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Vanadium doped graphitic carbon nitride for high performance lithium-sulfur batteries

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# Equal contribution

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1. Experimental section

1.1 Preparation of g-C_3N_4

60 g dicyandiamide was divided and loaded into three porcelain boats, which were heated in a tube furnace (Model: OTF-1200X) under air atmosphereat a rate of 5°C/min from room temperature to 550°C and held for 240 min. The yellow powder obtained after cooling to room temperature is the graphitic phase carbon nitride (g-C_3N_4).

1.2 Preparation of gC_3N_4-ND

A gas flask containing acetonitrile, placed in a water bath at 60 °C, was connected to upstream of the tube furnace with argon as the carrier gas. 2 g graphitic phase carbon nitride (g-C_3N_4) was laid flat in a porcelain boat and placed in the tube furnace and heated from room temperature to 500 °C for 240 min at a rate of 5 °C per

minute. After cooling to room temperature, the reddish-brown powder obtained is gC_3N_4-ND.

1.3 Preparation of V@gC_3N_4-ND1

2 g of gC_3N_4-ND (2g) was mixed with 2 g of vanadium acetylacetonate and dispersed in 500 ml of ethanol. The mixture was then dried in a blast drying oven (Model: 2X24) until the ethanol in the solution had evaporated completely, resulting in a solid complex of gC_3N_4-ND and vanadium acetylacetonate. The solid complex was placed in a tube furnace and maintained in an argon atmosphere for 120 min at a heating rate of 5 °C/min up to 550 °C. The black solid obtained was V@gC_3N_4-ND1. V@gC_3N_4-1 was prepared in exactly the same way as V@gC_3N_4-ND1, the only difference being that g-C_3N_4 was the support rather than the gC_3N_4-ND.

1.4 Preparation of V@gC_3N_4-ND2

The dried solid complex was placed in a tube furnace under an argon atmosphere and heated to 170 °C for 30 minutes at a rate of 5 °C per minute, then to 550 °C for 120 minutes at the same rate. The black solid obtained was V@gC_3N_4-ND2. V@gC_3N_4-2 was prepared in exactly the same way as V@gC_3N_4-ND2. The only difference is that g-C_3N_4 is the support rather than the gC_3N_4-ND.

1.5 Battery assembly

The prepared catalyst was mixed with the conductive carbon black and the binder polyvinylidene fluoride (PVDF) in a mass ratio of 8:1:1 and dispersed in isopropanol, which was then poured onto a PP separator (Celgard 2325) in a typical filtration process with a controlled surface loading of 0.4 mg cm^{-2}. The pre-dried commercial sulphur and BP2000 conductive carbon black (3:1 by mass) were ground and encapsulated in ampoules and kept at 155 °C for 12 h to prepare the carbon and sulphur composite (S@BP2000). Next, S@BP2000, Super P and PVDF were mixed

in a 7:2:1 mass ratio and dispersed in N-methyl-pyrrolidone (NMP). The resulting slurry was coated onto a clean aluminium foil and dried at 85 °C for 12 h to obtain a cathode. The coating thickness was controlled so that the surface loading of sulphur was approximately 1.2 g cm^{-2}. The batteries were assembled in a glove box filled with argon gas (water <0.01 ppm, oxygen <0.01 ppm) using LIR 2016 cases. The cathode, 25 µl electrolyte, modified separator, 15 µl electrolyte, and lithium tabs were placed in the positive case and sealed with the negative case before being encapsulated by a sealer for 3 s at approx. 1 MPa. The high sulphur loading battery was made with 0.2 M Li_2S_8 as active material on GDS 3250 carbon paper, the rest of the battery assembly conditions remaining unchanged.

1.6 Characterization methods

The morphology of the prepared samples was characterized by scanning electron microscopy (SEM, Nova Nano SEM 450, USA). Powder X-ray diffraction (XRD, S17 Lab XRD-7000 s, Japan) was used to analyse the crystal structure of the samples in the range of 5-80°. X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, UK) was used to investigate the valence states of the different elements.

