Biopolymer as Stabilizer and Adhesive To in Situ Precipitate CuS Nanocrystals on Cellulose Nanofibers for Preparing Multifunctional Composite Papers

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**ABSTRACT:** In order to solve the uneven distribution of copper sulfide nanocrystals (CuS-NCs) on cellulose nanofibers (CNFs), this work reports a feasible method to in situ precipitate CuS-NCs on CNF by utilizing biopolymers (lignin, xylan, or starch) as stabilizer and adhesive for fabricating the multifunctional composite papers. In the presence of biopolymers, CuS-NCs deposited in situ on CNF could be capped and stabilized by the biopolymers molecular chains for uniform distribution. Subsequently, biopolymers could anchor CuS-NCs on CNF by the hydrogen bonding. Compared to the composite paper with lignin or xylan as stabilizer and adhesive, CuS-NCs/starch/CNF paper showed the highest content and most uniform and continuous distribution of CuS-NCs, which not only enhanced the conductivity of composite paper to 10.12 S/cm but also increased the reaction rate constant on photocatalytic degradation of rhodamine B to 0.317 min⁻¹. The reaction rate constant is higher than most of the other reported CuS photocatalysts to date. It indicates that our method has a potential to be a novel strategy to precipitate nanocrystals uniformly on cellulose fibers for fabricating the multifunctional composite paper.

**INTRODUCTION**

Copper sulfide (CuS), a p-type semiconductor with a 1.2−2.0 eV of direct band gap,¹ has been extensively applied in industry and biomedical field due to its typical optical, electronic, physical, and chemical properties, for instance, as cathode materials in lithium rechargeable batteries, light-emitting diodes, solar cells, photocatalytic degradation of organic pollutants, photothermal ablation of tumor cells, and biology markers.²−⁷ So far, there have been only few reports on CuS-NC-based multifunctional composite paper. Cellulose nanofibers (CNFs), a low-cost raw material from renewable resources, can disperse well in aqueous solution by their large number of hydroxyl groups, which provided them with a good ability to disperse in aqueous medium. And hydroxyl group also provided a nucleation site for CuS-NCs by binding [Cu(NH₃)₄]²⁺.¹⁵ In the presence of biopolymers, CuS-NCs were unevenly distributed on CNF (as shown in Figure 1i). Therefore, a stabilizer and adhesive is necessary for dispersing and anchoring CuS-NCs on CNF. Recent reports show that the biopolymers could act as stabilizer during the growth of nanocrystals.¹³−¹⁵ In the presence of biopolymers, the formed nanocrystals could be capped and stabilized by the biopolymer chains.¹⁴ On the other hand, biopolymers could also anchor nanocrystals on CNF by hydrogen bonding as an adhesive.¹⁶

In this study, a new type of multifunctional composite paper was fabricated by utilizing the biopolymers (lignin, xylan, or starch) as stabilizer and adhesive for in situ precipitation of CuS-NCs on CNF. The effects of the three types of biopolymers on improving the distribution of CuS-NCs on CNF were contrasted, and the electrical conductivity and photocatalytic activity of composite papers were evaluated.

