Preparation and Printing Performance of Visible Light Photochromic Paper Based on PMoA-PWA/ZnO/PVP Composite

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Abstract: The recyclable paper based on photochromic materials not only reduces the pollution in the paper manufacture process, but also reduces the pollution caused by the use of ink, which receives wide attention. In this paper, a series of phosphomolybdic acid–phosphotungstic acid/ZnO/polyvinylpyrrolidone (PMoA-PWA/ZnO/PVP) hybrid films, which had different ratio of PMoA/PWA, was prepared by the ultrasonic composite method. The results indicated that the hybrid film prepared when the ratio of PMoA to PWA was 3 had the best photochromic performance. In this system, ZnO was the photosensitizer, while PMoA/PWA was the chromophore. The photochromic mechanism of the PMoA-PWA/ZnO/PVP hybrid film was based on the photogenerated electron transfer mechanism. ZnO generated photoelectron under the excitation of visible light, then PMoA and PWA obtained the photoelectron and produced photoreduction reaction to generate heteropolyblue. The visible light photochromic paper was prepared by loaded PMoA-PWA/ZnO/PVP hybrid film (A3) on A4 paper. Application tests showed that the prepared paper had extremely stable, excellent and reversible visible light photochromic properties, whether it was printing patterns or words, and could replace ordinary paper to realize the reuse of paper.

Keywords: ink-free printing paper; visible light; photochromic performance; heteropoly acid; ZnO; polyvinylpyrrolidone

1. Introduction

Paper product-related industries are still heavily polluting industries. If the paper used in our lives can be reused, this will greatly reduce the demand for paper, which will also reduce the pollution brought by the paper industry [1,2]. Recyclable paper based on photochromic materials [3–6], which use light-source printing, not only reduces the pollution in the paper manufacture process, but also reduces the pollution caused by the use of ink, which can be said to be “two birds”. Therefore, in order to control the pollution generated by the paper product-related industries from the source, in order to realize ink-free printing and paper recycling, ink-free printing technology has become the primary way to solve this problem [7–9]. Inspired by this, the UV photochromic material was loaded onto the paper and a printing device was made using a UV laser as the light source [10]. According to the characteristics that the UV photochromic material could change color under ultraviolet light irradiation and fading in air, the paper could be reused. Compared with ultraviolet light, which is 7% of sunlight, visible light accounts for nearly 40% of sunlight, and the energy of visible light is lower than the energy of ultraviolet light, so the excitation energy barrier required for photochromic materials that can respond to visible light must be lower than that of ultraviolet photochromic materials [10]. Therefore, the study of visible light photochromic materials is of great significance for the wider application of ink-free printing technology in the future. At the same time, compared with ultraviolet light, visible light can obviously reduce the cost of ink-free printing.
At present, the research on photochromic materials mainly focuses on Keggin-type heteropoly acids, especially phosphomolybdic acid [11,12] and phosphotungstic acid [13]. Scholars have used different preparation methods to compound heteropoly acids into different organic/inorganic materials to construct heteropoly acid-based composite photochromic materials. Through the interface interaction between the two, the charge transfer ability of heteropoly compounds was improved, and the excitation energy required for the photochromic reaction of the composite materials was reduced. Huang et al. [14] fabricated a PVP/PMoA film via layer-by-layer assembly with ultrasonic pretreatment and found that ultrasonic cavitation enhanced the photochromic capabilities of the PVP/PMoA film. Zhang Wei [15] prepared a series of heteropoly acid/ethyl cellulose (PMoA/EC), phosphomolybdic acid/polyvinylpyrrolidone (PMoA/PVP) and phosphomolybdic acid/silica/ZnFe$_2$O$_4$ (PMoA/SiO$_2$/ZnFe$_2$O$_4$) photochromic nanocomposite films that can respond to visible light by compounding heteropoly acid with organic polymer or inorganic semiconductor nanomaterial excited by visible light. Visible light photochromic materials can also be prepared by compounding with the photosensitive materials TiO$_2$ or ZnO [16,17]. The photochromic reaction was carried out according to the transfer mechanism of photogenerated electrons. Jagadeesh Babu et al. [18] reported that the altered band gap of TiO$_{2-x}$ rationally promoted the visible light absorption, and the RGO sheets present in the composites suppressed the electron–hole recombination, which accelerated the charge transfer. Due to the advantages of rapid carrier mobility and overwhelming production capacity of active protons under bandgap excitation, ZnO was considered as a potential candidate for high-efficiency photocatalyst materials [19–21]. Song et al. [20] fabricated a novel photochromic heteropolyacid-based composite film consisting of phosphomolybdic acid (PMoA), ZnO and polyvinylpyrrolidone (PVP) by a sol–gel process. After visible light irradiation, the PMoA/ZnO/PVP varied from slight yellow to blue, while undergoing an opposite color change upon heating. Wang Xuan et al. [21] prepared inorganic nanomaterials from ZnO by a calcination method, hydrothermal synthesis method and electrospinning method, and then combined it with heteropoly acid to prepare a ZnO/PMoA composite film system with excellent visible photochromic properties and pointed out that a Zn-O-Mo bond charge transfer bridge was formed at the interface between ZnO prepared by hydrothermal synthesis and PMoA.

