Functionalization of Cellulose Paper by Coating Nano Metal-Organic Frameworks for Use as Photochromic Material

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Summary: The cellulose paper-based functional materials modified by Zn-NDI and Cu-NDI were prepared by the coating method. The chemical structures were characterized by FTIR, XRD, UV-vis and SEM, and the photochromic properties of the composite functional materials were studied. The results showed that Zn-NDI and Cu-NDI were successfully prepared and retained on the surface of copy paper, the wavelength of photochromic reaction is between 300-400 nm of MOFs materials. Optical analysis confirmed that the NDI/paper, Zn-NDI/paper and Cu-NDI/paper changed from tan to wheat, light green to olive, and dark tan to brown after 60 seconds of exposure to hernia light irradiations, the MOFs coated paper returned to its original color when it was placed in the dark for 4 hours. The above results indicated that the prepared Zn-NDI and Cu-NDI coated paper composites exhibited excellent photochromic ability and had potential applications in the field of anti-counterfeiting packaging materials.

Keywords: Coating; Metal Organic Frameworks; Cellulose; Paper; Photochromic.

Introduction

Photochromic materials are a series of materials that change color under light or electromagnetic current. [1] Among photochromic materials, spiropyran, [2] azobenzene, [3] fulgide, [4] spiroxamine, [5] rare earth metals, [6] diarylethene derivatives [7] and redox active cores [8] have been extensively investigated for several decades. Photochromic materials have attracted wide attention in the fields of anti-counterfeiting coatings, photochromic glass and lens applications due to their significant property of color change.[9, 10]

Metal-organic frameworks are a class of porous materials composed of metal centers and organic ligands through coordination bonds.[11, 12]. The highly porous crystalline frameworks exhibited enormous potential in luminescent, drug delivery, magnetic etc. due to the functional organic ligands. Besides, its organic ligand structural extends the application in sensors and anti-counterfeiting when applying external stimuli.[13] Compared with traditional organic photochromic materials, 1,4,5,8-naphthalimide (NDI) had advantages of redox centers, good thermal stability and high fluorescence quantum yield.[14] In addition, thanks to the molecular structure of NDI, it had strong absorption in the visible light region and effectively avoids rapid characteristic behavior. Therefore, NDI was introduced to form MOFs with metal ions.

Cellulose paper is a kind of degradable green polymer functional material composed of plant fibers which has been widely applied in printing, writing and packaging.[15,16] To develop value added cellulose paper, photochromic paper was prepared by mixing photochromic compounds with fiber suspension during the papermaking, either being coating on the surface of paper.[17, 18] Tian *et al*. (2014) reported[19], photochromic paper with enhanced fluorescent properties, was prepared by addition of spiropyran derivatives into the cellulose pulp through a normal papermaking process. However, the retention issue of spiropyran derivatives limited its application in paper. Rad and Mahdavian (2016) [20] prepared photochromic paper by coating spiropyran functionalized latex particles on the surface of filter paper, which exhibited photochromic behavior under UV lights.

In this work, two types of MOFs were synthesized from Zn/Cu and NDI. We believe the photochromic behavior of NDI can deliver paper with excellent color change property, and the preparation process which helps to improve the fast discoloration behavior, can be potentially used as anti-counterfeit package material.

Experimental

Materials

1,4,5,8-naphthalene-tetracarboxylic acid

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dianhydride (AR), 5-aminoisophthalic acid (AR) were purchased from Mackline BioChemical Co., Ltd. (Shanghai China), acetic acid (AR), $Zn(NO_3)_2{\cdot}6H_2O$ (AR), $CuAc_2{\cdot}1H_2O$ (AR), N,N'-dimethylformamide (DMF, AR), and ethanol (EtOH, AR) were obtained from Hongyan Chemical Co., Ltd. (Chongqing China). White glue was from Panda Co., Ltd. (Shanghai China).

Preparation procedure of N, N'-bis(5-isophthalic acid) naphthalenediimide (H_4BINDI)

The synthesis of H_4BINDI as followed by a reported procedure.[3] 3.35 g, 12.5 m mol 1,4,5,8-naphthalene-tetracarboxylic acid dianhydride was taken dissolved in 100 ml acetic acid and stirred for 10 min. 4.5 g, 25.0 m mol 5-aminoisophthalic acid was used to the above solution and the suspension was refluxed for 12h at 60 ℃. The crude product was precipitated with 100 ml of deionized water at room temperature and washed several times with EtOH. The obtained product was dried in vacuum (5h, 60℃) and recrystallized from DMF.