**RESULTS AND DISCUSSION**

In Situ Precipitation of CuS-NCs on Biopolymer-Coated CNFs. The distribution of NCs in paper network affects the applications of the composite papers. The in situ precipitation technology is beneficial to the uniform distribution of NCs on cellulose fibers.²⁰,²¹ Figure 1 shows the fabrication of composite fibers. First, the CuS-NCs/CNFs were synthesized as shown in Figure 1A. CNFs possessed large amounts of hydroxyl groups, which provided them with a good ability to disperse in aqueous medium. And hydroxyl group also provided a nucleation site for CuS-NCs by binding [Cu(NH₃)₄]²⁺. Finally, the addition of S²⁻ led to the nucleation and growth of CuS-NCs in the [Cu(NH₃)₄]²⁺ enrichment for in situ precipitation of the CNF. In this case, CuS-NCs were unevenly distributed on CNF (as shown in the scanning electron microscopy (SEM) image in Figure 1i).
To improve the distribution of CuS-NCs on CNFs, natural biopolymers (e.g., lignin, xylan, or starch) are introduced as a "green" stabilizer and adhesive during the in situ precipitation of CuS-NCs on CNFs. The CuS-NCs/biopolymer/CNF composite fibers were fabricated as shown in Figure 1B. The dissolved biopolymers formed a composite template with CNF by hydrogen bonding. Then, \([\text{Cu}(\text{NH}_3)_4]^{2+}\) enriched on biopolymer/CNF hybrid chains, which provided the nucleation sites for crystallization of CuS-NCs. Finally, \(S^{2−}\) led to the nucleation and growth of CuS-NCs in the \([\text{Cu}(\text{NH}_3)_4]^{2+}\) enrichment for in situ precipitation on the CNF. In the presence of biopolymers, CuS-NCs deposited in situ on CNF could be capped and stabilized by the biopolymers molecular chains for uniform distribution. Subsequently, biopolymers could anchor CuS-NCs on CNF by the hydrogen bonding after drying. The SEM images (Figure 1 ii−iv) show the morphologies of CuS-NCs/biopolymer/CNF composite fibers. The precipitation of CuS-NCs on CuS-NCs/lignin/CNFs composite fiber formed a nanosheet with uneven distribution (Figure 1 ii). But the uniform distribution of CuS-NCs could be observed on CuS-NCs/xylan/CNF composite fiber (Figure 1 iii) and CuS-NCs/starch/CNF composite fiber (Figure 1 iv). It indicates that the distribution of CuS-NCs was strongly related to the molecular configuration and properties of biopolymers. For example, lignin contains a large amount of hydroxyl groups and shows the properties of aliphatic compounds and aromatic compounds,\(^{13}\) which can be used as a stabilizer for nanocrystals. However, its ability to control the growth orientation of nanocrystals is poor because of its relatively short molecular chains.\(^{22}\) In addition, the binding ability between lignin and cellulose fibers is relatively weak,\(^{23}\) which is not beneficial to anchoring CuS-NCs on CNFs. Compared to lignin, the xylan and starch molecules not only possess a large number of hydroxyl groups but also have long helical chains or random coils,\(^{24,25}\) which could cap and stabilize nanocrystals more effectively. Notably, the nanoparticles on CuS-NCs/starch/CNF composite fiber (Figure 1 iv) were smaller and showed a more uniform distribution than on CuS-NCs/xylan/CNF composite fiber (Figure 1 iii). Due to the presence of long B-chains with widely spaced side chains in amylopectins,\(^{26}\) the molecular structure of starch was more conducive to stabilizing and anchoring CuS-NCs on CNF.

**Fourier Transform Infrared (FT-IR), X-ray Diffraction (XRD), and Thermogravimetric Analysis (TGA) of Composite Papers.** The interaction between biopolymers and CNF was studied by FT-IR spectra. FT-IR spectra of biopolymers, CNF paper, CuS-NCs/CNF paper, and CuS-NCs/biopolymer/CNF paper are shown in Figure 2. There were absorption peaks at 3500 and 3429 cm\(^{-1}\) for CNF paper and biopolymers, respectively, which were all assigned to −OH stretching.\(^{27,28}\) In contrast, the absorption at 3500 cm\(^{-1}\) for CuS-NCs/CNF paper did not decrease, confirming there is no hydrogen bonding between CuS-NCs and CNF. Noteworthily, from the FT-IR spectrum of CuS-NCs/biopolymer/CNF paper, it was found that the absorbance at 3500 and 3429
the phase of CuS-NCs was CuS2 due to the superposition of CuS, Cu1.96S, Cu1.94S, Cu1.8S, Cu7S4, and Cu2S. Eventually, shadowing the conductivity and photocatalytic activity of composite papers, the characteristic diffraction peaks (corresponding to facets (100), (101), (102), (103), (006), (110), (108), and (116)) of CuS appeared on CuS-NCs/CNF paper, which match with the peaks in JCPDS (no. 06-0464). It demonstrates that CuS-NCs were successfully precipitated on the CNF. Actually, the phase of CuS-NCs transformed from CuS at the “copper-rich” side to Cu2S at the “copper-deficient” side during in situ precipitation, such as CuS, Cu1.8S, Cu1.6S, Cu1.4S, Cu1.2S, and Cu1S. Eventually, the phase of CuS-NCs was CuS2 due to the sufficient and fully released S2− from Na2S, which could be demonstrated by the characteristic diffraction peaks type of CuS-NCs in composite papers. The significant characteristic diffraction peaks of CuS also appeared on CuS-NCs/lignin/CNF paper, but the characteristic diffraction peaks were obviously weakened on CuS-NCs/xylan/CNF paper and CuS-NCs/starch/CNF paper. It can be explained that the helical chains or random coils structure of xylan and starch molecules was more conducive to capping and stabilizing CuS-NCs, thus shadowing the diffraction peaks of CuS-NCs.31

