Dramatic Enhancement of CO₂ Photoreduction by Biodegradable Light-Management Paper

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Photocatalytic reduction of CO₂ with H₂O vapor is gaining increased interest because it is a promising “green chemistry” route for the direct conversion of CO₂ to value-added chemicals driven by solar energy. To increase the efficiency of photocatalytic conversion, most efforts are made by exploring various photocatalysts while little effort on advanced light management. For the first time, it is demonstrated that bio-degradable transparent paper with excellent light diffusivity can effectively enhance the light utilization of photocatalytic reactions when attached on the device surface, and thus greatly increase the conversion efficiency. As a proof-of-concept, a graphitic carbon nitride (g-C₃N₄) photocatalyst with transparent paper attached, exhibited 1.5 times higher photocatalytic activity than bare g-C₃N₄ in the reduction of CO₂ under visible light irradiation. The improved catalytic performance can be ascribed to the (1) refractive index matching and (2) enhanced light absorption via prolonged light traveling path in transparent paper, which decreases the light reflection at surface and traps the absorbed light inside, leading to an increased light absorption at the active layer of the device. The transparent paper with a controllable light management behavior has an unprecedented potential for applications in photocatalysis as a general method for improved light utilization.

Carbon dioxide (CO₂), which accounts for more than 63% of the long-lived greenhouse gases (e.g., CH₄, N₂O), has been released tremendously from fossil fuel combustion in the past decades.[1,2] The conversion of atmospheric CO₂ into industrially favorable chemicals is highly desired for the sake of environmental protection and human society sustainability. Recently, a newly found sustainable path is the photocatalytic reduction of CO₂ with H₂O into value-added fuels by semiconductors. This path helps with atmospheric CO₂ reduction and partly solves energy problems as well.[3,4] Unfortunately, CO₂ photoreduction in engineered systems still suffers from low conversion yields, resulting from the fast electron-hole recombination of semiconductors, weak light harvesting, and backward reactions.[5–7] Strategies to resolve those challenges have been an area of intense research. Previous efforts on the enhancement of CO₂ reduction efficiency have generally focused on the development of highly efficient semiconductor photocatalysts such as constructing various nanostructures, doping with metal or nonmetal elements, and coupling with semiconductor composites.[8–14] Despite their important role, the development of those novel photocatalysts could have high energy-cost, contain cumbersome steps, or not environmentally friendly.

Recent studies show that light management to enhance the light trapping inside an active layer is critical for improving the efficiency of optoelectronic devices such as thin film solar cells and photoelectrochemical cells.[15–24] Transparent paper made of wood fibers is an environmentally friendly and renewable material that has excellent optical transparency (>90%) and tunable transmission haze (50–70%).[25–28] In general terms, the photocatalytic substrates require high optical transparency but also prefer high optical haze to increase the light scattering and consequently the absorption in the active semiconductor materials, and thus may enhance the photocatalytic efficiency. As far as we know, no report has been published on the utilization of light management techniques in the photocatalytic system.

In this work, we demonstrate for the first time the successful use of a green, biodegradable, transparent paper as a light management substrate to enhance the light utilization for a photocatalyst and thus improve its performance in the CO₂ photocatalytic reduction. A metal-free photocatalyst, graphitic carbon nitride (g-C₃N₄), was used for demonstration because of the advantage of its visible-light response, high chemical/thermal stability, low-cost synthesis, and most importantly,
appropriate band positions for CO$_2$ photoreduction.$^{[29–32]}$ As shown in Figure 1, g-C$_3$N$_4$ was first coated onto a macroporous nickel foam substrate because the gas molecules including reactants and produced gaseous fuels can easily diffuse in this 3D porous substrate. Then, a piece of transparent paper was attached on the surface of the g-C$_3$N$_4$. The transparent paper with a high haze can efficiently increase the visible light scattering and consequently improve its absorption in the g-C$_3$N$_4$ photocatalyst.

