

Facile synthesis of graphene-AgVO₃ nanocomposite with excellent supercapacitor performance

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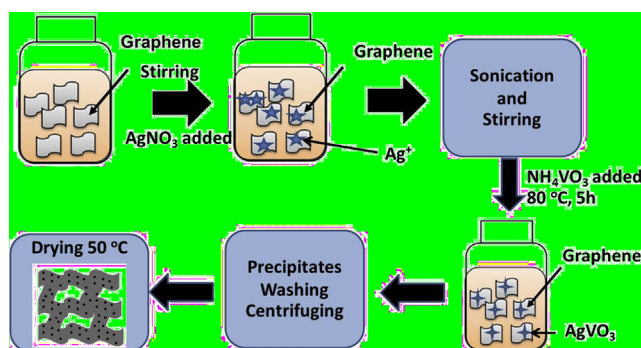
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HIGHLIGHTS

- Graphene-AgVO₃ nanocomposites were synthesized for supercapacitor application.
- The specific capacitance, cycle stability, and rate capability can be enhanced.
- Both the power and energy densities could be improved with the incorporation of AgVO₃.

GRAPHICAL ABSTRACT



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ABSTRACT

The graphene-AgVO₃ nanocomposites (GA30) were synthesized by facile one-step chemical-bath method. SEM and TEM images of the synthesized nanocomposites indicate that this method is possible to anchor the AgVO₃ nanoparticles onto the graphene surface. Galvanostatic charge-discharge (GCD) shows that specific capacitance, cycle stability, and rate capability of the supercapacitor device can be enhanced with AgVO₃ incorporation. The GA30 shows a high energy density of 10 Wh/kg at a power density of 25 W/kg as well as a high power density of 2045 W/kg at an energy density of 6 Wh/kg, which are much higher than those of graphene/activated carbon composites (GC30) and previous reported graphene-based composites. The improvement in specific capacitance, cycle stability, energy density and powder density of the graphene would be attributed to the special microstructure with high-rate transportation of both electrolyte ions and electrons due to the incorporation of AgVO₃.

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1. Introduction

The supercapacitors have attracted a great attention in recent years, since they exhibit cost-effectiveness, light weight, long life

time, broad operating temperature range, high power density, and eco-friendly energy storage [1,2]. Graphene shows the most interesting properties, i.e., electronic conductivity, mechanical flexibility, chemical stability, etc. [3–5], so the graphene-based materials are the potential electrode materials of supercapacitors. However, as-prepared graphene sheets tend to form irreversible agglomerates [6,7], the restacking of graphene layers would reduce the ion accessible surface area and the electrolyte diffusion [8]. So, the pure graphene electrodes usually have a low specific capacitance, for example, Stoller et al. reported the promising application of chemically modified graphene for supercapacitors with specific capacitance of 99 and 135 F/g in organic and aqueous electrolyte, respectively [9]. Therefore, many researchers are focusing on the graphene-based composites to further enhance specific capacitance of supercapacitors, i.e., MnO_2 [10,11], NiMoO_4 [12], ZnO [13], Co_3O_4 [14], etc. After incorporation of these materials onto graphene, the supercapacitor performance can be significantly enhanced. AgVO_3 , as a cathode active material in lithium primary batteries for implantable medical devices, shows high energy density and long-term stability [15]. Liang et al. [16] reported that the three-dimensional (3D) porous composite aerogels can be prepared via an innovative in situ hydrothermal method assisted by a freeze-drying process. The hybrid structure demonstrated that the one-dimensional (1D) AgVO_3 nanowires were uniformly dispersed on two-dimensional (2D) graphene nanosheet surfaces, resulting in the high discharge capacity, excellent capability, and good cycling stability for lithium ion batteries. Thus, AgVO_3 may have great improvement for the supercapacitor performance of graphene. Herein, the graphene- AgVO_3 nanocomposites were fabricated by using a facile precipitation method. AgNO_3 and NH_4VO_3 were selected as the precursor for the preparation of AgVO_3 . The in situ synthesized AgVO_3 anchor onto graphene surface can be the spacers and resulting in special microstructure of graphene with high-rate transportation of both electrolyte ions and electrons. The properties of prepared electrodes and supercapacitors have been studied.

