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Full Length Article

Finding of coal organic microspheres during hydrothermal treatment of brown coal

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HIGHLIGHTS

- A series of organic microspheres are produced from brown coal by hydrothermal method.
- Coal organic microspheres can be directly obtained from difference brown coals.
- These microspheres have the diameter of 0.2–3.8 μm and carbon yields above 29%.
- Some microspheres contained holes, indicating their potential role as microcapsules.
- Using these microspheres as the template, ZnO hollow microspheres are synthesized.

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ABSTRACT

Solid wastes or extracts directly obtained from brown coals by a single hydrothermal treatment were found to be composed of a series of novel coal organic microspheres (COM). Treatment using a flow of water at 350 °C and 20 MPa for 90 min produced COM from three brown coals with carbon yields above 29% and diameters ranging of 0.2–3.8 μm. The spherical morphology of COM changes slightly with different resources, and some microcapsules were observed in all three COM samples. A recycling experiment on COM indicates their potential application as carriers and/or supporters after modification. Through comparison, it is demonstrated that COM differ completely from carbonaceous microspheres or hydrochars obtained from hydrothermal carbonization of carbohydrates, both in mechanism and starting materials. In addition, considering COM as a template, zinc oxide hollow microspheres were synthesized successfully. These results indicate that a series of new substitutes with stable supply are provided to organic microspheres, and a waste or by-product of through the hydrothermal treatment of brown coal is transformed to a valuable advanced material. Given their uniform morphology, high yields, and availability from a variety of low-cost natural resources with worldwide abundance, COM are expected to play a major role in chemical and materials science applications.

1. Introduction

Organic microspheres (OM), or carbonaceous microspheres ("carbonaceous" is usually used to describe the carbonization of biomass), have been widely used in the fields of materials science, chemistry, biology, and medicine [1–8]. OM are generally produced from monomer or polymerized synthetic and natural materials. To date, the natural resource for OM production has been limited to specific carbohydrate biomasses, such as glucose, xylose, maltose, sucrose, and starch [9–11]. As these materials are highly sought-after, expensive, and an energy source for the human body, a cheaper and widely abundant substitute with a stable supply is required for the development of OM.

Coal has increasingly become the feedstock for the production of advanced materials, as it is cheap, abundant worldwide, and, in this application, is believed to be environmentally friendly and sustainable [12]. To date, the applications of coal in materials science have focused on the production of carbon materials, such as activated carbon [13,14], carbon fibres [15–17], fullerenes [18], and graphene [19–21], and inorganic materials using the mineral matter in coal, such as zeolite [22]. These carbon materials are products of coal pyrolysis at high temperatures. However, no materials have been produced using coal organic matter. Moreover, no one has yet succeeded in directly converting the natural organic molecules in coal to materials with uniform morphology using a green and efficient method under mild conditions.

