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Single-step flash-heat synthesis of red phosphorus/graphene flame-retardant composite as flexible anodes for sodium-ion batteries

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ABSTRACT

Red phosphorus (RP) has attracted considerable attention as the anode for high-performance Na-ion batteries, owing to its low cost and high theoretical specific capacity of ~ 2,600 mAh/g. In this study, a facile single-step flash-heat treatment was developed to achieve the reduction of graphene oxide (GO) and the simultaneous deposition of RP onto the reduced graphene oxide (rGO) sheets. The resulting RP/rGO composite was shown to be a promising candidate for overcoming the issues associated with the poor electronic conductivity and large volume variation of RP during cycling. The RP/rGO flexible film anode delivered an average capacity of 1,625 mAh/g during 200 cycles at a charge/discharge current density of 1 A/g. Average charge capacities of 1,786, 1,597, 1,324, and 679 mAh/g at 1, 2, 4, and 6 A/g current densities were obtained in the rate capability tests. Moreover, owing to the RP component, the RP/rGO film presented superior flame retardancy compared to an rGO film. This work thus introduces a highly accessible synthesis method to prepare flexible and safe RP anodes with superior electrochemical performance toward Na-ion storage.

1 Introduction

Li-ion batteries have achieved considerable success as power sources of portable devices and electrical vehicles because of their superior specific energy density, Coulombic efficiency, and cycling stability [1, 2]. Na-ion batteries represent one of the main alternatives to the Li-ion ones, and have attracted increasing attention because of the abundance of sodium in both the earth's crust and the oceans [3–6]. Phosphorus plays a major role among various anode materials for Na-ion batteries, owing to its high theoretical specific capacity of ~ 2,600 mAh/g [7]. Despite the excellent performance of black P toward

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Na-ion storage [8–10], red P (RP) is the most cost-effective allotrope among phosphorus forms with adequate chemical stability for battery applications. Moreover, the incorporation of RP can potentially enhance the flame retardancy of the electrodes, because this material has been widely used as an effective flame retardant additive for decades [11]. However, micron-sized RP particles have been proven unsuitable for stable Na-ion storage, owing to their poor electronic conductivity and huge volume expansion during the sodiation process [12]. To produce nanosized RP, several studies utilizing the ball-milling technique with conductive materials such as carbon nanotubes, carbon nanofibers and graphene stacks have been reported [13–15]. Despite the encouraging improvements achieved in these studies, various complex issues ascribed to the simple mechanical mixing, such as the non-uniform particle size and the poor contact between the RP active material and the conductive platforms, still hamper the optimization of the electrochemical performance of RP anodes. Traditional vaporization–condensation methods, recently employed to prepare RP anodes, led to impressive performance enhancements relative to the micron-sized RP particles, owing to the uniform size of the RP particles and the good contact between the active material and the conductive scaffold [16–19]. However, the sophisticated synthetic processes involved in such methods, which involve sealing in quartz ampoules, introduce significant challenges associated with their productivity and scalability.

Herein, we report a facile flash-heat treatment to grow nanosized RP on the surface of reduced graphene oxide (rGO) sheets and in the void spaces between rGO layers; in particular, the RP deposition and GO reduction were completed simultaneously in a single-step heat treatment. The synthesis method of the RP/rGO composite is described schematically in Fig. 1. As shown in Fig. 1(a), the RP and GO precursors were arranged in a RP/GO/RP three-layer structure inside a ceramic boat with a ceramic cover, and then loaded in a tube furnace under Ar/H_2 atmosphere. The boat was initially placed on the side of the heating zone; after heating the furnace to 500 °C, the boat was moved into the heating zone, as shown in Fig. 1(b). As soon as P condensation was observed on a quartz tube placed downstream of the gas flow, the boat was immediately moved back to the original position, as illustrated in Fig. 1(c). Then, the boat was maintained at 300 °C for 6 h to convert white P to red P through a cooling-down process. The structure of the resulting RP/rGO composite, schematically shown in Fig. 1(d), combines several advantages: 1) Nanosized RP can shorten the ion diffusion length and thus enhance both ionic and electronic kinetics in the anode; 2) the RP particles occupy the gaps between the rGO sheets conformally, which protect them against volume variations during intercalation and extraction of Na ions; 3) the rGO network can provide an electron pathway and thus increase the electronic conductivity of the RP anode. Furthermore, the flash-heat treatment process reported here is simpler and more cost-effective than the traditional ball-milling and vaporization–

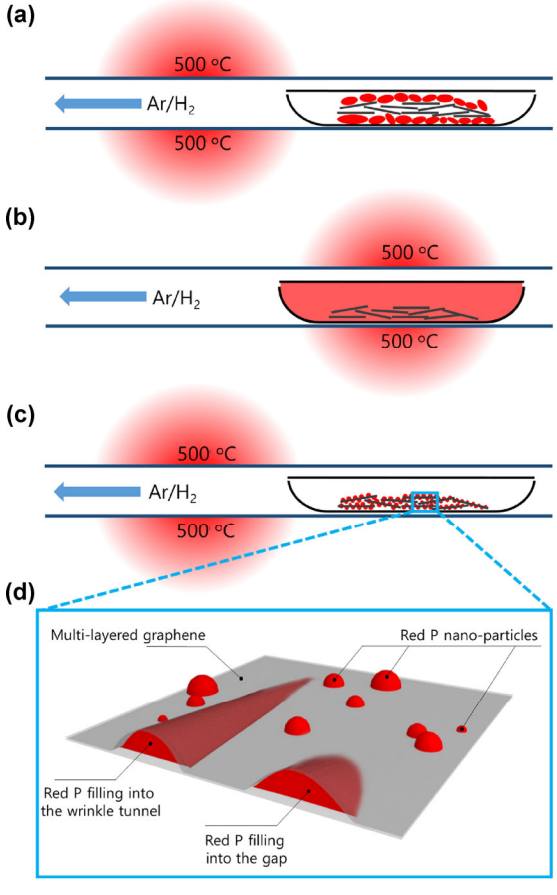

Figure 1 Schematic diagrams of the synthesis process of the RP/rGO composite: (a) pre-heat treatment; (b) flash-heat treatment; (c) cooling-down stage. (d) Schematic illustration of the nanostructure of the resulting RP/rGO composite.