2. Experimental details

Graphene powder (Wuxi Admas Technology, China) was dispersed in distilled (DI) water followed by ultrasonication for 1 h and stirring for 1 h to produce a homogeneous dispersion. AgNO_3 was added into the graphene solution and stirred for 12 h. Then the NH_4VO_3 was added into the solution followed by stirring for 5 h at 80 °C. Finally, the precipitated powder was washed by DI water and ethanol, and dried in an oven at 50 °C for 12 h. The as-synthesized graphene- AgVO_3 nanocomposite with 30 wt% of AgVO_3 is labeled as GA30. For comparison, the graphene-30 wt% activated carbon composite was also prepared by using the similar methods (GC30).

The morphologies of obtained nanocomposites were observed by scanning electron microscope (SEM, Hitachi S4800) and a transmission electron microscope (TEM, JEOL-ARM200F). X-ray diffraction (XRD) was characterized by an X-ray diffractometer (Rigaku A/MAX-Rb). X-ray photoelectron spectroscopy (XPS) was operated at 150 W with monochromatic Al K α (1486.6 eV) radiation with an ESCALAB 250. C 1s peak at 284.6 eV was the reference to analysis the binding energies of all elements.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on an Autolab electrochemical workstation. The GA30 and GC30 composite were used as a working electrode. A platinum foil and Ag/AgCl electrodes were used as the counter and reference electrodes, respectively. The testing was carried out at room temperature with a 6 M KOH solution as an electrolyte. The EIS measurements were performed over the frequency range, 0.1 Hz to 100 kHz, at the open circuit potential with

alternate current amplitude of 5 mV. The working electrodes were fabricated by mixing the as-synthesized composite (80 wt%) with 15 wt% acetylene black and 5 wt% polytetrafluorene binder. The mixed materials were rolled to a film and pressed onto nickel foam current collectors. Furthermore, the coin-type (2032) supercapacitor was also fabricated with two same electrodes. Galvanostatic charge-discharge (GCD) and the cycle stability were measured by LANHE battery testing system (Wuhan LANHE Electronic Co., Ltd.). The specific capacitance (C_s) of the electrode was calculated using the following equation: $C_s = 4It/mV$, where C_s , I , t , m , and V are the specific capacitance (F/g), discharging current (A), discharging time (s), mass of total active materials (g), and discharging potential range (V), respectively. The energy density and powder density of GA30 and GC30 can be calculated by the following equations [17]: $E = 0.5 CV^2/3.6$ and $P = E \times 3600/t$, where C is the device capacitance ($C = C_s/4$), V in V is the voltage during the discharge process after IR drop and t in seconds is the discharge process time.

3. Results and discussion

The AgVO_3 was employed to improve the supercapacitor performance of graphene using a one-step chemical-bath method (Fig. 1(a)). As shown in Fig. 1(a), the graphene was firstly dispersed in DI water using ultra sonication, then AgNO_3 was added in the graphene dispersion with 12 h stirring, resulting in the formation of homogeneous graphene- Ag^+ dispersion. Finally, the NH_4VO_3 was added into the solution followed by stirring for 5 h at 80 °C, the graphene- AgVO_3 nanocomposites can be prepared using the facile one-step chemical-bath method. The morphology of the GA30 was revealed by SEM and TEM. Fig. 1(b) and (c) show the SEM and TEM images of the synthesized nanocomposites respectively, the results indicate that the AgVO_3 nanoparticles can anchor onto the graphene surface.