1.7 Electrochemical tests

Cyclic voltammetry (CV) was tested at 1.7-2.8 V with a sweep rate of 0.1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was tested at a frequency of 0.01-10^5 Hz using the battery open circuit voltage as the starting voltage. The battery was assembled using GDS 3250 carbon paper as the working electrode and a lithium sheet as the reference electrode, with the counter electrodes separated by a PP separator. 20 µl of 0.2 M Li_2S_8 was added dropwise to the working electrode side and 20 µl of electrolyte to the counter electrode side. The batteries were first discharged at 0.112 mA to a voltage of 2.1 V with open circuit voltage as the starting voltage, then discharged at 2.05 V and the response current versus time was recorded and a Li_2S

deposition curve was obtained. The test platforms were LAND 3002A and CHE 760e respectively.

Figure S1. SEM images of (a) gC_3N_4-ND. (b) g-C_3N_4. (c) V@gC_3N_4-1. (d) V@gC_3N_4-2. (e) V@gC_3N_4-ND1. (f) V@gC_3N_4-ND2.

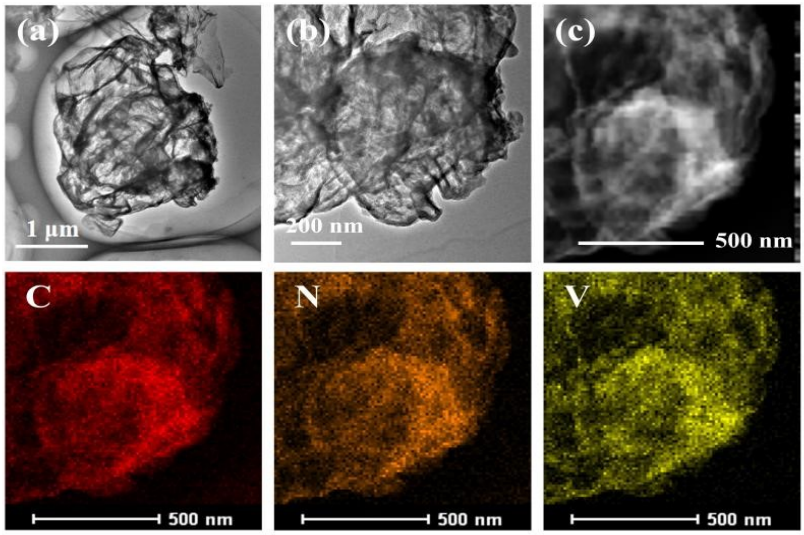

Figure S2. (a,b) High-resolution TEM image and (c) STEM image of V@gC_3N_4-ND2 and the corresponding elemental mapping of C, N, and V.

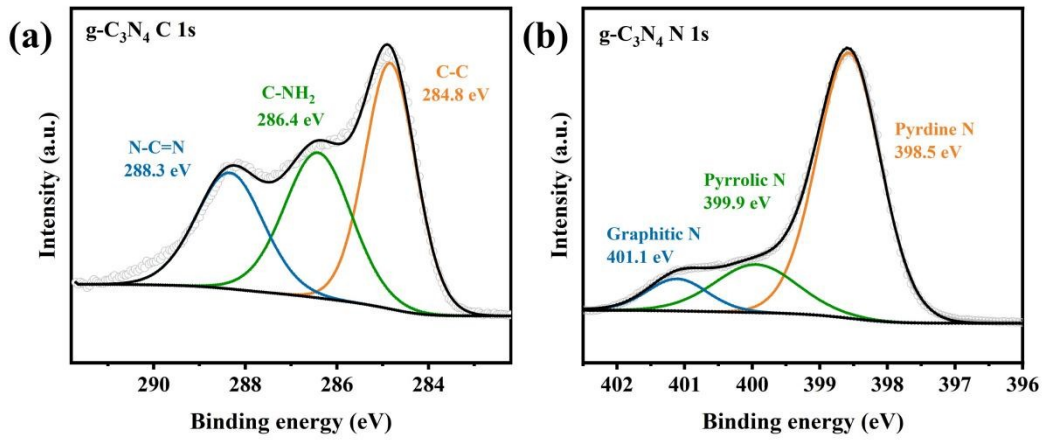

Figure S3. High-resolution (a) C 1s and (b) N 1s XPS spectra of g-C_3N_4.

