

Supplementary Information for

1-Dimensional AgVO₃ Nanowires Hybrid with 2-Dimensional Graphene Nanosheets to Create 3-Dimensional Composite Aerogels and its Improved Electrochemical Property

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Part I. Experimental details

Preparation

Preparation of Graphene Oxide

Graphene Oxide (GO) was synthesized from KS-6 using a modified Hummers method.¹ Briefly, KS-6 (2.0 g) was added to concentrated sulfuric acid (46 mL) under strongly stirring at 0 °C, and then potassium permanganate (6 g) was added slowly to keep the temperature of the suspension lower than 20 °C for 30 min. After this, the reaction system was transferred to a 35 °C water bath with stirring for 2 h, forming a thick paste. Next, 100 mL of water was added slowly to the above solution. Subsequently, the reaction system was transferred to a 95 °C water bath under vigorous agitation for another 15 min. Then, the suspension was diluted by 280 mL of water and treated with 6 mL of H₂O₂ (30%) to reduce residual permanganate to soluble manganese ions, and the color of solution turned from brown to golden yellow. Finally, the mixture was filtered and washed with 1:10 HCl aqueous solution (1000 mL) to remove metal ions followed by repeated washing with water and centrifugation to remove the acid, and dried in a vacuum oven at 60 °C for 24 h to obtain GO.

Preparation of AgVO₃ nanowires/Graphene Composite Aerogels, Pure Graphene Aerogels

AgVO₃ nanowires/Graphene Composite Aerogels were synthesized by using a hydrothermal method assisted by freeze-drying process. Firstly, GO (120 mg) was dispersed in 40 mL of water by sonication to make a GO aqueous dispersion. Next, NH₄VO₃ (0.46792g) was added to the GO aqueous dispersion and heated at 80 °C to completely dissolve NH₄VO₃. At the same time, AgNO₃ (0.67948 g) was dissolved in another 40 mL of water. After this, the GO aqueous dispersion with NH₄VO₃ was slowly added into the AgNO₃ solution with strongly stirring. Subsequently, the mixture was sealed in a 100 mL Teflon-lined autoclave and hydrothermally treated at 180 °C for 72 h. Finally, the resulting hybrid hydrogels were dialysis for 3 days in deionized water to remove the residual reducing agents, and freeze-dried (5×10^{-2} mbar at $T \leq -46$ °C) for 24 h to obtain AgVO₃ nanowires/graphene composite aerogels. For comparison, we have synthesized pure graphene aerogels. Typically, GO (120 mg) was dispersed in 80 mL of water by sonication, reaching a concentration up to 1.5 mg mL⁻¹. The resulting brown dispersion was sealed in an autoclave and heated at 180 °C for 72 h. The amount of GO used was 15% of AgVO₃ by weight, which was theoretically fabricated from 0.67948 g AgNO₃.

Characterization

The morphology and crystalline structure of the samples was investigated by field emission scanning electron microscopy (FE-SEM, Zeiss Supra 55) and high resolution transmission electron microscopy (HRTEM, JEM-2100F). X-ray diffraction (XRD) patterns were carried on a Shimadzu XRD-6000 diffractometer using Cu-K α radiation ($\lambda = 0.15406$ nm). Raman spectra were performed with a Renishaw RM2000 confocal Raman spectrometer with a 532 nm excitation laser. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Thermo Scientific ESCALAB 250 instrument equipped with Mg-K α X-ray source (1253.6 eV) at a pass energy of 30.0 eV. The binding energies obtained in the XPS analysis were calibrated for specimen charging by referencing the C 1s to 284.6 eV. The specific surface areas and the pore-size distributions were obtained at 77 K using the Brunauer-Emmett-Teller (BET) method with a Micromeritics ASAP2020 surface area and porosity analyzer. Before measurements, the samples were degassed at 80 °C for 12 h. The N₂ adsorption -desorption isotherm is fitted based on the Brunauer-Emmett-Teller (BET) model. The pore size distribution analysis is determined by the Barrett-Joyner-Halenda (BJH) method.

