

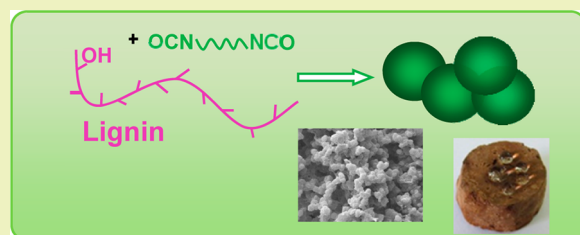
# Renewable Lignin-Based Xerogels with Self-Cleaning Properties and Superhydrophobicity

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## S Supporting Information

**ABSTRACT:** A novel dissocyanate-modified lignin xerogel is facilely prepared using renewable lignin as precursors via a sol–gel process and ambient pressure drying method. The xerogel possesses high performance in self-cleaning and superhydrophobicity with no need for further hydrophobic modification. Furthermore, the xerogel obtained can find potential applications in absorbents, coatings, and scaffolds.

**KEYWORDS:** Lignin, Xerogels, Self-cleaning, Superhydrophobicity, One-pot reaction



## INTRODUCTION

Xerogels/aerogels are low density nanoporous solids consisting of a three-dimensional (3D) open-cell network with in-filling air in the interfaces.<sup>1–3</sup> The interconnected structure with continuous nanopores can provide efficient mass transfer of the liquid or gas substances. Because of their exceptional large specific area, high porosity, adjustable framework, and surface properties, these porous materials are expected to have excellent performances as supercapacitors, sensors, thermal and acoustic insulation, catalyst supports, and absorbents for water purifications.<sup>1–8</sup> Various techniques have been employed for fabrication of xerogels/aerogels, including templates, chemical vapor deposition, pyrolysis treatment, and hydrothermal carbonization processes. However, most of those methods were not widely used in many situations because of certain drawbacks such as template consumptions, high energy cost, expensive chemicals, and the requirement of complicated and unusual fabrication devices.<sup>1–3</sup> Thus, great effort should be dedicated to develop a cost-effective and eco-friendly approach to prepare robust functional xerogels/aerogels under the pressing practical requirements.

Recently, there is an increasing trend to study and utilize renewable natural materials as a result of environmental protection and a growing shortage of oil resources. Lignin, as a plant cell wall component, is a heterogeneous and amorphous polymer of a phenolic nature, being the second most abundant renewable natural polymer and the largest contributor to soil organic matter.<sup>9,10</sup> The paper industry produces a large amount of lignin each year, but about 98% of this biomass is directly poured into nearby waters or burned in an energy-recovery step.<sup>11</sup> So far, the technologies of lignin extraction from plants have been well developed,<sup>12,13</sup> and versatile applications of

lignin has been investigated, such as raw materials for pyrolysis oil,<sup>14–17</sup> binders,<sup>18</sup> dispersant agents,<sup>19</sup> electrodes,<sup>20</sup> heavy metal absorbents,<sup>21</sup> and components for composites and copolymers.<sup>22–27</sup> Very recently, our group has found that lignin nanoparticles are ideal particle emulsifiers to commendably stabilize oil-in-water emulsions with pH responsibility and even oil-in-water high internal phase emulsions (internal phase can reach up to 91.7%),<sup>28,29</sup> expanding the industrial applications of lignin. While it is far away from being enough to activate the lignin market, much more significant applications should be exploited to make the best use of this easy to obtain, renewable, and eco-friendly natural resource.

On the basis of the structural model of lignin, lignin has many hydroxylic groups, and several attempts have been made to obtain highly valuable lignin-based products by taking advantage of this property, providing much inspiration for the effective utilization of lignin.<sup>25,26</sup> In this work, a simple and straightforward method was successfully developed to prepare superhydrophobic lignin-derived xerogels for the first time. To be specific, monolithic polyurethane organogel was first achieved by the condensation polymerization of lignin and modified dissocyanate (MMDI, Lupranate MM103C, BASF) in a THF solution, and then ambient pressure drying was applied to the as-prepared organogel resulting in a lignin-based xerogel. Interestingly, the obtained xerogels simultaneously possess low surface energy and great water repellence, exhibiting multifunctional characteristics including self-cleaning and selective oil absorption, demonstrating that they are ideal absorbents for

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removing oils or organic solvents from water for oil spill cleanup or industrial wastewater purification.

