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Photochromic transparent wood for photo-switchable smart window applications†

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Transparent wood with high optical transmittance, excellent thermal insulation and high toughness has attracted significant attention as an energy-saving building material. Many research efforts were dedicated to functional transparent wood, from luminescent to electrochromic transparent wood. However, photochromic transparent wood that is highly desirable and critical for smart window applications has been rarely studied. Herein, we experimentally demonstrate photochromic transparent wood with photo-switching of transmittance in the visible light region and color tuning properties. The photochromic transparent wood was obtained by infiltrating the lignin modified wood template with a mixture of photochromic material 3′,3′-dimethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-indoline]-1′-ethanol (DNSE) and pre-polymerized methyl methacrylate (MMA). This photochromic transparent wood exhibits a vibrant purple-to-colorless color change under the illumination of light. In addition, dichroic dye material doped photochromic woods were studied for providing more color change choices. The proposed photochromic transparent wood shows potential applications in mechanically robust, energy-efficient, photo-switchable, and colorful smart windows on a large scale.

Introduction

The desire to reduce residential building energy consumption that accounts for nearly 40% in the total energy consumption has motivated the development of energy-saving building materials with good light transmittance and thermal insulating properties.[1] Glass is mainly used in building windows for transmitting light. However, it suffers from shattering and brittleness in case of failure, resulting in potential safety issues. Recently, transparent wood (TW), composed of lignin removed or lignin modified bleached wood infiltrated with a refractive index-matching polymer matrix (PMMA) or epoxy, has attracted significant attention in energy-saving building materials due to the combined good optical transmittance, low thermal conductivity, and favorable mechanical toughness with shatterproof features.[2–6] To improve the properties of transparent wood for real applications, large-size,[7] centimeter thick[8] or flexible transparent wood,[9,10] as well as rapid and efficient preparation[11,12] of transparent wood has been intensively explored for energy-efficient building materials or solar cell application.[13,14]

In addition, transparent wood shows significant potential in multi-functionalities due to the macro-scale channels and nanopores in the cell wall.[15] W. Gan *et al.* reported the fabrication of a transparent magnetic wood based on filling the index matching methyl methacrylate and magnetic Fe_3O_4 nanoparticles into the delignified wood template.[16] W. Gan *et al.* also demonstrated luminescent and transparent wood composites using the index matching poly(methyl methacrylate) (PMMA) and luminescent γ-Fe_2O_3@YVO_4:Eu^{3+} nanoparticles.[17] Y. Li *et al.* fabricated luminescent transparent wood by the impregnation of quantum dots dispersed in a PMMA/oligomer liquid mixture.[18] Q. Fu *et al.* studied transparent plywood with load-bearing and luminescent properties through controlling lamination angles and cellulose content.[19] Lasing and random lasing from dye-doped transparent wood were reported separately.[20,21] Heat-shielding transparent wood was prepared by filling Cs_xWO_3.[22] Particularly, a smart window based on transparent wood containing electrochromic material was demonstrated using poly(3,4-ethylenedioxy-thiophene):poly(styrene sulfonate) (PEDOT:PSS) as the transparent conducting electrode, leading to a vibrant magenta-to-clear color change. It exhibited practical application in fabricating mechanically robust, energy-efficient smart windows on a large scale.[23] However, the smart window based on the photochromic transparent wood, which is capable of controlling incident irradiations onto a building by light, is quite useful in improving the building's energy efficiency but has rarely been investigated.

In this study, we experimentally demonstrate the photochromic transparent wood with photo-switching of transmittance in the visible light region and color tuning properties. The photochromic transparent wood was obtained by infiltrating the lignin modified wood template with a mixture of photochromic material 3′,3′-dimethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-indoline]-1′-ethanol

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(DNSE) and pre-polymerized methyl methacrylate (MMA). The microstructural and optical properties of the photochromic material doped transparent wood were investigated and characterized. The proposed photochromic transparent wood shows potential applications in mechanically robust, energy-efficient, photo-switchable and colorful smart windows on a large scale.

