Lignocellulose aerogel and amorphous silica nanoparticles from rice husks

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Abstract

Rice Husks (RHs) are one of the most abundant sources of biomass in the world due to rice consumption. Lignocellulose and silica are two of the main components of RHs, which allow RHs to be applied in different areas. Lignocellulose can be partially dissolved in 1-butyl-3-methylimidazolium chloride (BMIMCl), which is a simple way of competing with the traditional extraction methods that suffer from high chemical consumption. A lignocellulose freeze gel is obtained via a cyclic liquid nitrogen freeze-thaw (NFT) process. Multi-functional self-assembled lignocellulose aerogel is obtained after CO2 supercritical drying. Based on the aerogel’s special properties, two routes are developed for practical applications. On one hand, the aerogel is coated to exhibit a superhydrophobic property that can be applied as an absorbent for oil spills. On the other hand, a carbon aerogel is synthesized via a pyrolysis process, resulting in a porous amorphous carbon. The residue after partially dissolving lignocellulose in BMIMCl is further calcined to obtain amorphous silica nanoparticles, achieving a comprehensive application of RHs.

Keywords: Rice husks, Lignocellulose, Carbon aerogel, Silica

1 Introduction

Rice husks (RHs) are one of the most abundant sources of biomass in the world because of the massive amount of rice consumed by the human population. There are two main components in RHs: silica (ca. 15–28 wt.%) and lignocellulose (LC) (ca. 72–85 wt.%) [1–3]. If isolated, the silica from RHs [4, 5] can be used to prepare various silicon-based materials, including silicon carbide [6], silicon nitride [7], silicon tetrachloride [8], silicon [9], and zeolite [10]. These materials have widespread applications in semiconductors [10], abrasive materials [10], pigments [11], catalyst supports [12], biomedicine [13], luminescence [14–17], etc. LC is a natural polymer, containing lignin, cellulose, and hemicellulose [18]. LC can be used to prepare biochemicals, such as bioethanol and xylitol [19], as well as quantum dots [20]. Of the three major contents of LC, cellulose is abundantly available in nature, and has been used by humans for a wide range of applications for thousands of years [21]. Recently, cellulose has become an attractive sustainable resource and been applied across several areas, including cellulose gas barrier films [22], sensors [23], cellulose nanocrystals [23], and aerogels [24]. However, the extraction process of RH cellulose is very complex and time consuming [25]. Ionic liquids (ILs) were reported to be able to effectively dissolve cellulose and lignin [26, 27] because the ions in ILs can serve as the acceptor of hydrogen bonds, which helps to isolate the lignocellulose from RHs [28, 29]. As such, ILs are a good working medium to directly extract LC from RH biomass, and dissolve those organic components to form a homogeneous system.

Aerogels are a group of materials with a 3-D porous network structure. Their ultra-low density, high surface area, and large porosity make them attractive for many applications, including catalyst supports [30], artificial muscles [31], supercapacitors [32], and absorption materials [33–37]. Carbon aerogels are particularly promising...
due to their high conductivity [38]. Graphene and carbon nanotubes from chemical vapor deposition (CVD), and resorcinol-formaldehyde aerogels derived from pyrolysis are the two main routes to prepare carbon aerogels [39, 40]. However, the precursors are very expensive, and some of the chemicals used are also not friendly to the environment.

Since ILs are able to effectively dissolve LC from RHs [18], under a subsequent series of treatments of a liquid nitrogen freeze–thaw (NFT) process [41, 42], water regeneration, and CO$_2$ supercritical drying, self-assembled LC aerogels can potentially be prepared [41]. In addition to their practical applications, such as absorption materials for various chemicals (e.g., oil spill cleanup) thanks to their high porosity and surface area, such self-assembled LC aerogels may also help researchers better understand the mechanism of the self-assembly of LC and collagen fibrils, two of the most abundant fibers in nature. How LC (predominately in plants) and collagen (predominately in animal bodies) fibrils self-assemble into larger scale structures in living body still remains a mystery [43].

Carbon aerogels can be further obtained via high temperature pyrolysis of LC aerogels under an inert atmosphere. The porous structure can be maintained and the entire organic components can be converted into carbon. Their remarkable chemical and physical properties make carbon aerogels promising for various applications, such as supercapacitors [44–46], catalyst supports [47, 48], and gas storage [48].

Biomass has recently become increasingly attractive because they are renewable. Both the inorganic and organic components in biomass can be potentially applied to different areas. But the major problem facing biomass utilization is the trade-off between efficiency and waste. For example, to extract high purity silica from RHs, traditionally the organic components are wasted and vice versa. Therefore, a route to derive both organic and inorganic components from RHs is highly describable and should be more sustainable.

Herein, we report a comprehensive strategy to prepare both LC aerogel and amorphous silica nanoparticles from RHs. The LC aerogel has a high surface area with a mesoporous structure. By surface modification with a hydrophobic agent, the aerogel with a hydrophobic surface was prepared. The carbon aerogel was further prepared by pyrolyzing the LC aerogel under an inert atmosphere. The residue from IL treated RHs was further calcined to prepare amorphous silica nanoparticles. These three processes demonstrate a good example to convert biomass into value added products, as well as the promising future of green chemistry.

