

# Direct Preparation of Hollow Nanospheres with Kraft Lignin: A Facile Strategy for Effective Utilization of Biomass Waste

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This work discusses the preparation and characterization of hollow nanospheres based on kraft lignin (KL). Kraft lignin is a by-product of the papermaking industry and an abundant renewable resource. It was determined that adding water to a KL/THF solution induced KL to form hollow nanospheres *via* self-assembly. Scanning electron microscopy and transmission electron microscopy confirmed the hollow nanosphere morphology. The shell thickness of the hollow nanospheres was tunable by adjusting the initial KL concentration in THF, making the nanospheres a potential material for the encapsulation and controlled release of guest molecules. Ultraviolet (UV) and Fourier transform infrared (FTIR) spectroscopy confirmed the  $\pi$ - $\pi$  stacking of aromatic rings as an important and distinctive mechanism for the formation of hollow KL nanospheres. The nanospheres were obtained simply and inexpensively, and they exhibited the characteristics of biocompatibility, biodegradability, and low toxicity. These advantages make hollow KL nanospheres attractive for applications in nanoscience and nanotechnology. This study developed an economically feasible and facile strategy for the effective use of biomass waste in sustainable chemistry.

*Keywords:* Kraft lignin; Hollow nanosphere; Self-assembly; Sustainable chemistry; Renewable resources

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## INTRODUCTION

Lignin is one of the most abundant natural organic polymers, second only to cellulose by mass. As the most abundant natural aromatic polymer, lignin has a highly branched three-dimensional phenolic structure. Although lignin's exact structure remains virtually unknown, its structural components are widely accepted as three types of phenylpropanoid units: para-hydroxybenzene, guaiacyl, and syringyl (Chakar and Ragauskas 2004). Most industrial lignin is a by-product of the paper pulping process, so lignin has long been given the label of a "waste material". Kraft lignin (KL), recovered from the black liquor of paper pulping, has the highest proportion of industrial lignin. A major portion of KL is incinerated for the production of process steam and energy. In addition, KL could be used for biochemicals and biofuels (after chemical degradation or pyrolysis), polymer materials by blending, heavy metal adsorbents, carbon fibers, and many types of industrial dispersants after chemical modification (Vishtal and Kraslawski 2011; Lin *et al.* 2012; Cui *et al.* 2013; Lou *et al.* 2013). However, the existing products have mostly low-value

applications. The use of KL in high-value-added applications still requires exploration.

The fabrication of hollow polymer nanospheres or nanocapsules has attracted considerable interest in both theoretical and applied research fields (Zoldesi and Imhof 2005; Blanazs *et al.* 2009; Du and O'Reilly 2009; Velev and Gupta 2009). Because they can encapsulate guest molecules in their interior, hollow spheres have great potential for applications such as drug storage and delivery (Kataoka *et al.* 2012), separation (Wang *et al.* 1998), adsorbents, microreactors (Vriezema *et al.* 2005), catalysts (Lu *et al.* 2015), supercapacitors (Liu *et al.* 2014), and medical examination and diagnosis (Salata 2004). Methods for the fabrication of hollow spheres have been extensively reported, including template synthesis (Liu and Basu 2009), self-assembly (Breitenkamp and Emrick 2003), emulsion polymerization (Jang and Ha 2002), core removal of dendrimers (Zimmerman *et al.* 2002), and direct polymerization reaction (Kim *et al.* 2010); however, the most commonly used raw materials are synthetic polymers.

Kraft lignin can be considered an amphiphilic biopolymer because of the presence of both hydrophilic and hydrophobic groups. Similar to amphiphilic block copolymers, KL should, in principle, be able to form nanostructures by self-assembly. However, KL has been unexplored for the preparation of nanostructures because of its intricate structure. The authors have recently shown that KL, after chemical modification by acetylating, can form lignin-based solid spheres by self-assembly (Qian *et al.* 2014a,b). That work led us to the idea to use this procedure for exploiting more nanomaterials produced by lignin.

