Preparation and properties of lignin-based carbon/ZnO photocatalytic materials

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Abstract
Lignin-based carbon/zinc oxide (LCZ) composites with excellent porous structures were prepared by a one-step carbonization method using lignin as the carbon source. The effects of different carbonization conditions (temperature, carbonization time and QAL addition) on the pore structure of the composites were investigated. The results showed that the obtained LCZ composite had the largest specific surface area (317.765 m² g⁻¹) and pore volume (0.4344 mL g⁻¹) when the QAL addition was 4 g and carbonization at 600 °C for 2 h (LCZ-600-2-4). This porous structure enables a tighter bond between the lignin-based carbon and ZnO. The photodegradation performance of the prepared LCZ under simulated solar light (500 W Xe lamp) irradiation was improved for the rapid transfer of photogenerated electrons. Compared with pure ZnO, the degradation rate of LCZ reached 92% and 91% of methyl orange (MO) and rhodamine B (Rh B) in 2 h. LCZ was tested for material stability, and it showed good acid–base stability and the degradation rate of RhB kept above 80% after five cycles. This simple and scalable method opens up a green pathway for the preparation of photoelectric conversion materials.

Keywords Lignin-based carbon · ZnO · Photocatalytic materials

1 Introduction
Due to the continuous development of industry, environmental pollution and resource crisis have become problems that restrict human development and survival [1]. Especially, the environmental pollution caused by a large amount of industrial waste is very serious, such as the large amount of paper black liquor produced by paper industry and the large amount of dye waste liquid produced by printing and dyeing industry [2–4]. Therefore, the preparation of bio-waste into functional composite materials is the suitable and effective way to solve this problem [5–8]. Photocatalysts based on carbon/semiconductor composites have great potential for application in organic wastewater treatment and have been extensively studied in recent years [9, 10]. Various carbon/semiconductor nanostructures with excellent photocatalytic properties have been reported [11–13]. Among the many semiconductor photocatalytic materials, ZnO has received increasing attention due to its excellent electrical [14], optical [15], and environmental friendliness [16]. However, the low quantum efficiency and photocorrosion of ZnO severely limit its application in photocatalysis, which can be solved by doping or combining with carbon materials to aid the separation and migration of photogenerated electrons and holes [17, 18].

In industrial applications, it would make more sense to fully consider the economic benefits and environmental pollution. Industrial lignin is considered as a promising precursor for carbon materials due to its high abundance, good reproducibility, and low cost [19–21]. According to the findings, lignin has been described as a random, three-dimensional network polymer comprised of phenolhydroxyl, methoxyl and carboxyl active functional groups, which are very beneficial to form neat uniform composite structures with ZnO nanoparticles [22–25].

In this paper, LCZ composites with good solar light photocatalytic properties were prepared using lignin as the carbon source by a low-cost and environmentally friendly process. Since the porous carbon structure of the composites provides abundant adsorption sites, these adsorption sites become the active sites for the reaction during
photodegradation. The addition of lignin-based carbon significantly increased the solar light absorption of LCZ, effectively inhibited the complexation of photogenerated electron–hole pairs, and significantly improved the adsorption and photocatalytic performance of LCZ. This simple and scalable method opens up a green pathway for the preparation of photoelectric conversion materials.

2 Materials and methods

2.1 Experiment materials

Alkali lignin (AL) is provided by Shanghai Yunzhe New Material Technology Co., Ltd. sodium oxalate (Na$_2$C$_2$O$_4$), sodium hydroxide (NaOH), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O), rhodamine B (Rh B) and methyl orange (MO) were commercially purchased from Shanghai Titan Scientific Co., Ltd. All other chemicals were of analytic grade and used as-received without any further purification. Rh B(20 mg L$^{-1}$) and MO(20 mg L$^{-1}$) were used as representative organic dye molecule to characterize the photocatalytic properties of the as-prepared LCZ.