2 Results & discussion

The entire process for preparing self-assembled LC aerogel, carbon aerogel, and silica nanoparticles is shown in Fig. 1. RHs, which contain a high content of LC, were partially dissolved in BMIMCl after 4 h of treatment at 85 °C [18, 28]. The LC IL solution was obtained after centrifugation, and subsequently treated by the NFT process to induce gelation [22, 42]. First, the IL solution containing LC was frozen by liquid nitrogen, during which the IL solvent began to freeze, so that it contained a frozen and unfrozen liquid micro-phase [42]. After freezing for 6 h, cellulose, hemicellulose, and lignin were extruded by the completely frozen IL crystalline. In this process, the gaps between cellulose macromolecules shrunk. The molecules were then crosslinked by physically twisted crosslinking points [42]. Finally, a gel formed during a slow thawing process due to an increasing strength of the physical crosslinking with an increasing temperature. By utilizing CO$_2$ supercritical drying, a low-density LC aerogel was obtained. As shown in Fig. 1, the self-assembled LC aerogel was light enough to stand on a dandelion. The density of the LC aerogel was measured to be 0.129 g/cm$^3$. This approach to prepare light aerogel is advantageous because of three reasons. First, the formation process does not use any crosslinking agent, which may cause environmental and health issues. Second, the process is very facile. The self-assembly thermodynamic process minimizes the utilization of chemicals. Third, RH biomass, sometime treated as a biowaste, was used as the staring material.

The cross section of the LC aerogel derived from RHs was characterized by SEM and the images are presented in Fig. 2a and b, which show that the LC IL solution formed a steady network structure with a dense porosity. The higher resolution SEM image indicates that the LC fibers interconnected at physical crosslinking points [22, 42]. The result suggests that the cyclic water regeneration could effectively remove IL, eliminating the barrier of the following gelation process. Overall, the NFT process successfully led to the formation of a hydrogel from the IL LC solution. With the assistance of CO$_2$ supercritical drying, the hydrogel could maintain its porous network structure to form an aerogel, promising for a wide variety of applications depending on the porous structure [42].

Self-assembled LC aerogel is a porous material that contains an abundance of carbon. Thus, carbon aerogel could be generated from LC aerogel in an inert atmosphere under elevated temperatures. As shown in Fig. 2c and d, the porous network structure was well maintained throughout the high temperature pyrolysis, which indicates that the LC aerogel could maintain its structure at elevated temperatures. The inert atmosphere also contributed to minimizing the damage to the porous structure. The lignin and hemicellulose wrapped around cellulose were changed to spheres after pyrolysis and attached to the carbonized cellulose structure [49].
Fig. 1 Flow chart of the process to prepare LC aerogel, carbon aerogel, and RH silica

Fig. 2 a SEM image of the LC aerogel synthesized after 5 cycles of NFT; b enlarged area of Figure; c SEM images of the carbon aerogel prepared via the pyrolysis of LC aerogel under 1000°C for 2 h; d enlarged area of Figure (c)
Figure 3a shows the XRD patterns of the LC aerogel and RH cellulose. The results show that RH cellulose bears the typical cellulose I structure according to the characteristic diffraction peaks (002), (101), and (040), at 15.5°, 22.1°, and 34.7°, respectively [50]. The LC aerogel was obtained after water regeneration and CO₂ supercritical drying. It mainly showed one broad hump at ca. 21.1°, indicating that the regenerated LC has a lower degree of crystallinity than the raw cellulose, which is expected [51]. According to the previous reports [52, 53], the regenerated cellulose or lignocellulose possess a cellulose II structure with a characteristic peak (002) at 12.1°, which is also shown in the XRD pattern of the LC aerogel. The lower crystallinity of the regenerated LC is due to some of the intrinsic inter- and intra-molecular hydrogen bonds and destruction of crystallized structures of cellulose in the dissolving process [51]. However, the intensity of the (002) peak of the LC aerogel is relatively low as shown in Fig. 3a, due to the fact that lignin restrained the swelling of cellulose molecules in IL and limited the solubility of cellulose molecules at relatively low temperatures (85 °C) [42, 53, 54].

As shown in Fig. 3b, the N₂ adsorption-desorption curves of the LC aerogel and carbon aerogel prepared at 1000 °C are of type IV, suggesting that the two types of aerogels are mesoporous. The curves also indicate that the LC aerogel formed a mesoporous network structure after cyclic NFT thermodynamic crosslinking, and the carbon aerogel maintained a porous structure after pyrolysis. Based on the isotherms, the specific surface area (SSA) and pore property data were calculated and are summarized in Table 1. The LC aerogel derived from RHs has a relatively higher total specific surface area (SSA (total)) of 106.5 m²/g, compared to the literature data of 80.7 m²/g [22]. The main reason is most likely because RHs contain a high cellulose content [55], which could minimize the effect of lignin in the solution, and assist the formation of a porous network structure. The LC aerogel also has a high SSA (meso)/SSA (total) ratio, which is probably due to the low surface tension at the supercritical CO₂/hydrogel interface during CO₂ supercritical drying. After the conversion of LC aerogel to carbon aerogel, the SSA (total) of the carbon aerogel sample reached 217.3 m²/g.

