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Self-assembled three-dimensional hierarchical porous V$_2$O$_5$/graphene hybrid aerogels for supercapacitors with high energy density and long cycle life

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This paper describes the synthesis of hierarchical porous vanadium pentoxide (V$_2$O$_5$)/graphene hybrid aerogel through a low-cost and facile sol–gel method. The V$_2$O$_5$/graphene hybrid aerogel is synthesized through the in-situ growth of V$_2$O$_5$ nanofibers on graphene sheets. The V$_2$O$_5$/graphene hybrid aerogel-based supercapacitors exhibit enhanced specific capacitance (486 F g$^{-1}$), high energy density (68 Wh kg$^{-1}$) and outstanding cycle performance. These effects are attributed to the unique hierarchical porous structure of the hybrid aerogel.

Supercapacitors, which are also called electrochemical capacitors or ultracapacitors, bridge the gap between batteries and conventional solid-state and electrolytic capacitors because these supercapacitors exhibit high power density, superior rate capability, rapid charging/discharging rate, long operating lifetimes, and low maintenance cost.$^1$–$^2$ However, the energy density of supercapacitors is significantly lower than batteries and fuel cells.$^3$ The energy density (E) of a supercapacitor is governed by the specific capacitance (C) and cell potential (V) of a supercapacitor according to the equation $E = \frac{1}{2}CV^2$.$^4$ Thus, supercapacitors should enhance specific capacitance, which largely depends on the specific surface area of electrode materials.$^5$ Supercapacitors based on aerogels, especially carbonaceous aerogels (e.g., carbon, carbon nanotube, and graphene aerogels), exhibit a specific capacitance of 128 F g$^{-1}$; this high specific capacitance is attributed to the unique three-dimensional (3D) porous structure, low density, high conductivity, and large specific surface area of carbonaceous aerogels.$^6$–$^{11}$ Metal oxide/carbon hybrid aerogels have recently attracted considerable attention because these metal oxide/carbon hybrid aerogels exhibit composite structure of electrochemical double layer capacitors (EDLCs) and pseudocapacitors; these metal oxide/carbon hybrid aerogels exhibit higher capacitance than carbon-based supercapacitors, such as manganese oxide/carbon aerogel microbead composite (368 F g$^{-1}$),$^{12}$ nickel oxide/carbon aerogel composite (356 F g$^{-1}$),$^{13}$ tin oxide/graphene (310 F g$^{-1}$),$^{14}$ and manganese oxide/graphene hybrid aerogel (242 F g$^{-1}$)$^{15}$.

Composite aerogels are generally prepared by fabricating 3D aerogel skeletons and depositing or adsorbing active materials.$^8$–$^{16,17}$ Hydrothermal process is another feasible pathway of preparing composite aerogels; in this technique, a 3D framework structure of aerogel forms and combines with active materials.$^{18}$–$^{20}$ However, these methods exhibit poor compatibility and weak interaction between modified materials and aerogel substrates. A nonhomogeneous and unstable structure seriously affects electrochemical performance of supercapacitors.$^{18}$ To date, producing functional aerogel electrode materials for supercapacitors through appropriate routes remain a challenge.

This paper reports a mild and facile one-pot sol–gel process to synthesize 3D V$_2$O$_5$/graphene hybrid aerogel (V$_2$O$_5$/GN-Ae) by in-situ self-assembly of V$_2$O$_5$ nanofibers and graphene sheets for the first time. The V$_2$O$_5$/GN-Ae exhibits 3D hierarchical porous structure, good mechanical strength, and stable pore geometry and pore size. The hybrid aerogel-based supercapacitors demonstrate enhanced specific capacitance, high power and energy densities, and excellent cycle stability. These properties are attributed to the synergistic effect of the EDLCs (graphene) and the pseudocapacitors (V$_2$O$_5$). Moreover, the V$_2$O$_5$/GN-Ae aerogels do not require harsh
conditions during fabrication compared with common aerogel composites. Thus, the V$_2$O$_5$/GN-Ae aerogels are easily controlled and mass produced.