Synthesis of MOFs (Zn/Cu-NDI)

0.34 g 2 m mol H_4BINDI was dissolved in 20 ml mixture solution of DMF and EtOH (12.5:7.5). 0.34 g 2 m mol H_4BINDI was dissolved in 20 ml mixture solution of DMF and EtOH (12.5:7.5). 1.21g 4 mmol $Zn(NO_3)_2{\cdot}6H_2O$ or $CuAc_2{\cdot}1H_2O$ were dissolved in 20 ml DMF/EtOH (5:3). Then, the above solutions were mixed together and transferred into a Teflon autoclave, and reacted at 140 ° C for 4 hours. After the product was cooled to room temperature, it was washed 5 times with DMF and EtOH.

Preparation of MOFs (Zn/Cu-NDI) or NDI coated paper

10 g white glue were evenly coated on usual copy paper (30 cm × 21 cm), then a mixture which containing 1% Zn/Cu-NDI or NDI ethanol solution was coated on copy paper by using a glass rods.

Characterization

ATR-FTIR spectra of Zn/Cu-NDI powder and Zn/Cu-NDI coated paper were recorded on a Bruker Victory 22, 32 scans were accumulated from 400 to 4000 cm^{-1}. The crystal structure of samples were characterized by X-ray diffraction (XRD) using a D/max 2200PC X-ray diffractometer with a Cu Kα (λ=0.1542 nm) anode. The surface morphology and cross section of the samples were observed by a HITACHI-S4800 Scanning Electron Microscope. The samples were coated with Pt. The UV-vis spectrums of all samples were achieved using a Cary 100 spectrometer to perform absorption spectroscopy analysis. Photochromic properties were measured under a Hernia light (120-1100 nm).

Results and Discussion

The preparation of MOFs (Zn-NDI/Cu-NDI) and NDI coated paper

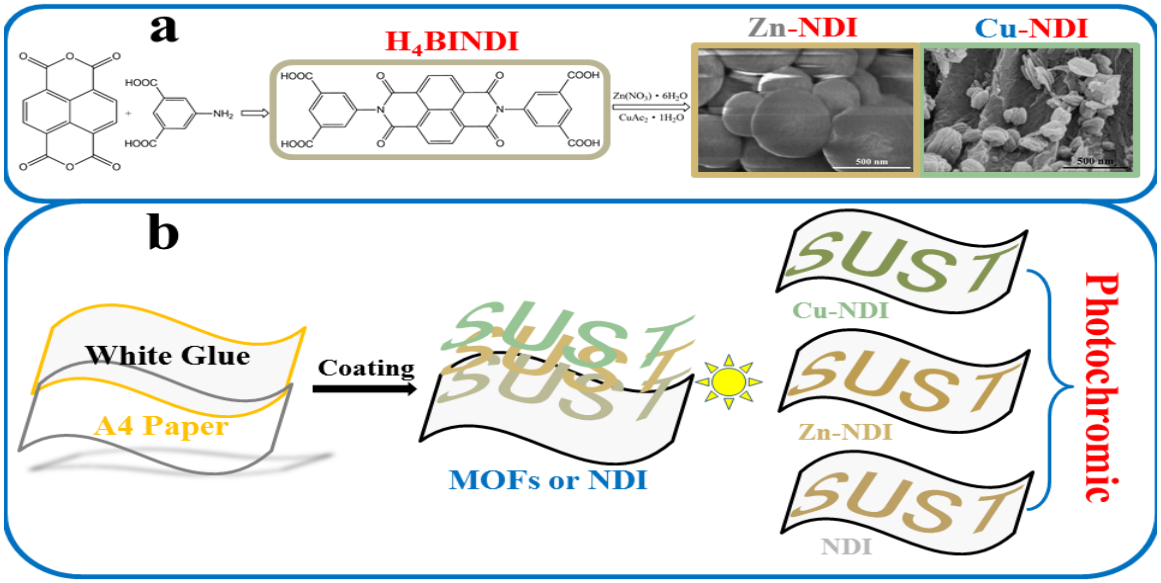

Fig. 1: The schematic of the concept of preparing Zn/Cu-NDI and NDI coated on paper.