The XRD pattern of the GA30 is shown in Fig. 2(a). The diffraction peaks reveal that all the plane reflections of the AgVO_3 crystal

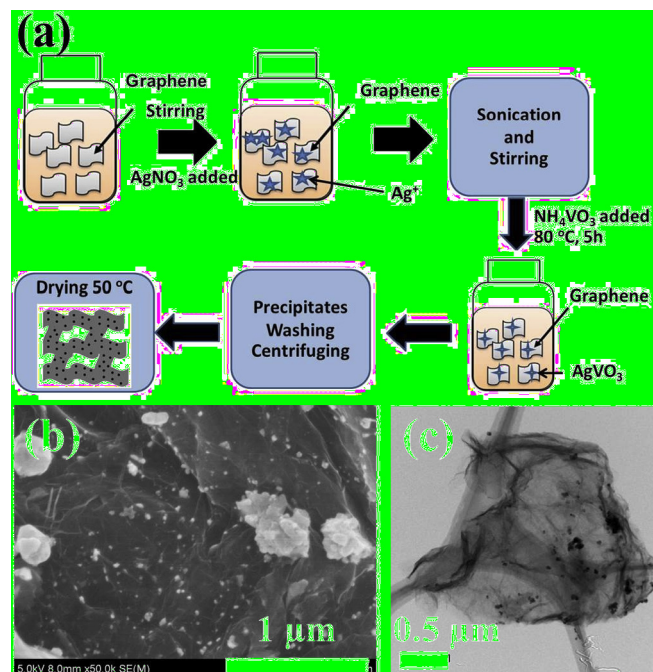


Fig. 1. (a) Synthesis illustration of graphene- AgVO_3 nanocomposites, (b) SEM image of graphene- AgVO_3 nanocomposites, (c) TEM image of graphene- AgVO_3 nanocomposites.

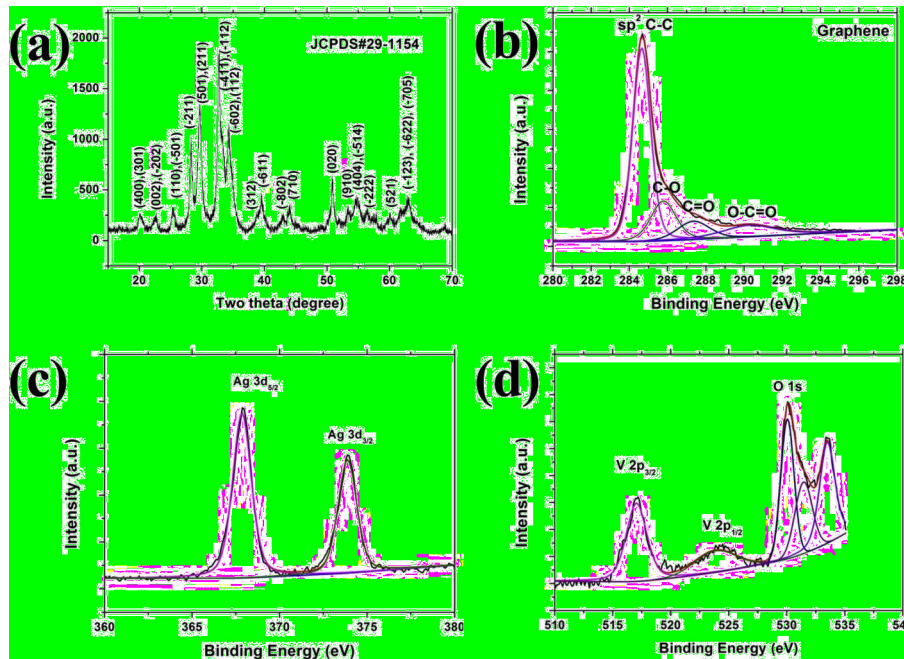


Fig. 2. XRD pattern of SEM image of graphene- AgVO_3 nanocomposites, and high resolution XPS spectra of SEM image of graphene- AgVO_3 nanocomposites (b) C1s, (c) Ag 3d, (d) V2p and O1s.

