



# Preparation and formation mechanism of size-controlled lignin based microsphere by reverse phase polymerization



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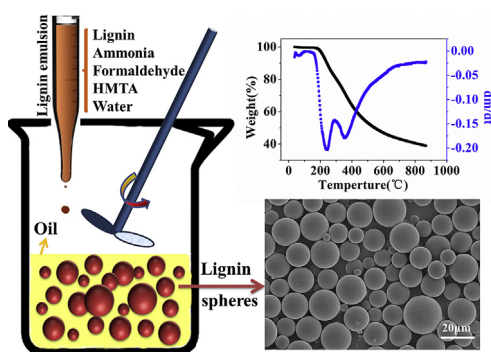
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## HIGHLIGHTS

- Lignin based microsphere was prepared by reverse phase polymerization.
- The mechanism was studied by elemental analysis, FT–IR and thermogravimetric analysis.
- The lignin emulsion plays a vital role on size distribution and surface morphology.
- Lignin based microsphere showed excellent thermal stability.
- Lignin based activated microsphere is a promising material for high performance SCs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Commercial lignin, by-product of enzymatic hydrolysis of biomass for bioethanol production, was used to prepare lignin based microsphere by reverse phase polymerization. The reverse phase polymerization had favorable influence on the morphology, size distribution and thermal stability by coordinating solid content and dispersed phase content of lignin emulsion. The carbonization yield at 870 °C of lignin based microsphere reaches to 38.87% by improving 5% from lignin precursor 33.43%, at solid content 0.059 and dispersed phase content 0.050. The mechanism is postulated based on the results from elemental analysis, FT–IR spectroscopy and thermogravimetric analysis. Furthermore, the lignin based microsphere could directly carbonize without pre-oxidation process. Hence, the reverse phase polymerization is a meaningful and possible industrial process. And the gravimetric capacitance of lignin based activated carbon microsphere (LAC-M) is as high as 334 F g<sup>-1</sup>, and even after 10,000 cycles at 1 A g<sup>-1</sup> a specific capacity of 286 F g<sup>-1</sup> remains. Thus, LAC-M is a promising material for high performance SCs.

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## 1. Introduction

Lignin, the second most abundant biopolymer after cellulose, is a high carbon content renewable resource in nature. It is a polyphenol with a three dimensional structure consisting of randomly

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cross-linked phenyl propane building blocks, namely, *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) [1]. Commercial lignin comes mainly from by-product of various industrial processes such as the organosolv pulping process, sulfite pulping methods used in the paper and pulp industry and enzymatic hydrolysis of biomass for bioethanol production. Commercial lignin offers advantages of abundance, low cost, biocompatibility, high carbon content and sufficient oxygen-containing functional groups, etc., making it a potential polymer for the carbon material, for example, activated carbons, carbon fibers and composite materials [2–4].

The application of lignin based carbon materials has made claim on the morphology of lignin precursor. Lignin based carbon sphere, carbon fiber, activated carbon sphere and activated carbon fiber are better choices for practical application. It is challenging to make specific shape for lignin because its softening point temperature is higher than the decomposition temperature. So most lignin need to undergo pretreatment to change thermal properties or be blended with other thermoplastic polymers to increase its plasticity performance before forming process [5,6]. The research on lignin based carbon materials started fifty years ago, and several methods, physical and chemical treatment, had been described to synthesize activated carbons and carbon fiber used in adsorption [7], lithium ion battery [8] or supercapacitor [9] from commercial lignins. Especially lignin based carbon fiber had been prepared by melting spinning, dry spinning [10] or wet spinning successfully [11]. However, the preparation of lignin based microsphere and properties of such material are also important to its potential applications on adsorption or supercapacitor, yet not to have been explored.

Most recently, Techniques reported on synthesizing Nano/micro spherical structured materials include self-assembly [12,13], colloidal dispersion [14] and emulsion polymerization [15,16] were introduced. Lee KP [17] reported directed synthesis of poly (ortho-toluidine)-metal (gold and palladium) composite Nano spheres via self-assembly method. Zhang J [18] presented a facile and large-scale fabrication of poly (acrylic acid) (PAA) hollow Nano gels via an in situ Pickering miniemulsion polymerization method. Gomes VG developed a facile route for the synthesis of high yield graphene-polymer nanocomposites in the aqueous phase and polymer brush nanocomposite from “NH<sub>2</sub>-terminated CNT” substrate via emulsion polymerization [19,20]. Many commercial available polymers and copolymers manufactured by the suspension polymerization process have been used for industrial applications because of easy manufacturing feature with spherical polymer particles. In addition, the polymer particles could be easily combined to form copolymers and hybrid materials with other monomers, respectively. Lignin, replacing part of polyphenols, can be used to prepare thermosetting lignin based phenolic resin microsphere, for its rich hydroxyl group of molecules [21,22]. Furthermore, the genius of lignin molecule, three dimensional structures consisting of randomly cross-linked phenyl propane building blocks give lignin based microsphere potential application on activated carbon for supercapacitors.