In this paper, the ZnO nanomaterials, phosphomolybdic acid and phosphotungstic acid were combined in the organic polymer polyethylpyrrolidone ethanol system with different concentration ratios by the ultrasonic dispersion compounding method, and the heteropoly-acid-based multi-component visible light photochromic hybrid film system was constructed by drip coating. The PMoA-PWA/ZnO/PVP hybrid thin films with the best visible light response and good reversibility were selected through the phototropism test, and the photochromic mechanism of visible photochromic composite films was studied according to the energy-level transition characteristics of ZnO and the charge transfer mechanism of the charge transfer bridge of heteropoly acids. Finally, the PMoA-PWA/ZnO/PVP hybrid thin film with the best photochromic performance was selected and loaded on ordinary A4 paper to prepare visible light photochromic paper. Its application was tested and the stability and reversibility of its photochromic properties were investigated.

2. Experiment

2.1. Preparation

2.1.1. Preparation of PMoA-PWA/ZnO/PVP Hybrid Film

Zinc acetate dihydrate (Zn(OOCC$_2$H$_5$)$_2$·2H$_2$O, analytical reagent, Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China, 8.23 g), which was used as the Zn precursor, was dissolved in anhydrous ethanol (262.75 mL) and stirred in a water bath (60 °C) for 0.5 h. Slowly, 2.25 mL of ethanolamine (MEA, HOCH$_2$CH$_2$NH$_2$, analytical reagent, Sinopharm Chemical Reagent Co., Ltd.), which was used as the stabilizer, was added dropwise to the stirred solution, and stirring was continued in a water bath (60 °C) until a homogeneous and transparent solution was formed. The solutions were aged at room temperature for 24 h
to form a zinc oxide sol, labeled No. 1. A 3.6866 g aliquot of \( \text{H}_3\text{PMo}_{12}\text{O}_{40} \) (PMoA, analytical reagent, Sinopharm Chemical Reagent Co., Ltd.) was mixed with 50 mL absolute alcohol ethanol (analytical reagent, Sinopharm Chemical Reagent Co., Ltd.) to form solution No. 2 with a concentration of 0.4 mol/mL. A 2.3042 g aliquot of \( \text{H}_3\text{O}_{40}\text{PW}_{12} \) (PWA, analytical reagent, Sinopharm Chemical Reagent Co., Ltd.) was mixed with 20 mL absolute alcohol ethanol (analytical reagent, Sinopharm Chemical Reagent Co., Ltd.) to form solution No. 3 with a concentration of 0.4 mol/mL. A 1.00 g aliquot of polyvinylpyrrolidone (PVPd, analytical reagent, Mw = 50,000) was mixed with 100 mL absolute alcohol ethanol (analytical reagent, Sinopharm Chemical Reagent Co., Ltd.) to form solution No. 4 with a concentration of 0.01 g/mL. Solution No. 1 and solution No. 2 were mixed at a ratio of 7:3. Then, under the condition of continuous stirring, we dripped an appropriate amount of the above mixed solution into solution No. 3 to prepare the PMoA:PWA concentration ratios of 1:1, 2:1, 3:1 and 4:1 to form 10 mL mixed solutions. A pipetting gun was used to drop this mixed solution into solution No. 4 with constant stirring. Then, we dropped this mixed solution onto a quartz substrate to form a PMoA-PWA/ZnO/PVP hybrid thin film with an amount of 100 \( \mu \)L. We recorded the sample number as \( A_i \) (i = 1, 2, 3, 4).