Experiments

Fig. 1 shows the schematic of the fabrication of transparent wood. Basswood slabs were parallelly cut along the growth direction of the tree, in order to obtain the original wood (OW). The slabs were about 30 mm long, 25 mm wide and 0.2 mm thick. The chemicals used for removing lignin contents from the wood were sodium silicate (from Tianjin Damao), sodium hydroxide (from Sinopharm), magnesium sulfate (from Aladdin), diethylene triamine pentaacetic acid (DTPA, Aladdin), and H_2O_2 (from Macklin). Methyl methacrylate was purchased from Macklin for the synthesis of infiltrated polymer using 2,2-azobisisobutyronitrile (AIBN, J&K Scientific Ltd) as the initiator. The solvents used were ethanol (from Shanghai Lingfeng), acetone (from Shanghai Lingfeng), and deionized (DI) water. 3′,3′-Dimethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-indoline]-1′-ethanol was purchased from Beijing MREDA Technology.

It was reported that basswood contains about 20 wt% lignin and 80% hemicellulose and cellulose.[27] In our experiment, the Basswood as the original wood underwent the lignin modification (step I in Fig. 1) process,[5] which led to the removal of only the chromophoric structure while retaining most of the lignin of the wood. Then, the OW was immersed in the lignin modification solution, which consisted of deionized water, sodium silicate (3.0 wt%), sodium hydroxide solution (3.0 wt%), magnesium sulfate (0.1 wt%), DTPA (0.1 wt%), and then H_2O_2 (4.0 wt%), at temperature of 70 °C till the wood was bleached by H_2O_2. The obtained lignin modified wood (LMW) was then thoroughly washed with DI water and kept in ethanol.

To obtain the photochromic material (DNSE) doped transparent wood, the filling materials were used to fill the lignin modified wood. 25 mL MMA doped with 0.3 wt% (0.0697 g) thermal initiator AIBN was firstly pre-polymerized at 75 °C[18] and then mixed with 0.05 wt% (0.0116 g) DNSE by stirring till the color of MMA mixture solution changed from purple to colorless. Next, the LMW was immersed in the MMA mixture solution and then placed in a vacuum drying oven, where the mixture solution was filled into the LMW. Here, multiple filling procedures can be applied to achieve complete filling. Finally, the LMW filled with MMA mixture solution was assembled between two glass substrates. It was then wrapped in tin foil, placed in an oven, and polymerized at 75 °C for 4 hours, leading to a transparent wood.

Results and discussion

Fig. 2(a–c) demonstrate the surface-view (longitudinal section) scanning electron microscopy (SEM) images of wood microstructures for original wood, lignin modified wood, and transparent wood, respectively. The original wood is opaque and brown in color (Fig. 2(a) – inset), which is due to the existence of lignin that would absorb visible light. During the process of lignin modification, the color of the wood gradually changes to white (Fig. 2(b) – inset) because of the increased light reflection at the interface of the nano/micro-sized channel and the microstructure of wood. After infiltrating the polymer, the refractive index mismatch reduces significantly, and the light reflection also suppresses drastically, resulting in a transparent wood with high transparency (Fig. 2(c) – inset). Fig. 2(d–f) demonstrate the cross-sectional (perpendicular to the surface) SEM images of wood microstructures for original wood, lignin modified wood, and transparent wood, respectively. It can be seen that the microstructure in wood has been preserved well during the lignin modification process, where the well-aligned channels allow the infiltration of the polymer doped with DNSE in our experiment. It is worth noting that the cross-section of transparent wood demonstrates a good and complete polymer filling into nano/micro-sized channels of the wood. Besides reducing

