High Stability and Recyclable Cellulose-based Fluorescent Paper Derived from Waste Bagasse for Anti-counterfeiting

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Abstract

Developing fluorescent paper-based materials with recyclable, environmental friendly, excellent stable and uniform performances are still an urgent challenge at present. Herein, a simple, green, and high-efficiency method for the fabrication of high stability and recyclable cellulose-based fluorescent paper from waste bagasse via Hantzsch reaction is proposed. Compared to the pristine paper, the surface modification showed little effect on the morphology, mechanical properties, thermal performance and appearance. Meanwhile, the good writing and printing ability of the paper still remained. The prepared paper showed excellent fluorescence performance, which is very stable even treated with acidic, alkaline, and different solvents for 24 h. It can be processed into different security patterns. What's more, this strategy could be extended by using other compositions with aldehyde groups. Considering their functional and recyclable features, as well as the convenient and efficient fabrication process, our fluorescent papers hold great potential to be applied in many fields such as anti-counterfeiting.

Introduction

The counterfeiting of banknotes, invoices, certificates, pharmaceutical, etc., is an increasingly serious and long-standing worldwide problem, which has a serious negative impact on corporate reputation, human health and the normal order of economic development (Gao et al., 2018; Kalytchuk et al., 2018; Liu et al., 2019; Zhang et al., 2022). Hence, anti-counterfeiting technology is of great significance to help enterprises, consumers and governments reduce the economic losses caused by counterfeit goods such as paper money, medicine, food, clothing, and microelectronics (Qin et al., 2021; Ren et al., 2020; Scheuer and Yifat, 2015). The use of fluorescent anti-counterfeiting as a preferred technology has attracted great attention for practical application in banknotes, brands, and documents due to their extraordinary superiority with regard to a fast response, visualization, extra security features (Long et al., 2019; Xu et al., 2017). Recently, a large quantity of synthetic polymer luminescent materials with high fluorescence efficiency, including nanostructures, carbon dots, and organic-inorganic complexes, as well as organic dyes have been widely reported and utilized in anti-counterfeiting (Dai et al., 2019; Liu et al., 2017; Qu et al., 2012; Waiskopf et al., 2021; Zhang et al., 2019). However, the application of the above-mentioned synthetic polymer fluorescent materials is limited by the disadvantages such as complex preparation process, bio-refractory, biological incompatibility and toxicity (Lei et al., 2018; Masruchin et al., 2018; Pan et al., 2015; Sarrazin et al., 2007), but also involved serious environmental problems due to difficulty in biodegradation.

Cellulose has been widely studied during the past decades due to its inexpensive, eco-friendly, biodegradable and renewable properties (Fu et al., 2020; Hansson et al., 2009; Nawaz et al., 2020; Peng et al., 2016). Cellulose contains many hydroxyl groups, therefore, it could be used to incorporate various functional groups into the cellulose backbone to produce a variety of derivatives, such as cellulose esters, and ethers (Fox et al., 2011; Heinze and Liebert, 2001; Liu et al., 2020). Among them, cellulose paper-based fluorescent materials had attracted great attention due to their environmental-friendly features, wide applications, and low-cost (Zhang et al., 2021). Chen et al. reported a chiral photonic paper made of

cholesterol-cellulose nanocrystals and polycations, which can be rewritten and used in anti-counterfeiting fields such as watermarking technology and optical encryption (Chen et al., 2021). Abdollahi et al. developed a novel multicolor photoluminescent ink for information encryption and confidentiality on cellulosic paper (Abdollahi et al., 2020). Although the aforementioned works have enhanced the anticounterfeiting capabilities of fluorescent materials, there still involved several problems such as tedious synthesis processes, aggregation-caused quenching and photochemical side reactions (Wang et al., 2014). Besides, it is extremely difficult for fluorophores to achieve the homogeneous distribution at molecular level in the matrix by conventional blending process. Moreover, most of the fluorophore groups were deposited on the fibers, resulting in fluorescence uniformity and poor stability, which limit their practical application.