structure [18]. However, no obvious peak related to graphene was observed because of its low intensity. To understand further the surface information of the GA30 sample, the composition, chemical bonding, and the states of each element on the surface were studied by XPS. Fig. 2(b) represents the high-resolution C1s spectra. The C1s spectra can be fitted into four main peaks. The high-intensity peak located at 284.6 eV represents the sp^2 hybridized graphitic carbon. Three peaks centered at 285.8 eV, 287.4 eV, and 290.2 eV can be attributed to the C-O, C=O, and O-C=O groups, respectively. These peaks indicate that graphene is existed in the GA30 [19]. The detailed Ag 3d spectra are shown in Fig. 2(c), which shows the doublets characteristic of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ at 367.9 eV and 373.9 eV, respectively. The V 2p spectra (Fig. 2(d)) also show the doublets characteristic of V $2p_{3/2}$ and V $2p_{1/2}$ at 517.0 eV and 523.9 eV, respectively. Furthermore, the O 1s spectra (Fig. 2(d)) exhibit three peaks located at 530.0 eV, 531.4 eV, and 533.5 eV. The peaks at 530.0 eV and 531.4 eV can be assigned to lattice oxygen in the AgVO_3 , while the observed peak of O 1s at 533.5 eV may be ascribed to adsorbed oxygen [20]. According to the previous research [21,22], the appearance of Ag 3d and V 2p peaks can be identified as Ag^+ and V^{5+} , respectively. The XPS results further confirm the formation of AgVO_3 phase in the GA30 sample, which is in good agreement with the XRD, SEM, and TEM analysis.

To know the electrochemical properties of GA30 and GC30 electrode, the CV and EIS were investigated in 6 M KOH aqueous

electrolyte. Fig. 3(a) shows the CV measurement results of GA30 and GC30 at scanning rate of 20 mV/s. It can be seen that the CV curves of GA30 exhibit a better squareness than that of GC30, which reveal that GA30 nanocomposites have a larger capacitance than the graphene-activated carbon composites. Furthermore, the CV curves of the GA30 electrode at different scan rates from 5 to 20 mV/s were also measured (Fig. 3(b)). The CV shapes do not change significantly, indicating rapid ions transportation and good rate capability. The EIS of GA30 exhibits a semicircle with smaller diameter in high-frequency region comparing with the GC30 (Fig. 3(c)), which reveals that GA30 exhibits a smaller charge transfer resistance and lower impedance at the electrode/electrolyte interface due to the AgVO_3 incorporation. Moreover, the GA30 has approximately vertical line in low frequency region, it means that the GA30 has a smaller diffusive resistance of the ion diffusion from electrolyte solution to electrode surface than that of GC30.

The two-electrode symmetric supercapacitor was further assembled, and the capacitance performance of the supercapacitor device was tested. Fig. 4(a) shows the GCD curves at different current densities for symmetric supercapacitor of GA30. The nearly symmetric curves with a slight inflection in a potential range of 0–1 V indicate a good capacitive behavior. The specific capacitance of the GA30 and GC30 as a function of discharge current density is shown in Fig. 4(b). The specific capacitance decreases with the

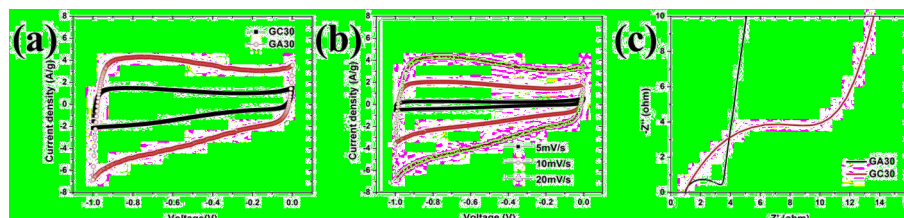


Fig. 3. (a) CV curves of GA30 and GC30 at scan rate of 20 mV/s, (b) CV curves of GA30 at different scan rate, (c) EIS of GA30 and GC30.