2.1.2. Preparation of Visible Light Photochromic Paper

We used a pipette to measure 2 mL 21PMoA-7PWA/9ZnO mixed solution \( A_3 \), and slowly added it dropwise to 100 mL of PVP ethanol solution under constant stirring. After fully stirring for 30 min, ultrasonic compounding was performed for 1 h. And then, after stirring fully for 1 h, the transparent light yellow compound solution was obtained. The whole process was carried out under dark conditions. Then, the A4 paper was completely soaked in the above solution for 2 h, and then it was taken out and hung in the air. The paper was put in a dark box when it was completely dried. The preparation process of the visible light photochromic paper was carried out under dark conditions because the composite system had excellent visible light photochromic properties.

2.2. Characterization

TEM images of the sample were obtained on a JEM-200CX (JEOL, Tokyo, Japan) transmission electron microscopy with 250 kV acceleration voltage by the dropping complex solution onto the copper grids. Photochromic property measurements were performed on a V-500 UV–optical spectrophotometer (JASCO, Tokyo, Japan) in the range of 350–900 nm with an optical detection resolution of 1 nm. XPS measurements were performed on an ESCALAB 250 photoelectron spectrometer (Thermo, Waltham, MA, USA) with an AlK\( \alpha \) (1486.6 eV) and MgK\( \alpha \) (1253.6 eV) mono X-ray source to obtain the information of chemical binding energy of the hybrid film.

2.3. Photochromic Experiments

Photochromic properties experiments were performed with a 75 W xenon light source (PLS-SXE, Beijing Perfectlight Technology Co., Ltd., Beijing, China) filtered by a UV filter (pass above 422 nm wavelength) as the optical-light source. The straight-line distance between the light and the hybrid thin film was 150 mm. The hybrid film was exposed to air during the process of visible light irradiation. Under visible light irradiation, the hybrid thin film responded to visible light and generated a photochromic reaction, which turned to blue from colorless. The color response of the film to visible light can be expressed by the change of the absorption peak on the absorbance curve of the film. After irradiation for a certain time, the in situ absorbance curve of the film was obtained. The irradiation time was recorded until the curve was the same as the former one. Then, the film was sheltered from light under air conditions and the absorption spectra were measured at regular intervals to monitor the bleaching process. At the same time, we put the colored film in a drying oven at 100 °C for 30 min to test the absorption curve of the film. We repeatedly irradiated the film with visible light; it then faded under heating conditions. We recorded the absorption curve after coloring and fading and drew the film coloring–fading
cycle experiment diagram. We repeated the process of irradiating the film with visible light and fading under heating conditions and recorded the absorption curves after staining and fading. Finally, the experimental diagram of the film coloring–fading cycle was obtained.

2.4. Application Test of the Visible Light Photochromic Paper

The visible light photochromic paper was put in an opaque box and sent to Changchun New Industry Optoelectronic Technology Co., Ltd. (Changchun, China) for the application test. The test contents were as follows: the company used an inkless printing device prepared with a visible light source laser as the light source to print simple patterns, complex patterns and words on the prepared visible light photochromic paper, and took photos of the printed visible light photochromic paper.

3. Results and Discussion

3.1. TEM Analysis

The microstructures of the ZnO, PMoA-PWA and PMoA-PWA/ZnO/PVP hybrid films were measured by transmission electron microscopy; images are shown in Figure 1. It can be seen that the ZnO nanoparticles exhibited a rod-like structure with an average diameter of 100–160 nm (Figure 1a), and PMoA and PWA particles exhibited spherical structures with an average diameter of 10 nm (Figure 1b). From Figure 1c, spherical PMoA or PWA was found to be wrapped around the outer surface of ZnO nanotubes, resulting in roughness, and ZnO was not completely covered by PMoA or PWA. As shown in Figure 1d, ZnO displayed a clear and structurally ideal surface, and the lattice fringe spacing of ZnO was measured at 0.248 nm. The same microstructure of ZnO was present in the PMoA-PWA/ZnO/PVP hybrid film (Figure 1f), which indicated that the entry of PMoA or PWA into the ZnO lattice did not occur.

3.2. Photochromic Behavior

The UV–vis absorption spectra of PMoA-PWA/ZnO/PVP hybrid films Ai (i = 1, 2, 3, 4) in the coloration process are illustrated in Figure 2. There was no significant absorption
peak in the range of 350–900 nm before irradiation. After the irradiation of visible light, the color of the four hybrid films turned from light yellow to blue and broad absorption bands appeared at 775 nm in the UV–vis absorption spectra of the four hybrid films, which indicated that PMoA-PWA/ZnO/PVP hybrid films could respond to visible light.