2.2 Experiment methods

2.2.1 Preparation of lignin-based carbon/ZnO materials (LCZ)

The quaternized alkali lignin (QAL) with positively charged functional group was synthesized from alkali lignin by a simple quaternization process, which can combine well with the negatively charged ZnO [26]. 6.7 g of Na$_2$C$_2$O$_4$ and 14.87 g of Zn(NO$_3$)$_2$·6H$_2$O were prepared into 200 mL of solution, respectively. Then the Zn(NO$_3$)$_2$ solution was dropped into the Na$_2$C$_2$O$_4$ solution with constant stirring to obtain a mixed solution of dispersed ZnC$_2$O$_4$. Then a certain amount of QAL powder was added into the ZnC$_2$O$_4$ mixed solution and stirred for 30 min. The obtained mixture was filtered and dried to obtain the ZnC$_2$O$_4$/QAL precursor, and the LCZ composites were prepared by carbonization in a tube furnace under N$_2$ atmosphere. An overview of the flowchart of the synthetic pathways for the LCZ was shown in Fig. 1.

2.2.2 Preparation of LCZ under different factors

The LCZs were prepared by the above-mentioned preparation method under different factors. firstly, the mass of QAL added was fixed at 1 g, the carbonization time was 2 h, and then the carbonization temperatures were adjusted to 400 °C, 500 °C, 600 °C, 700 °C, and 800 °C, respectively. The prepared LCZs were noted as LCZ-400-2-1, LCZ-500-2-1, LCZ-600-2-1, LCZ-700-2-1 and LCZ-800-2-1.

The carbonization temperature was set to 600 °C, the mass of QAL added to the mixture was 1 g, and the carbonization times were adjusted to 1 h, 2 h, 3 h, 4 h, and 5 h. The prepared LCZs were noted as LCZ-600-1-1, LCZ-600-2-1, LCZ-600-3-1, LCZ-600-4-1, and LCZ-600-5-1.

The carbonation time and carbonation temperature were set to 2 h and 600 °C, respectively. 1 g, 2 g, 3 g, 4 g, and 5 g of QAL mass were then added to the mixture, respectively. The prepared LCZs were noted as LCZ-600-2-1, LCZ-600-2-2, LCZ-600-2-3, LCZ-600-2-4, LCZ-600-2-5.

2.3 Characterization

The micro-morphology and structure analysis of LCZ and ZnO were investigated by field-emission scanning electron microscope (SEM, S-4800). X-ray diffraction (XRD) patterns were obtained by a Bruker D8 advance (Bruker, Germany) diffractometer using Cu-Ka radiation ($\lambda=0.154$ nm).
in the scattering range (2θ) of 10–80° with a scanning rate of 2°/min. The Raman spectra of the prepared LCZ and ZnO were recorded on a (LabR AMA Ramis, France) micro-Raman spectrometer excited at 633 nm. The specific surface area of the sample was analyzed by using the Brunauer–Emmett–Teller (BET) method with a Tristar II 3020 automated surface area and pore size analyzer (Micromeritics Corp., USA). UV–Vis diffuse reflectance spectra of ZnO and LCZ were recorded from 200 to 800 nm using a UV–Vis spectrophotometer (UV-2600, Shimadzu, Japan). The photo-luminescence (PL) spectra were recorded on a Hitachi F4500 instrument with an excitation light of 365 nm at room temperature.

### 2.4 Photocatalytic degradation performance test of LCZ

The photocatalytic degradation of MO and RhB were used as a model re-action for the evaluation of the photocatalytic activity of the LCZ. The experiment to determine photocatalytic degradation of MO was carried out as follows: A mixture of MO (20 mg L⁻¹, 100 mL) and prepared samples (50 mg) was illuminated with simulated solar light (500 W Xe lamp) under stirring in a photochemical re-action instrument (GG-GHX-V, Shanghai Guigo Industrial Co., Ltd., Shanghai, China). Before light illumination, the mixture was stirred for 30 min in the dark to reach the adsorption–desorption equi-librium. The temperature of the MO solution was maintained at 20 °C using circulating water. During the illumination, 15 mL of the MO mixture together with the catalyst was removed at each time point and centrifuged immediately to remove the catalyst. The concentration of the removed MO solution was measured by absorbance at the maximum absorption wavelength using UV–Vis spectrophotometry. The percentage of degradation of MO was calculated by \( \frac{C}{C_0} \) (calculated by \( \frac{A}{A_0} \)). Here, \( C \) is the concentration of MO at each irradiated time interval, and \( C_0 \) is the initial concentration of MO solution. \( A \) is the absorbance at the maximum absorption wavelength of the MO solution at each irradiated time interval, and \( A_0 \) is the initial concentration of the MO solution. The photocatalytic degradation tests of RhB were performed following the same procedure as for MO.