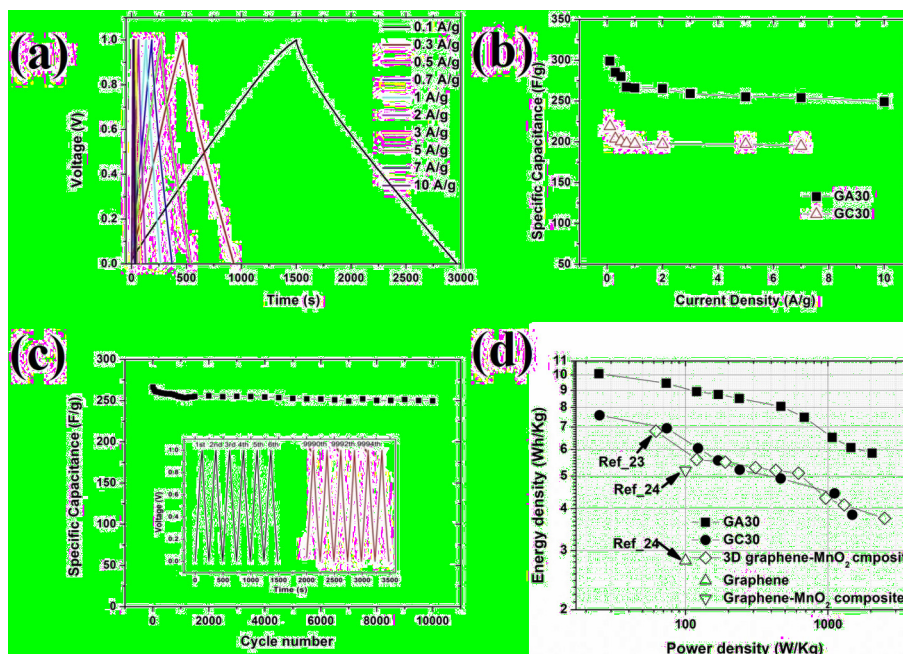


Fig. 4. GCD curves of GA30 at different current density, (b) specific capacitance of GA30 and GC30 as a function of current density, (c) cycle stability of GA30 (insert: initial and last 6 GCD cycle), (d) Ragone plots, compared with the values of similar symmetrical systems from refs 23 and 24.

current density increasing for both the GA30 and GC30 devices. The GA30 device exhibits much better capacitive performances than that of GC30. At 10 A/g, the GA30 still have a high Cs of 250 F/g, corresponding good rate retentions of 83.3%.

The long-term cyclic stability of GA30 devices was evaluated at a current density of 1 A/g within a potential range of 0–1 V (Fig. 4(c)). Fig. 4(c) and the inserted GCD curves show the stable performance of GA30 devices after 10000 cycles. The outstanding cycle stability also indicate that the AgVO_3 nanoparticles are firmly combine together with graphene frameworks which led to the excellent structural stability and porous structure for the electrolyte transport. The Ragone curves are also plotted in Fig. 4(d). The symmetric supercapacitor GA30 exhibits a high energy density of 10 Wh/kg at a power density of 25 W/kg for a 1 V window voltage, which are much higher than that of graphene/activated carbon composites (GC30). It also preserves 60% of its energy density as the power density increases to 2045 W/kg. These values are superior to the similar previously reported symmetrical systems 3D graphene- MnO_2 composite//3D graphene- MnO_2 composite (6.8 Wh/kg) [23], graphene//graphene (2.8 Wh/kg) [24], MnO_2 -graphene composite// MnO_2 -graphene composite (5.2 Wh/kg) [24]. The results demonstrate that the AgVO_3 nanoparticles can be anchored onto the graphene surface by this facile chemical bath method. The AgVO_3 nanoparticles could serves as a spacer to separate the thin graphene sheets, preventing them from stacking like pieces of paper. The obtained electrochemical, GCD, rate ability, and cycle stability can indicate that the incorporation of AgVO_3 can significantly enhance both energy and powder densities, which would be attributed to the special microstructure with high-rate transportation of both electrolyte ions and electrons due to the incorporation of AgVO_3 . The present results show an efficient way to enhance energy and powder densities of supercapacitors, and the influence of AgVO_3 percent will be further studied in our future work. In addition, the energy density could also be enhanced by using the asymmetrical supercapacitor design. Further study is still under way.

4. Conclusions

In summary, two kinds of graphene-based composite materials (GA30 and GC30) were prepared by simple chemical-bath methods. The excellent electrochemical performance of GA30 can be achieved due to the AgVO_3 anchored onto the graphene. The symmetric supercapacitor of GA30 exhibits a high energy density of 10 Wh/kg at a power density of 25 W/kg as well as a high power density of 2045 W/kg at an energy density of 6 Wh/kg, which are much higher than that of GC30. The present results afford a facile and efficient method to construct graphene for the improvement of the high capacitive performance of energy storage devices.

Acknowledgments

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