In the present study it was discovered that KL can easily form hollow nanospheres *via* self-assembly in a mixture of water and tetrahydrofuran (THF). The most exciting aspect of this study is that these hollow nanospheres are obtained by a completely physicochemical process, without the need for any chemical modification. Moreover, it was also found that both the size and the shell thickness of these nanospheres can be easily controlled, which would allow the permeability of the nanospheres to be adapted to the desired application. The hollow nanospheres prepared from KL have several obvious advantages over other techniques. First, the preparation process is very simple. The products are obtained simply by mixing the two solvents, which makes this method a facile strategy to perform on an industrial scale. Furthermore, the cost of the raw materials is very low. For example, the Chinese market price of KL is approximately 150 to 300 dollars per ton, which is competitive with synthetic polymers for the same purpose. Moreover, the natural properties of KL also provide many advantages. Lignin itself has high biocompatibility and biodegradability, low toxicity, ultraviolet resistance (Qian *et al.* 2015), oxidation resistance (Faustino *et al.* 2010), and good pH and temperature responsiveness. These properties make lignin a suitable material for the shells of the hollow nanospheres. For example, it was demonstrated that lignin microcapsules can realize the purpose of drug release and they are not cytotoxic and readily incorporated in the animal cells (Tortora *et al.* 2014). With so many advantages, hollow KL nanospheres are highly attractive materials, with possible applications in the materials industry, agriculture, food, biology, medicine, and life sciences.

In this work, hollow KL nanospheres were directly prepared *via* self-assembly in a mixed THF and water solvent system. The influence of the preparation conditions on the morphology of the hollow nanospheres was also studied. The structural characters of the hollow nanospheres and their aggregation mechanism were characterized and revealed by a series of characterization methods. The preparation for hollow KL nanospheres is expected to potentially be a valuable and environmentally sustainable route for waste utilization and green chemistry.

## EXPERIMENTAL

### Materials

Kraft lignin, provided by the Jinan Shengquan Group Co., Ltd. in the Shandong province of China, was obtained from black pulping liquor using acid precipitation. The product was used directly from the factory, without any further treatment. The water used in the experiment was ultrapure water. Other reagents were purchased commercially as analytical-grade products and used without further purification.

### Preparation

Hollow KL nanospheres were prepared by first dissolving KL in THF. The KL/THF solution was bath sonicated for 2 to 3 min and later allowed to stand for approximately 72 h to allow sufficient time to dissolve as much KL as possible. The supernatant was removed to be used as a stock solution for preparing the hollow spheres. The concentration of the stock solution was tested against a pre-prepared UV standard curve.

To prepare the hollow spheres, 3.0 mL of KL/THF stock solution was first added to a serum bottle; then, ultrapure water was added to the bottle dropwise using a peristaltic pump at a rate of 0.02 mL/sec until the water content was 90 wt.%. The solution was continually stirred with a magnetic bar as the water was being added.

For the DLS and UV measurements, a sample was prepared as described above. Next, the sample solution was placed in a dialysis bag with a molecular cut-off of 1000 g/mol and dialyzed for three days with continuously renewed ultrapure water to remove the THF.

After dialysis, the concentration of the solution was again tested by the pre-prepared UV standard curve. For UV and FTIR measurements, the KL samples from the supernatant of the KL/THF solution that were not used to form the hollow spheres were concentrated by rotary evaporation to ensure the consistency of their chemical composition. For the FTIR study, the two samples were treated further with freeze drying.

### Characterization

A commercial laser light scattering (LLS) instrument (ALV/CGS-3, ALV GmbH, Germany), equipped with a multi-digital time correlator (ALV-7004) and a solid-state He-Ne laser (JDS-Uniphase, output power = 22 mW, 632.8 nm), was used to measure the scattered light intensity and the hydrodynamic radius. The temperature for the LLS measurement was maintained at 20 °C.

The TEM was performed using a JEM-2100F microscope (JEOL, Japan). A drop of the hollow KL nanosphere solution was deposited onto copper grids coated with a thin carbon film and then dried at room temperature. Scanning electron micrograph observations were conducted on an FEI Nova Nano SEM 430 microscope (FEI, Holland), as shown in Fig. 2, and using a Zeiss Merlin microscope (Zeiss, Germany), as shown in Fig. 4. The specimens for the SEM observations were prepared by depositing a drop of each solution onto silicon substrates.