TGA images of the CNF composite papers are shown in Figure 4. The initial degradation temperature of CuS NCs/CNF paper was lower than that of CNF paper due to the pyrolysis of CuS at ~200 °C.32 Then, the initial degradation temperature of composite papers with biopolymers (CuS-NCs/lignin/CNF paper, CuS-NCs/xylan/CNF paper, and CuS-NCs/starch/CNF paper) shifted to lower temperature due to the carbonization of biopolymers under nitrogen flow. In addition, the weight residue of composite papers is higher than that of CNF paper because of the stabilization of biopolymers in the CNF network. Compared to CuS-NCs/CNF paper, the weight residue of CuS-NCs/lignin/CNF paper and CuS-NCs/xylan/CNF paper are lower, indicating the decrease of CuS-NCs retention. This is in agreement with the CuS-NCs content in composite papers in Table 1 (30.82% of CuS-NCs in CuS-NCs/CNF paper; 22.73% of CuS-NCs in CuS-NCs/lignin/CNF paper; 17.73% of CuS-NCs in CuS-NCs/xylan/CNF paper). The higher CuS-NCs content in CuS-NCs/CNF paper can be explained by the large CuS-NCs in CuS-NCs/CNF paper (SEM image in Figure 5a), which resulted in the increase of retention of CuS-NCs. Due to the stabilizing effect of lignin and xylan, the large CuS-NCs in CuS-NCs/lignin/CNF paper and CuS-NCs/xylan/CNF paper were reduced in size (SEM images in Figure 5c), while the lower CuS-NCs content in CuS-NCs/lignin/CNF paper and CuS-NCs/xylan/CNF paper suggests that the lignin and xylan possessed a weaker ability to anchor CuS-NCs on CNF. Interestingly, CuS-NCs/starch/CNF paper showed the highest weight residue, which is in agreement with 35.48% of CuS-NCs content in CuS-NCs/starch/CNF paper in Table 1. Due to the stabilizing effect of starch, large CuS-NCs in CuS-NCs/starch/CNF paper were the fewest (SEM image in Figure 5g), while the highest CuS-NCs content in CuS-NCs/starch/CNF paper indicates that the starch provided a strong ability to anchor CuS-NCs on CNF for increasing the retention of CuS-NCs. It should be noted that due to the low content of biopolymers in the composite papers (8.5 wt % of lignin, 8.5 wt % of xylan, and 4.4 wt % of starch), the quantity after high-temperature carbonization was very low, which did not affect the weight residue result. In addition, the lack of formation of biopolymers would not affect the conductivity and photocatalytic activity of composite papers.

