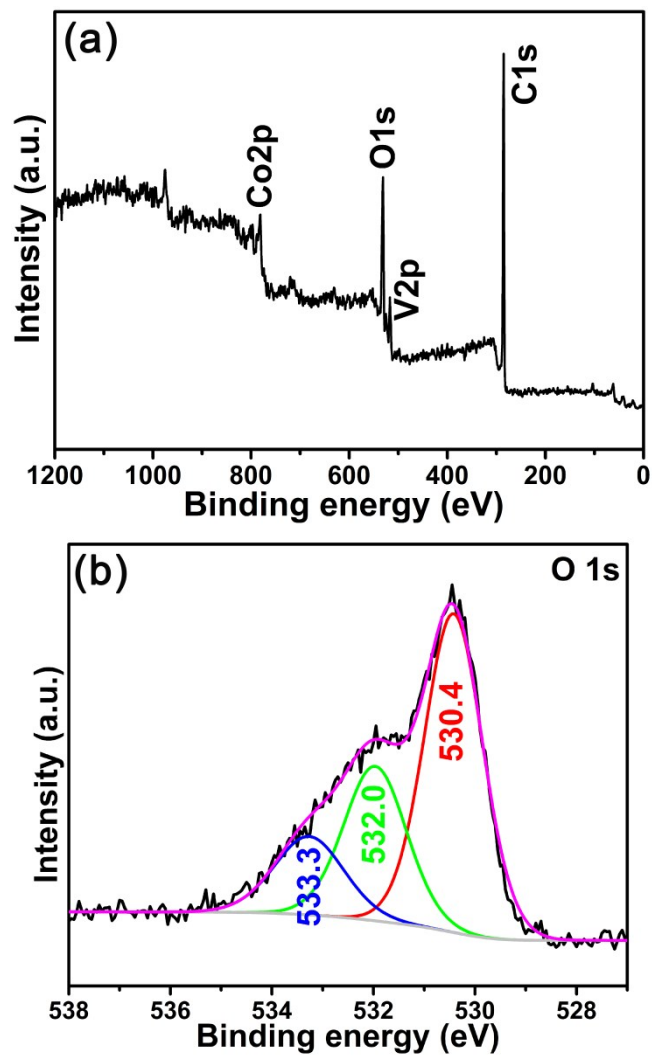


**Fig. S2** TG curve of CoVO/rGO composite.

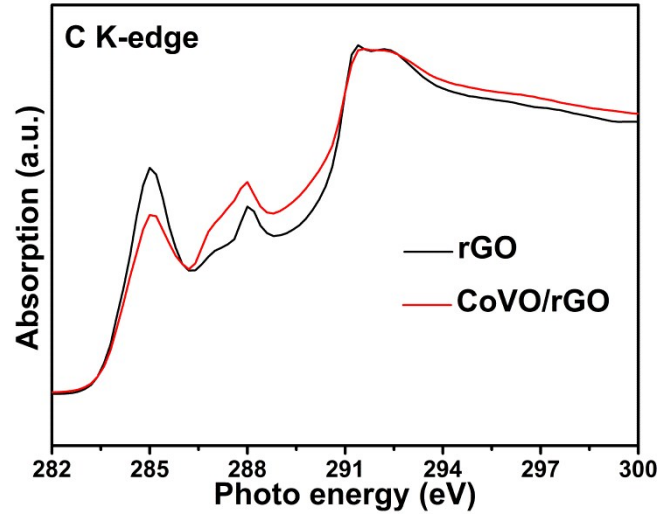
TGA curves for CoVO/rGO composite can be divided into two parts: from 45 °C to 200 °C and from 200 °C to 600 °C. In the first part, a mass loss of approximately 0.5% (wt %) is observed below 200 °C on the TG curve, which can be attributed to the desorption of adsorbed gaseous molecules (e.g., CO<sub>2</sub>, H<sub>2</sub>O). In the second part, the Co<sub>1.8</sub>V<sub>1.2</sub>O<sub>4</sub> phase was oxidized into Co<sub>3</sub>V<sub>2</sub>O<sub>8</sub> (Fig. S3), accompanying the complete removal of carbon. Based on the remaining weight percent of Co<sub>3</sub>V<sub>2</sub>O<sub>8</sub>, we can calculate the weight percent of 75.1% for Co<sub>1.8</sub>V<sub>1.2</sub>O<sub>4</sub>. Thus, the carbon content for the CoVO/rGO composite is approximately 24.4% (1 – 0.5% – 75.1%).



**Fig. S3** The XRD pattern of sample after TG test. All the diffraction peaks are consistent with the standard Co<sub>3</sub>V<sub>2</sub>O<sub>8</sub> phase (JCPDS No. 70-1393).