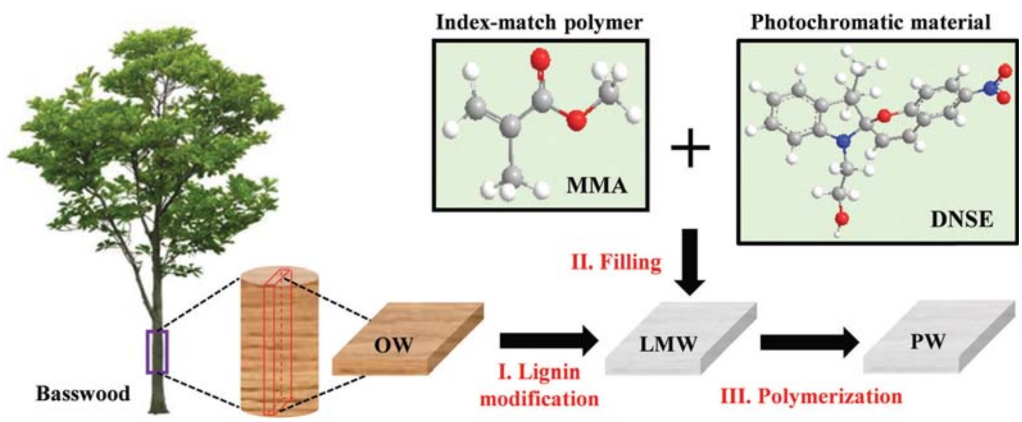

Fig. 1 Schematic of photochromic material doped transparent wood fabrication process. A Basswood was cut parallel to OW slab, and then treated with lignin modification by only removing chromophoric structure to obtain LMW. A mixture of thermal initiator AIBN doped pre-polymer MMA solution and photochromic material DNSE was filled into the LMW through vacuum process. After polymerization at 75 °C for 4 h, the PW was obtained (OW: original wood; LMW: lignin modified wood; PW: photochromic wood).

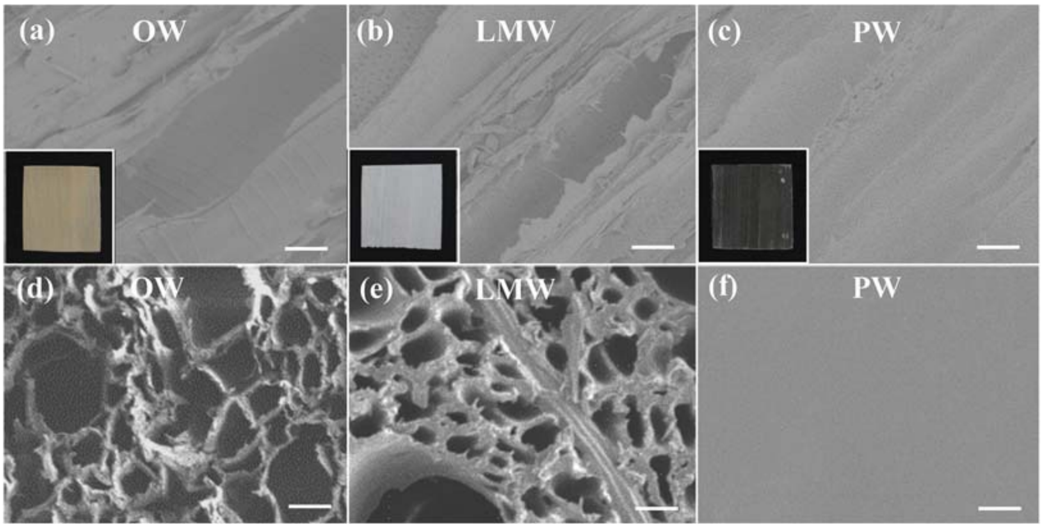

Fig. 2 Surface-view (longitudinal section) SEM images of wood microstructures for (a) original wood, (b) lignin modified wood and (c) transparent wood. The insets show optical images of OW in brown color, LMW in white color, and transparent PW, respectively. Cross-sectional (perpendicular to the surface) SEM images of wood microstructures for (d) original wood, (e) lignin modified wood and (f) transparent wood. Scale bar is 20 μm.

the light scattering through index match, the polymer filling can also improve the mechanical strength of wood/polymer composite by gluing wood cellulose nanofibers together.