As shown in Fig. 1b, a significantly color change occurred for all MOFs samples (NDI, Zn-NDI and Cu-NDI) coated paper, revealing their photochromic property.

Paper is a flexible composite material with a three-dimensional structure, which typically prepared by wet-forming technique. For uncoated paper, the typical average diameter of the pores between cellulose fibers is 2-10 μm.[21] As shown in Fig. 1a, Zn-NDI had a larger particle size (in the range of 200-500 nm) compared with Cu-NDI (in the range of 100-200 nm). The difference in size between the MOFs and the pores in paper resulted in the loss of MOFs particulates on paper surface, thus, affecting their photochromic behavior. Owing to avoid MOFs fell into the pores, white glue was adopted to coat on the surface of the copy paper. Besides, white glue was colorless and does not affect the photochromic performance of MOFs.

Fig.1b illustrate the difference in color change of the Zn/Cu-NDI coated paper and the NDI coated paper under hernia light. This can be explained by the photochromic behavior of NDI and MOFs; which incorporated of metal ions (Zn or Cu) with NDI structures.

FTIR and XRD Spectrum Analysis

Fig. 2 displayed the chemical structure of NDI, Zn-NDI and Cu-NDI by ATR-FTIR. The absorption peak of -CON- was found around 1670 cm^{-1}, and which located around 1250 cm^{-1} belonged to 1,4,5,8-naphthalene-tetracarboxylic acid dianhydride substituted with N element. The strong adsorption band around 1708 cm^{-1} and weakly adsorption band 3100 cm^{-1} due to the carboxyl groups of NDI. These data proved the NDI was synthesized successfully and existed in the composite. In addition, the absorption peak near 474 cm^{-1} is the characteristic vibration peak of -Zn-O-, and the absorption peak near 747 cm^{-1} was the characteristic absorption vibration peak of -Cu-O-.[14] These results suggested that Zn/Cu had been generated with NDI.