### 2.5 Material stability test of LCZ

The basic operation of the pH stability experiment was described in 2.4, where the pH of the used Rh B solution was only adjusted by pH electronic meter. The basic operation of the cyclic stability test was described in 2.4. After completing the photocatalytic experiments, the remaining solution was filtered. The residue was washed with distilled water and anhydrous ethanol several times to removal the residue of RhB. The dried powder was used as catalyst in the following photocatalytic experiment. This experiment was repeated five times.

### 3 Results and discussion

#### 3.1 Structural characterization

Figure 2 showed the N₂ adsorption–desorption isotherms and the pore size distribution obtained by the BJH algorithm for all samples LTC-T-X-Y tested at 77 K temperature. It could be seen that the adsorption isotherm of LCZ belonged to type IV line type in the IUPAC classification [27]. For all samples, the relative pressure was smaller for N₂ adsorption in the low-pressure, indicated that there was less microporous filling. In addition, the hysteresis of the desorption curve in the medium-pressure and the low adsorption at a \( P/P_0 \) of 0.99 in the high-pressure indicated the presence of fewer macropores and a large number of mesopores in LCZ. When the carbonization time and QAL addition were constant, the adsorption capacity of the high-pressure increased gradually with the increase of the regulation temperature, and the desorption curves were also more hysteresis. That was because more mesopores and macropores appeared after the carbonization temperature increased, and the specific surface area and pore volume also increased. As shown in Table 1, the specific surface area reached a maximum value of 310.249 m² g⁻¹ at a carbonization temperature of 600 °C, indicating that more mesopores were produced and the specific surface area increased at a carbonization temperature of 600 °C. The pore volume reached a maximum value of 0.3976 mL g⁻¹ at a carbonization temperature of 600 °C. However, more macropores were produced after the carbonation temperature over 600 °C, which increased the pore volume, but too many macropores reduced the specific surface area.

When the carbonization temperature and QAL addition were constant, it could be found that there was little change in the high-pressure, while the adsorption amount in the medium-pressure was increased and the hysteresis of the desorption curve is more severe, indicated that more mesopores were generated with increasing carbonation time. As shown in Table 1, the specific surface area reached a maximum value of 310.249 m² g⁻¹ at 2 h, while the pore volume also reached a maximum value of 0.3976 mL g⁻¹.

The amount of regulated QAL addition was continuously increased when the carbonation temperature and carbonation time were constant, it could be found that the maximum specific surface area of 317.765 m² g⁻¹ and the maximum pore volume of 0.4344 mL g⁻¹ can be achieved at the addition of 4 g of QAL. It was showed that QAL addition affects the number of pore creation, but relatively too much QAL may reduce pore generation by self-encapsulation of the
carbon layer and collapse of the pore channel. As shown in the pore size distribution diagram, the pore size of LCZ was mainly concentrated between 1 and 30 nm, a large number of mesopores were distributed between 2 and 10 nm, and a small number of micropores and macropores existed. In summary, LTC-600-2-4 with excellent pore structure was obtained when carbonized at 600 °C for 2 h and the addition of QAL was 4 g.