Figure 1. TEM images of ZnO (a), PMoA-PWA (b), and PMoA-PWA/ZnO/PVP hybrid films (c), and HRTEM images of ZnO (d), PMoA-PWA (e), and PMoA/ZnO/PVP hybrid films (f).

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Figure 2. UV–vis spectra of PMoA-PWA/ZnO/PVP hybrid film sample Ai (i = 1, 2, 3, 4).

Comparing the UV–vis absorption spectra of A1–A4 in Figure 2, it was found that, after 6 min, 7 min, 7 min, and 6 min of visible light irradiation, respectively, the UV–vis absorption spectra of the hybrid films Ai (i = 1, 2, 3, 4) all had new features at 775 nm. At the same time, the absorption peak intensity of the hybrid films Ai (i = 1, 2, 3, 4) reached the maximum; their saturated absorbance values reached 0.141, 0.213, 0.266 and 0.206, respectively. The above result showed that the PMoA-PWA/ZnO/PVP hybrid film system prepared in this experiment had excellent photochromic properties of visible light. The ratio of PMoA:PWA of 3:1 was the best, and the saturated absorbance of the characteristic absorption peak was as high as 0.266. This was because, under the premise of ensuring the PMoA:ZnO ratio of 7:3 in the PMoA-PWA/ZnO/PVP hybrid film system, adding PWA components increased the specific gravity of the chromophore groups (PMoA, PWA) and reduced the proportion of ZnO in the system. In the hybrid film system, when PMoA:PWA was 3:1, the saturated absorbance was the highest, indicating that the ratio of the chromophore to the photosensitizer ZnO was the best; when PMoA:PWA was greater than 3:1, the proportion of the PWA component decreased, the chromophore group decreased and the photosensitizer ZnO was excessive, so the saturated absorbance of the hybrid film decreased; when PMoA:PWA was less than 3:1, the specific gravity of PWA increased, the chromogenic group was excessive and the photosensitizer ZnO was insufficient, so the saturated absorbance of the composite film also decreased. Therefore, when preparing the PMoA-PWA/ZnO/PVP hybrid film, the best ratio of PMoA:PWA was 3:1 and the ratio of PMoA:PWA:ZnO in the system was 21:7:9. Therefore, the hybrid film prepared when the ratio of PMoA to PWA was 3 (A3) was used in subsequent studies.
The fading process of the colored hybrid film $A_3$ is shown in Figure 3. As shown in Figure 3, the absorbance of the colored hybrid film sample $A_3$ was almost unchanged after being stored in vacuum for three days. When exposed to air, the hybrid film began to fade slowly, which indicated that oxygen played a key role in the bleaching process of the hybrid film. When the colored film faded in the air for three days, the absorbance of the hybrid film decreased to 74%, 55% and 46% of the saturated absorbance after one, two and three days, respectively, which indicated that the fading rate of the hybrid film gradually decreased with the prolong of time. When the colored hybrid film was heated at 100 °C for 30 min, the absorbance of the hybrid film would be rapidly reduced to 10% of the saturated absorbance, which indicated that heating accelerated the discoloration rate of the hybrid film.

![Figure 3. Bleaching process of PMoA-PWA/ZnO/PVP hybrid film after irradiation.](image)

The reversibility of the coloration–decoloration cycles of the hybrid film is shown in Figure 4. As shown in Figure 4, the saturated absorbance of the hybrid film over seven coloration–discoloration cycles was almost unchanged and the original absorbance increased slightly (but was almost unchanged). This showed that the hybrid film prepared in this experiment had high stability and good reversibility. After seven cycles of experiments, the hybrid film was still firmly adhered to the substrate, which indicated that the film had good adhesion and stable physical properties.

![Figure 4. Coloration–discoloration cycle diagram of PMoA-PWA/ZnO/PVP hybrid film at 775 nm.](image)
3.3. Photochromic Mechanism

In order to explore the photochromic mechanism of the PMoA-PWA/ZnO/PVP hybrid film under visible light, we studied the electronic structure changes of Mo 3d and W 4f in the hybrid film before and after irradiation by XPS spectroscopy in Figure 5.