Electrochemical measurements were investigated using coin-cells with lithium metal as the counter and reference electrode. The working electrode was composed of 70% active materials, 20% acetylene black, and 10% polyvinylidene difluoride (PVDF) binder by weight. The above mixture was pressed onto an aluminum foil which served as a current collector. The electrode was dried at 120 °C in vacuum for 12 h. The electrolyte was 1 M LiPF₆ in EC-EMC-DMC (1: 1: 1 volume ratio). The cells were assembled in an argon-filled glove box. Galvanostatic discharge-charge measurements were performed at a potential range of 3.7-1.5 V vs. Li⁺/Li using a LAND-CT2001A test system (Wuhan, China) at room temperature. Cyclic voltammetry (CV) was carried out at a scan rate of 0.1 mV s⁻¹ using a CHI650D work station (Chenhua, Shanghai). The specific capacity and current density were based on the whole composite material.

Part II. Supplementary Figures

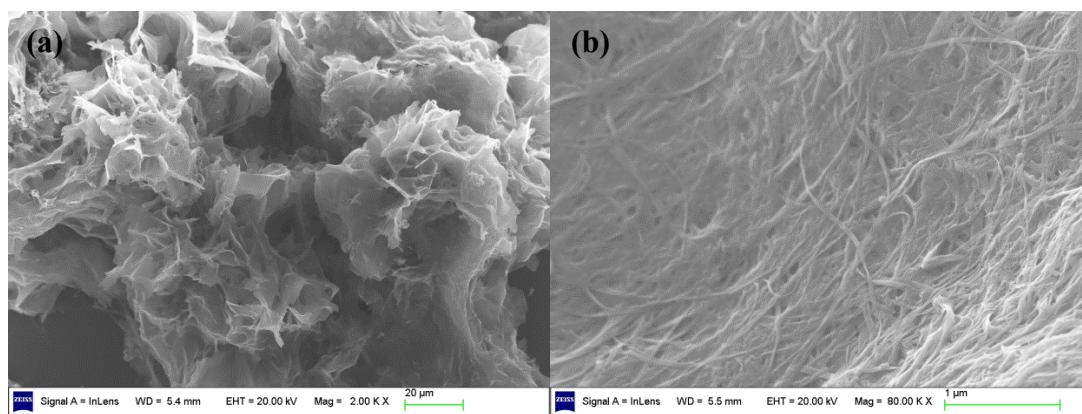


Fig. S1 SEM images of AgVO_3 /graphene composite hydrogels after hydrothermal self-assembly at 180 °C for 72 h.

