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Xanthoceras sorbifolia husks-derived porous carbon for sodium-ion and lithium-sulfur batteries

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ABSTRACT

Sodium-ion batteries (NIBs) and lithium-sulfur batteries (LSBs) have attracted increasing research attention as promising energy storage systems. And renewable biomass-derived carbon materials play an important role in improving their electrochemical performance due to their heteroatoms-doping, electrical conductivity and exceptional porous structure. Here, xanthoceras sorbifolia husks have been employed to prepare amorphous porous carbon (XSH-PC) for NIBs and LSBs. As an anode material for NIBs, XSH-PC delivers a reversible specific capacity of 269.5 mA h g^{-1} at 0.05 A g^{-1} with initial coulombic efficiency as high as 65.9%, and retains stable capacity of 113 mA h g^{-1} after 500 cycles at 1 A g^{-1}. As well, after sulfur loading, as obtained XSH-PC/S composite shows stable coulombic efficiencies of 100 ± 0.3% and a reversible specific capacity of 442.4 mA h g^{-1} after 500 cycles at 2 A g^{-1} with a low average capacity decay rate of 0.065% per cycle when used for LSBs. These excellent electrochemical properties can be attributed to the unique structure of XSH-PC showing mesoporous structure with abundant carbon edge defects and large specific surface areas. These results illuminate the potential application of xanthoceras sorbifolia husks-derived porous carbon in NIBs and LSBs.

1. Introduction

With the increasing consumption of fossil energy sources and the ever-worsening ecological environment, there is an increasing urgency to develop clean and high-efficiency renewable energy resources such as solar and wind energies. And electrochemical energy storage systems such as rechargeable batteries are vital to storage these renewable energies for peak shift operation [1]. Among these rechargeable batteries, sodium-ion batteries (NIBs) and lithium-sulfur batteries (LSBs) have attracted increasing research attention as promising energy storage systems due to their low cost raw materials and/or high energy densities [2]. As one of the most promising energy storage devices, NIBs have the most competitive advantage of low cost for earth abundance of sodium [3–5]. As well, LSBs have drawn increasing research attention in the view of large theoretical energy density (2500 Wh kg^{-1}) and natural abundance of sulfur [6,7].

Carbonaceous materials have been extensively investigated for LSBs and NIBs [8–12]. The well-known disadvantages, such as high electrical resistance of the sulfur and polysulfides shuttle, have restricted the practical application of LSBs [12]. And these issues can be effectively solved by composing sulfur with porous carbon materials, in which carbonaceous skeleton could improve electrical conductivity of sulfur-based electrodes and the internal interconnected pores as efficient polysulfide reservoirs could inhibit polysulfide shuttle during cycling [7,12–21]. As well, although graphite could reversibly storage only a small amount of sodium atoms due to the mismatching of graphite interlayer distance (0.334 nm) with the sodium ions (0.102 nm) [11,22,23], amorphous carbon materials have become the most promising anode materials for NIBs in view of high capacity (~300 mA h g^{-1}), low cost, and abundance. To prepare these carbon materials with well-designed structure, biomass has been one of the most promising carbon sources due to its renewability, low cost, environment-friendly and exceptional porous structure [8,9,24,25]. And lots of biomass-derived carbon materials deliver superior electrochemical energy storage performance for LSBs and NIBs applications [8,9,13,17,24–28].

Here, xanthoceras sorbifolia husks were employed as renewable resource to prepared amorphous porous carbon, and potential applications of xanthoceras sorbifolia husks-derived porous carbon (XSH-PC) in LSBs and NIBs have been investigated in detail. As a major woody energy plant, xanthoceras sorbifolia is widely planted (may be over 5×10^5 ha by 2020) in northwest China and its seeds can be used to produce biodiesel, as well as husks have been widely investigated for use as medicine, health food, furfural, bioenergy and carbon materials