Bagasse is considered as one of the largest agro-industrial by-products of sugar industry (Mohapatra and Singh, 2021; Valladares-Diestra et al., 2021). After the extraction of sucrose from sugar cane, the huge amount of bagasse has become a challenge for treatment and disposal. It was reported that bagasse has an annual global production of 1044.8 million tons, and about 50% of bagasse is used for energy to support the processing plant and the remainder is not used (Chourasia et al., 2021; Pandey et al., 2000; Tye et al., 2016). Traditional methods of treating bagasse including incineration, landfill, and compost, which will cause certain environmental pollution in the long-term (Somerville et al., 2010). Thus, the full utilization of waste bagasse is an important step towards carbon neutrality. The main component of bagasse after purified is cellulose, and it is also widely applied in the field of papermaking (Li et al., 2017; Sun et al., 2004). However, this simple recycling method has not realized the high-value utilization of cellulosic materials. Thus, it is still a big challenge to fabricate functional paper from waste bagasse to improve the added value.

In this work, we presented a novel cellulose-based fluorescent paper with recyclable and stable properties derived from waste bagasse. Firstly, as shown in Fig. 1, the acetoacetyl groups were introduced on the bagasse cellulose fiber through simple surface esterification modification, and the cellulose acetoacetate (CAA) paper was obtained through the typical paper-making process. Then, a cellulose-based fluorescent paper was fabricated based on the CAA paper via Hantzsch reaction, which is mild, efficient and environmentally friendly process. The fluorescence 1, 4-dihydropyridine (DHP) ring was introduced on the CAA paper in the presence of acetoacetyl, aldehydes and amines components (Liu et al., 2018; Wu et al., 2017). Besides, the fluorescence groups are firmly connected to the surface of cellulose fiber through the stable covalent bonds to avoid the aggregation quenching effect caused by molecular movement. The structure and properties of these fluorescent papers were comprehensively investigated.

Experimental Section

Materials

Bagasse was produced from Guangxi Dongtang Paper Co., Ltd., *tert*-butyl acetoacetate (*t*-BAA, 95%), *N,N*-dimethylformamide (DMF, 99.9%), formaldehyde (FA, 37 wt% in water), ammonium acetate (98%). All

other chemicals were purchased from Shanghai Maclean Biochemical Technology Co., Ltd. They were used without further purification.

Preparation of CAA-based paper

Bagasse cellulose fiber was purified by pretreatment, chemical pulping, bleaching process. The synthesis of CAA paper was carried out according to our previous reported with little change (Guo et al., 2021). In brief, dried bagasse fiber (10.00 g) was dispersed in 400 mL DMF, the mixture was heated to 110°C. Subsequently, *t*-BAA (51.72 g) was slowly added dropwise with stirring for 6 h. After the reaction, the products were washed with ethanol, then dried for use. Whereafter, CAA fiber (6.28 g) was added to the deflaker, and the fiber was evenly dispersed at 10000 revolutions. Then it is formed via wet papermaking technology on the fast Kaiser process forming machine, and dried at 90°C for 15 min to obtain CAA paper.

Preparation of cellulose-based fluorescent paper

Ammonium acetate (77.00 mg) and formaldehyde (80.00 μ L) were dissolved in ethanol solution (80 wt%). CAA paper (5.11 g) and the solution were introduced into a beaker, which was subsequently stirred at room temperature for 2 h. Upon completion of the reaction, the paper was removed from the reaction mixture and repeatedly washed with deionized water and finally dried at 80°C for 2 h. The resulting paper was named as CAA-FA. The other fluorescent paper samples were prepared via different aldehydes (PPA, DBA, VA, BA) as described above method, and the samples obtained were named CAA-PPA, CAA-DBA, CAA-VA and CAA-BA, respectively.