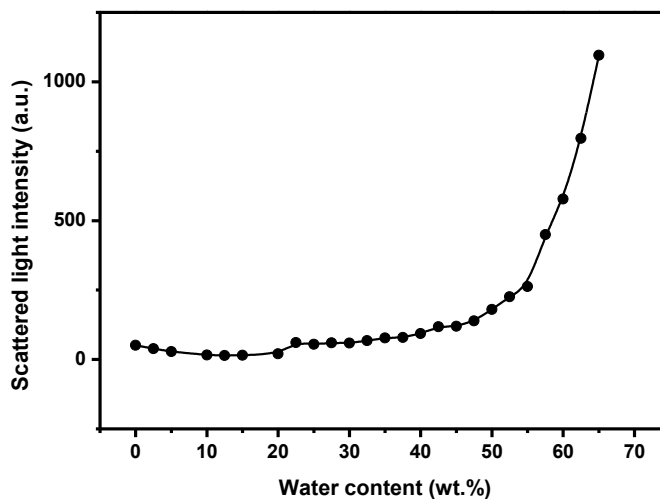
The UV spectra were measured with a UV-Vis spectrophotometer (UV-2450, Shimadzu Corp., Japan). Fourier transform infrared spectra were recorded in the 500 to 4000  $\text{cm}^{-1}$  range on a Vector 333 FT-IR spectrometer (Bruker Corp., Germany).

## RESULTS AND DISCUSSION

### Preparation and Characterization

The solvent environment had a pivotal role in the aggregation of KL. Relatively speaking, THF is a better solvent for KL than water. For the preparation of KL nanospheres, the KL/THF solution was first obtained as mentioned in the experimental section. Next, water was added dropwise to the KL/THF solution. As water was added to the system, the solvent environment became progressively worse for KL, and the KL molecules were driven to self-assemble with the slow addition of water to the system.

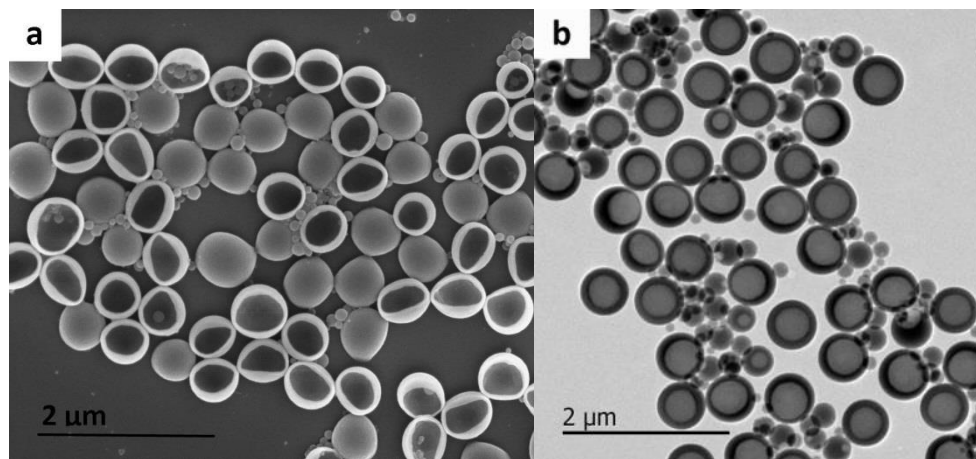
Figure 1 presents the experimental curves of the scattered light intensity from the solutions as a function of the added water content. Because scattered light intensity is proportional to polymer concentration and aggregate molecular weight, the increase of scattered light intensity reflect the molecular weight increase of the aggregate (Yu *et al.* 1998). When the water content was relatively low, the scattered light intensity changed very little, implying that the KL aggregates did not yet form appreciably. However, when the water content rose to approximately 50 wt.%, the scattered light intensity increased noticeably. The rapid increase in the scattered light intensity indicates that the KL aggregates formed quickly.



**Fig. 1.** Scattered light intensity *versus* the added water content in the solution. The initial KL concentration in THF was 2.0 mg/mL