The electronic structures of Mo 3d before and after irradiation are shown in Figure 5a,b. The binding energies (BEs) of Mo 3d had two spin–orbit configurations, Mo3d5/2 and Mo3d3/2, which were obtained by Gaussian spectral decomposition. As shown in Figure 5b, the characteristic signal of Mo5+ was detected in the PMoA-PWA/ZnO/PVP hybrid film after visible light irradiation, which indicated that the PMoA in the hybrid film underwent a photoreduction reaction under visible light irradiation. In Figure 5a, the characteristic signal of Mo5+ was also observed, which was caused by the X-ray excitation of the hybrid film before irradiation.

The binding energies of Mo3d5/2 and Mo3d3/2 in the hybrid film before and after irradiation are shown in Table 1. The binding energies of Mo3d5/2 and Mo3d3/2 were reduced after irradiation, which showed that the chemical microenvironment of the Mo atom had changed after irradiation. The proportion of Mo atoms occupied by Mo5+ before and after irradiation was calculated as shown in Table 1. It can be seen that the Mo5+/Mo ratio was 0.40 before irradiation, and the ratio of Mo5+/Mo reached 0.53 after irradiation, which can be attributed to the intervalence charge transfer, and the Mo6+ in the hybrid film underwent a photoreduction reaction. 
Table 1. Binding energies of Mo 3d energy level and Mo$^{5+}$/Mo ratios in PMoA-PWA/ZnO/PVP hybrid film after visible light irradiation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mo(^{5+})</th>
<th>Mo(^{6+})</th>
<th>Mo(^{5+}$/Mo Ration</th>
</tr>
</thead>
<tbody>
<tr>
<td>before illumination</td>
<td>232.66</td>
<td>235.69</td>
<td>231.16</td>
</tr>
<tr>
<td>after illumination</td>
<td>232.32</td>
<td>235.45</td>
<td>231.11</td>
</tr>
</tbody>
</table>

The electronic structure of W 4f before and after irradiation is shown in Figure 5c,d. The binding energy of W 4f can be divided into two configurations of spin–orbit merger, W\(4f_5/2\) and W\(4f_3/2\), which were obtained by Gaussian spectral decomposition. The binding energies of W\(4f_5/2\) and W\(4f_3/2\) before and after irradiation are shown in Table 2. It can be seen from Figure 5d that, after visible light irradiation, the characteristic signal of W$^{5+}$ was detected in the PMoA-PWA/ZnO/PVP hybrid film, which indicated that the PWA in the hybrid film underwent a photoreduction reaction under visible light irradiation.

Table 2. The binding energies of W 4f energy level and W$^{5+}$/W ratios in PMoA-PWA/ZnO/PVP hybrid film before and after visible light irradiation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>W$^{5+}$</th>
<th>W$^{6+}$</th>
<th>W$^{5+}$/W Ration</th>
</tr>
</thead>
<tbody>
<tr>
<td>before</td>
<td>— —</td>
<td>35.62</td>
<td>37.75 — —</td>
</tr>
<tr>
<td>after</td>
<td>34.96</td>
<td>37.33</td>
<td>35.26 37.40 0.49</td>
</tr>
</tbody>
</table>

It can be seen from Table 2 that the BE values of W\(4f_5/2\) and W\(4f_3/2\) after irradiation were both reduced, which indicated that the chemical microenvironment of W atoms had changed. The ratio of W$^{5+}$/W reached 0.49 after the irradiation, which indicated that, during the irradiation process, the W$^{6+}$ in the hybrid film underwent a photoreduction reaction to generate W$^{5+}$.

The photochromic energy level of the PMoA-PWA/ZnO/PVP hybrid film system is shown in Figure 6. The valence band bottom of ZnO was significantly lower than that of PMoA, which indicated that the electrons in ZnO can more easily enter PMoA. As a visible light photosensitizer, ZnO can generate photogenerated electrons under the excitation of visible light. The conduction bands of PMoA and PWA were both lower than the conduction band of ZnO, which facilitated the injection of excited electrons into the conduction band of PMoA or PWA. In this reaction, ZnO acted as a visible light photosensitizer and electron donor to generate photogenerated electrons under the excitation of visible light and transferred electrons to the conduction bands of PMoA and PWA through the relative energy level difference between the conduction bands of PMoA and PWA. PMoA and PWA obtained electrons to undergo a photoreduction reaction, Mo$^{6+}$ was reduced to Mo$^{5+}$, W$^{6+}$ was reduced to W$^{5+}$ and heteropoly blue was formed. This is consistent with the conclusion drawn from the XPS analysis. Therefore, the photochromic mechanism of the PMoA-PWA/ZnO/PVP hybrid film was based on the photogenerated electron transfer mechanism.
PMoA-PWA/ZnO/PVP hybrid film was based on the photogenerated electron transfer mechanism.