Paper recycling process

Papers were torn into pieces and then soaked in water. Next, a disintegrator was used to slush the paper pieces back into fiber dispersions. The fiber dispersions were then made into paper again following the procedure described above. Five rounds of recycling were carried out in total.

Characterization

SEM observations were performed with Merlin (Zeiss, Germany) equipped with an energy-dispersive X-ray spectrometer. FT-IR spectra were obtained with a Nicolet IS50 (Thermo Fisher Scientific, America). The spectra were recorded with width ranging from 500 to 4000 cm^{-1} , and resolution of 2 cm^{-1} . X-ray photoelectron spectroscopy (XPS) (KratOs, UK) conducted experiments to study the surface composition of paper. The samples were heated from 30 to 600 °C at a heating rate of 10 °C/min to obtain TG and DTG curves (TG 209 F1, Netzsch, Germany). The mechanical tensile properties of CAA-FA paper were tested three times by INSTRON 5565 universal materials testing machine. The content of different elements of bagasse and CAA-FA paper was measured by an elemental analyzer (Elementar, Germany). The multi-position automatic sampling X-ray diffractometer (XRD, X'pert Powder, Panalytical, Netherlands) was used to measure the crystallinity of the fluorescent paper with at a conventional wide-angle 5° to 80° and a scanning speed of 12°/ min. The crystallinity indexes (CI) of bagasse CAA-FA fibers were calculated using the Segal method according reference (Qin et al., 2022). The fluorescence spectra

were obtained using a fluorescence spectrometer (Edinburgh, FLS980, UK). The air permeability was obtained using a paper densometer (L&W 166, Sweden). The whiteness was obtained using a Elrepho 070 (Sweden).

Results And Discussion

As shown in Fig. 1, covalent graft of acetoacetyl groups on the surface of cellulose fibers is performed by transesterification of the t-BAA molecule with hydroxyl groups. In order to speed up the reaction rate of acetoacetyl group, transesterification reaction was carried out in DMF solution as dilution medium at 110°C (Liu et al., 2016). Subsequently, as shown in Fig. 1 and Fig. 2a, functional paper with fluorescence effect was prepared by covalently modifying CAA fiber with formaldehyde through Hantzsch multicomponent reaction at room temperature. On one hand, the appearance color of CAA-FA paper has no obvious change compared to pristine bagasse paper (Fig. 2b-d). On the other hand, it was clearly that the smooth and flat surface, natural wrinkle and deformation were well preserved in the fluorescent paper through SEM images, which have almost complete cellular wall (Fig. 2e-g). These results demonstrate that the modification caused minimum damage to the surface morphology and microstructure. In addition, as shown in Fig. 2h-j, EDS mapping clearly showed the distribution of C, O and N elements. The N elements appeared in CAA-FA papers were uniformly distributed on the surface of cellulose fiber, indicating the DHP ring was formed via the Hantzsch reaction.

The elemental analysis of fluorescent paper is shown in Table. S1. The increase of carbon content in CAA-FA paper indicated that the acetoacetyl group was grafted to the surface of the fiber. The significant increase in nitrogen content (0.19%) further confirmed that the DHP rings were formed on the surface of fibers.

The chemical structure could also be determined by FT-IR spectra. As shown in Fig. 3a, the peaks at 1705 and 1745 cm^{-1} are from the stretching of acetoacetyl group, and the intensity of the peaks is weakened significantly. The strong signals at 1561 and 3284 cm^{-1} are assigned to the bending vibration and the stretching vibration of the N-H bond, respectively (Zhang et al., 2020). Besides, the stretching vibration absorption peak of C=C at 1655 cm^{-1} was also observed, indicating the existence of DHP rings.