Transparent paper with excellent optical transparency, low surface roughness, and high optical haze was prepared by vacuum filtration of a 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized wood fiber solution. Figure 2a,b shows the scanning electron microscope (SEM) images of the synthesized transparent paper made from microsized wood fibers with an average diameter of $\approx$30 $\mu$m. This transparent paper presents a high optical transmittance of over 90% and transmission haze of $\approx$60% in a wavelength range of 400–1100 nm (Figure 2c,d). The high transmission haze results from the large forward scattering effect of the transparent paper, which can be visualized in the inset of Figure 2d. When a red laser is passed through, the transparent paper gives a high intensity and highly scattered light pattern on the surface of target. A control experiment was also applied to glass for comparison and the result is shown in Figure S1 of the Supporting Information. Since the transmission haze of glass is very low ($\approx$1%), the transmitted light is scattered only slightly as visualized by a small illuminated area on the wall behind the transparent paper. The angular dependence of the light scattering effect of transparent paper was evaluated on an optical setup with a rotating stage, and the scattering angle range is defined as the scattered light, which illustrates a light intensity larger than 5% of the peak transmission intensity at 0°. The scattering angle distribution of the transmitted light is displayed in Figure 2e, which presents a Gaussian-like pattern with a maximum scattering angle of $\approx$36°. Figure 2f illustrates the light reflection of the transparent paper. It is a low reflection where a value less than 8% is observed in the wavelength range of visible light.

Transparent paper provides excellent optical transmittance while simultaneously offering a largely modulated light scattering behavior, which exhibits great potential applications as an efficient light management coating or substrate for many optoelectronic devices.$^{[33–35]}$ Analogously, light management also plays a crucial role in photocatalytic systems. Herein, the photocatalytic performance of the metal-free g-C$_3$N$_4$ attached with a piece of transparent paper (denoted as g-C$_3$N$_4$@T-paper) was conducted on a gas phase photoreduction system in the presence of CO$_2$ and H$_2$O vapor under perpendicular visible-light irradiation, the detailed procedure is included in the Experimental Section. Control experiments were conducted without photocatalyst or light irradiation, and no product was found, thus confirming that both the photocatalyst and light irradiation are two essential conditions for the CO$_2$ photoreduction. Figure 3a gives the evolution of the main product CO as a function of irradiation time over g-C$_3$N$_4$@T-paper and bare g-C$_3$N$_4$. From the curves, it is observed that the CO yield is increased with the irradiation time and the g-C$_3$N$_4$@T-paper exhibits a higher activity than bare g-C$_3$N$_4$. After 24 h of visible-light irradiation, the yield of CO on the g-C$_3$N$_4$@T-paper was up to 3.85 $\mu$mol g$^{-1}$ cat., which is about 1.5 times higher than that of bare g-C$_3$N$_4$. The enhanced photocatalytic performance...
is mainly due to the combination of the enhanced forward scattering effect of transparent paper, as well as the index matching effect between gas and the g-C₃N₄ photocatalyst after attaching the transparent paper to the top surface of a photoactive layer. Figure 3b shows the UV–vis diffuse reflectance spectra of the g-C₃N₄ with and without transparent paper in the range of 350–800 nm. It is apparent that the UV–vis spectrum of the g-C₃N₄@T-paper displays a significant adsorption between 400 and 800 nm with respect to that of bare g-C₃N₄. Therefore, the transparent paper is functioning as (i) the light trapping layer with an enlarged photon traveling path in the photoactive layer of the CO₂ photoreduction system and (ii) the antireflection coating as an index matching layer between the g-C₃N₄ photocatalyst and gas.

To reveal the possible incident angle-independent optical properties of the transparent paper, the transmission of our transparent paper and a commercial transparent poly(ethylene terephlate) (PET) film was investigated and compared by utilizing different incident angles with a single mode 420 nm laser, and the relative values compared to the transmittance of perpendicular incident light (=90%) are plotted in Figure 4a. Here, the incident light was collimated before illuminating on the surface of the sample with a spot size of ~500 µm, and the incident angle is defined as the angle between the incident light and normal direction of the substrate. When the incident angle is 0° (perpendicular illumination), the plastic PET film and transparent paper exhibit similar transmission. While the transmission of PET film gradually decreases with larger incident angles, the transparent paper maintains a higher transmission across all angles.