LC is hydrophilic due to the hydroxyl groups present on the structures of lignin, cellulose, and hemicellulose. It was reported that a hydrophobic coating could be applied on a recycled cellulose aerogel to make it oleophilic [33]. One of the main incentives to convert cellulose aerogels to be hydrophobic is because hydrophobic aerogels can repel water and attract oil, making them promising for applications such as oil spill cleaning [56].

Figure 4a and b shows the water contact angles (WCAs) of 132.5° and 130.5° on an external and a freshly fractured surface of the coated LC aerogel, respectively. This result suggests that the hydrophobic modification by MTMS vapor can reach deep into the LC aerogel, and the entire 3-D porous structure was converted to be hydrophobic.

In order to investigate the potential oil absorption performance of the surface-modified LC aerogel, pump oil stained by Sudan III dye (to show a high visibility) was adopted for the demonstration, and the result is presented in Fig. 4c. The surface modified

| Sample            | SSA (total) [m²/g] | SSA (meso) [m²/g] | SSA (micro) [m²/g] | SSA (meso) /SSA (total) [%] | SSA (micro) /SSA (total) [%] |
|-------------------|-------------------|------------------|-------------------|-----------------------------|-----------------------------|
| LC aerogel        | 106.5             | 100.2            | 6.2               | 94.1                        | 5.8                         |
| Carbon aerogel    | 217.3             | 55.5             | 143.6             | 25.5                        | 66.1                        |

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LC aerogel can easily and quickly absorb the pump oil. At the beginning of the test, the stained pump oil was floating on water surface. Upon direct contact with the aerogel, the oil was quickly absorbed. After the completion of the absorption, the oil was completely removed and no stained oil was visibly detected on the water surface. The result suggests that the modified LC aerogel could effectively absorb oil from water surface, offering an environmentally-friendly alternative option for oil spill cleaning.

RH residue after IL treatment was rinsed by DI water and dried in an oven. After that, the residue was calcined at 700 °C for 2 h to synthesize silica [1, 9, 11, 12]. The XRD patterns shown in Fig. 5a indicate that the silica derived from the IL treated RH residue (RH-IL-silica) remained to be amorphous. It exhibits a similar XRD pattern as the silica derived from HCl treated RHs (RH-HCl-silica), a widely adopted process to synthesize silica from RHs [18]. Figure 5b shows the SEM image of RH-IL-silica, which exhibits as nanoparticles with a diameter of ca. 40–80 nm. Considering IL treated RH residue is a byproduct, using this residue to prepare silica contributes to the comprehensive application strategy of RH biomass, which improves the utilization efficiency of RHs and broadens the applications of RH biomass [18]. Due to the amorphous phase and relative high surface area, the silica derived from RHs can be used as a filler in plastics, rubbers, and personal care products, and as the starting material for various silicon-containing materials [10].
3 Conclusion
In summary, the LC in RHs could be successfully dissolved into IL (BMIMCl) to form a homogenous solution. LC aerogel with a 3-D porous network structure was prepared by treating the LC IL solution by the NFT process followed by freeze drying. After the MTMS vapor treatment, the LC aerogel turned from hydrophilic to hydrophobic. Such a modified LC aerogel could potentially find uses in absorption applications, such as cleaning oil spills. The LC aerogel can be easily converted to carbon aerogel with a high surface area through a facile pyrolysis process. Meanwhile, amorphous silica nanoparticles could be prepared from the IL treated RH residue, leading to a comprehensive utilization of RH biomass.

4 Supplementary information
Supplementary information accompanies this paper at https://doi.org/10.4.

Additional file 1. The experimental part is available in the supporting information.

Abbreviations
RHs: Rice Husks; BMIMCl: 1-butyl-3-methylimidazolium chloride; NFT: Nitrogen freeze-thaw; LC: Lignocellulose; ILS: Ionic liquids; CVD: Chemical vapor deposition; MTMS: Methyltrimethoxysilane; FE-SEM: Field emission scanning electron microscope; XRD: X-ray diffraction; BET: Brunauer–Emmett–Teller; SSA: Specific surface area; WCAs: Water contact angles; RH-HCl-silica: Silica derived from HCl treated RHs

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Authors’ contributions
LS and ZW designed the project. ZW led the project, and ATS, WRTT, JL, and HW participated in the characterizations. HS and WW provided valuable suggestions to optimize the synthesis route. LS and HW co-supervised the project. ZW wrote the first draft. LS, ATS and HW revised the manuscript. All authors read and approved the final manuscript.

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