XPS experiment was carried out to further investigate the surface composition and confirm various functional groups on fluorescent paper, as described in Fig. 3b. In the wide-scan spectra, the signals of C1s (282.65 eV, at%) and O1s (530.94 eV, at%) are observed for both original cellulose fiber and CAA-FA paper samples. The appearance of a new peak at 400 eV assigned to N1s only in the spectrum of the CAA-FA paper further confirmed the occurrence of reaction. A blow-up of the N1s peak was showed in Fig. S1, which was subjected to peak differentiating and imitating to consist of N-H and C-N-C binding energies at 397.3 and 399.5 eV, respectively. In addition, the bonding energies of C=O, C-N, and C=C also emerged in the blow-up spectra of C1s and O1s confirming the presence of DHP rings.

The thermal stability of fluorescent paper was evaluated by TG test. As shown in Fig. 3c, the maximum decomposition temperature of CAA-FA paper is 350°C. It is a little bit lower than that for native cellulose (366°C), mainly due to the introduction of DHP ring. It indicated that a little quantity of anchored DHP ring on the fiber surface was not sufficient to have a significant effect on the thermal degradation of the fibers.

One of the advantages of surface modification is that the physical structure and crystalline region of cellulose fibers could be retained eventually, due to the reaction being carried out on the surface-accessible cellulose chain of the fiber. The results of XRD (Fig. S2) showed that the original crystalline allomorph (cellulose β) (Chang and Zhang, 2011; Sun et al., 2020) of the cellulose fibers was retained after esterification and Hantzsch reaction. However, the crystallinity of CAA-FA fiber (Cl: 79.3%) was slightly reduced compared to that of cellulose (Cl: 91.0%). Hydrogen bonds maintained the stability of crystalline structures. However, hydrogen bonds were broken after hydrogen atoms of hydroxyl groups were replaced, and the degree of crystallinity was reduced accordingly (Liu et al., 2021).

The mechanism property of obtained paper was evaluated by tensile test, as presented in Fig. 3d. The tensile stress of CAA-FA paper is 29.6 MPa, which is slightly lower than that of bagasse. However, the elongation at break of CAA-FA paper is 2.97%, which is slightly higher than 0.41% of the original cellulose paper. The balance between strength and flexibility was a long-term challenge. High strength was often obtained at the cost of flexibility (Guan et al., 2020). Although the final CAA-FA paper only maintains 93% tensile strength of the bagasse fibers, it can withstand more than 150 times its own weight. The bonding strength is mainly formed through the hydrogen bonds interactions between the cellulose hydroxyl groups (Ling et al., 2018). However, the number of hydrogen bonds reduce due to the hydrogen atoms in the hydroxyl groups on the cellulose was replaced, leading to the decrease of mechanical strength and increased air permeability of the CAA-FA paper. Besides, the whiteness measurement demonstrated that the Hantzsch reaction showed little effect on the whiteness of CAA-FA paper (Fig. 3e). Similar as regular paper, CAA-FA paper can be used as a common paper for text writing and design printing. As shown in Fig. 3f, the Chinese characters written on the paper and the printed 'SCUT' pattern was clearly visible.

The effects of the reaction time on the fluorescence of the materials were explored, as presented in Fig. 4a-b. It is worth noting that a strong emission could be achieved within 10 min at ambient temperature. It could be attributed to the high efficiency of Hantzsch reaction and high fluorescence yield of the DHP ring. In addition, with the increase of reaction time, the fluorescence of paper became brighter and the brightness gradually tends to be stable. Fluorescent spectroscopy was also employed to monitor the progress of the Hantzsch reaction (Fig. 4c-d). The maximum excitation wavelength of fluorescent paper obtained by different reaction time appeared at 380 nm, under these conditions, a broad emission spectrum rang from 400 to 600 nm was observed (Wang et al., 2021). For most cellulose-based fluorescence materials, such as nanofilm, cellulose-based microgel or waterborne ink etc., the time for preparation ranges from 30 to 360 min. Therefore, our CAA-FA paper has a great advantage of rapid preparation to obtain fluorescence properties. It revealed that Hantzsch multicomponent reaction is more efficient than other methods. In addition, this reaction is highly atom-economic with only water as the by-