Figure 2. Characterizations of the transparent paper. a,b) SEM images, c) light transmittance, d) transmission haze and the visual effect of light scattering effect (inset), e) scattering angular distribution with arbitrary y-axis and x-axis units, and f) light reflection of the transparent paper.

Figure 3. a) Yield of CO as functions of irradiation time over g-C₃N₄ photocatalyst with and without transparent paper under perpendicular visible-light, and b) UV–vis diffusion reflectance spectra of the g-C₃N₄ with and without transparent paper.
angle up to 80°, the transmission of our transparent paper
remains constant up to 60° incident angle and slowly decreases
to ≈84% at 80° incident angle. Comparably, the transmission
for the PET film drops ≈62.2% during the change from perpen-
dicular illumination to 80° illumination while the transparent
paper only exhibits ≈16% drop. Besides the 420 nm blue light,
we have also evaluated the performance of transparent paper
using other different wavelengths including red (630 nm) and
green (530 nm), thereby covering three main components in
the visible-light spectrum. As can be observed in Figure 4a,
there is minimal variation of the transmission for three dif-
ferent wavelengths, indicating a strong broadband effect of
light passage.

Similarly, Figure 4b gives profile of the relative transmis-
sion haze values of transparent paper versus incident angle
under different wavelengths. Interestingly, the haze value stays
constant with an incident angle from 0° to 80°, yielding a uni-
form light scattering capability that is almost independent of
the position of the light source. Based on the excellent optical
properties outlined above, it is expected that the haze effect of

Figure 4. The relative intensity of a) transmission and b) haze versus incident angle under different wavelengths using the standard transmittance or
haze of perpendicular incident light as the reference. Yield of CO as functions of irradiation time over g-C$_3$N$_4$ photocatalyst with and without T-paper
under c) 45° incident angle and d) 70° incident angle. e) The schematic diagram of the light scattering and reflecting behaviors on the g-C$_3$N$_4$ photocatalyst
with and without T-paper with different incident angles.
the transparent paper can cause the incident angle-independent photocatalytic performance. To verify this, the photocatalytic activity of devices under illumination from different incident angles was measured by illuminating the devices with parallel visible light. As demonstrated in Figure 4c,d, the photocatalytic activity of g-C₃N₄@T-paper is almost always stable even when the light angle is varied from 0° to 45°, and sometimes up to 70°. While the corresponding activity on bare g-C₃N₄ without T-paper decreases significantly after increasing the incident angles, indicating a lower light utilization in the bare g-C₃N₄. The bare g-C₃N₄ exhibits a refractive index of about 1.95. Our transparent paper is composed of cellulose fibers with a refractive index close to 1.5, which is between that of gas (n = 1) and that of the g-C₃N₄ photocatalyst. Thus, when intimately coated on top of the g-C₃N₄, a reduced light reflection can be observed compared with that from the bare g-C₃N₄ surface. Thus, a low reflection was obtained (Figure 4e). In addition, after passing through the transparent paper, light reaches into the active photocatalytic layer, then the transparent paper with a suitable size was attached on the surface of g-C₃N₄. Figure S4 of the Supporting Information indicates that this g-C₃N₄ has a platelet-like morphology with an average particle size of 5–12 µm.

**Structural Characterization:** The optical properties of the transparent paper were measured using a UV–vis Spectrometer Lambda 35 containing an integrating sphere (PerkinElmer, USA). The micromorphologies were characterized by an SEM using a TESCAN VEGA-3-SBH SEM operated at 25 kV. The crystal structure of the g-C₃N₄ photocatalyst was identified by using an XRD (Rigaku D/MAX-2550VB/PC) with Cu Kα radiation (λ = 1.5406 Å). The accelerating voltage and the applied current were 40 kV and 40 mA, respectively (scanning step: 0.02° per second) in the 2θ range of 10°–80°. The diffuse reflectance spectrum of the g-C₃N₄ over a range of 200–800 nm was recorded by a Shimadzu UV-2401 spectrophotometer, and its surface area was measured by the nitrogen sorption analysis at 77 K using multipoint Brunauer–Emmett–Teller method.