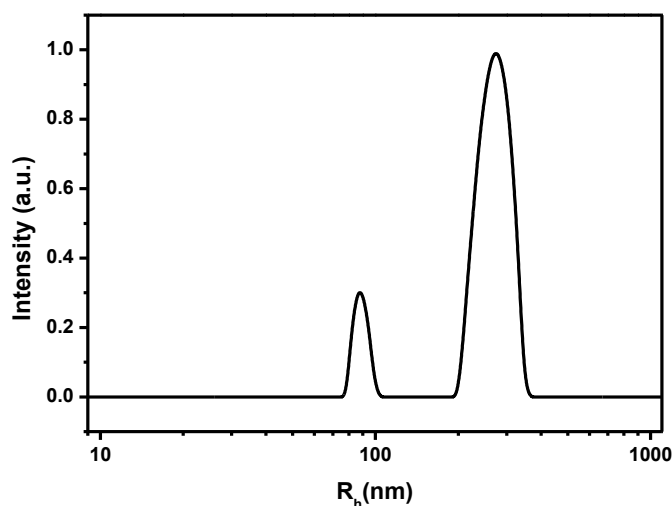
The morphologies of the aggregates were investigated by SEM and TEM, as indicated in Fig. 2. The morphologies of the particles depend considerably on the preparation conditions (as will be discussed later). Therefore, in this section, we first started with an initial concentration of 2.0 mg/mL of KL in THF for imaging and observation, which led to the formation of a representative type of aggregate. The remarkable hollow sphere morphology of the aggregates can be observed by SEM and TEM. Clearly, the SEM image (Fig. 2a) shows a hollow interior surrounded by a shell with a certain thickness, but many of the larger spheres have irregular gaping holes. Because SEM images were obtained under a vacuum, which completely dried the samples, the solvent in the interior of the sample was evacuated, leaving the walls of the sphere broken and gaping open. However, high contrast between the central and outer parts of the aggregates in the TEM

images (Fig. 2b) shows how the hollow spheres typically appear under TEM. There were two resulting particle size ranges visible in the images; the larger particles tend to be approximately 500 to 600 nm, while the smaller ones were approximately 100 to 200 nm.



**Fig. 2.** (a) SEM and (b) TEM images of the hollow KL nanospheres. The initial KL concentration in THF was 2.0 mg/mL

The particle sizes of the samples prepared under the above conditions were measured by DLS. The DLS results in Fig. 3 show a bimodal distribution of the hydrodynamic radius, which agrees well with the SEM and TEM images. The bimodal distribution of the particles may be attributed to the broad molecular weight distribution of KL.



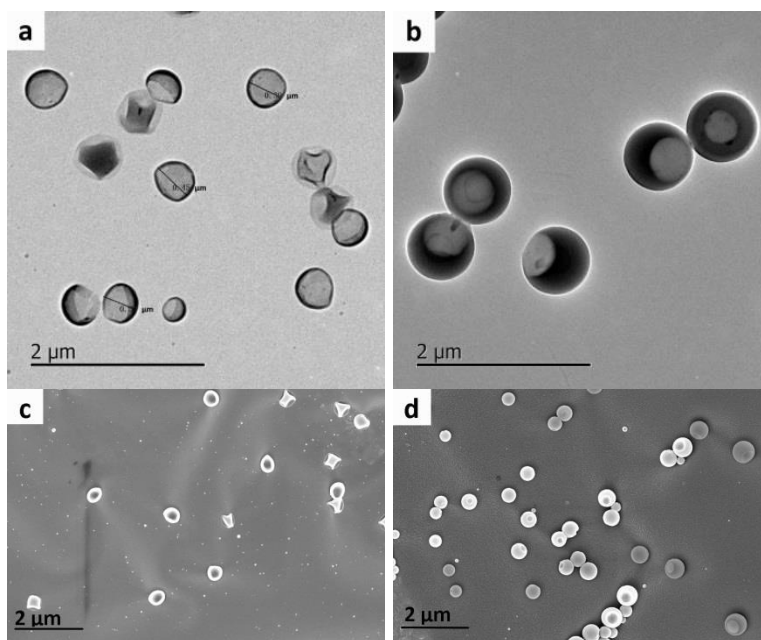
**Fig. 3.** Hydrodynamic radius ( $R_h$ ) distribution of the hollow KL nanospheres in aqueous solutions. The initial KL concentration in THF was 2.0 mg/mL

As a natural biomacromolecule, KL has a wide range of molecular weights, and the physicochemical properties also vary between different size molecules, especially because of their amphiphilic character. While water is added to the solution, KL molecules with different amphiphilic properties respond differently to the changing solvent environment.

A higher content of hydrophobic KL molecules aggregate more easily, and the rate at which different size KL molecules aggregate also differs. As a result, the sizes of the aggregates were somewhat different in this experiment.

### Control of Morphology

Different morphologies are often needed for various applications of hollow nanospheres (Letchford and Burt 2007). Therefore, we explored how to adjust the morphologies of hollow KL nanospheres. In general, many factors affect the morphology of polymer nanospheres. For this system, the initial KL concentration in THF was a simple variable to change, so it was selected for exploring how to adjust the morphology.