The chemical structure of photochromic material DNSE is demonstrated in Fig. 3(a). A reversible photo-switching can be triggered by ultraviolet (UV) or green light, corresponding to two structures of DNSE called spiropyran[24] and merocyanine.[25] Under UV irradiation, the carbon–oxygen (C–O) bond of the spiropyran structure will be broken due to electronic transition from nitrogen atom to oxygen atom between the ring structures of spiropyran molecules, leading to a transition from a ring-close to ring-open structure. The C–O bond breaks at the picosecond level, and subsequently, the discoloration rate of the spiropyran occurs extremely fast. The DNSE molecule then rotates locally and forms a coplanar merocyanine structure with quinone, resulting in a purple color. Conversely, under green light irradiation or heating,

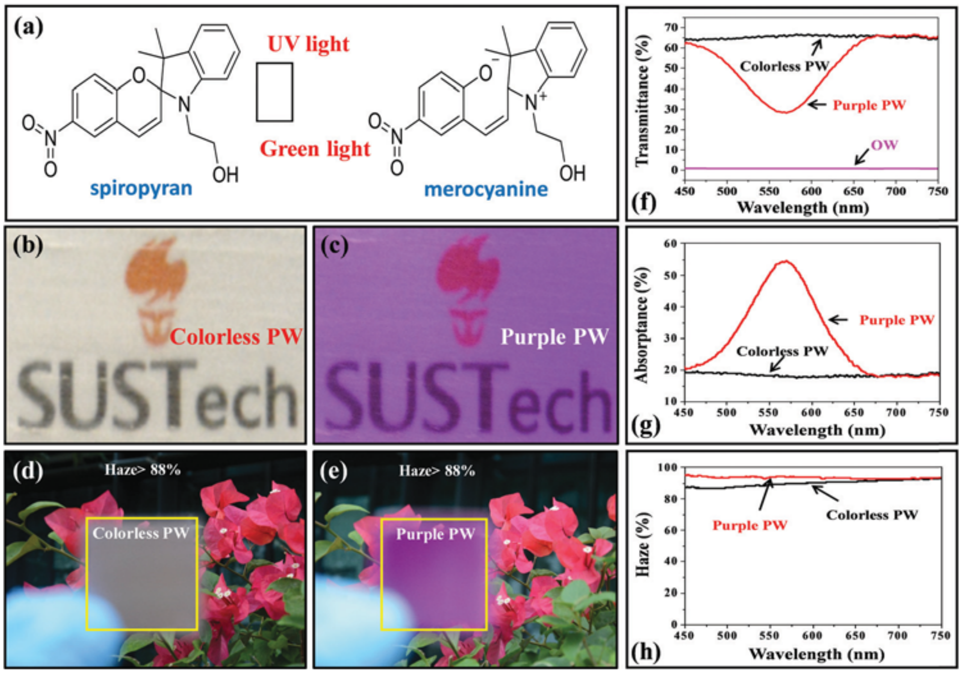

Fig. 3 (a) Chemical structure of spiropyran and merocyanine. The reversible photo switch can be triggered by UV or green light. Photo images of SUSTech logo with (b) colorless PW (spiropyran) and (c) purple PW (merocyanine). Outdoor views of flowers with (d) colorless PW and (e) purple PW. The hazes in both cases are as high as 88%, providing excellent block effects. (f) Transmittance of OW, colorless PW, and purple PW. (g) Absorbance of colorless PW and purple PW. (h) Haze of colorless PW and purple PW.

the C–O bond is connected due to an electronic transition from the oxygen atom to nitrogen atom, which leads to a transition from a ring-open to ring-close structure. Photochromic materials of spiropyran are well-known for the reversible "ring-open" and "ring-close" forms. The photo image of our university (SUSTech) logo with colorless transparent wood, and with purple transparent wood is shown in Fig. 3(b and c), respectively. Herein, UV light with 356 nm and a power of 12 mW was used for the illumination of photo-switching, which takes 10 s for completing the transition from colorless to purple PW. In contrary, it takes 52 s for the completion of transition from purple to colorless PW with a green light of wavelength 532 nm and a power of 2.5 mW (shown in Video S1, ESI†). It is worth noting that the transition from purple to colorless can be accelerated by heating. The higher the heating temperature, the shorter the time needed for transition. Therefore, the transparent wood can be easily controlled by UV or green light to switch the color between colorless and purple while doping photochromic material DNSE into the transparent wood. In both the cases, the PW was highly transparent, and the logo beneath was clearly visible.