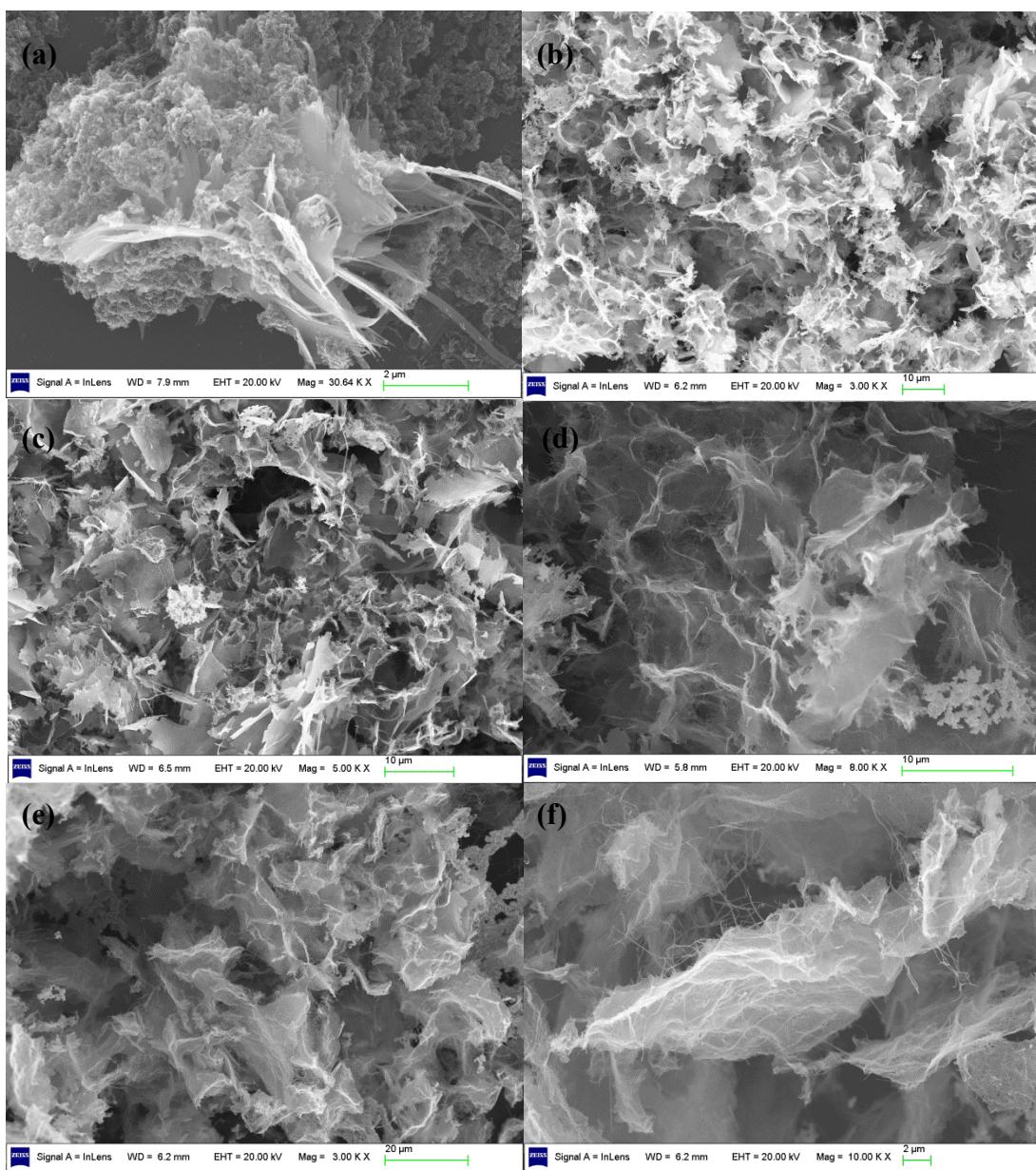


Fig. S2 SEM images of AgVO_3 /graphene composite aerogels after hydrothermal self-assembly at 180 °C for (a) 12 h, (b) 24 h, (c) 48 h, (d) 72 h, and (e, f) 96 h.