The structures of pure ZnO and LTC-600-2-4 were tested by XRD diffraction. As shown in Fig. 3, the characteristic peaks of ZnO appeared at 2θ of 31.8°, 34.3°, 36.2°, 47.5°, 56.6°, 62.9°, 67.9°, 69.2°, which correspond to the ZnO peaks.
crystals at (100), (002), (101), (102), (110), (103), (200), (112), (201), respectively. The characteristic peaks and positions of LTC-600-2-4 and ZnO are consistent, indicating that lignin did not destroy the crystalline structure of ZnO. This was because the intensity of the amorphous characteristic peaks of lignin carbon at 20–30° was much weaker than that of the ZnO. Moreover, the amount of lignin carbon in the composites was relatively small, which made it difficult to observe the characteristic peaks of lignin carbon in the XRD spectra. This was similar to most reported XRD results of graphene/ZnO composites [20, 21].

To further investigate the structure of LTC-600-2-4, Raman spectroscopy was performed on the composites. As shown in Fig. 4, the characteristic peaks D peak (1340 cm\(^{-1}\)) and G peak (1590 cm\(^{-1}\)) of lignin carbon could be observed. The D-band reflected the degree of defects in the carbon structure, and the G-band was due to the vibration of sp\(^2\)-hybridized carbon atoms in the two-dimensional direction of the hexagonal lattice. The obtained LTC-600-2-4 was similar to C/ZnO reported by other researchers using other carbon materials [19–21]. The strength ratio of G-band to D-band (I\(_G\)/I\(_D\)) was used to express the degree of graphitization of carbon in the composite. The smaller the I\(_G\)/I\(_D\) carbon value, the higher the degree of graphitization of the material. The low degree of graphitization of the prepared LTC-600-2-4 could be clearly seen from the figure.

### 3.2 Morphology and microstructure characterization

The micro-morphology and structure analysis of ZnO and LCZ-600-2-4 were investigated by SEM and TEM. As shown in Fig. 5a, ZnO had a typical nanoparticle structure with diameters ranging from about 50–180 nm, and pure ZnO nanoparticles exhibited a severe agglomeration behavior. As shown in Fig. 5c, d, LCZ-600-2-4 was composed of lignin carbon and ZnO nanoparticles. It could also be seen that the ZnO nanoparticles were well dispersed and tightly bound to the lignin carbon nanosheets, and the particle size of ZnO in the composite was much smaller than that of pure ZnO in Fig. 5b, d and f. The transfer process of photogenerated electrons and holes was closely related to the surface contact between carbon and semiconductor, and the high specific surface area and pore volume of LCZ-600-2-4 provides a rich site for ZnO. This tight interfacial contact was expected to improve the transfer process of photogenerated electrons and holes, thus improving and enhancing their photocatalytic performance.

The elemental composition and content of LCZ-600-2-4 was analyzed by X-ray energy spectrometry (EDS). As shown in Table 1, the specific surface area and pore volume of the LTCs were measured. The low degree of graphitization of the prepared LTC-600-2-4 could be clearly seen from the figure.

### Table 1 Pore parameters of LTCs

| Sample          | Specific surface area/m\(^2\) g\(^{-1}\) | Pore volume/mL g\(^{-1}\) |
|-----------------|----------------------------------------|--------------------------|
| LCZ-400-2-1     | 107.365                                | 0.2898                   |
| LCZ-500-2-1     | 136.907                                | 0.3667                   |
| LCZ-600-2-1     | 310.249                                | 0.3976                   |
| LCZ-700-2-1     | 228.186                                | 0.3181                   |
| LCZ-800-2-1     | 158.116                                | 0.2708                   |
| LCZ-600-1-1     | 183.596                                | 0.3354                   |
| LCZ-600-2-1     | 310.249                                | 0.3976                   |
| LCZ-600-3-1     | 292.426                                | 0.2632                   |
| LCZ-600-4-1     | 205.314                                | 0.2880                   |
| LCZ-600-5-1     | 168.167                                | 0.2259                   |
| LCZ-600-2-1     | 310.249                                | 0.3976                   |
| LCZ-600-2-2     | 149.841                                | 0.1776                   |
| LCZ-600-2-3     | 210.249                                | 0.3976                   |
| LCZ-600-2-4     | 317.765                                | 0.4344                   |
| LCZ-600-2-5     | 217.686                                | 0.3214                   |

![Fig. 3 XRD patterns of ZnO, LCZ-600-2-4](image)

![Fig. 4 Raman spectra of ZnO and LCZ-600-2-4](image)
shown in Fig. 6a, LCZ-600-2-4 contained C, O and Zn elements and their atomic percentages are 62.57%, 16.64% and 20.79%, respectively. The O and Zn atomic ratio was close to 1:1, which further indicates that the LCZ-600-2-4 composite was successfully prepared.