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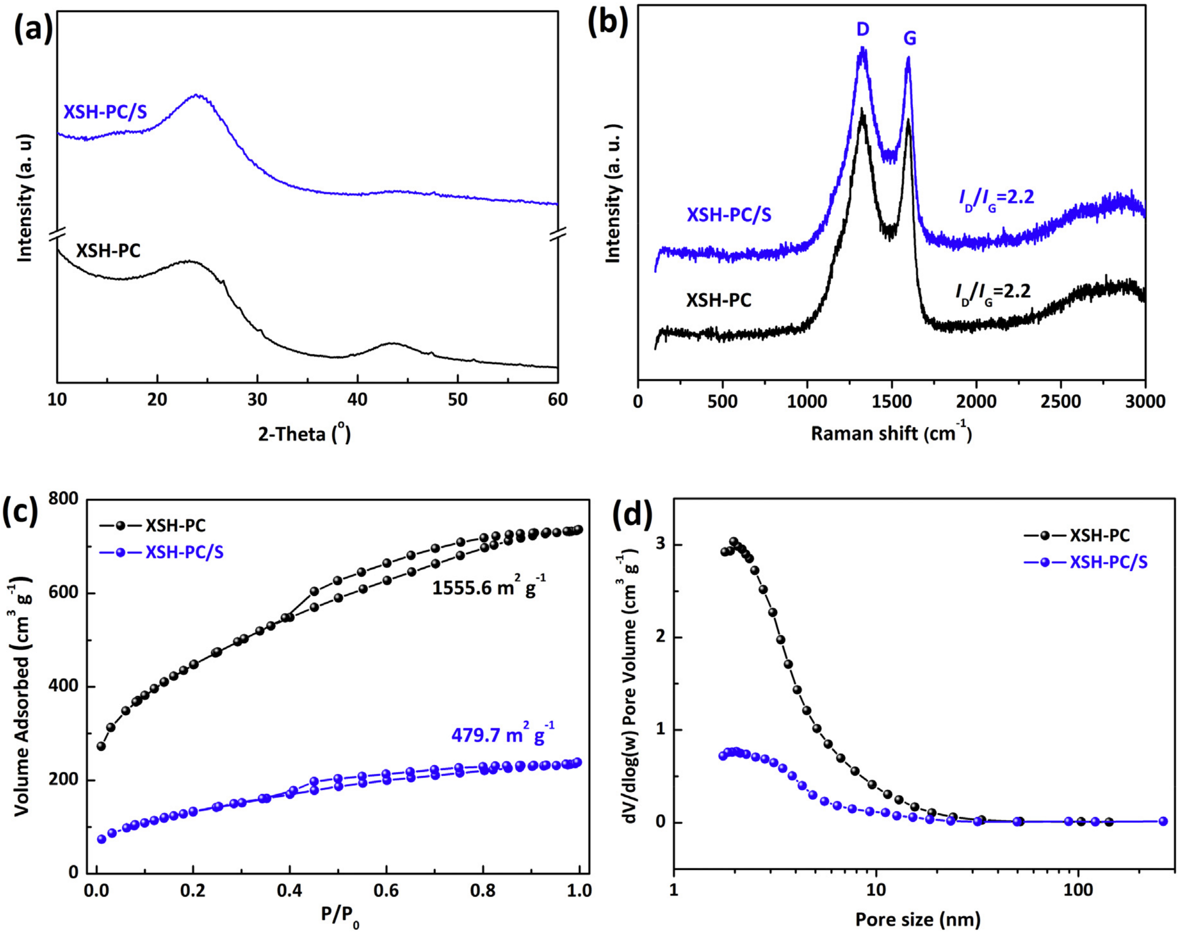

Fig. 1. (a) XRD patterns, (b) Raman spectra, (c) N_2 adsorption-desorption isotherms, (d) pore-size distributions of XSH-PC and XSH-PC/S.

[29]. Annual xanthoceras sorbifolia seeds production varies widely from 122 kg ha^{-1} to 2543 kg ha^{-1}. Considering the desiccated husks/seeds ratio of about 1.1:1, ~5 × 10^5 tons of xanthoceras sorbifolia husks could be produced annually [29]. This represents a significant potential resource for biomass-derived carbon. In this study, an attempt was done to investigate the electrochemical energy storage performance of XSH-PC material for LSBs and NIBs. Benefiting from its unique structure showing mesoporous structure with abundant carbon edge defects and large specific surface areas, the as-obtained XSH-PC and XSH-PC/S electrodes deliver excellent electrochemical properties including high initial coulombic efficiency, large reversible specific capacity, and good cycling performance when used for NIBs and LSBs, respectively.

2. Experimental details

2.1. Preparation of bare XSH-PC and XSH-PC/S composite

XSH-PC was prepared via a facile thermal carbonization of xanthoceras sorbifolia husks. Firstly, the collected husks were dehydrated in a vacuum oven at 80 °C for 24 h, and then pulverized. After being co-ground with $ZnCl_2$ (as pore-forming agent, the optimal mass ratio of husks and $ZnCl_2$ is 1:3), the obtained mixture was transferred to the horizontal alumina tube furnace and thermal carbonized at 800 °C for 3 h in a flowing nitrogen atmosphere. After that, the black XSH-PC was collected and washed with 2 M HCl aqueous solution to remove the impurities, following deionized water for several times before being dried at 80 °C overnight. The XSH-PC/S was prepared through a modified melt-diffusion process. Typically, the as-obtained XSH-PC matrix and sublimed sulfur were co-ground together with a mass ratio of 2:3, and then heated in a sealed stainless-steel vessel at 155 °C for 12 h followed by 180 °C for another 24 h. After cooling to ambient temperature naturally, the composite was soaked in toluene under stirring for 1 h to remove the redundant sulfur on the external surface. Finally, the XSH-PC/S sample was collected by suction filtration, washed thoroughly with anhydrous ethanol, and then dried in vacuum at 60 °C.

2.2. Physical characterizations

To characterize the morphology, structure and composition of the as-prepared materials, the powder *X*-ray diffraction (XRD, PANalytical B.V. Empyrean, Netherlands, operating with Cu K_α radiation of $\lambda = 0.15416$ nm), Raman spectra (Invia Refl, Renishaw, UK), *X*-ray photoelectron spectra (XPS, PHI-5702 spectrometer, USA, Al K_α *X*-ray radiation as the *X*-ray excitation source), field emission scanning electron microscopy (SEM, Ultra Plus, Carl Zeiss, Germany), and transmission electron microscopy (TEM, FEI TECNAI TF20, operating at 200 kV) were performed. All XRD patterns were analysed using Jade 5.0 software of Material Data, Inc. The sulfur content in XSH-PC/S was examined under a N_2 atmosphere with a heating rate of 5 °C min^{-1} using a thermogravimetric analyser (TGA, PrekinElmer, U.S.A.). The Brunauer-Emmett-Teller (BET) specific surface area and the pore size distribution were investigated by nitrogen sorption isotherms (ASAP-2010, MICROMERITICS, USA).

2.3. Electrochemical performance characterizations

The detailed electrochemical properties of XSH-PC and XSH-PC/S