product and can be carried out under benign conditions. It will be a huge advantage for the large-scale production of such functional materials. The photochromism of CAA-FA paper is shown in Fig. 4e. DHP ring is a 6π electron system with two unconjugated double bonds, which exhibits extremely active chemical properties (Fan et al., 2018). It shows an emission wavelength at 465 nm within the fluorescence spectra, which is derived from the $\pi \rightarrow \pi^*$ transition of C=C bonds. The $\pi \rightarrow \pi^*$ electrons rotate around the C=C bond to form the single excited state (Fig. 4f). Efficient energy dissipation, the lifetime of the single excited state is short and often occurs with fluorescence (Schuster et al., 1993).

Fluorescence optical image of the CAA-FA paper was exhibited in Fig. S3. Strong blue photoluminescence was observed from the CAA-FA paper upon exposure to UV light of 365 nm, which will further broaden the application fields of CAA-FA paper. As shown in Fig. 5a, observed under sunshine, the pattern was hidden, whereas it appeared with fluorescence when observed under 365 nm UV light. Such characteristics induce dual-security levels to the documents marked with this type of paper, which widely used in the field of information encryption. Moreover, the fluorescent patterns were clearly visible when CAA-FA paper is used in banknotes for anti-counterfeiting, as presented in Fig. 5b. It indicated that this approach is an efficient method for increasing security in currency anti-counterfeiting and authentication technologies or security documents. In addition, CAA-FA paper could also be used for warning labels, which the pattern showed bright blue under UV light to achieve warning effect, it greatly expands the application range of paper (Fig. 5c). The overall CAA-FA paper recycling process was shown in Fig. 5d. With the increase of the number of recycling of CAA-FA paper, its fluorescence performance has no obvious changed. The excitation and emission wavelengths of CAA-FA paper peak at 389 and 465 nm, respectively, and fluorescence quenching does not occur with the increase of cycles (Fig. S4). Therefore, the number of recycling runs and the total service life of the fluorescent paper can therefore be increased substantially.

The fluorescence stability of CAA-FA paper is extremely important for further practical application. From the macroscopic observation, the CAA-FA paper after long-term storage still emits bright fluorescence under ultraviolet radiation, as presented in Fig. S6. The emission spectra of the CAA-FA paper peaked at 380 nm under the excitation of 465 nm external light, which indicate the fluorescence spectra of the CAA-FA paper showed no obvious change. In addition, it can be found that under the excitation light of 365 nm, the paper samples treated with different reagents all show strong blue fluorescence (Fig. S7). After being soaked in different organic solvents for 24 h, the fluorescence spectrum of CAA-FA paper subjected to ultraviolet radiation is similar to that before the treatment, and the maximum emission peak still appearing at 380 nm (Fig. S8). Besides, the CAA-FA paper also possessed good fluorescent stability even treat with acid or base solution. After they were immersed in acid or alkali solution for at least 24 h, the patterns also exhibited clear fluorescence under UV light (Fig. S9). The maximum emission spectrum of sample was 381 nm, which no significant change in fluorescence spectrum compared with before soaking (Fig. S10). These results further confirm that the fluorophores in CAA-FA paper are firmly anchored to the surface of cellulose molecular chain by covalent bond. Therefore, the responsive make the CAA-FA paper an excellent candidate in the field of anti-counterfeiting materials. Moreover, in view of the stable fluorescence properties and uniform luminescence of CAA-FA paper offer advantages including ease of synthesis and handling as well as potential applications for the anti-counterfeiting and labelling

fields, and making soft materials, which serve for ID-card and credit card protection and other security applications.