### 3.3 Optical properties characterization

The optical properties of pure ZnO and LCZ-600-2-4 were measured by UV–vis diffuse reflectance spectroscopy. As shown in Fig. 7a, the sample exhibited a typical strong light absorption in the UV region due to the promotion of electrons from the valence band (VB) to the conduction band (CB) of ZnO. Due to the benzene ring structure and the presence of double bonds, LCZ-600-2-4 exhibited a higher UV absorption than pure ZnO. In addition, LCZ-600-2-4 showed enhanced absorption intensity in visible light due to the absorption of background light by lignin-based carbon compared to pure ZnO.

The band gap energies ($E_g$) were determined from the Tauc spectra of $(\alpha h\nu)^2$ versus photon energy (h$\nu$) as depicted in Fig. 7b. The band gap energy of the semiconductors has been calculated by the Kubelka–Munk method [28]. The relationship between the photon energy (h$\nu$) and the absorption coefficient ($\alpha$) for the direct band gap semiconductor can be determined by the following equation:

$$\alpha = B_d(h\nu - E_g)^{1/2}\hbar$$

where the $B_d$ is the absorption constant for direct transitions, and $\alpha$ can be determined from the scattering and reflectance spectra according to the Kubelka–Munk theory. The band gap energies calculated from the intercept of the tangents to the plots are approximately 3.03 and 2.74 eV, corresponding to pure ZnO and LCZ-600-2-4, respectively. It showed that the absorption band-edges of the composites have red-shifted. The absorption edge of LCZ-600-2-4 showed a red shift compared to the pure ZnO, which is beneficial to enhance the photocatalytic performance.
The photoluminescence (PL) spectra of ZnO and LCZ-600-2-4 were shown in Fig. 8. The pure ZnO had a high and broad photoluminescence peak at about 500 nm, which indicated that there were many photogenerated electron/hole pairs in the pure ZnO. However, the photogenerated electrons and holes had a high probability of recombination. The luminescence intensity of LCZ-600-2-4 was much lower than that of pure ZnO. The significant decrease in photoluminescence intensity indicates that the recombination probability of photogenerated electrons and holes was greatly reduced and the electron–hole separation efficiency was significantly improved. The photogenerated electrons were effectively transferred to the lignin-based carbon with better conductivity, which greatly improved the photocatalytic activity.

### 3.4 Evaluation of photocatalytic performance

The photocatalytic performance of the prepared LCZ-600-2-4 composites was evaluated by simulating the photodegradation rate of organic dye pollutants under solar irradiation, and anionic dye MO and cationic dye Rh B were selected as pollutant models. The results are shown in Fig. 9a and b. The results showed that the LCZ-600-2-4 composite had good photodegradation effect on both MO and Rh B, while the photodegradation effect of pure ZnO solar visible light was very poor. Compared with pure ZnO, LCZ-600-2-4 degraded MO up to 92% and Rh B up to 91% in 2 h. After compounding with lignin carbon, LCZ-600-2-4 with rich pore structure provided a large number of adsorption sites and reactive sites for photocatalytic degradation.
Table 2 is the comparison of the characteristic parameters for the LCZ-600-2-4 photocatalyst and other hybrid ZnO photocatalysts related to this work. Although experimental conditions such as light source, value and concentration of dye solution and photocatalyst mass are different, the photocatalysis performance can still be a rough evaluation. The photocatalysis performance of the prepared LCZ-600-2-4 is similar to or superior to the photocatalysis performance in other reports. The prepared lignin-based carbon nanosheets have great potential for the replacement of the expensive graphene in the field of photocatalysis.