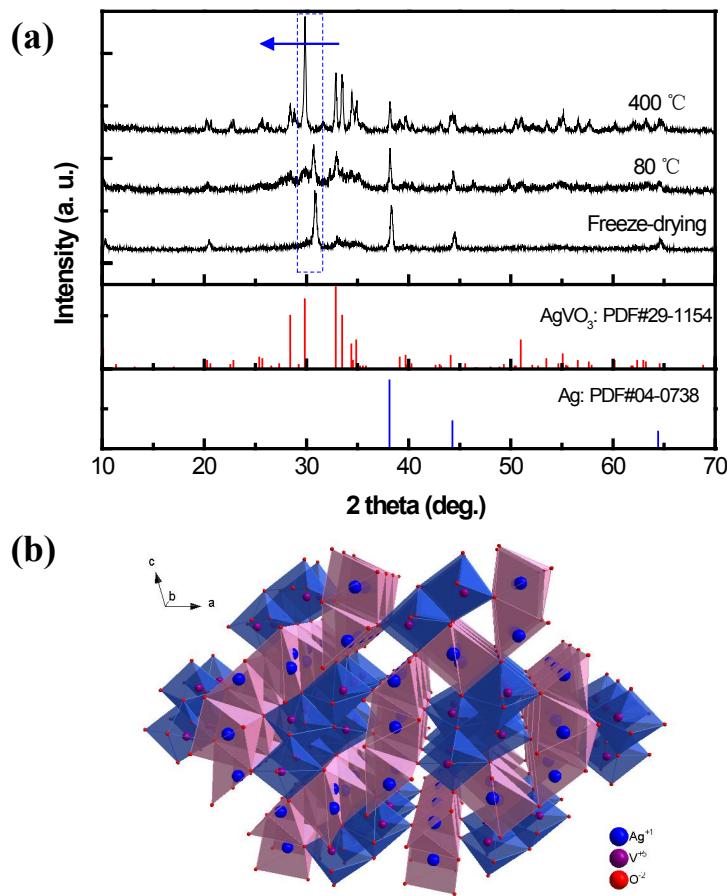


Fig. S3 (a) XRD patterns of AgVO₃/GAs after freeze-drying, 80 °C for 12 h in vacuum, and 400 °C for 2 h in air. (b) Crystal structure of β-AgVO₃.

The structure of AgVO₃/GAs was confirmed by X-ray diffraction (XRD). Fig. S3a displays XRD patterns of AgVO₃/GAs at different post treatment conditions, which are freeze-drying, 80 °C for 12 h in vacuum, and 400 °C for 2 h in air, respectively. The composite aerogels after freeze-drying consist of part of low crystallinity of AgVO₃ nanowires and some Ag particles (JCPDS card no. 04-0738), in which these Ag particles were incompletely used to prepare AgVO₃. However, with the improved treatment temperatures, the diffraction peaks intensity of Ag particles is gradually weakening, in contrast, the peaks of AgVO₃ become increasing sharp and intense, and all peaks can be readily indexed to the monoclinic β-AgVO₃ (JCPDS card no. 29-1154). No apparent diffraction peak of graphene is attributed to the small amount (13%) in the composite aerogels. Meanwhile, it is worth

noting that the diffraction peak at 29.837° for JCPDS card no. 29-1154 shifts to larger degree after freeze-drying, due to the decreased distance between the vanadium oxide sheets. With respect to β -AgVO₃ crystal structure (Fig. S3b), the silver interlayer is between the vanadium oxide sheets, and hence the shortage of Ag in silver interlayer of AgVO₃ leads to the shrunken layer distance after freeze-drying.