**Fig. 4.** (a, b) TEM and (c, d) SEM images of the hollow KL nanospheres obtained at two different initial KL concentrations: a and c, 0.5 mg/mL; b and d, 5.0 mg/mL

Representative SEM and TEM images of the nanospheres obtained from two different initial KL concentrations are shown in Fig. 4. For convenience of comparison, only the larger nanospheres obtained at each condition were selected for imaging. The morphologies obtained from two different initial concentrations are visibly different from each other. At the lower initial concentration (0.5 mg/mL), the nanospheres have a smaller particle size and a thinner shell that easily collapses. At the higher initial concentration (5.0 mg/mL), the nanospheres have a larger particle size and a thicker shell. The nanospheres with thicker shells are shape-persistent, meaning they can maintain their integrity even in a dry state. This effect can be easily understood with respect to initial KL concentration. When the initial concentration was lower, the KL molecules were more diffuse, and there were not enough KL molecules to form robust nanospheres, so they were relatively small and their walls were thinner. Meanwhile, at the higher initial concentration, the molecules were much closer to each other, and there were more molecules present to form the nanospheres. Thus, their size was relatively larger and their shell was thicker.

This facile fabrication method allowed us to obtain hollow nanospheres with tunable shell thicknesses and therefore tunable properties. The shell thickness of these hollow nanospheres is, particularly in the context of applications, of great interest. For

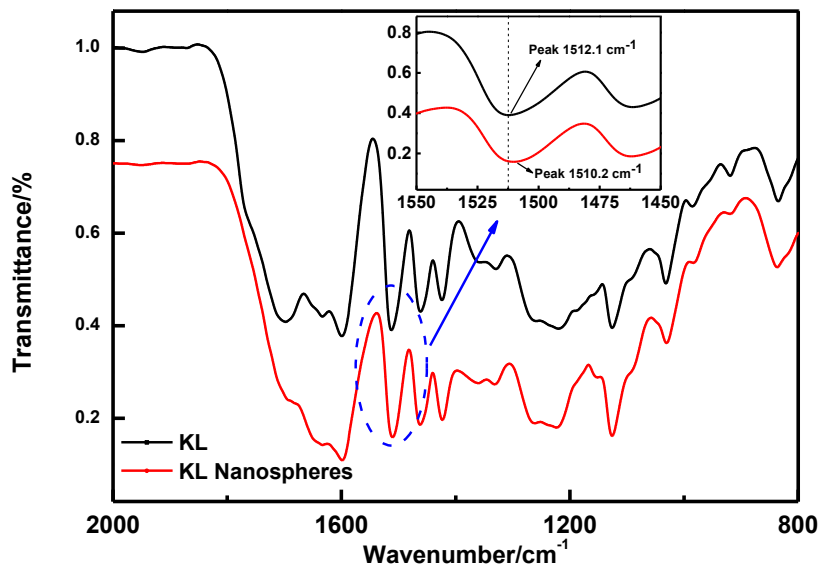
example, the thickness of the shells would allow control of properties such as permeability, degradation kinetics, rigidity, and mechanical strength (Balasubramanian *et al.* 2013). Hence, more possibilities for different applications can be derived from their tunable properties.

### Mechanism of Nanosphere Formation

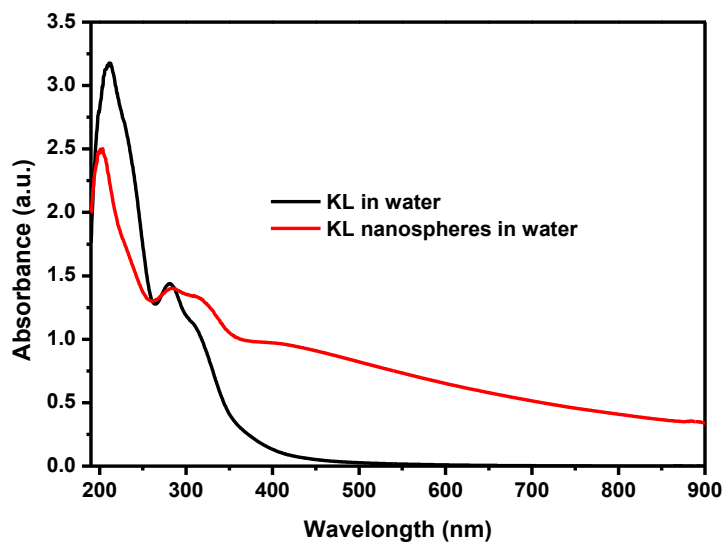
Although the method for preparing hollow KL nanospheres is similar to those of other hollow nanospheres that involve block copolymers (Cameron *et al.* 1999), the assembly process for hollow KL nanospheres should be distinctive because of the differences in the molecular structure and their aggregation mechanism. Previous studies showed that the KL in THF existed mainly as mono-molecules and intermolecular associations, having the more irregular conformation (Li *et al.* 2015). Obviously, there exist some intermolecular interactions that drive the KL from the irregular conformation to the uniform spherical structure. Noncovalent interactions, such as the hydrophobic effect and hydrogen bond interactions, promoted the aggregation of the KL molecules as water was added to the KL/THF solution, similar to the behaviour of block copolymers. Nevertheless, previous studies have suggested that lignin is a flat and disk-like macromolecule in solution (Vainio *et al.* 2004), and lignin molecules tend to form aggregates in solution (Contreras *et al.* 2008). The  $\pi$ - $\pi$  stacking among the benzene groups is considered a distinctive characteristic for the aggregation of KL (Guerra *et al.* 2007; Deng *et al.* 2012). To explore whether  $\pi$ - $\pi$  stacking played a role when the KL molecules gathered to form the nanospheres, further studies were carried out by UV and FTIR spectroscopy.