**Effect of CuS-NCs Distribution on Electrical Conductivity and Photocatalytic Activity of Composite Papers.** The distribution of CuS-NCs on CNFs may have a significant effect on the performance of composite papers. In the presence of biopolymers, CuS-NCs deposited in situ on CNF could be capped and stabilized by the biopolymer molecular chains for uniform distribution. With the drying process of composite paper, the hydrogen bonding between the biopolymer and CNF was enhanced, and the CuS-NCs were firmly anchored on the CNF to prepare composite paper that results in uniform distribution of CuS-NCs. As shown in Figure 5a, the light bulb connected with CuS-NCs/CNF paper presented the weakest light. This is because of the lowest conductivity of CuS-NCs/CNF paper (0.94 S/cm). Although the CuS-NCs content in CuS-NCs/CNF paper was higher than that in CuS-NCs/lignin/CNF paper and CuS-NCs/xylan/CNF paper (Table 1) due to the formation of large CuS-NCs in CNF network without biopolymers as stabilizer (SEM image in Figure 5a), the uneven and discontinuous distribution of CuS-NCs on CNF (Figure 5b) was not conducive to the conduction of electrons between fibers, resulting in the lowest conductivity of CuS-NCs/CNF paper. In contrast, the light...
bulb connected with CuS-NCs/lignin/CNF paper, CuS-NCs/xylan/CNF paper, or CuS-NCs/starch/CNF paper showed a stronger light (Figure 5c,e,g). It suggests that the addition of biopolymers was beneficial to the improvement of conductivity of composite papers (2.78 S/cm for CuS-NCs/lignin/CNF paper, 3.33 S/cm for CuS-NCs/xylan/CNF paper, and 10.12

| Sample              | CuS-NCs/CNF paper | CuS-NCs/lignin/CNF paper | CuS-NCs/xylan/CNF paper | CuS-NCs/starch/CNF paper |
|---------------------|-------------------|--------------------------|-------------------------|--------------------------|
| CuS-NCs content (%)| 30.82             | 22.73                    | 17.71                   | 35.48                    |

Figure 5. Electrical conductivity of composite papers. Optical images of light bulb connected with (a) CuS-NCs/CNF paper, (c) CuS-NCs/lignin/CNF paper, (e) CuS-NCs/xylan/CNF paper, and (g) CuS-NCs/starch/CNF paper. The insets show the SEM surface morphology images and conductivity of the corresponding papers. (b, d, f, h) Magnified SEM surface morphology images of the corresponding papers.
S/cm for CuS-NCs/starch/CNF paper). Biopolymer acted as a stabilizer and adhesive to promote the uniform and continuous distribution of CuS-NCs on CNF (Figure 5d,f,h), which contributed to improving the electrical conduction between the CNF and increasing the conductivity of composite papers. Although the CuS-NCs content in CuS-NCs/lignin/CNF paper and CuS-NCs/xylan/CNF paper was lower (Table 1), the uniform and continuous distribution of CuS-NCs on CNF (Figure 5d,f) was beneficial to improve the conduction of electrons between fibers. This is the reason for their higher conductivity than CuS-NCs/CNF paper. Noteworthily, CuS-NCs/starch/CNFs composite paper possessed the highest conductivity, due to the presence of long B-chains with widely spaced side chains in amylopectins and the molecular structure of starch more conducive to stabilizing and anchoring CuS-NCs on CNF, resulting in the highest content (Table 1) and most uniform and continuous distribution of CuS-NCs (Figure 5h).

**Figure 6.** Photodegradation of RhB dye in NIR laser: UV−vis absorption spectra of RhB without composite paper (a) and with CuS-NCs/CNF paper (b), CuS-NCs/lignin/CNF paper (c), CuS-NCs/xylan/CNF paper (d), and CuS-NCs/starch/CNF paper (e) acting as photocatalyst at different time intervals. The insets indicate the decolorization reaction. (f) Influence of photocatalyst type on the reaction rate. (g) Reusable performance of the four kinds of photocatalyst. (h) Stability of composite papers. 1: CuS-NCs/CNF paper; 2: CuS-NCs/lignin/CNF paper; 3: CuS-NCs/xylan/CNF paper; 4: CuS-NCs/starch/CNF paper; R: rubbing the sheets on both sides for 100 times each, followed by immersing in deionized water; W: washing the sheets 100 times with deionized water in the beaker, followed by immersing in it; S: sheets immersing in deionized water after sonication for 30 min at 360 W; 0’: sheets before photodegradation; 5’: sheets after 5 times photodegradation; 10’: sheets after 10 times photodegradation.
Otela et al.\textsuperscript{33} reported highly conductive CuS nanoparticle films via electrophoretic deposition. The traditional spin-casting method can yield CuS films with a conductivity of 5.7 S/cm. In contrast, the CuS nanoparticle films prepared by electrophoretic deposition consistently have an order of magnitude higher conductivity (up to 75 S/cm) due to the formation of smaller CuS nanoparticles and thinner film. Lee et al.\textsuperscript{34} reported a CuS-multiwalled carbon nanotube (MWCNT) hybrid nanostructures by in situ growing of CuS-NCs on MWCNTs. The uniform growth of small CuS-NCs on MWCNTs improved the electrochemical performance of composites as solar cells. In our study, CuS-NCs were deposited in situ on CNFs with lignin, xylan, or starch as stabilizer and adhesive to form a uniform and continuous CuS-NCs cladding structure in composite paper. This is the reason for the high conductivity of composite papers. In contrast, CuS-NCs/starch/CNFs composite paper showed the highest conductivity due to the smallest CuS-NCs and the most uniform cladding structure in composite paper.