Fig. 3(d and e) show the real photo of colorless PW and purple PW for an outdoor case. The high optical haze (more than 88%) provides an excellent block effect to both colorless and purple PW in outdoor or indoor situations. Herein, the distance between the objects and PW was around 10 cm. The block effect from high haze will be significant when the distance is larger than 10 mm. Therefore, the optical switchable photochromic wood possesses optical properties of high transmittance (transparency) for an object beneath (closely attached) and high haze (opaque) for an object behind (>10 mm). Fig. 3(f) shows the transmittance of original wood, colorless transparent wood, and purple transparent wood in the visible spectrum. For the original wood, the transmittance was close to 1%, indicating an opaque wood. A good optical transmittance of around 65% was achieved for colorless PW. It was noticed that the absorbance of colorless PW was around 20% (Fig. 3(g)), resulting in a relatively lower transmittance in our experiment. The transmittance spectra were measured with an unpolarized probe light beam using a UV-vis-NIR microspectrophotometer (20/30 PVTM, CRAIC). The light beam was focused to a probing area of 50×50 μm^2 using a

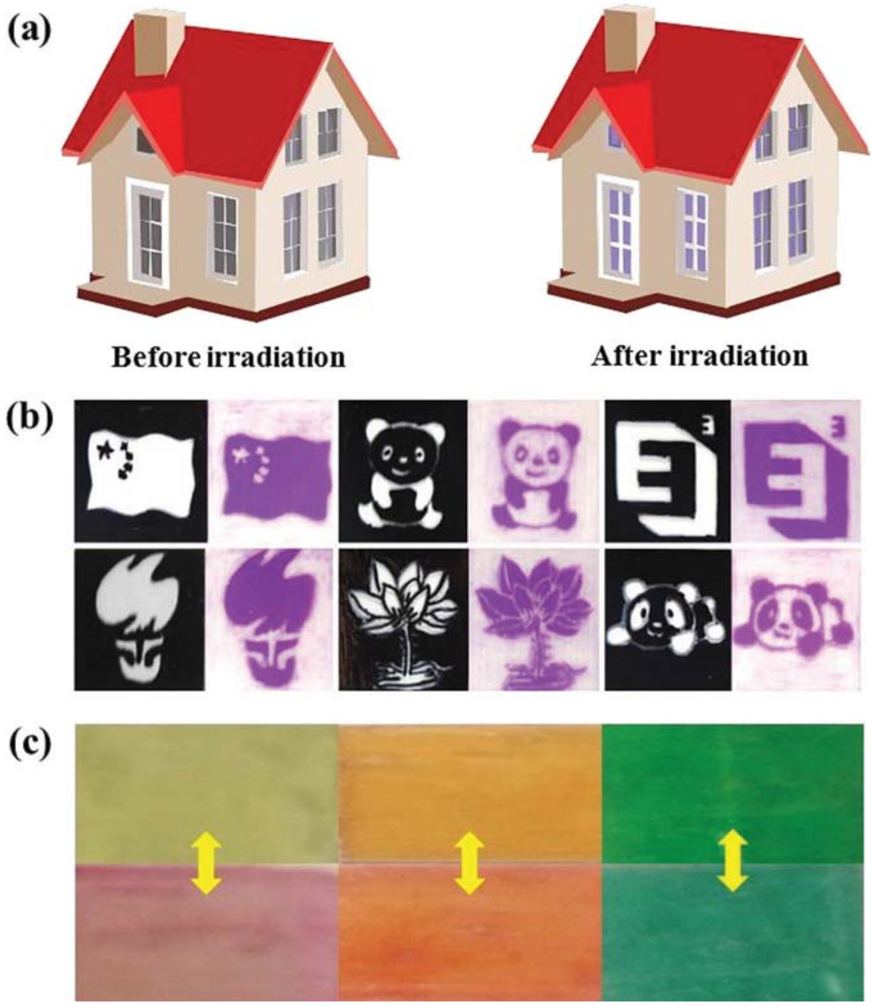

Fig. 4 (a) Schematic of PW windows on building before irradiation and after irradiation. (b) Photochromic wood exposed through a photo-mask to generate different pictures. (c) Colorful PW doped with dichroic dye material. PW in the top figures with colors of light yellow, yellow and green were captured before UV irradiation, and PW in the bottom figures with colors of light purple, orange and dark green were captured after UV irradiation.

10× objective lens (the working distance was 7.4 mm) combined with a variable aperture. The transmittance can be further improved by reducing the thickness of the wood slab. After UV irradiation, the TW doped with DNSE transits to purple PW, leading to a low transmittance centered at a wavelength of around 570 nm. The low transmittance was due to the intense absorption of merocyanine, as shown in Fig. 3(g). The absorption band in the visible region was the result of the π-electron transition in the ring-open structure.[26] Besides transmittance, the haze was another important parameter for PW performance. Fig. 3(h) demonstrates high optical haze of around 90% and 95% for colorless PW and purple PW, respectively. Therefore, the colorless transparent wood demonstrates good optical transmittance of approximately 65% and a high optical haze of 90%. The doped DNSE adds the function of photo-switching into the transparent wood, making it optically switchable and colorful.