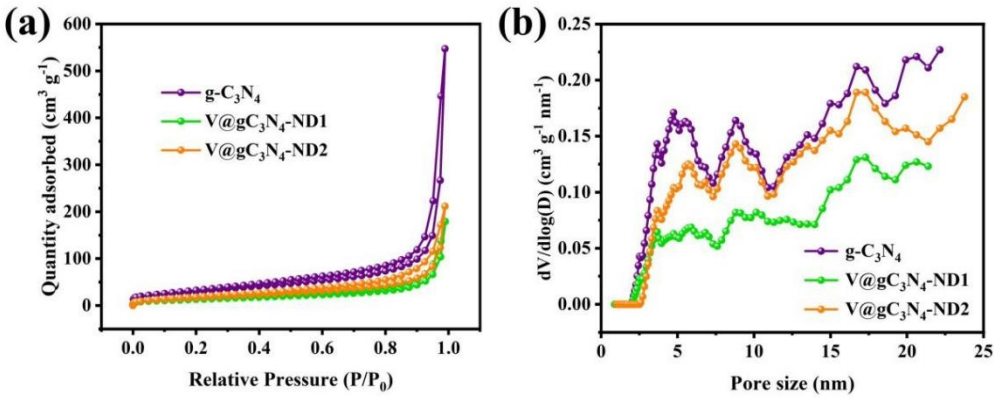

Figure S4. (a) N_2 adsorption/desorption isotherms and (b) pore size distributions of different catalysts.

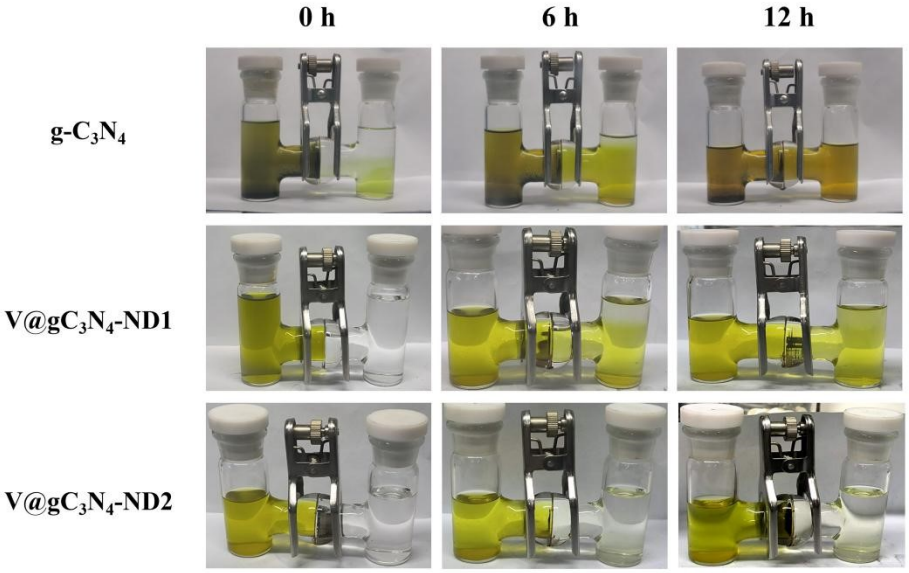

Figure S5. Polysulfide diffusion tests of the g-C_3N_4/PP, V@gC_3N_4-ND1/PP and V@gC_3N_4-ND2/PP separators.

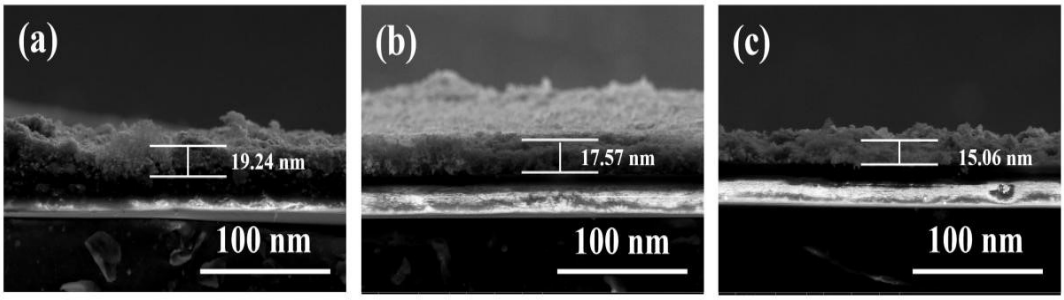

Figure S6. Coss-sectional SEM images of the g-C_3N_4, V@gC_3N_4-ND1 and V@gC_3N_4-ND2 modified separators.