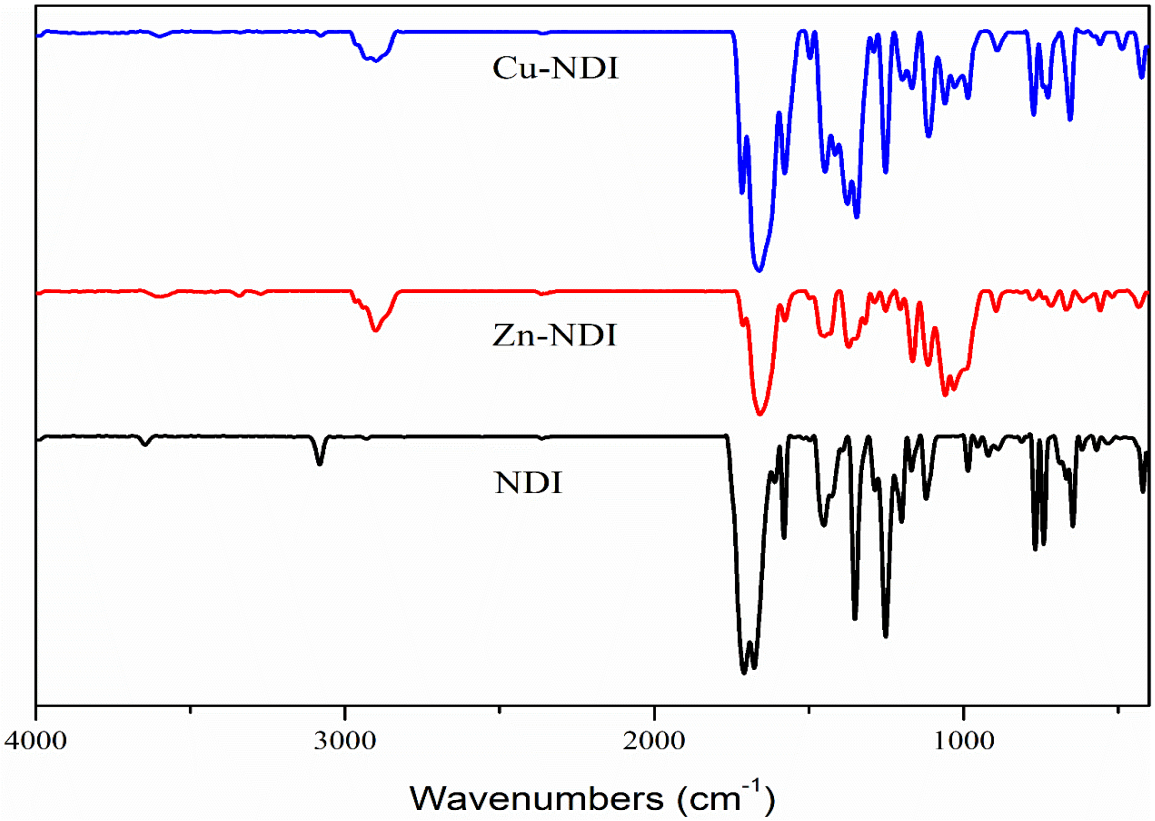

Fig. 2: The FTIR patterns of NDI, Zn-NDI and Cu-NDI.

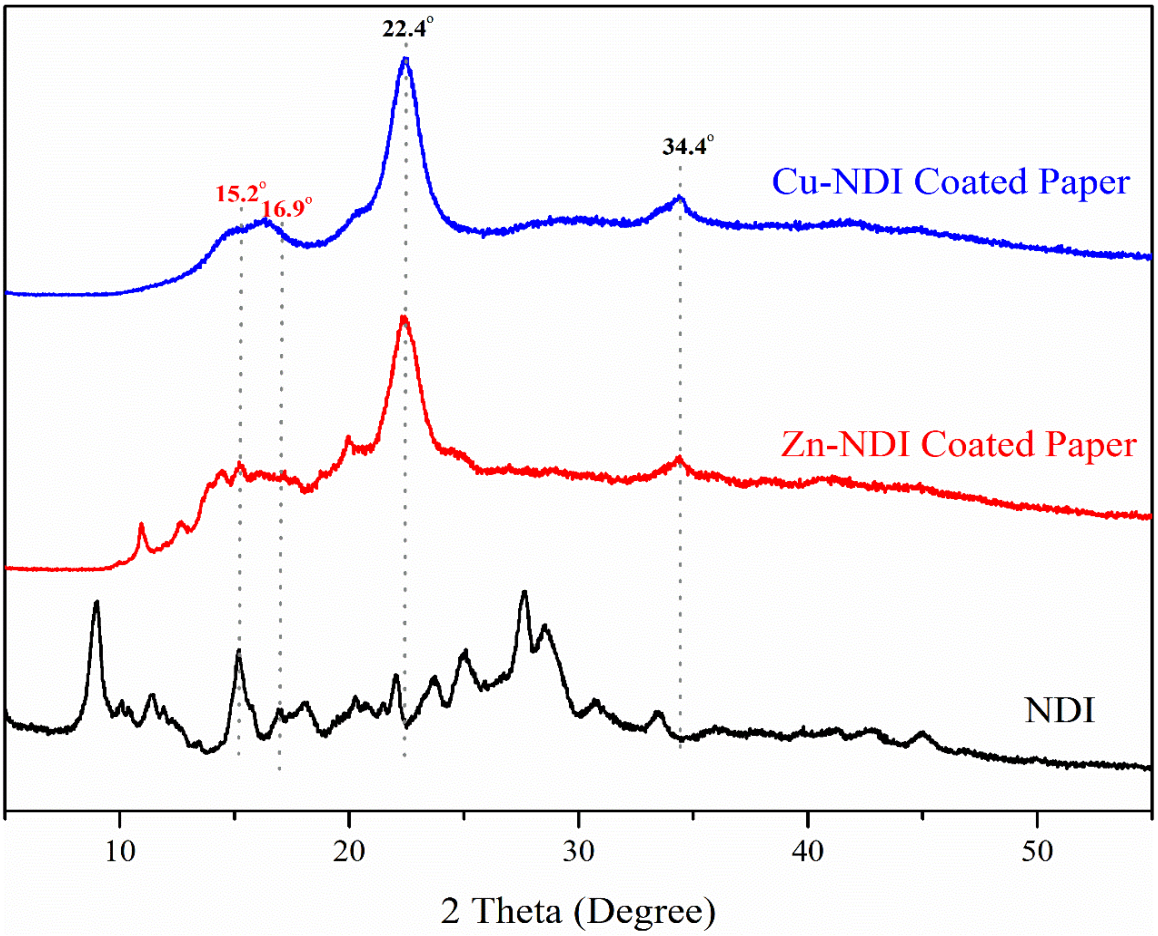

Fig. 3: The XRD spectrum of Zn-NDI and Cu-NDI coated on copy paper and NDI.