Fig. 1 shows the preparation and structure of the V$_2$O$_5$/graphene hybrid aerogel. First, we prepared a functionalized V$_2$O$_5$ sol from a relatively cheap commercial V$_2$O$_5$ powder. Cheap V$_2$O$_5$ powder was used to avoid the use of costly vanadium precursors (e.g., vanadium oxytripropoxide and metavanadate) (Experimental Section in ESI†). The as-prepared light yellow sol was composed of vanadium oxide (VO$_x$) oligomers; Scheme S1† shows the possible chemical reaction pathway in producing V$_2$O$_5$ sol.21-23 Graphene oxide (GO) aqueous solution was then added in the V$_2$O$_5$ sol under vigorous stirring to induce hydrolysis and in-situ recombination of the GO sheets and the VO$_x$ oligomers. A dark red VO$_x$/GO hybrid gel was obtained after about 5 min because of the rapid formation of vanadium intermediate phases and growth of nanofibers. The gel was aged for 2 day,24 and the gel gradually changed to a deep green hydrogel (VO$_x$/GO-Hy), which indicated the presence of V$^{4+}$.25 The VO$_x$/GO hybrid aerogel (VO$_x$/GO-Ae) was obtained after solvent replacement, and supercritical CO$_2$ drying or freeze drying was performed. Shrinkage was not observed during the drying process because of the stable skeleton structure of the 3D architecture. The as-prepared aerogel was then annealed in air at 300 °C to thermally reduce the graphene is reduced, and a mixture of the V$_2$O$_5$ and graphene is present in the as-prepared aerogel (Figs. S2 and S3 in ESI†). Moreover, the GO is reduced, and a mixture of the V$_2$O$_5$ and graphene is present in the as-prepared aerogel (Figs. S2 and S3 in ESI†). The morphology and structure of the as-prepared aerogels are further investigated by field emission-scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM). Figs. 3b and 3c illustrate that the 3D VO$_x$ architecture is composed of randomly arranged VO$_x$ nanofibers. The curled nanofibers are typically several micrometers long and dozens of nanometers in diameter. The noncrystalline VO$_x$ nanofibers become shorter and straight after the aerogel is thermally treated because the V$_2$O$_5$ partly crystallized (Figs. 3e, 3f, and S4 in ESI†). This result corresponds to the result of X-ray diffraction (Fig. S5†). Figs. 3h, 3i, 3k, and 3l strongly confirm that the V$_2$O$_5$ nanofibers grow along the graphene sheets during the treatment. This result validates the oxidation of V$^{4+}$.32 Obviously, the color of the graphene composite aerogels is darker than the V$_2$O$_5$ aerogels because the presence of graphene in the graphene composite aerogels. The results of the Fourier transform infrared (FTIR) spectrophotometry and Raman spectroscopy show that the GO is reduced, and a mixture of the V$_2$O$_5$ and graphene is present in the as-prepared aerogel (Fig. S2 and S3 in ESI†). Moreover, the aerogel exhibits uniform color, which indicates that the V$_2$O$_5$ and graphene sheets are homogeneously incorporated in the aerogel.

The morphology and structure of the as-prepared aerogels are further investigated by field emission-scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM). Figs. 3b and 3c illustrate that the 3D VO$_x$ architecture is composed of randomly arranged VO$_x$ nanofibers. The curled nanofibers are typically several micrometers long and dozens of nanometers in diameter. The noncrystalline VO$_x$ nanofibers become shorter and straight after the aerogel is thermally treated because the V$_2$O$_5$ partly crystallized (Figs. 3e, 3f, and S4 in ESI†). This result corresponds to the result of X-ray diffraction (Fig. S5†). Figs. 3h, 3i, 3k, and 3l strongly confirm that the V$_2$O$_5$ nanofibers grow along the graphene sheets during
hydrolysis. GO can disperse in water and form a stable dispersion.\textsuperscript{33} TheVO\textsubscript{x} oligomers coordinate with GO at the start of hydrolysis, and a homogeneous 3D structure forms, which benefits from the good dispersity of the GO. The network structure is “frozen” and preserved because of the gelation process; thus, uniform incorporation is observed (Figs. 3m to 3p).

The densities of the V\textsubscript{2}O\textsubscript{5} aerogel and the V\textsubscript{2}O\textsubscript{5}/GN hybrid aerogel are 26.3 and 27.7 mg cm\textsuperscript{-3}, respectively. The weight of the hybrid aerogel is so light that it can be lifted by a feather (Fig. 4a). Fig. 4b shows that the V\textsubscript{2}O\textsubscript{5}/graphene composite aerogel exhibits excellent mechanical property. Moreover, the aerogel is strong enough to support a 100 g weight, which indicates the excellent stability of the 3D aerogel structure.