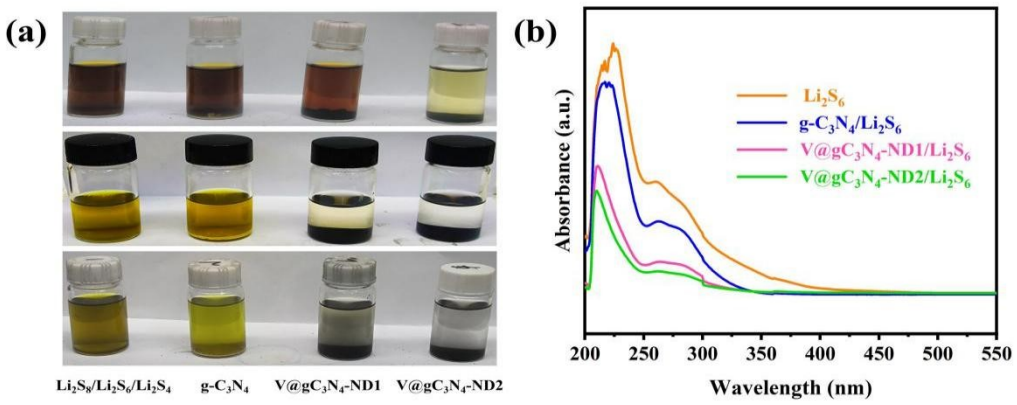

Figure S7. (a) Photographs and (b) UV−vis spectra of different samples soaked in the Li_2S_6 solution.

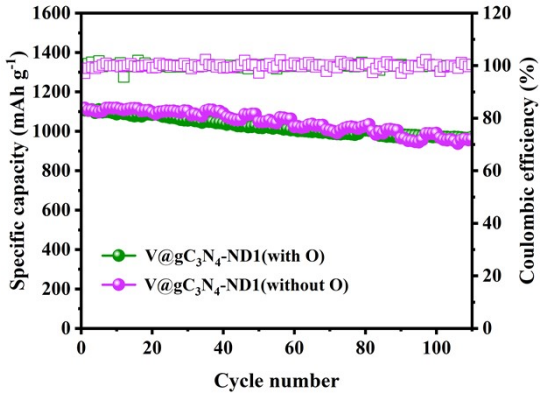

Figure S8. Cycle performances of the batteries assembled with oxygen-containing and oxygen-free V@gC_3N_4-ND1/PP separators at 0.5C.

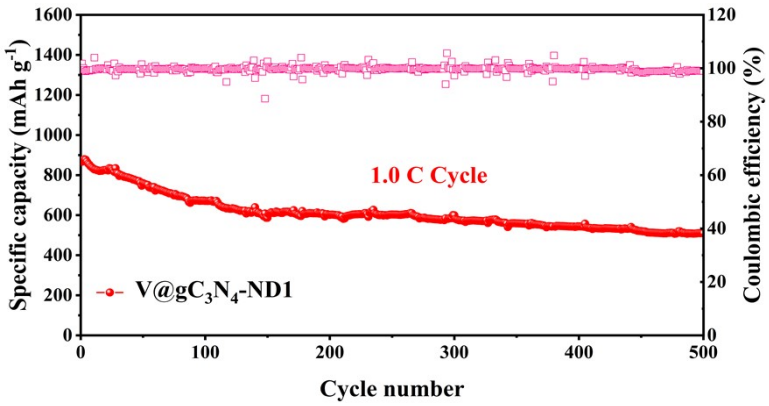

Figure S9. Cycle performance of the battery assembled with V@gC_3N_4-ND1/PP separator at 1C.

Table S1. Atomic percentage for several samples by EDS

Element	g-C_3N_4	gC_3N_4-ND	V@gC_3N_4-1	V@gC_3N_4-2	V@gC_3N_4-ND1	V@gC_3N_4-ND2
C	38.55	37.2	41.82	38.88	40.14	40.91
N	61.45	62.8	46.98	42.4	40.67	43.76
O	-	-	8.6	15.57	15.96	11.87
V	-	-	2.6	3.15	3.23	3.46