As shown in Fig. 3, X-ray diffraction (XRD) curves showed the crystalline structure of Zn/Cu-NDI coated paper NDI. The characteristic diffraction peaks of NDI were located at 2θ = 15.2° and 16.9°, and becomes weaker after forming Zn-NDI and Cu-NDI.[22] Regarding the formation of Zn-NDI and Cu-NDI coated paper, the typical diffraction peaks of NDI still existed, indicating that both Zn and Cu were coordinated with NDI. The similar result also reported by Banerjee *et al.*[23] For MOFs (Zn-NDI and Cu-NDI) coated paper, 2θ = 14.9°, 16.4°, 22.7° and 34.5° can be attributed to the typical diffraction peaks of cellulose fiber. The analysis of the above data showed that NDI and Zn/Cu have formed two MOFs through coordination and successfully prepared paper-based functional materials based on MOFs modification.

SEM Morphology Analysis

Fig 4 showed the micro-topography of all samples. It can be seen from Fig 4a that the white glue was evenly coated on the surface of the copy paper, and the cross-sectional morphology of the composite material displayed that the white glue formed a smooth layer of 2~2.5 μm on the surface of the paper (Fig 4b). The scanning electron microscopy images of Fig. 4c and d also showed essentially the NDI coated paper composing of NDI with a particle size of 200 nm in one-dimensional direction. As shown in Fig. 4e and f, Zn-NDI had typical diameters of 200-500 nm and coated on the copy paper, SEM images clearly recorded the perfect spherical shape of the Zn-NDI with uniform shapes. Besides, as shown in Fig. 4g, under the same conditions, the Cu-NDI crystals (in a range of 100-200 nm) exhibited the regular geometry.

