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Improving photoreduction of CO_2 with homogeneously dispersed nanoscale TiO_2 catalysts

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Significantly improved photoconversion of CO_2 was achieved with photocatalysts of nanoscale TiO_2 particles homogeneously dispersed in porous cavities of optically transparent ionomer membrane thin films.

Carbon sequestration by photocatalytic reduction of CO_2 is of significant interest to the research community.[1–6] Nanoscale semiconductors have been used as photocatalysts in the photoconversion.[7–11] For example, Henglein first reported the photoreduction of CO_2 to formic acid by using SiO_2-stabilized ZnS quantum dots as catalyst and 2-propanol as sacrificial electron donor in an aqueous solution.[7] The photoreaction efficiencies with quantum-sized semiconductor photocatalysts are considerably higher than those with corresponding bulk semiconductors. For the photoconversion of CO_2 to formate over ZnS nanoparticles, a quantum efficiency of 23% was achieved.[8] The more effective photocatalysis with the nanoscale semiconductors is attributed to an increase in the band gap and a decrease in the recombination of photogenerated electron–hole pairs.[9–11] Despite the recent advances, however, the direct photocatalytic reduction of CO_2 remains a difficult and challenging task. Among the efforts made to improve the CO_2 photoconversion is the use of liquid or supercritical CO_2,[12–14] in which the CO_2 concentration is substantially higher than that in an aqueous solution. For example, Mizuno *et al.* reported that the photoreduction of CO_2 with colloidal TiO_2–Cu as catalyst was significantly more efficient in supercritical CO_2 than in aqueous CO_2 solution.[12] The heterogeneous photocatalytic conversion of CO_2 depends sensitively on the dispersion of the nanoscale semiconductors. The agglomeration of the nanoparticles is a critical problem associated with several photocatalyst platforms. Commercial colloidal TiO_2 (Degussa), for example, aggregates significantly in suspension, which not only reduces the active surface area but also compromises the desired photoreaction conditions due to a severe scattering effect.[14–16] In the work reported here we immobilized TiO_2 nanoparticles in porous cavities of the commercial ionomer membrane Nafion (Du Pont Co.). The homogeneously dispersed nanoscale TiO_2 photocatalysts in Nafion thin films allowed the heterogeneous photoreduction of CO_2 under an optically homogeneous reaction condition, resulting in significantly improved photoconversion.

The TiO_2 nanoparticles in Nafion films were prepared by a procedure reported previously.[17] Briefly, purified and dried Nafion-112 films (supplied by Du Pont Co.) were soaked in a solution of $Ti(OC_3H_7)_4$ in isopropanol (0.5 M) for 48 h. Upon repeated washing and rinsing with isopropanol and acetone, the films were immersed in boiling water for the hydrolysis of $Ti(OC_3H_7)_4$ in the membrane structure to form TiO_2 nanoparticles.[17] The TiO_2-loaded films appeared similar to the blank films, except for a light yellowish color. The films were characterized by UV/vis absorption (Fig. 1), X-ray powder diffraction analysis (anatase TiO_2, Fig. 1 inset), and TEM (specimen from cross-sectional microtone, Fig. 2). The results show that the embedded TiO_2 nanoparticles in different films have similar average sizes (~4 nm in diameter) and also similar size distribution standard deviations (~0.5 nm). The TiO_2 loadings in the films are about 10 wt% (1.3 mmol-TiO_2/g-Nafion), estimated gravimetrically and confirmed by UV/vis absorption results.

The optically transparent Nafion films embedded with TiO_2 nanoparticles were used in the photocatalytic reduction reaction of liquid CO_2 (high-purity SCF-grade) in a cylindrical high-pressure optical cell (1.7 cm inner diameter and 8 cm long) with two quartz windows (Fig. 2). In a typical experiment for the photoreduction, one or more of the films was arranged in the optical cell to be parallel to the quartz windows (thus perpendicular to the incident light, Fig. 2). The optical cell was purged with CO_2 gas for 30 min, and then filled with the liquid CO_2 to a final pressure of 2000 psia. After photoirradiation with a xenon arc source (990 W, Ushio Electronics Co.) through a water filter for 5 h, the optical cell was depressurized and this was immediately followed by the addition of deoxygenated water (or D_2O, 2 mL).[14] The reaction products in the resulting aqueous solution were analyzed quantitatively by using ^1H NMR (with D_2O) and HPLC techniques. Blank Nafion films were used as control under the same experimental conditions, but no reaction products were detected as expected. For reference, commercially available TiO_2 powders (Degussa, 50 mg) were

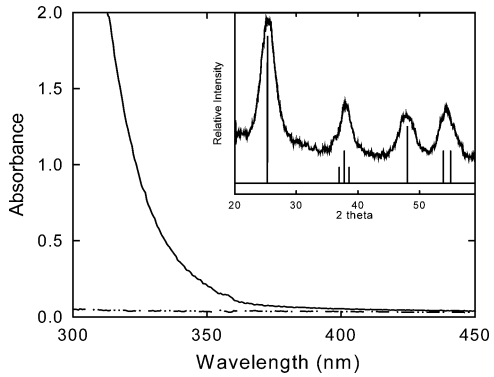

Fig. 1 UV/vis absorption spectra of Nafion-112 films with (——) and without (— . .—) embedded TiO_2 nanoparticles. Inset: powder X-ray diffraction pattern of the TiO_2-loaded Nafion film.