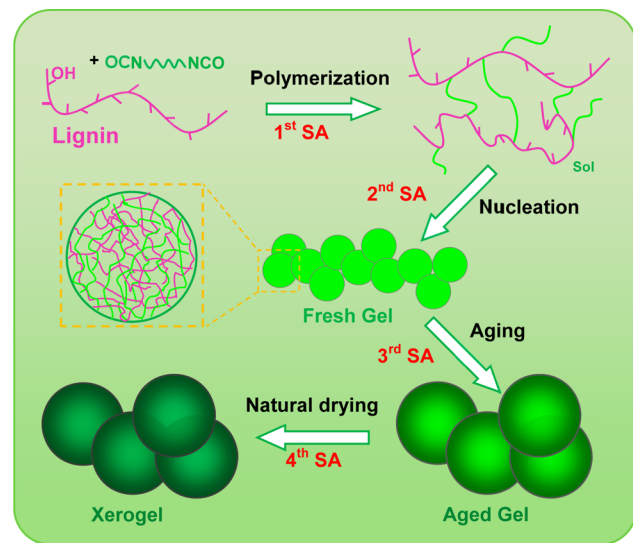
## EXPERIMENTAL SECTION

The number of hydroxyl groups of lignin used in this work is 2.189 mmol/g. Various lignin-based xerogels were prepared based on different monomer ratios and concentrations shown in Table S1 of the Supporting Information. In a typical experiment, 0.5 g of lignin and 0.4 g of MMDI were dissolved in 4.0 mL of THF. Followed by adding 20  $\mu\text{L}$  of triethylamine (TEA), the polymerization was activated and stayed for 4 h at room temperature to achieve an organogel. Finally, the xerogel was obtained by ambient pressure drying of the organogel. If there is no special declaration, the xerogel refers to sample 3 in Table S1 of the Supporting Information.

## RESULTS AND DISCUSSION

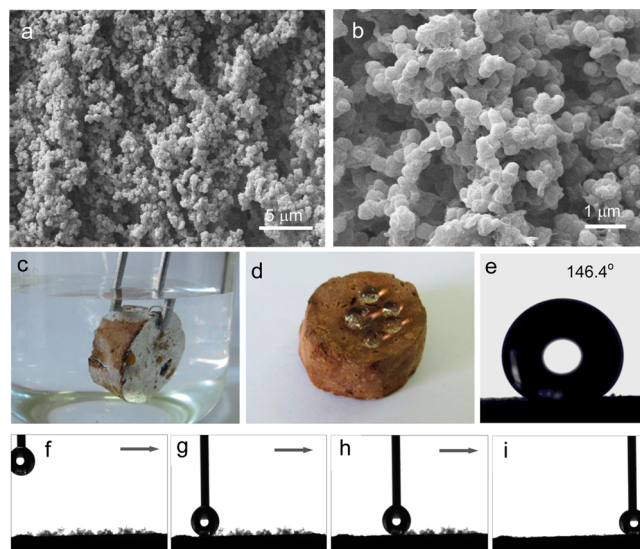
The formation of lignin-based xerogels is illustrated in Scheme 1. Three structural evolution procedures were involved in the

### Scheme 1. Schematic Representation of Formation of Lignin-Based Xerogels by Controlling Phase Separation in the Sol-Gel Process and Subsequent Ambient Pressure Drying



whole sol–gel process, including cross-linking polymerization between lignin and MMDI, spontaneous assembly of sol nanoparticles, and an aging process to form a framework of nanoparticles. First, as we know, the phenolic building blocks of lignin, namely, p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, differ in the substitution of the 3 and 5 position of the aromatic ring. These hydroxyl-rich groups on the side chains make it possible for lignin to dissolve in THF solution and react with MMDI by the catalytic action of triethylamine. With the development of polymerization between lignin and MMDI, chemically cross-linked polyurethane was obtained (Figure S1, Supporting Information). Compared with the FTIR spectrum of MMDI, the absorption peak of  $-\text{NCO}$  of the xerogel at  $2270\text{ cm}^{-1}$  disappeared, indicating that the  $-\text{NCO}$  groups have been totally consumed in the reaction with  $-\text{OH}$  of lignin. At the same time, the density of hydroxyl groups reduced sharply resulting in a more hydrophobic polymer, and its solubility in the polar THF solution reduced accordingly. Therefore, lignin nanoparticles can be achieved by the effect of phase separation, which creates