Photocatalysis is a process that when a semiconductor materials absorbs light, the absorption of photon energy is equal to or more than the band gap of the semiconductor, and then generates electrons and holes, which can further produce free radicals in the system to oxidize the semiconductor.\textsuperscript{35} For composite papers as photocatalyst, near-infrared (NIR) light as a light source can provide an energy to create electron–hole pairs on the surface of CuS-NCs for triggering the photocatalytic step. The excited electron reacts with dissolved O$_2$ to form O$_2^-$, and the holes react with surface hydroxyl groups to form OH$^+$ radicals, which will oxidize the organic dye. In case of RhB, the characteristic absorption peak at 552 nm was used to monitor the photocatalytic dye degradation reaction.

As shown in Figure 6, the photocatalytic activities of four composite papers were estimated by monitoring the decreased intensity of RhB at 552 nm under various NIR laser (808 nm, 1.5 W/cm$^2$) exposure times. The RhB did not degrade under NIR laser irradiation in the absence of composite papers (Figure 6a). With composite papers as photocatalyst, the time required for the composite papers with lignin, xylan, or starch as stabilizer and adhesive to completely degrade RhB (<20 min, Figure 6c–e) was shorter than that of CuS-NCs/CNF paper (24 min, Figure 6b). In addition, Figure 6f shows that photocatalytic decomposition reaction constant (k) increased following the increase of uniform distribution of CuS-NCs on CNFs. Notably, the k value in CuS-NCs/starch/CNFs group is 0.317 min$^{-1}$, which is higher than most of the other CuS photocatalysts reported to date.\textsuperscript{36,37} It can be explained by the high content (Table 1) and uniform distribution of CuS-NCs (Figure 5h) in CuS-NCs/starch/CNFs paper. The measured specific surface areas of the composite papers based on N$_2$ were 181.8 m$^2$/g for CuS-NCs/CNF paper, 246.7 m$^2$/g for CuS-NCs/lignin/CNF paper, 284.5 m$^2$/g for CuS-NCs/xylan/CNF paper, and 365.3 m$^2$/g for CuS-NCs/starch/CNF paper. It indicates that improving the distribution of CuS-NCs on CNFs by biopolymers could increase the specific surface area of CuS-NCs, resulting in more unsaturated surface coordination sites exposed to the reactants and decreasing the degradation time. Furthermore, the use of composite paper as photocatalyst can avoid secondary pollution and is beneficial to the recycling. As shown in Figure 6g, RhB maintained comparatively high degradation efficiency without any significant decrease even after running for 10 cycles with composite paper as photocatalyst. Compared to other composite papers, RhB showed the highest degradation efficiency with CuS-NCs/starch/CNF paper as photocatalyst because of its highest content and most uniform distribution of CuS-NCs.