In the UV and FTIR studies, two forms of KL samples were compared. One sample was KL that did not form hollow nanospheres (hereafter referred as “KL”), which was obtained by first dissolving KL in an alkaline solution and then dialyzing it against ultrapure water to remove the alkali. The other sample was the hollow KL nanospheres, which were obtained by dialyzing the sample solutions with ultrapure water to remove the THF. Thus, the chemical compositions of these two samples were the same, but the aggregate form of KL was different: one sample formed hollow nanospheres, while the other did not. The FTIR spectra for the KL and the hollow KL nanospheres are shown in Fig. 5. The peak related to the aromatic units of KL at  $1512.1\text{ cm}^{-1}$  shifted to  $1510.2\text{ cm}^{-1}$  for hollow KL nanospheres, a positive movement of  $2.1\text{ cm}^{-1}$  in peak shift. Because the two samples' chemical compositions were identical, the peak shift can only be attributed to the lignin's aromatic groups being in different aggregating environments (Pillai and Rennekar 2009). The lower wave numbers provided direct evidence that hollow KL nanospheres have stronger  $\pi$ - $\pi$  interactions among the aromatic groups than KL.

In Fig. 6, the UV absorption spectra of KL and hollow KL nanospheres in aqueous solution are quite different, despite their identical chemical compositions. This result also indicates that the aggregating environments of the aromatic rings in the KL and the KL nanospheres were significantly different. A previous study showed that the typical  $\pi$ - $\pi$  aggregation mechanism of the KL aromatic groups is J-aggregation (Deng *et al.* 2011). According to molecular excitation-coupling theory, the enhancement of J-aggregation results in a red shift in the UV spectra; thus, the red shift in Fig. 6 indicates that the J-aggregation in the hollow KL nanospheres is enhanced; therefore,  $\pi$ - $\pi$  aggregation is enhanced. The UV analysis agreed with the FTIR results, which further confirms that  $\pi$ - $\pi$  interactions among the aromatic groups play a crucial role in the formation of hollow KL nanospheres.



**Fig. 5.** FTIR spectra of KL and hollow KL nanospheres. Note the shift related to aromatic skeletal vibration at 1512 cm<sup>-1</sup>



**Fig. 6.** Ultraviolet-Vis absorption spectra of KL and hollow KL nanospheres in aqueous solutions. The absorbencies at  $\lambda_{280\text{ nm}}$  were adjusted to be similar to each other.

The hollow KL nanospheres obtained by this method have many advantages, such as simple preparation, low cost, biocompatibility, and biodegradability. Therefore, we believe that these new, hollow KL nanospheres possess great potential for desirable applications. This novel finding encourages further study with KL to serve both industrial and sustainable chemistry. Although we did not perform encapsulation and controlled release experiments, which were beyond the scope of this paper, future work will focus on these applications.



## CONCLUSIONS

1. It was demonstrated that KL can directly form hollow nanospheres by self-assembly. This preparation method only requires the addition of water to a KL solution in THF, and does not require further processing.
2. Furthermore, hollow nanospheres with tunable shell thicknesses can be obtained by adjusting the initial KL concentration.
3. The  $\pi$ - $\pi$  stacking of aromatic rings is an important and distinctive mechanism for the formation of hollow KL nanospheres.

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