**Photocatalytic Performance Tests:** The photocatalytic performance was evaluated via a CO₂ photoreduction experiment under a 500 W xenon lamp light irradiation with a 420 nm filter. The reactions were performed in a homemade 2700 mL stainless steel reactor at 25 °C and 110 KPa pressure. A powdered g-C₃N₄ photocatalyst (100 mg) was evenly coated on the surface of macroporous nickel foam substrate to form a photoactive layer, then the transparent paper with a suitable size was attached on the surface of the g-C₃N₄ photoactive layer. Figure S4 of the Supporting Information shows the cross-section SEM image of this sandwich-like active substrate. The thickness of transparent paper and g-C₃N₄ photoactive layer are measured to be about 60 and 150 µm, respectively. This sandwich-like active substrate was fixed into the center of the reactor. Prior to illumination, the reactor was evacuated several times and then purged with a CO₂ + H₂O mixture at about 20 mL min⁻¹ for 2 h in the dark until reaching an adsorption–desorption balance, and then exposed to a light source for 24 h for every cycle. As can be seen from Figure 5, no apparent deactivation of the g-C₃N₄@T-paper was observed after five consecutive runs (the CO₂ photoreduction efficiency declined by only 3%), indicating that the transparent paper possesses good stability during the gas-phase photocatalytic reaction.

In conclusion, highly transparent paper with a high optical haze has been prepared by vacuum filtration of the TEMPO-oxidized wood fibers, and utilized as a light management substrate for photocatalytic CO₂ reduction. A comprehensive analysis shows that the prepared transparent paper possesses incident angle-independent optical properties which make it a viable effective light manager with applications in photocatalytic systems. In the first demonstration, it was found that coating the transparent paper on the surface of g-C₃N₄ photocatalyst layer lead to significantly enhanced photocatalytic performance in the reduction of CO₂ with H₂O vapor. This comes as a result of the effective light scattering and increased light absorption within the photocatalyst. The exciting findings of this study will provide a general strategy for the future development of high-performance photocatalytic systems with efficient light management.

**Experimental Section**

**Transparent Paper and g-C₃N₄ Photocatalyst Preparation:** Transparent paper was prepared by vacuum filtration of the TEMPO-oxidized wood fibers suggested in the previous report.[35] In a typical process, bleached softwood pulp extracted from the southern yellow pine trees was dispersed into a 1 wt% fiber suspension with distilled water and then treated in a TEMPO/NaBr/NaClO system at pH 10.5. The mixture was continuously stirred for an additional 4–6 h until the color of the water changed from yellow to colorless. After that the TEMPO-oxidized wood pulp was diluted to about 0.2 wt% in solution with deionized water. This diluted pulp was then used to fabricate transparent paper by filtration method using a 9 cm filter membrane (0.65 µm PVDF, Millipore, USA). The resulting wet paper was sandwiched between two stacks of regular filter paper and dried at room temperature under a pressure of 4 Mpa. g-C₃N₄ was synthesized by direct pyrolysis of melamine at 550 °C according to the literature.[35] Typically, 10 g of melamine powder was put into a alumina crucible with a cover, then heated to 550 °C in the muffle furnace for 2 h at a heating rate of 10 °C min⁻¹. A typical X-ray diffractometer (XRD) pattern of the prepared g-C₃N₄ is shown in Figure S2 of the Supporting Information. The SEM image in Figure S3 of the Supporting Information indicates that this g-C₃N₄ has a platelet-like morphology with an average particle size of 5–12 µm.
gas phase volume concentrations of CO$_2$ and H$_2$O were controlled at about 95.5% and 4.5%. (The H$_2$O vapor was bubbled into the reactor by CO$_2$, and the corresponding initial concentrations of CO$_2$ and H$_2$O in the reactor were about 1865.6 and 35.8 mg L$^{-1}$, respectively.) After that, the reactor was tightly closed and the lamp was switched on to start the experiment. The gas-phase products were collected every hour and analyzed online by gas chromatography (LH 9890B) equipped with flame ionization detector and thermal conductivity detector. Nitrogen (N$_2$) was used as the carrier gas.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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CO$_2$ photoreduction, high haze, high transmittance, light management, transparent paper

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