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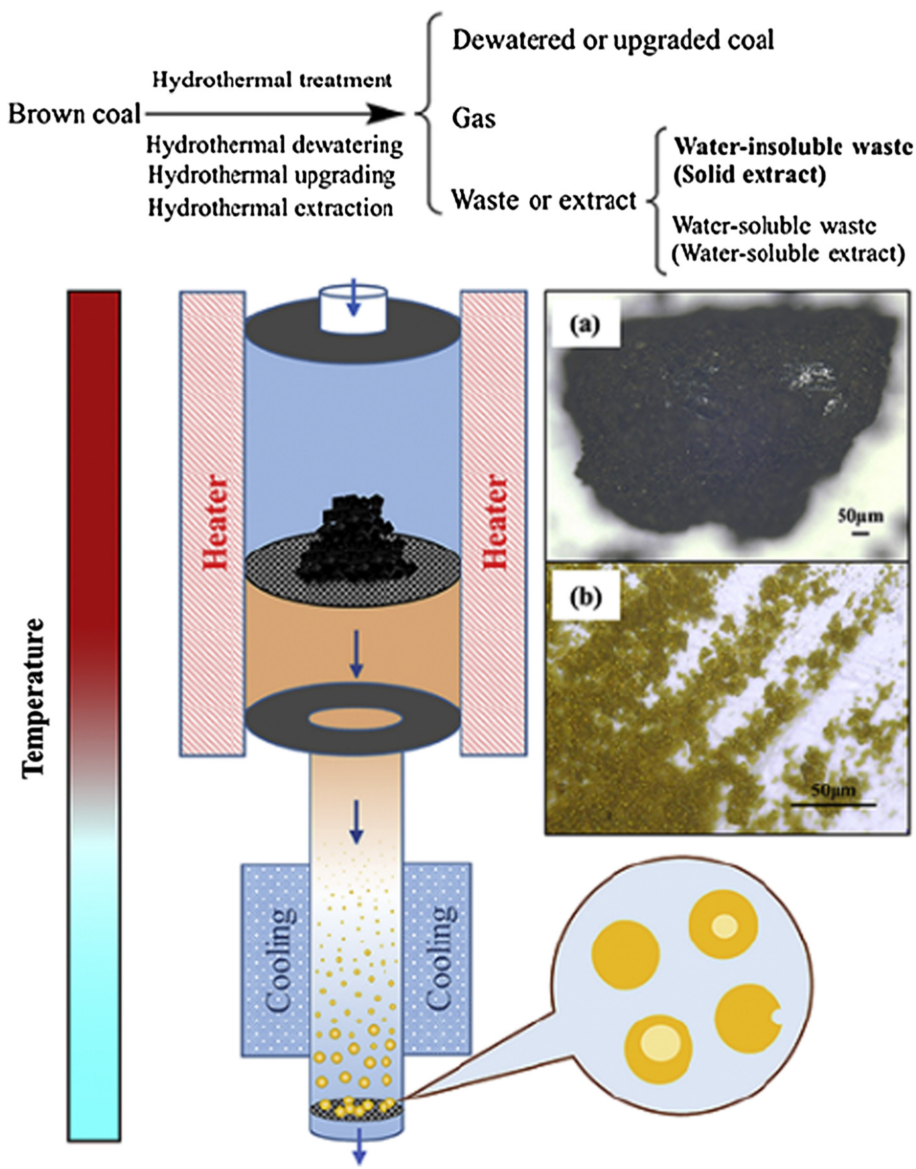
Brown coal and lignite exist in abundant minable reserves worldwide and are cheap compared with bituminous coals. These low-rank coals have high moisture contents and low heating values due to intrinsic oxygen functional groups, and high spontaneous combustibility after drying [12]. Hydrothermal treatment is a coal upgrading process that uses hot water as the only reaction/extraction medium, always at ⩽350 °C and ⩽20 MPa, which is suitable for low-rank coal because the water inherent in the coal can be used as a reaction medium. During the process, the decomposition of oxygen functional groups occurs and leads to dewatering and a consequent increase in the heating value [23–26]. Through hydrothermal treatment, brown coals are separated into three parts: the treated coal (the main product), gas, and waste (extracts, removed from the coal due to its solubility in hot water, including water-insoluble and water-soluble parts at room temperature and pressure). Treated coal with lower moisture and oxygen contents and a higher heating value is usually the target product, and the process is called hydrothermal dewatering or upgrading; correspondingly the treated coal is known as dewatered coal (DC) or upgraded coal (UC), as shown in Scheme 1. It has been shown that DC or UC (UC is used in this article) is an important fuel for burning, liquefaction, or gasification. Extracts, especially water-insoluble or solid extracts at room temperature and pressure, have also been studied. There exist a number of characterizations of the solid extract [24–26]; however, there has been only one report about its application, which is a hydrothermal gasification process to convert both water-insoluble and water-soluble extracts into gaseous fuel using catalyst [23]. Here we examine the solid extract morphologically and explore its application in material science.

A hydrothermal extraction process under the same condition was executed on three brown coals (Loy Yang coal, LY; Nei Meng coal, NM; Yun Nan coal, YN) in a flow of hot water using a semi-batch type extractor. The information of the raw coals are shown in Table S1; schematic diagrams of the apparatus and process are shown in Fig. S1 and Scheme 1. Solid extracts obtained from LY, NM, and YN are denoted as LYOM, NMOM, and YNOM, respectively, as listed in Table 1.



Scheme 1. Illustration of the previous studies on hydrothermal treatment of brown coal and a schematic diagram for the formation of solid extract from brown coal. The insets are microscope images of (a) LY and (b) LYOM.