One potential application of photo-switchable transparent wood is to be used as building windows. Under the condition of abundant sunlight, the PW window will be exposed to a high dose of UV rays in sunlight. It will absorb the UV light and gradually turn into purple color, which will lower the total light exposure in the indoor room, thereby making the window colorful. In contrast, under the condition of relatively poor solar radiation, the photochromic materials doped PW will return to the colorless state, which increases the total light exposure in the indoor room and makes the window transparent and colorless. Fig. 4(a) depicts the schematic of PW windows in a building before irradiation and after irradiation. Fig. 4(b) shows the photochromic wood exposed through a photo-mask to generate different pictures such as the national flag, panda, the logo of our department, the logo of SUSTech, and lotus. In the case of PW region behind the white part of the photomask, the PW will be exposed to UV light due to which it will become purple in color. In contrary, for PW region behind the black part of the photomask, the PW will not be exposed to the UV light and will stay in the colorless state. Further, three kinds of dichroic dye colored light yellow, yellow and green were mixed with our photochromic material to generate more colors. Fig. 4(c) shows the photos of dichroic dye material doped PW before UV irradiation (top three figures) and after UV irradiation (bottom three figures). It can be seen that the colors light yellow, yellow and green can be photo-switched to light purple, orange and dark green by UV light, and can be photo-switched back by green light. Besides the window application, the photo-switchable PW can also be used as anti-counterfeiting materials and other light-control rewritable materials or in photonic devices. However, it is noticed that the proposed photochromic transparent wood with the property of blocking transmission in the colored state is preferable only in summer and not in winter.

Conclusion

In summary, photochromic transparent wood, with photo-switching of transmittance in the visible light region and color tuning properties, has been demonstrated for potential smart window application. The photochromic transparent wood was obtained by infiltrating the lignin modified wood template with a mixture of photochromic material 3′,3′-dimethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-indoline]-1′-ethanol (DNSE) and pre-polymerized methyl methacrylate (MMA). This photochromic transparent wood exhibits a vibrant purple-to-colorless color change under the illumination of light. In addition, dichroic dye material doped photochromic woods were also studied for providing more color change choices. The proposed photochromic transparent wood shows potential applications in mechanically robust, energy-efficient, photo-switchable and colorful smart windows on a large scale, as well as anti-counterfeiting materials and other light-control rewritable materials or photonic devices.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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