The stability of composite papers is shown in Figure 6h. The deionized water of soaked composite papers was all clear without dark green of CuS-NCs after rubbing, washing, or sonication, which proves that there was no significant leaking of CuS-NCs from composite papers. It suggests the good stability of CuS-NCs in composite papers due to the stabilizer and adhesive effect of biopolymers. We also studied the stability of the composite papers in cycle photodegradation. As shown in Figure 6h, the CuS-NCs/CNF paper collapsed a little after 10 times photocatalysis. Except for this, the other composite papers did not collapse after 5 or 10 times photodegradation due to the adhesive effect of biopolymers in composite papers. Therefore, the use of composite papers as photocatalyst can avoid secondary pollution and is beneficial to the recycling.

### CONCLUSIONS

In summary, we report a feasible method to in situ precipitate CuS-NCs on CNF by utilizing biopolymers (lignin, xylan, or starch) as stabilizer and adhesive for fabricating the multifunctional composite papers. The biopolymers could cap and stabilize the in situ deposited CuS-NCs and anchor CuS-NCs on CNF by hydrogen bonding. Compared to the composite paper with lignin or xylan as stabilizer and adhesive, CuS-NCs/starch/CNF paper showed the highest content and most uniform and continuous distribution of CuS-NCs, inducing the highest conductivity and reaction rate constant on the photocatalytic degradation of rhodamine B. This novel strategy provides an alternative for uniform and stable deposition of nanocrystals on cellulose fibers.

### EXPERIMENTAL SECTION

#### Materials

CNFs were purchased from Intelligent Chemicals Pty Ltd (Guangzhou, China). Their average fiber length and fiber diameter were 4–6 μm and 10–50 nm, respectively. Lignin (M$_\text{w}$: 1700 g/mol) was recovered from soda pulping effluent of the State Key Laboratory of Pulp & Paper Engineering (Guangzhou, China). The functional groups attached to lignin benzene rings and side chain include –OH$_3$ (16.0%), –C=O, COOH (7.2%), OH alcohol, OH phenolic (2.6%), and so on. This lignin was hydrophobic and was well dispersed in sodium hydroxide (NaOH) solution. Xylan (M$_\text{w}$: 4.9 × 10$^4$ g/mol) isolated from bagasse was purchased from Shanghai Yuanye Biotechnology Co., Ltd. (Shanghai, China). The sugar composition was as follows: 87.35% xylose, 9.28% arabinose, 0.81% glucose, 0.50% galactose, and 2.06% glucuronic acid. This xylan was hydrophobic and well dispersed in NaOH solution. Corn stalk (M$_\text{w}$: 2.7 × 10$^4$ g/mol) without any chemical treatment was purchased from Shanghai Yuanye Biotechnology Co., Ltd. (Shanghai, China). The amylose/amylopectin ratio of starch was 1:3. This starch was hydrophilic and was well dispersed after cooking. Sodium hydroxide (NaOH), hydrogen peroxide (H$_2$O$_2$), ammonia (25–28%), copper sulfate (CuSO$_4$·5H$_2$O), and sodium sulfide nonahydrate (Na$_2$S·9H$_2$O) were all of analytical grade.

#### Preparation of Composite Papers

CuSO$_4$·5H$_2$O (0.4 g) was dissolved in water (50 mL). Then, diluted ammonia (7 M,
Lignin and xylan were dissolved in 2 wt % aqueous NaOH, respectively, to prepare 0.04 wt % 50 mL lignin/NaOH solution and xylan/NaOH solution; starch was cooked in deionized water with stirring at 95 °C for 1 h to prepare 0.02 wt % 50 mL starch aqueous solution. The above three solutions were added into 50 mL of CNFs pulp (homogenized by D-130 homogenizer, dry weight of 0.126 g) and stirred at a given temperature (room temperature for lignin and xylan, 90 °C for starch) for 30 min. Then, the \([\text{Cu(NH}_3\text{)}_4]^{2+}\) solution was added into the above mixture and stirred for 1 h at the corresponding temperature. Finally, \(\text{Na}_2\text{S}\cdot\text{9H}_2\text{O}\) (4 wt %, 20 mL) was added dropwise to the above solution under stirring at the corresponding temperature and reacted for 30 min. After the reaction, the suspensions were dialyzed until \(\text{S}_2\)− was completely removed (the dialysate was tested with \(\text{CuCl}_2\) until no precipitate appeared). After dialysis, the volume of the suspensions was 200 mL and wet sheets were obtained by suction filtration of 100 mL suspensions with 0.22 μm membrane. Then, the wet sheets were dried at 60 °C to prepare the composite papers. The unified composite paper specifications are as follows: 12.56 cm² size; 0.15 ± 0.008 mm thickness; and 50 g/m² basis weight. In addition, the composite fibers for SEM observation were obtained after dialyzed suspension lyophilizing at −40 °C for 36 h. The filtrate was titrated with sulfuric acid to calculate the mass of CuS-NCs detached from the wet sheets, and the CuS-NCs content in composite paper was estimated by the following equation