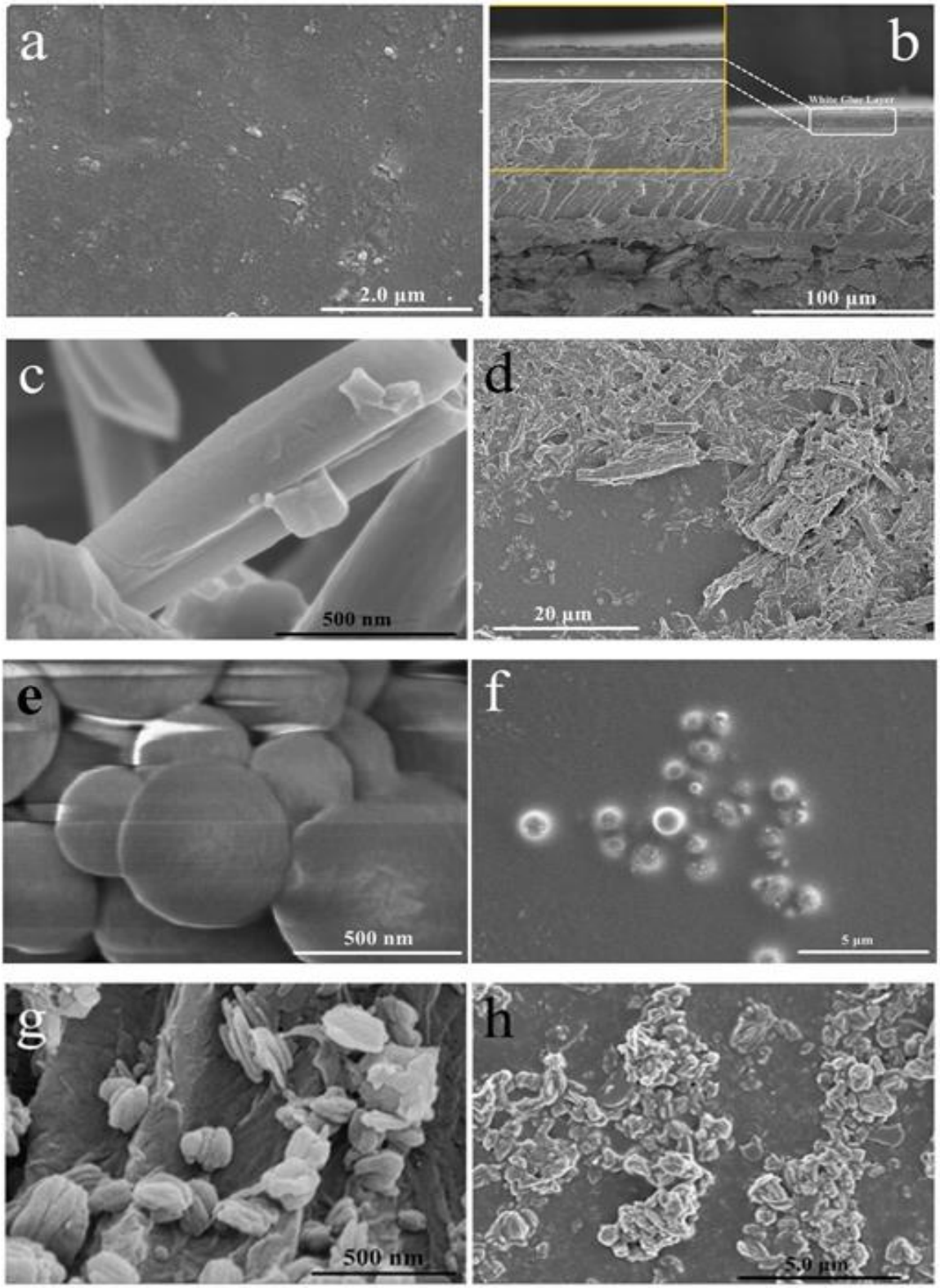

Fig. 4: The SEM morphology: the top view of white glue coated paper (a), the section view of white glue coated paper (b), NDI (c), NDI coated paper (d), Zn-NDI (e), Zn-NDI coated paper (f), Cu-NDI (g) and Cu-NDI coated paper (h).

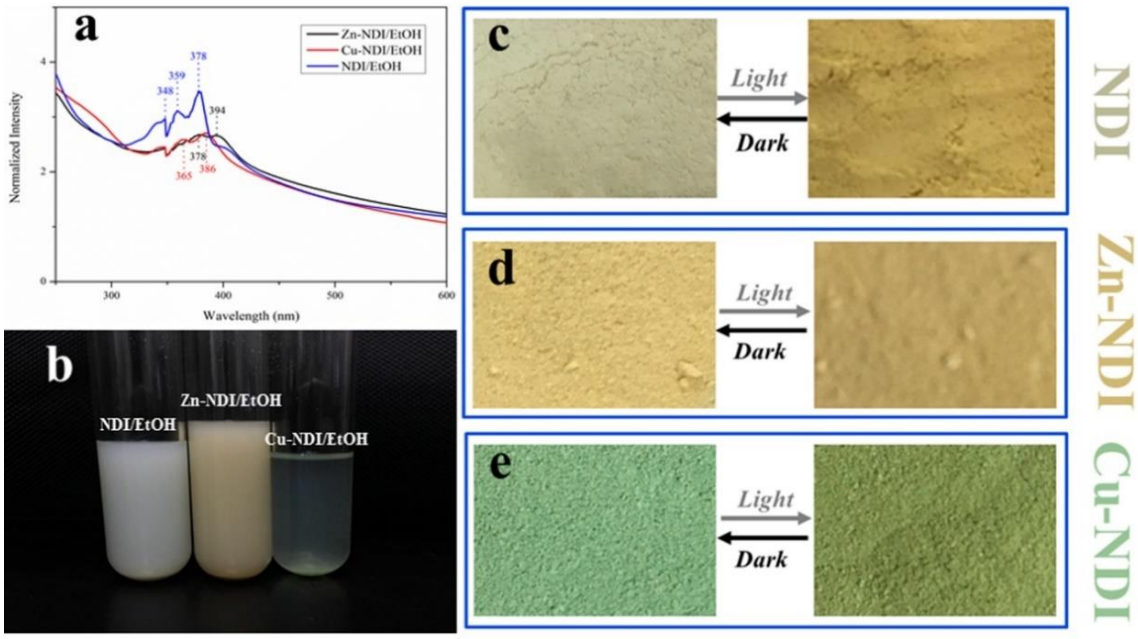

Fig. 5: UV-vis spectrum of Zn-NDI/EtOH, Cu-NDI/EtOH and NDI/EtOH (a), 1% concentration of NDI/EtOH, Zn-NDI/EtOH and Cu-NDI/EtOH mixture solution (b), optic pictures of NDI, Zn-NDI and Cu-NDI before and after irradiation under hernia light (c, d and e).