Hence, the objective of this study was to prepare lignin based microsphere via reverse phase polymerization from commercial lignin, examine the physical and chemical changes of lignin precursor during the reverse phase polymerization, explore the influence of preparation conditions (lignin emulsion solid content and dispersed phase content) on the lignin based sphere diameter distribution and surface appearance, and make clear the optimal lignin emulsion solid content and dispersed phase content range where the reverse phase polymerization work effectively. What's more the influence of reverse phase polymerization on the properties of lignin based microsphere was studied by thermogravimetric analysis, differential scanning calorimetry (DSC), XRD, X-ray

photoelectron spectroscopy (XPS) and Field emission scanning electron microscope (FESEM). And then the application of lignin based microsphere on activated carbon for supercapacitors was explored preliminarily.

## 2. Material and methods

### 2.1. Lignin precursor and lignin base microsphere processing

Commercial lignin, by-product of enzymatic hydrolysis of biomass for bioethanol production from Yanghai chemical co., LTD in Shandong province, China, was used as the main raw material to prepare lignin based microsphere. It underwent purification treatment to get rid of the adverse ash and some organic impurity, aiming to improve the purity and stability of lignin. Table 1 contains the main properties of the lignin precursor. The elemental analysis of the lignin precursor indicated that it composed mainly of carbon, hydrogen and oxygen. The content of nitrogen is very small. The C/H and C/O ratio of the lignin precursor reflects some degree of aromaticity and methoxy group in the lignin precursor. And the ash content is 0.17% measured by GB/T 2295-2008 technique.

Lignin based microsphere was prepared by reverse phase polymerization and reaction mechanism of lignin based microsphere is phenol-formaldehyde condensation, hydroxyl group of lignin molecules and formaldehyde. Olive oil from MERYER CO., LTD in Shanghai, china, was continuous phase and the dispersed phase was lignin precursor emulsion. The emulsion solid content is 0.059. Ammonia, Hexamethylenetetramine and formaldehyde were purchased from Tianjin Jiangtian chemical technology co., LTD in Tianjin, China. Ammonia was used as catalyst, and Hexamethylenetetramine (HMTA) was curing agent. 1.0 g Lignin mixing with 1.8 g Ammonia and 0.09 g Hexamethylenetetramine, was dissolved in water, at the mass ratio of 1:5. When the lignin dissolved totally and then 6 g formaldehyde was added into emulsion. And the dispersed phase content was 0.050. Condensation and curing reaction of lignin precursor and formaldehyde kept at 94 ± 2 °C for 2 h in 300 ml oil phase. After cooling down to room temperature, the lignin based microsphere by centrifuge separation was washed with hexyl hydride until no trace of oil remains. Finally, the obtained lignin based microsphere was dried at 80 °C for 12 h. In order to expound the effect of the emulsion solid content and dispersed phase content on lignin based microsphere diameter distribution and surface appearance, three different emulsion solid content (0.041, 0.059 and 0.079) and dispersed phase content (0.024, 0.048 and 0.072) were applied.

The lignin based microsphere was firstly carbonized at 600 °C for 1 h. The obtained lignin based carbon microsphere was dispersed in KOH aqueous at a mass ratio of 1:3, dried at 80 °C for 12 h and activated at 800 °C for 2 h under nitrogen in a tube furnace. Sample was washed with 1M HCl solution and sufficient water repeatedly till a neutral pH was obtained. Finally, the sample was dried at 80 °C for 24 h. For a better understanding of the lignin based microsphere, the lignin precursor was also treatment as mentioned before. Activation samples were named as LAC-M and LAC-P, representing the lignin based microsphere activated sample

**Table 1**  
Main properties of the Lignin precursor.

Raw Materials	Elemental Analysis (wt %)					Ash (wt %)
	C	H	N	O <sup>a</sup>	C/H <sup>b</sup>	
Lignin precursor	62.28	5.47	0.74	31.51	0.95	0.17

<sup>a</sup> By difference.

<sup>b</sup> Carbon to hydrogen atom ratio.

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