**Fig. S4** (a) The overall XPS spectra of CoVO/rGO composite, which clearly indicates the coexistence of elements Co, V, C, and O. (b) XPS spectra of O 1s region for CoVO/rGO composite.

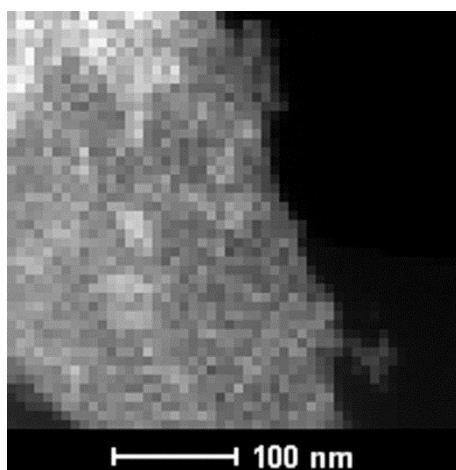


**Fig. S5** C K-edge XANES of rGO and CoVO/rGO. Compared to rGO, CoVO/rGO displays an obvious increase of C K-edge peak intensity at ca. 288 eV, corresponding to carbon atoms in rGO bonded with oxygen species. This strongly indicates the generation of metal–oxygen–carbon bonds in CoVO/rGO,<sup>[1,2]</sup> which is in agreement with XPS result.

**Related references:**

- [1] X. Zhou, L.-J. Wan, and Y.-G. Guo, *Adv. Mater.*, 2013, **25**, 2152–2157.
- [2] W. Huang, H. Wang, J. Zhou, J. Wang, P. N. Duchesne, D. Muir, P. Zhang, N. Han, F. Zhao, M. Zeng, *Nat. Commun.*, 2015, **6**, 10035.





**Fig. S6** The corresponding TEM image for elemental mapping of CoVO/rGO composite.

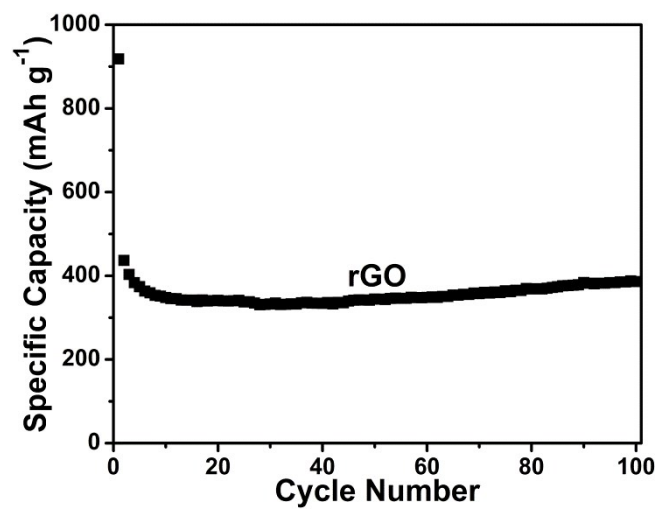


Fig. S7 Cycling performance of the rGO electrode at  $100 \text{ mA g}^{-1}$ .

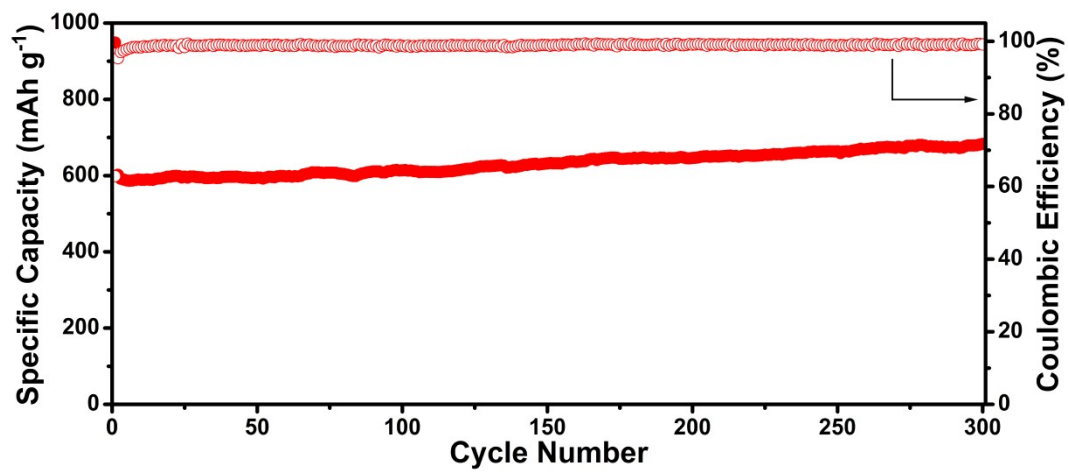
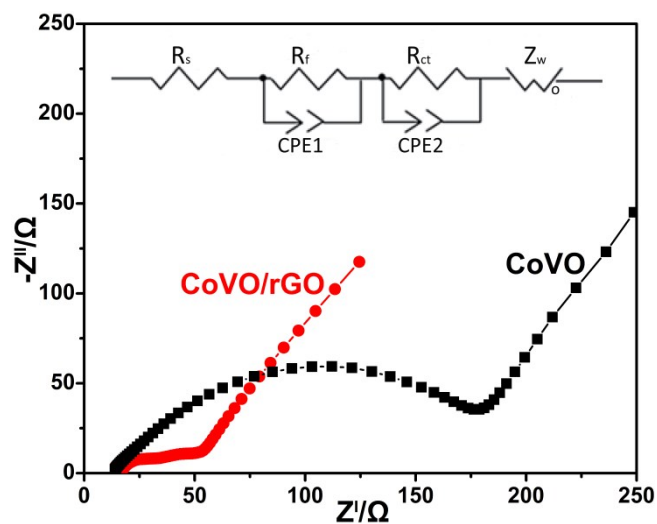


