Two-Dimensional Nanoporous MnO$_2$ with Enhanced Supercapacitor Performance

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1. Background

In recent decades, supercapacitors have attracted much attention because of their higher power density, longer cycle life than batteries, and their higher energy density compared to conventional capacitors [1]. MnO$_2$ is known as a promising electrode material for applications in supercapacitors and has raised much interest because of its environmental friendliness, low cost, and high theoretical specific capacitance [2]. Unfortunately, MnO$_2$ usually delivers a low specific capacitance due to a low specific surface area. To a great extent, nanoscale MnO$_2$ particles possess large surface area and relatively high specific capacitance, but the microstructure is easily damaged during electrochemical cycling, giving a relatively poor electrochemical stability [3]. Graphitic carbon nitride with the C$_3$N$_4$ stoichiometry is considered as an analogue of graphite, and possesses a stacked 2D structure, which composed of the condensed tri-s-triazine subunits with a periodic array of carbon vacancies [4-6]. As far as we know, transmitting the morphology of 2D nanoporous structure from C$_3$N$_4$ to as-prepared metal oxides has rarely been reported.

2. Aims

The in situ formation of MnO$_2$ nanoparticles on the framework of Carbon Nitride (C$_3$N$_4$) may result in the same structure of MnO$_2$ by morphology transmission, leading to the improved electrochemical performance like capacitance. Our purpose is to design a facile and green route for the synthesis of 2D nanoporous MnO$_2$ as stable electrode materials for enhanced performance supercapacitor.

3. Methods

As shown in Figure 1, C$_3$N$_4$ dispersion was produced by exfoliation of bulk C$_3$N$_4$ in NMP by bath sonication [8]. With the introduction of KMnO$_4$, aqueous solution into the C$_3$N$_4$ dispersion system, the carbon atoms of C$_3$N$_4$ framework would react with MnO$_2$ in situ to form nanoporous MnO$_2$. The mixture was kept standing under ambient conditions for 12 h, at which time all the carbon atoms of C$_3$N$_4$ were replaced by MnO$_2$ molecules, then the samples of 2D nanoporous MnO$_2$ can be achieved.

4. Results

The electrochemical performance of 2D nanoporous MnO$_2$ was characterized using CV and galvanostatic charge-discharge measurements in 1 M Na$_2$SO$_4$ solution. As shown in Figure 2, the rectangular and symmetric CV curves of as-synthesized MnO$_2$ indicate the ideal capacitive behavior of the as-fabricated electrode. And it exhibits a good capacitance, reaching 327.31 F·g$^{-1}$, which is much more competitive than pure C$_3$N$_4$ (9.15 F·g$^{-1}$) and nano-MnO$_2$ (211.2 F·g$^{-1}$) [7]. Moreover, during the charging and discharging steps there is still around 86% initial capacitance retention even when the current density increases 20 times. Additionally, when the charge-discharge was cycled at 500 mA·g$^{-1}$, there is only a slight decrease in capacitance of less than 15% even after 1000 cycles, demonstrating a great stability.

5. Conclusions

A general procedure by in situ substituting the carbon atoms in the framework of C$_3$N$_4$ to produce 2D nanoporous MnO$_2$ has been developed. The as-synthesized MnO$_2$ not only introduce more electrochemical active specific surfaces for absorption/desorption of electrolyte ions, but also bring additional interfaces at the periodic vacancies to facilitate charge transport during charging/discharging processes. The unique structural design for supercapacitors electrodes enables great performance enhancements compared to nanoscale MnO$_2$ electrodes, exhibiting high specific capacitances, excellent rate capability and cycling stability. Such 2D nanoporous material is expected to be a highly promising candidate for application in high-performance energy storage systems.

Reference