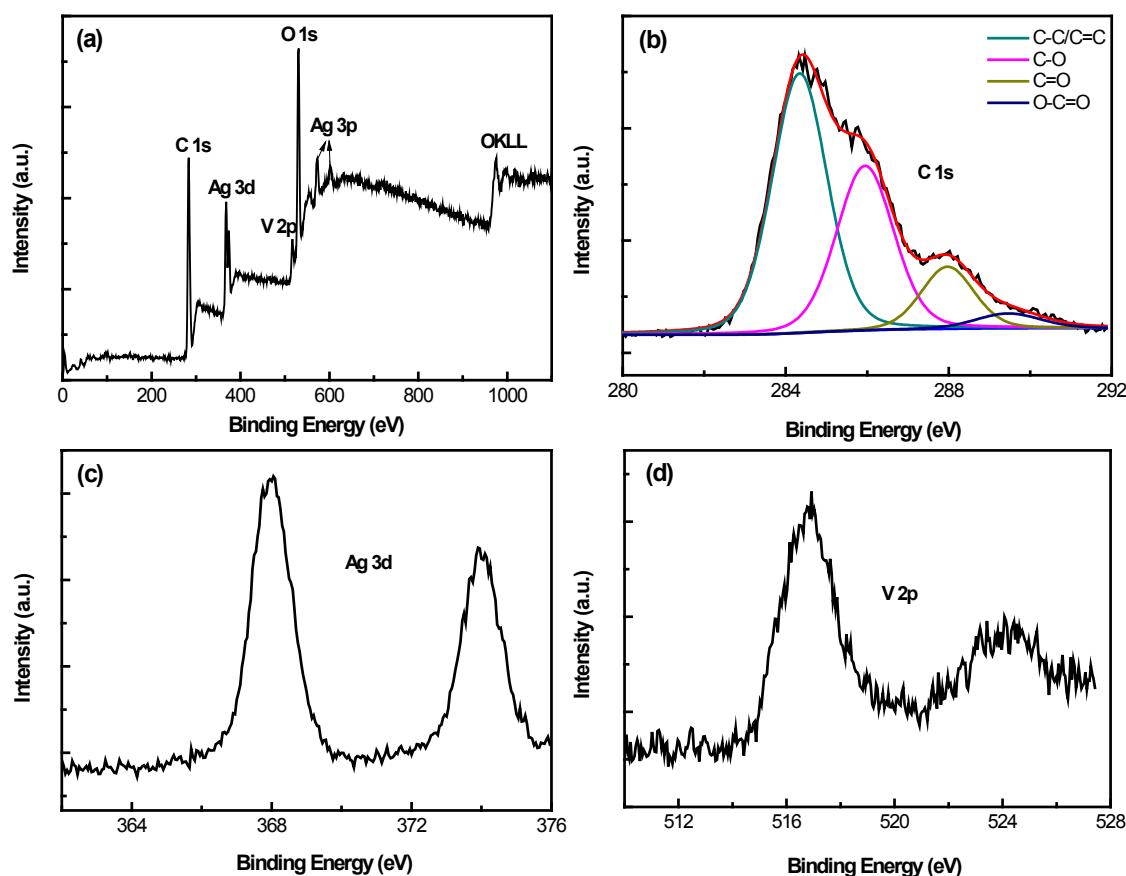


Fig. S4 (a) XPS survey spectrum of AgVO_3/GAs after freeze-drying. (b), (c), and (d) XPS core level spectra of C 1s, Ag 3d, and V 2p regions.

The chemical attribute of AgVO_3/GAs has been investigated by X-ray photoelectron spectroscopy (XPS) as shown in Fig. S4. No peaks of other elements except C, O, Ag, and V were observed in the survey spectrum (Fig. S4a), indicating the high purity of the composite aerogels. Fig. S4b shows C 1s XPS peaks at 284.34, 285.95, 287.97, and 289.46 eV, corresponding to C=C/C-C in aromatic rings, C-O (epoxy and alkoxy), carbonyl, and carboxyl groups, respectively. The corresponding components of Ag 3d and V 2p can be found in our previous work.²

Table S1 The comparison of electrochemical properties of different SVOs

Composition	Current density	Capacity (mAh g⁻¹) (cycle number)	Capacity retention (cycle number)
$\beta\text{-AgVO}_3$ nanowires ³	0.01 mA	302.1 (1)-90.6 (20)	30% (20)
Nanocrystalline $\text{Ag}_2\text{V}_4\text{O}_{11}$ ⁴	2C	305 (1)-100 (30)	32.8% (30)
$\text{Ag}_2\text{V}_4\text{O}_{11}$ /Ag nanobelts ⁵	20 mA g ⁻¹	276 (1)-30 (20)	10.9% (20)
$\beta\text{-Ag}_{0.33}\text{V}_2\text{O}_5$ nanoparticles ⁶	100 mA g ⁻¹	175 (1)-125 (30)	71.4% (30)
$\beta\text{-AgVO}_3$ nanorods ⁷	100 mA g ⁻¹	228.8 (1)-106 (30)	46.3% (30)
	400 mA g ⁻¹	202.7 (1)-65 (30)	32.1% (30)
$\beta\text{-AgVO}_3$ /PANI nanowires ⁸	30 mA g ⁻¹	211 (1)-131 (20)	62% (20)
This work	100 mA g ⁻¹	220 (1)-96 (50)	43.6% (50)
	50 mA g⁻¹	195.8 (1)-118.8 (50)	60.9% (50)
	100 mA g⁻¹	185 (1)-118.9 (50)	62.9% (50)
	400 mA g⁻¹	166.5 (1)-106.4 (50)	63.9% (50)
	800 mA g⁻¹	159.1 (1)-106.1 (50)	66.7% (50)
	1000 mA g⁻¹	143.9 (1)-116.4 (50)	80.9% (50)

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