Hantzsch multicomponent reaction require specific chemical moieties, which allow different reactants to be combined to quickly obtain diverse functional groups. 2-Phenylpropionaldehyde (PPA), 3,4-dimethoxybenzaldehyde (DBA), vanillic aldehyde (VA) and benzaldehyde (BA) used in place of formaldehyde to explore the modularization of the Hantzsch multicomponent reaction (Fig. 6a). According to Fig. 6b, it was clearly observed that DHP rings synthesized by different aldehydes still have strong fluorescence, and the paper showed bright blue under UV light. These papers exhibited bright fluorescent excitation and emission around 380 and 465 nm respectively, confirming the formation of DHP rings (Fig. 6c-d). It suggested that different pendant groups could be incorporated via this Hantzsch route. Through this strategy, aldehydes with additional chromophores could be conveniently immobilized on the DHP ring. It indicated that Hantzsch reaction can be used as template reaction to prepare various cellulose-based fluorescent materials, which greatly enriches the application of it in the modification of cellulose and its cellulose derivatives. It is worth noting that this reaction is a process where the by-product is water, which will greatly reduce the impact on the environment.

Conclusions

Novel recyclable and high stability fluorescent papers were developed from waste bagasse by using a simple, efficient and eco-friendly surface functionalization process. Compared to original fibers, there were no significant change in the morphology and structure for the modified fibers. The resulting CAA-FA paper showed the similar appearance as ordinary paper, and exhibited high thermal stability, good mechanical properties, and good writing/printing ability. A strong emission could be achieved within 10 min at ambient temperature due to the high efficiency of Hantzsch reaction. The covalent connection of DHP rings endow the paper with highly stable fluorescent performance. The bright fluorescent property of the paper could still be observed even treated with water, organic solvent, acid and alkali solution. In addition, strong fluorescence emission occurs in the CAA-FA paper even after 5 rounds of recycling. What's more, this surface functionalization strategy could be extended by using other compositions with aldehyde groups, to generate new DHP systems and allow tuneable emission wavelengths. In view of the mild reaction conditions, broad scope of substrates, intense and high stability fluorescence, this universal strategy shows great potential for rapid fabrication of recyclable fluorescent paper-based materials and further to be used in anti-counterfeiting.

Declarations

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Lei Guo: Conceptualization, Methodology, Investigation, Data Curation, Writing - original draft. **Hongchen Liu:** Conceptualization, Supervision, Writing - review & editing. **Fang Peng:** Methodology, Investigation, Data Curation. **Jian Kang:** Conceptualization, Supervision, Writing - review & editing. **Haisong Qi:** Conceptualization, Supervision, Writing - review & editing.

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Figures

Figure 1

Schematic diagram of the preparation of fluorescent paper from waste bagasse.

Figure 2

(a) Schematic diagram of chemical reaction for the preparation of CAA-FA, photograph of (b) bagasse, (c) CAA and (d) CAA-FA paper, (e) SEM image of bagasse, (f) CAA and (g) CAA-FA paper, EDS-Mapping of (h) carbon, (i) oxygen, (j) nitrogen in CAA-FA paper.

Figure 3

The (a) FT-IR, (b) XPS broad spectrum (c) TGA, (d) tensile-strain curve (e) whiteness and air permeability of bagasse and CAA-FA paper, (f) photographs of screen printed and writing on CAA-FA paper.

Figure 4

(a) The photographs of CAA-FA papers for different reaction times under sunlight, and (b) 365 nm UV light, the (c) excitation and (d) emission spectrum of different reaction times, (e) responsivity of the DHP rings toward UV light irradiation, (f) luminescence mechanism diagram of CAA-FA paper.

Figure 5

(a) Application of the CAA-FA paper for information encryption, (b) currency anti-counterfeiting, (c) the application of CAA-FA paper in warning labels, (d) the overall recycling process of CAA-FA paper.

Figure 6

(a) The Hantzsch reaction of CAA with other aldehyde compounds, (b) photographs of different fluorescent papers under UV light, the (c) excitation and (d) emission spectra of different fluorescent papers.

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