The pore structure of the V\textsubscript{2}O\textsubscript{5}/graphene composite aerogel is investigated by nitrogen adsorption–desorption measurements. Fig. 4c shows that the adsorption–desorption curves exhibit type-IV adsorption hysteresis loops. This finding indicates that the structure is mesoporous.\textsuperscript{34} Furthermore, the pore size distribution of the aerogel, which is calculated by the Barrett–Joyner–Halenda (BJH) method, ranges from 1 nm to 100 nm. This result demonstrates that the composite aerogel exhibits hierarchical macro-, meso-, and microporous structures (inset in Fig. 4c). The macropores can act as a bulk buffering reservoir for electrolytes to minimize diffusion distances to interior surfaces.\textsuperscript{35} The mesopores provide a large accessible surface area for ion transport/charge storage, and micropores strengthen the electric double layer capacitance.\textsuperscript{36, 37} Brunauer–Emmett–Teller (BET) analysis reveals that the specific surface area and total pore volume of the V\textsubscript{2}O\textsubscript{5}/graphene hybrid aerogel are 172 m\textsuperscript{2} g\textsuperscript{-1} and 0.53 cm\textsuperscript{3} g\textsuperscript{-1}. These values are higher than those of the as-prepared V\textsubscript{2}O\textsubscript{5} aerogel (60 m\textsuperscript{2} g\textsuperscript{-1} and 0.15 cm\textsuperscript{3} g\textsuperscript{-1}, respectively). The surface area of the V\textsubscript{2}O\textsubscript{5}/graphene hybrid aerogel is also higher compared with those of the 3D V\textsubscript{2}O\textsubscript{5} architecture (133 m\textsuperscript{2} g\textsuperscript{-1}),\textsuperscript{32} V\textsubscript{2}O\textsubscript{5}/graphene composite (64 m\textsuperscript{2} g\textsuperscript{-1}),\textsuperscript{38} graphene/Fe\textsubscript{3}O\textsubscript{4} nanoparticle aerogel (95.22 m\textsuperscript{2} g\textsuperscript{-1}),\textsuperscript{31} and MnO\textsubscript{2} nanowire/graphene composite (107 m\textsuperscript{2} g\textsuperscript{-1}).\textsuperscript{39}
in comparison with graphene hydrogel electrodes(1, ref. 41), V2O5 nanotube electrodes (*, ref. 42), graphene/V2O5 nanobelt composite electrodes(<, ref. 43) and MnO2 nanorod/graphene-V2O5 nanowire/graphene hybrid electrodes(\textcircled{4}, ref. 44) and (h) Electrochemical impedance spectra (EIS) of raw V2O5 powder, V2O5 aerogel and V2O5/GN aerogel composite. The unique hierarchical porous structure of the V2O5/graphene hybrid aerogel makes it an excellent candidate in energy storage. We evaluated the electrochemical behavior of the V2O5/graphene hybrid aerogel as electrodes of supercapacitors in symmetric two-electrode cells using 1 M Na2SO4 aqueous solution as electrolyte. For comparison, the electrochemical properties of V2O5 aerogel and raw V2O5 powder were also tested under the same conditions and the results are shown in Fig. 4d. The nearly rectangular cyclic voltammetry (CV) curve and redox peaks of the V2O5/graphene hybrid aerogel indicate the synergistic effect of the electrochemical double layer capacitors and pseudocapacitors. We also measured the galvanostatic charge/discharge behaviors of the V2O5/graphene hybrid aerogel at various current densities from 0.5 A g\(^{-1}\) to 10 A g\(^{-1}\) to understand the high electrochemical performance of the aerogel. Fig. 4e shows the results of the test conducted. The specific capacitance of the V2O5/graphene composite aerogel is 486 F g\(^{-1}\) at a current density of 0.5 A g\(^{-1}\). The obtained specific capacitance is much higher than the V2O5 aerogel (233 F g\(^{-1}\)) and raw V2O5 (157 F g\(^{-1}\)) (Figs. S6–8 in ESI†).

The cycle stability of the 3D hybrid aerogel is also evaluated at a constant current density of 10 A g\(^{-1}\). Fig. 4f shows that the V2O5/graphene hybrid aerogel exhibits excellent cycling performance even after 20000 charge–discharge cycles, and 90% of the specific capacitance is retained, which is comparable to EDLCs. Fig. 4g compares the energy density and power density derived from the galvanostatic charge/discharge characteristics of different prototype supercapacitors. Remarkably, the V2O5/graphene hybrid aerogel exhibits a high energy density of 68 Wh kg\(^{-1}\) at a power density of 250 W kg\(^{-1}\). This result indicates the outstanding high-energy performance of the V2O5/graphene hybrid aerogel. The enhanced specific capacitance, high power and energy densities, and long cycle life of the hybrid aerogel electrode is attributed to the unique hierarchical porous structure of the hybrid aerogel. The interconnected network of the V2O5 can shorten diffusion distances from external electrolytes to interior surfaces and improve ion accessibility in the 3D framework. The graphene sheets within the hybrid aerogel can serve as multi-dimensional pathways to transport electrons and reduce charge transfer resistance (Fig. 4h). Finally, the combined EDLCs and pseudocapacitors can simultaneously increase specific capacitance and cycling stability.\(^5, 31, 45\)

**Conclusions**

In summary, we successfully fabricated a V2O5/graphene hybrid aerogel at ambient pressure through a simple sol-gel method from commercial V2O5 powder for the first time. The V2O5 nanofibers are anchored and in-situ grown on the graphene surfaces through coordination effect. Thus, a homogeneous and stable hybrid aerogel structure formed. The fabricated 3D hybrid aerogel exhibits low density(27.7 mg cm\(^{-3}\)), large specific surface area (172 m\(^2\) g\(^{-1}\)), and favorable mechanical strength. Moreover, the 3D hybrid aerogel displays hierarchical macro-, meso-, and microporous structures. In addition, the V2O5/GN-Ae-based supercapacitor exhibits enhanced specific capacitance (486 F g\(^{-1}\)), high energy density (68 Wh kg\(^{-1}\)) and long cycle life (>20000 cycles). These effects are caused by the hierarchical porous structure of the aerogel. We believe that the fabricated 3D V2O5/graphene hybrid aerogel can be used in broad applications, such as lithium ion batteries, sensors, electronics, analysis, and adsorbents, because of the unique structure of these aerogels.

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A self-assembled three-dimensional hierarchical porous V$_2$O$_5$/graphene hybrid aerogel for high-performance supercapacitor.