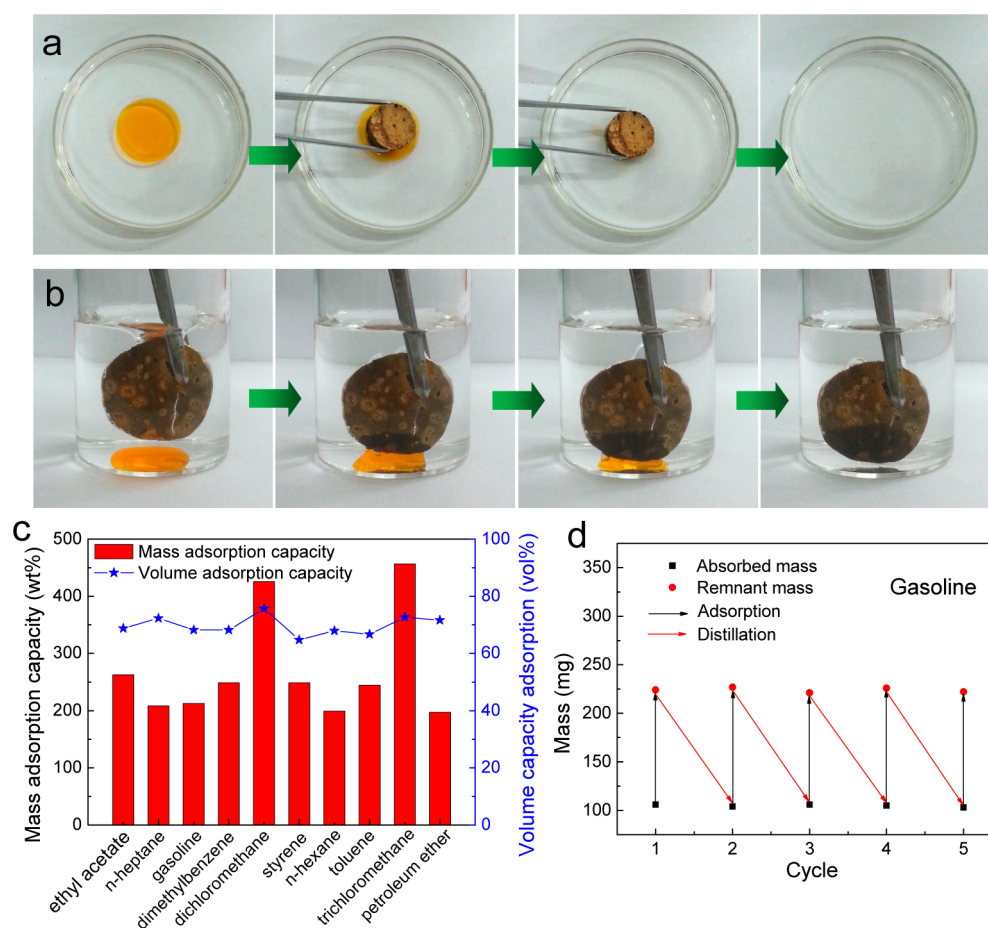
microscopic “regions of free liquid”. Followed by enough aging treatment, an organogel with a network of nanoparticles was generated and did not exhibit apparent shrinkage compared with the former sol solution (Figure S2, Supporting Information). Finally, lignin-based xerogel was obtained after natural drying under ambient pressure (inset, Figure 1a). The



**Figure 1.** (a,b) SEM images of the xerogels at different magnifications. (c) Mirror-like phenomenon can be observed on the lignin-based xerogel (submerged in water). (d) Water droplets exhibit spherical shapes on the surface of the xerogel. (e) The water contact angle on the surface of the xerogel. (f–i) The self-cleaning ability of the resultant xerogel through the removal of silica particles from the surface using a moving water droplet ( $5\ \mu\text{L}$ ).

number of hydroxyl groups of lignin used in this work is 2.189 mmol/g. After the reaction with MMDI, the number of hydroxyl groups would decrease. However, lignin was unsolvable at this time, and the determination of the number of hydroxyl groups became difficult.

Typical SEM images at different magnifications of lignin-based xerogels are shown in Figure 1a and b. The low magnification SEM image reveals that the xerogel surface possesses a randomly rough structure at the microscale of coralloid nanoparticle clusters. The high magnification SEM image shows that the coralloid nanoparticle clusters are composed of spherical nanoparticles, and the individual nanoparticle is not isolated but bonded together. The formation of this multiscale structure occurs because the nanoparticles are produced in the phase separation process and particle aggregates in the aging treatment section, resulting in coralloid particle clusters. Furthermore, effects of the concentration and ratio of the monomers to the xerogel structure are investigated (Figure S3, Supporting Information). Compared with the samples prepared based on different monomer concentrations, it was found that decreasing monomer concentration reduced the diameter of the nanoparticle and the xerogel porosity; when the monomer concentration is low enough, the porous structure cannot even be achieved. Moreover, fixing the lignin concentration at a suitable level and reducing the MMDI concentration leads to compacter particle networks. The above results can be traced to the fact that increasing the monomer concentration or eliminating hydroxyl groups by reacting with MMDI both



**Figure 2.** Snapshots of removal process of (a) *n*-hexane (dyed with Sudan I) floating on water and (b) dichloromethane (dyed with Sudan I) sinking below water using the hydrophobic xerogel. (c) Sorption efficiency of lignin-based xerogels for various organic liquids. (d) Regenerability of the xerogel for absorption of gasoline with the distillation method.

lead to a faster phase separation, which is beneficial to the porous structure formation. In other words, the porous structure of the xerogel is controllable by adjusting the monomer concentration or the ratio of lignin/MMDI.