Figure 6. Schematic presenting the electron transfer between PMoA, PWA and ZnO in PMoA-PWA/ZnO/PVP hybrid film. (a) Bandgaps of PMoA, ZnO and PWA. (b) Schematic diagram of LMCT.

3.4. Research on the Printing Performance of Visible Light Photochromic Paper

Figure 7 shows photographs of the paper with visible photochrom after printing on an ink-free printer. It can be seen that the prepared visible light photochromic paper was directly used for printing. Whether it was used for printing simple patterns, complex patterns or words, the printed contents could be clearly presented on the paper. There was not much difference between inkless printing and normal ink printing, which preliminarily showed that it was feasible to replace ordinary paper with visible light photochromic paper.

Figure 7. Photographs of the paper with visible photochrom after printing on an ink-free printer: (a) after printing simple pattern, (b) after printing complex pattern 1, (c) after printing complex pattern 2, (d) after printing words.

The photographs of visible light photochromic paper printed with patterns are shown in Figure 8. It can be seen that the pattern printed on the visible light photochromic paper was very clear in Figure 8a. After the patterned visible light photochromic paper
was put in a vacuum bag for three days, the pattern hardly changed (Figure 8b). This indicated that the pattern on the paper could be preserved intactly under vacuum condition. The patterned visible light photochromic paper was naturally faded in the air for three days, and the pattern on the visible light photochromic paper was a little fuzzy, but the outline of the pattern was still left (Figure 8c). This indicated that the patterned paper had a fading reaction in the air. The fading reaction was consistent with the fading rule of the photochromic hybrid film described above, and the paper cannot be directly used for printing at this time. The visible light photochromic paper printed with a pattern was heated at 100 °C for 30 min, and the content of the pattern was almost invisible (Figure 8d). This indicated that the heat treatment accelerated the fading rate of the visible light photochromic paper, which was the same as the fading rule of the hybrid film described above. From Figure 8e, it can be clearly seen that the visible light photochromic paper was still intact after seven repeated uses, which showed that the visible light photochromic paper had excellent, stable and reversible performance when it was applied to print a pattern.

In summary, the visible light photochromic paper prepared in this experiment had extremely stable, excellent and reversible visible light photochromic properties, whether for printing patterns or words. Results further showed that the visible light photochromic paper could replace ordinary paper to realize the reuse of paper. The success of the application test of visible light photochromic paper and the analysis results of printing performance in this experiment have laid a practical foundation for the daily use of the visible light photochromic paper.

4. Conclusions

In this paper, the PMoA-PWA/ZnO/PVP hybrid film was prepared by the ultrasonic composite method. Under the irradiation of visible light, the hybrid film changed from light yellow to dark blue. Under the irradiation of visible light, ZnO can generate photogenerated electrons. Because of the relative energy level difference between ZnO and the conduction band of PMoA and PWA, the photogenerated electrons generated by ZnO can be injected into PMoA and PWA, which underwent photoreduction reaction after obtaining photogenerated electrons: Mo$^{6+}$ was reduced to Mo$^{5+}$, W$^{6+}$ was reduced to W$^{5+}$ and heteropoly acid produced heteropoly blue. In order to study the application performance of the PMoA-PWA/ZnO/PVP hybrid film in paper recycling, visible light photochromic paper was prepared by loading the hybrid film on paper. Under the irradiation of visible
light, the visible light photochromic paper presented stable, reversible and excellent visible light photochromic properties, which provided a reliable practical basis for visible light photochromic paper to replace ordinary paper and to realize the reuse of paper. Because the excitation light source of the visible light photochromic paper was visible light and the cost was low, the application of visible light photochromic paper in real life in the future is very promising. Therefore, the successful research and development of visible photochromic paper in this experiment was of great guiding significance for the realization of paper reuse.

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References

20. Song, T.; Li, J.; Deng, Q.; Gao, Y. Preparation, characterization, photochromic properties, and mechanism of PMoA/ZnO/PVP composite film. *Molecules* 2023, 28, 7605. [CrossRef] [PubMed]


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