\[
C (%) = \frac{A_1 - A_2}{A} \times 100
\]

where \(A_1\) is the total weight of generated CuS-NCs, \(A_2\) is the weight of CuS-NCs detached from the wet sheets, and \(A\) is the weight of composite paper.

Characterization of Composite Papers. The morphological and structural characteristics of the composite fibers and composite papers were investigated using an EVO-18 scanning electron microscope (SEM, Zeiss, Germany). The FT-IR spectra were recorded on a Tensor 27 (Bruker, Germany) under dry air at room temperature by a KBr pellet method; each sample was scanned from 4000 to 500 cm⁻¹ with a resolution of 4 cm⁻¹. The composite papers for SEM were taken before and after photo-degradation for several times.

Electrical Conductivity and Photocatalytic Activity of Composite Papers. Sheet resistances \((R_s, \text{Ω/} \text{sq})\) of the composite papers were measured by a four-probe method using a multielectrical measurement system (FT-340, Ningbo, China), and the corresponding volume conductivities \((\sigma, \text{S/cm})\) were calculated by the formula: \(\sigma = 1/(R_s \cdot l)\), where \(l\) (cm) is the paper thickness. The composite papers for conductivity test were cut into 2 cm square sheets. The distance between electrodes was 2.35 mm, and the test current was 10 mA.

The composite papers (1.5 cm² size; 0.15 ± 0.008 mm thickness; 50 g/m² basis weight) were immersed in rhodamine B (RHB) solution (2.0 × 10⁻⁵ mol/L, 50 mL), followed by dropping 1 mL of \(\text{H}_2\text{O}_2\) and then NIR laser (808 nm, 1.5 W/cm²) irradiation on the composite paper through the RHB solution in the dark. The Optocouplers laser (MW-GX-808/1–5000 mW) was purchased from Leishi Optoelectronics Technology Co., Ltd. (Changchun, China). RHB solution (5 mL) was sucked out at designed time interval to test the UV–vis spectra by TU-1810 (Beijing, China) with a scan range of 800–400 nm. The kinetic study was performed by measuring the change in the intensity of the absorbance at 552 nm. The photocatalytic decomposition reaction of RHB can be modeled as a pseudo-first-order reaction with the kinetics expressed by the equation as follows

\[
\ln A = -kt
\]

where \(A\) is absorbance, \(t\) is the time, and \(k\) is reaction rate constant. So, the plot of \(\ln A\) vs \(t\) gives a straight line having a negative slope.

The reusable performance was investigated by the change of the degradation efficiency after several cycles of photocatalysis. We note that the rinse method of composite papers between the photocatalytic cycles was as follows: the composite papers were sandwiched from the RHB solution and 50 mL of deionized water was drawn several times with a dropper to wash the front and back surfaces of the composite papers. The degradation efficiency of RHB was calculated using the following equation

\[
X (%) = \frac{A_0 - A_1}{A_0} \times 100
\]

where \(A_0\) and \(A_1\) are the absorbances of RHB solution at 552 nm before and after photocatalytic reaction.

The stability of the composite papers was investigated after the following treatments: rubbing the sheets on both sides 100 times each, followed by immersing in deionized water; washing the sheets 100 times with deionized water in the beaker, followed by immersing in it; and immersing in deionized water after sonication by a KQ-600GKDV ultrasonic cleaner (Kunshan, China) for 30 min at 360 W. The images of the composite papers were taken before and after photo-degradation for several times.

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