The photo-degradation mechanism of LCZ composites for MO or Rh B in this experiment can be explained as follows (Fig. 10):

\[
\text{LCZ} + \text{hv} \rightarrow \text{ZnO}^+ + \text{LC}(e^-), \\
e^- + \text{O}_2 \rightarrow \cdot \text{O}_2^- \\
h^+ + \text{H}_2\text{O/OH}^- \rightarrow \cdot \text{OH} \\
\cdot \text{OH} \text{ or } \cdot \text{O}_2^- \text{ or } h^+ + \text{MO(Rh B)} \rightarrow \text{CO}_2 \text{ and H}_2\text{O}
\]

Table 2

| Photocatalyst      | Light source | Mass of photocatalyst | Value and concentration of dye solution | Degradation efficiency |
|--------------------|--------------|-----------------------|-----------------------------------------|------------------------|
| LCZ-600-2-4        | Xe (500 W)   | 50 mg                 | MO-100 mL (20 mg L\(^{-1}\))             | 92.0% (120 min)        |
| LCZ-600-2-4        | Xe (500 W)   | 50 mg                 | RhB-100 mL (20 mg L\(^{-1}\))            | 91.0% (120 min)        |
| LC/ZnO-2 [29]      | Xe (500 W)   | 30 mg                 | MO-60 mL (15 mg L\(^{-1}\))             | 98.9% (30 min)         |
| ZnO-10%RGO-NCs [30]| Xe (500 W)   | 20 mg                 | RhB-80 mL (10 ppm)                       | 98.2% (120 min)        |
| Cl-ZnO-NWAs/GF [31]| Xe (150 W)   | –                     | RhB-50 mL (5 mg L\(^{-1}\))             | 95.1% (75 min)         |
| ZnO-GO [32]        | Xe (200 W)   | 40 mg                 | MB-50 mL (20 mg L\(^{-1}\))             | 98.0% (50 min)         |
The QAL with positively charged functional groups can combine well with the negatively charged ZnO. The photogenerated electrons and holes generated by ZnO could be rapidly transferred to the lignin-based carbon through a tight interface, inhibiting the effective complexation of holes and electrons. The high specific surface area of LCZ-600-2-4 could facilitate the bulk loading of ZnO, and its porous structure could rapidly adsorb organic dyes onto the composite surface. The degradation of organic dyes in wastewater was further greatly enhanced.

### 3.5 Evaluation of material stability

It could be seen from Fig. 11a the photodegradation performance showed little difference under different pH conditions. The lignin carbon particles had a certain encapsulation effect, which reduced the excessive contact between ZnO and the degradation solution to a certain extent, indicated that the prepared LCZ-600-2-4 had good pH adaptability.

To further investigate the stability of the samples of LCZ-600-2-4, five successive recycling tests over the sample of LCZ-600-2-4 for photo-degradation of Rh B under solar light have been performed, and relevant experimental results were shown in Fig. 11b. It could be seen that the degradation rate of LCZ-600-2-4 could still maintain above 80% after five cycles. The slight decrease of degradation rate was due to the incomplete desorption of the adsorbed dyes in the dark reaction stage. The results indicated that the prepared composites had good cycling stability.

### 4 Conclusions

In this study, lignin-based porous carbon photocatalytic composite with high catalytic degradation rate under solar light was prepared. The obtained LCZ-600-2-4 composites had the largest specific surface area (317.765 m$^2$ g$^{-1}$) and pore volume (0.4344 mL g$^{-1}$). The high specific surface area of LCZ-600-2-4 sample provided a site for the ZnO particles, and the porous structure was more favorable for the rapid adsorption of pollutants. Each adsorption site was equivalent to a reaction site, which greatly enhances the photocatalytic activity of the composite. Compared with pure ZnO, the degradation rate of LCZ-600-2-4 reached 92% and 91% of methyl orange and rhodamine B in 2 h. Meanwhile, LCZ-600-2-4 had good acid–base stability and cyclic stability. Lignin-based carbon composite material may find various potential applications and display promising prospects.
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Declarations

Competing interest The authors have declared that no conflict of interest exists.

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