Fig. S8 Cycling performance and coulombic efficiency of the CoVO/rGO composite electrode at 2000 mA g<sup>-1</sup>.



**Fig. S9** Nyquist plots after five cycles at 100 mA g<sup>-1</sup> for CoVO and CoVO/rGO, respectively. The inset is the corresponding equivalent circuit.

**Table S1** Electrochemical impedance parameters of the CoVO and CoVO/rGO electrodes obtained from equivalent circuit fitting of experimental data.

Sample	Cycle number	Rs/Ohm	Rf/Ohm	Rct/Ohm
CoVO	after five cycle	13	66	130
CoVO/rGO	after five cycle	13	27	24

**Table S2** Electrochemical performance of recently reported cobalt vanadate anodes.

Anode	Rate performance (mA h g <sup>-1</sup> )	Cycling performance (mA h g <sup>-1</sup> )	Ref.
CoVO/rGO	789 (100 mA g <sup>-1</sup> )	683 at 300th cycles	This work
	628 (2000 mA g <sup>-1</sup> )	(2000 mA g <sup>-1</sup> )	
Co <sub>3</sub> V <sub>2</sub> O <sub>8</sub> ·nH <sub>2</sub> O HHPPs	800 (200 mA g <sup>-1</sup> )	847 at 255th cycles	26
	534 (2000 mA g <sup>-1</sup> )	(500 mA g <sup>-1</sup> )	
Co <sub>3</sub> V <sub>2</sub> O <sub>8</sub> Sponge	900 (100 mA g <sup>-1</sup> )	501 at 700th cycles	18
	543 (1600 mA g <sup>-1</sup> )	(1000 mA g <sup>-1</sup> )	
Co <sub>3</sub> V <sub>2</sub> O <sub>8</sub> -IHMs	923 (500 mA g <sup>-1</sup> )	562 at 300th cycles	24
	618 (2000 mA g <sup>-1</sup> )	(5000 mA g <sup>-1</sup> )	
rGO@Co <sub>3</sub> V <sub>2</sub> O <sub>8</sub> NPs	898 (200 mA g <sup>-1</sup> )	899 at 600th cycles	27
	471 (2000 mA g <sup>-1</sup> )	(200 mA g <sup>-1</sup> )	
Co <sub>3</sub> V <sub>2</sub> O <sub>8</sub> hollow nanofibers	970 (200 mA g <sup>-1</sup> )	1400 at 150th cycles	28
	570 (2000 mA g <sup>-1</sup> )	(500 mA g <sup>-1</sup> )	
T-Co <sub>3</sub> O <sub>4</sub> @Co <sub>3</sub> V <sub>2</sub> O <sub>8</sub>	916 (200 mA g <sup>-1</sup> )	706 at 500th cycles	29
	578 (2000 mA g <sup>-1</sup> )	(1000 mA g <sup>-1</sup> )	
Co <sub>3</sub> V <sub>2</sub> O <sub>8</sub> HMMSs	823 (100 mA g <sup>-1</sup> )	967 at 200th cycles	30
	545 (2000 mA g <sup>-1</sup> )	(500 mA g <sup>-1</sup> )	
Co <sub>2</sub> V <sub>2</sub> O <sub>7</sub> MHNPs	813 (200 mA g <sup>-1</sup> )	520 at 580th cycles	12
	518 (2000 mA g <sup>-1</sup> )	(2000 mA g <sup>-1</sup> )	
mCVO	650 (200 mA g <sup>-1</sup> )	623 at 500th cycles	31
	504 (1000 mA g <sup>-1</sup> )	(500 mA g <sup>-1</sup> )	
CVO-C-S	871 (100 mA g <sup>-1</sup> )	771 at 100th cycles	32
	389 (2000 mA g <sup>-1</sup> )	(200 mA g <sup>-1</sup> )	