The micronanoscale hierarchical structure on the lignin-based xerogel surface, which is similar to the multiscale structure of the lotus leaves surface, prevents the capillary permeability of the water enhancing the xerogel surface hydrophobicity.<sup>30</sup> Combined with the intrinsic hydrophobicity of the nanoparticle components (Figure S4, Supporting Information), the obtained xerogels consist of outstanding surface wettability. It was demonstrated that the xerogels consist of great water repellence with a water contact angle of 146.4° (Figure 1e). It is highlighted in Figure 1c and d that when immersed into water by an external force, the xerogel surface acts like a sliver mirror when viewed at a glancing angle, and the water droplets exhibit typical spherical shapes on the xerogel surface. In addition to the super-repellency, the resultant xerogel showed a low adhesion to water. The water droplet is hardly able to stick to the xerogel surface, allowing water droplets to roll off quite easily (Movie S1). This can be directly confirmed by the evolving contact process of a water droplet on the superhydrophobic xerogel surface (Figure 1f–i). The superhydrophobicity with a small sliding angle makes it possible to use the xerogel in the field of oil/water separation, especially when the density of oils is close to that of water. The mechanisms of the self-cleaning property and superhydropho-

bicity for the xerogels can be concluded as follows. First, the reaction between –NCO and –OH reduces the hydrophilicity of the polymer, resulting in nucleation and phase separation, and the porous structure consisting of nanoparticles is formed. With the aging treatment, the nanoparticles aggregate and lead to coralloid nanoparticle clusters, making the obtained xerogel possessing a micronanoscale hierarchical structure, which is similar to the lotus leaves. The superhydrophobicity roots in the intrinsic hydrophobicity of the obtained polymer. Moreover, the microscale rough surfaces that resulted from the coralloid nanoparticle clusters can effectively prevent the capillary action of water, tremendously enhancing the hydrophobicity of the obtained xerogels. Furthermore, the nanoscale structure that is rooted in the nanoparticles can effectively reduce the close contact between the solid and liquid and influence the shape, length, and continuity of the triple-phase contact line. Thus, it substantially reduces the rolling angle, making the rolling of the water droplets on the xerogels easy and exhibiting an excellent self-cleaning property.

Owing to their superhydrophobic surface, high porosity (75.1%; Figure S5, Supporting Information), and interconnected 3D framework, the lignin-based xerogels exhibit excellent selective oil absorption in the oil/water mixture.<sup>31–36</sup>

When a small piece of the xerogel was forced to the *n*-hexane layer on a water surface, the oil had been taken up completely in several seconds (Figure 2a, Movie S2, Supporting Information). In addition, the xerogel was forced into the

water for quick absorption of chloroform sinking at the bottom of water and also exhibits a quick oil recovery ability (Figure 2b, Movie S3, Supporting Information). Various oils and organic solvents can be absorbed by the xerogel, and the absorption capacity varied depending on density, viscosity, and surface tension of the absorbed liquids (Figure 2c). Furthermore, the regenerability of absorbent and the recoverability of pollutants also play important roles in pollution control and environmental protection.<sup>10</sup> As illustrated in Figure S6 of the Supporting Information, distillation is employed to recover pristine xerogel and harvest the pollutants, unlike the conventional combustion process, which will waste the precious raw materials. The absorption/distillation recycle test has been conducted on the gasoline/xerogel system. After gasoline has been absorbed, the xerogel was heated to 70 °C to release the gasoline vapor, and gasoline was recovered by cooling the vapor. Moreover, the recycle process was repeated at least five times (Figure 2d); the absorption capacity of the aerogel remained almost 100%, as the structure and size of the lignin-based xerogel were maintained perfectly during the entire process, exhibiting an ideal absorbent for recycling absorbed oil contaminants from water.

## CONCLUSION

In conclusion, we have developed a facile and low-cost method to fabricate a novel xerogel with self-cleaning properties and superhydrophobicity using lignin modified by dissociate. The obtained xerogel exhibits excellent selective oil absorption in the oil/water mixture, being an ideal absorbent for spilled oil cleanup. This method may open a new route to utilizing natural renewable resources to design and synthesis porous materials for a wide range of applications.

## ASSOCIATED CONTENT

### Supporting Information

Materials, formulations, and mechanical performance of lignin-based xerogels. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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