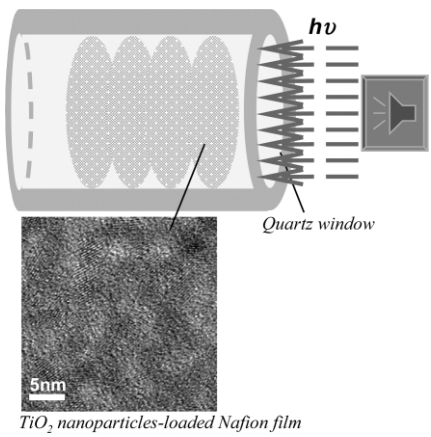

Fig. 2 Experimental setup for the photoreduction of liquid CO_2 with TiO_2-loaded Nafion films as photocatalyst. The TEM image is for a specimen from the cross-sectional microtone of a TiO_2-loaded film.

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suspended in liquid CO_2 in the optical cell for photoreduction under the same conditions. The suspension was stirred continuously during the photoirradiation, and the reaction products were similarly analyzed quantitatively.

The use of Degussa as photocatalyst suspended in liquid CO_2 yielded formic acid as the primary reduction product at 9 μmol/gram-TiO_2 and trace amount of methanol. This is comparable with the literature results under similar experimental conditions.[14] In the work by Mizuno *et al.*, the photoconversion product was also exclusively formic acid at 8.8 μmol/gram-TiO_2.[14] However, significantly more efficient photoreduction of CO_2 was achieved with the use of only a single TiO_2-loaded Nafion film as photocatalyst, producing not only formic acid at 190 μmol/gram-TiO_2 but also methanol at 280 μmol/gram-TiO_2 and acetic acid at 30 μmol/gram-TiO_2. Overall, the products correspond to the photoconversion of 530 μmol-CO_2 (or 23 mg-CO_2) per gram-TiO_2, which is at least 60-times higher than that with the use of suspended Degussa under otherwise the same photoreaction conditions. The more efficient photoreduction of CO_2 is credited to the homogeneous dispersion of TiO_2 nanoparticles in the Nafion thin film, which essentially eliminates the aggregation problem associated with the suspended Degussa and with other suspension-based configurations of photocatalysts.[14–16]

The optical transparency of the TiO_2-loaded Nafion thin film also makes it possible to more effectively utilize the incident light and maximize the nanoparticle surface area for the heterogeneous photoreduction in the parallel configuration of multiple films (Fig. 2). Significantly higher photoconversion of CO_2 was achieved with the use of multiple TiO_2-loaded Nafion thin films (Table 1). For example, the reaction with 4 films yielded 3.6-times more formic acid, twice as much methanol, and 50% more acetic acid in comparison with those with a single film under the same experimental conditions (Table 1). Shown in Fig. 3 is the photoconverted amount of CO_2 plotted against the number of films used in the photoirradiation. Obviously, the "stacking" of multiple

Table 1 Photoreduction of CO_2 with multiple TiO_2-loaded Nafion films

No of Films	HCOOH (μg)	CH_3OH (μg)	CH_3CO_2H (μg)
1	20	30	3.5
2	39	34	4.0
3	45	40	5.2
4	73	62	5.7

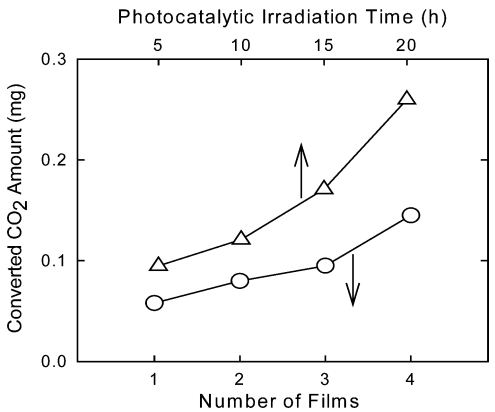

Fig. 3 Photoconverted CO_2 as functions of the number of TiO_2-loaded Nafion films (○) and the photoirradiation time with 3 films (Δ).

TiO_2-loaded Nafion thin films is an effective way to apply the homogeneously dispersed nanoscale catalysts for more efficient photoreduction of CO_2.

The photocatalytic conversion of CO_2 was further improved by increasing the photoirradiation time. The yields of formic acid, methanol and acetic acid are all higher with longer photoirradiation. As shown in Fig. 3 for the use of 3 TiO_2-loaded Nafion thin films in a parallel configuration, the amount of photoconverted CO_2 increased monotonically with the photoirradiation time under otherwise the same experimental conditions. Contrary to what was observed in the photoreduction with suspended nanoscale catalysts,[14] there was no deterioration in the photocatalytic activity for these TiO_2 nanoparticles embedded in Nafion thin films at longer irradiation times. For the use of 4 films, the photoirradiation for 20 h resulted in a total conversion of 0.3 mg CO_2.

The results of the photocatalytic reduction are reproducible, and most interestingly the TiO_2-loaded Nafion film as photocatalyst is stable with the photoirradiation and reusable in the repeated experiments. For example, a piece of the TiO_2-loaded Nafion film used in one photoreduction experiment was washed thoroughly with deionized water and reused in the next photoreduction experiment under the same experimental conditions, and then this process was repeated again. No meaningful difference (within 3%) in reaction products and yields was observed in the three repeated photoreduction experiments.

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