Furthermore, as shown in Fig. 4d, f and h, for NDI, Zn-NDI and Cu-NDI coated copy paper samples, MOFs crystals were readily observed on the surface of white glue coated copy paper. However, in the previous experiment of this work, NDI, Zn-NDI and Cu-NDI was tried to coat on the surface of paper directly, but the effect of photochromic was underdeveloped, due to the pore size (2~10 μm) formed by fibers constructed in the paper is much larger than the size of NDI and MOFs, so that it was hardly retained on the surface of paper.[21]

Photochromic behavior of MOFs coated paper materials

The UV-vis spectrum showed the absorption behavior of Zn-NDI/EtOH, Cu-NDI/EtOH and NDI/EtOH in 250~600 nm (Fig. 5a). As the n-π* and π-π* transitions of the aromatic carboxylic acid ester ligands, three characteristic absorption peaks appear in the region of 300-340 nm (λ = 348 nm, λ = 359 nm, and λ = 378 nm). The similar result was also reported by Hu *et al*.[24] As shown in Fig.5a, the red shift which belong to Cu-NDI (19 nm, 16 nm) were also shown on the NDI ligand linker, due to the p-conjugated frameworks, caused by the coordination formation of metal ions (cooper) and organic linker (NDI).[25] Similarly, the red-shift result was also observed in Zn-NDI sample.

Furthermore, all the samples (NDI, Zn-NDI and Cu-NDI) displayed color change properties under hernia light. As-synthesized NDI showed tan in color while the other MOFs showed light green (Cu-NDI) and dark tan (Zn-NDI) (Fig. 5c, d and e). When the NDI and MOFs crystal powders were exposed to hernia light for 60 seconds. NDI turned into wheat, Cu-NDI and Zn-NDI exhibited olive and brown color under otherwise the same condition.

1% NDI/EtOH, Zn-NDI/EtOH and Cu-NDI/EtOH mixture solution coated onto paper. Organic linker (NDI) and MOFs, delivered the coated paper with color change properties (*i.e*., tan changed to wheat, light green changed to olive and dark tan changed to brown) under hernia lights for 60s. Otherwise, the above sample was placed in a dark environment for 4 hours, and then restored to its original color. The reason was that with the conversion of light and dark conditions, oxygen free radicals or ligand free radicals were formed during the electron transfer process of NDI. Similarly, Mallick *et al*.

(2015) [13] reported the solvatochromic behavior of Mg-based porous MOFs in kinds of solvents (benzene, toluene, phenol, aniline etc. The results showed that Mg-based MOFs prepared from naphthalenediimide exhibited a fast and reversible photochromism effect, due to the electron deficient part of NDI organic linker, indicating that MOFs based on NDI can be used for benzene series organic solvent detection.

In our previous attempts, AKD (alkyl ketene dimer) and polyurethane was chosen to be the coating layer of copy paper. However, Zn-NDI/paper and Cu-NDI/paper showed the same wheat of NDI in color under hernia light for 30s, Prasath *et al.*[26] discovered that the carboxyl group of the polyurethane can form an ionic bond with the metal center, resulting in the loss of discoloration activity of MOFs, thus the coated paper composites behaved poor color change property.

In addition, the above experimental results also showed that the MOFs modified paper-based composite material which prepared by the coating method has potential application value in the fields of anti-counterfeiting, photochromic coated glass, special packaging, sensors, and diagnosis. [27]

Conclusion

(1) Photochromic paper was prepared by coating MOFs (Zn-NDI and Cu-NDI) on the surface of white glue pre-coated copy paper. SEM results displayed that coated paper with a white glue (thickness of about 2-2.5 μm) could effectively make up the pores between the fibers of the paper which without affected the paper structure, and improved the retention of MOFs on the paper.

(2) The photochromic properties of NDI/paper, Zn-NDI/paper and Cu-NDI/paper were investigated. The results showed that after being exposed to 60s, NDI/paper, Zn-NDI/paper and Cu-NDI/paper changed from tan to wheat, light green to olive, and dark tan to brown, respectively. After the above samples were left in the dark for 4 hours, the original colors were restored; this indicated that Zn-NDI/paper and Cu-NDI/paper were photochromic paper-based functional materials with fast and reversible effects. The above results demonstrated thus as-prepared MOFs coated paper composites had excellent color changing ability and had great potential in coating products including, anti-counterfeiting coating, and photochromic coating glass, special packaging, sensor and diagnosis.

Acknowledgments

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