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Short communication

Heterogeneous photocatalysis in titania-stabilized perfluorocarbon-in-water emulsions: Urea photosynthesis and chloroform photodegradation

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Abstract

The photocatalytic behaviour of perfluorodecalin-in-water emulsions stabilized by bare and Cu-modified nanodispersed TiO_2 has been studied using, as the model reactions, the simultaneous photoreduction of CO_2 and NO_3^- to urea and the oxidative photodegradation of $CHCl_3$. It has been shown that the employment of emulsified perfluorocarbons, capable of dissolving large quantities of gaseous substrates, as the carriers of TiO_2 photocatalyst permits one to improve the selectivity of photoreduction and to enhance the urea photoproduction rate (by two to seven times depending on the nitrate concentration) due to high acting concentration of CO_2 involved into light-induced reaction at the interface and possibility of stabilizing the reaction intermediates in the case of two-phase reaction medium. It has also been demonstrated that the ability of perfluorocarbons to dissolve both oxygen and organics leads to the enhancement of $CHCl_3$ photodegradation in the TiO_2-stabilized perfluorocarbon-in-water emulsion and allows for combining extraction with photocatalytic decontamination.

Keywords: Photocatalysis; Titania; Emulsion; Perfluorocarbon

1. Introduction

The ability of perfluorocarbons to physically dissolve significant quantities of oxygen and carbon dioxide [1–3] opens fresh opportunities for elaboration of novel photocatalytic systems in which high concentrations of CO_2 or O_2 involved in the light-driven reactions are attainable that favour their photoreduction. Being hydrophobic and therefore not miscible with water, perfluorocarbons can be readily emulsified in aqueous medium in the presence of surface-active stabilizing compounds [4]. As the emulsifying agent, the particles of finely divided solids which are partially wettable by both nonaqueous phase and water can also be used, the stabilizing of the resulted water continuous emulsion being the most pronounced if the contact angle of dispersed solid (as measured across the aqueous phase) is somewhat smaller than 90° [5,6]. One can expect that colloidal particles of titania are highly active and durable photocatalyst [7–10], which exhibits relatively low hydrophilicity (in the case of anatase, the water contact angle is 72° [7]) and can act as stabilizer of perfluorocarbon-in-water emulsions by residing at the interface. In such emulsions, the particles of titania appear at the same time in contact with an aqueous phase behaving as a sink for photoholes and nonaqueous phase with high concentration of oxygen or carbon dioxide that provides favourable conditions for their photocatalytic reduction; on the other hand, the possibility of concentrating of different organic compounds (substrates, intermediates, products) in the perfluorocarbon phase can also enhance the light-induced reactions occurring at the surface of emulsion drops where titania particles are held. In this study, the photocatalytic properties of titania-stabilized perfluorocarbon-in-water emulsions

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were investigated using, as the model reactions, the photoreduction of CO_2 in the presence of NO_3^- to urea and the oxidative photodegradation of chloroform; in the former case, isopropanol served as the hole scavenger, whereas the molecular oxygen played the role of sacrificial electron acceptor in a reduction half-reaction in the latter case.

2. Experimental

For the emulsion preparation, we have used perfluorodecalin (PFD) capable of dissolving large quantities of oxygen and carbon dioxide (the solubility of O_2 and CO_2 amounts 45 and 134 ml/100 ml, respectively). A highly dispersed commercial TiO_2 photocatalyst Hombikat UV100 from Shachtleben Chemie (100% pure anatase with a primary particle size of 5 nm) has been used as a stabilizing agent. Titania-stabilized PFD-in-water (PFD:TiO_2) emulsion was prepared by adding 6 ml of PFD (Aldrich) to 10 ml of aqueous suspension of TiO_2 (2 g/l) containing $NaNO_3$ and isopropanol (in the case of urea photosynthesis experiments) or chloroform (in the case of photodegradation experiments), followed by sonication of the obtained mixture for 10 s in the ice-cooled vessel. An average diameter of the emulsion drops in freshly prepared PFD:TiO_2 emulsion was ca. 7 μm.

The modification of titania photocatalyst with copper was performed in two steps: at first, a small amount (ca. 5×10^{-6} wt.%) of silver was deposited via photocatalytic reduction; thereupon, copper was deposited at 80 °C from slightly modified standard electroless plating bath [11] of the following composition: $CuSO_4$ (20 g/l) + EDTA (30 g/l) + NaOH (15 g/l) + KCNS (0.02 g/l) + HCHO (20 ml/l). The resultant copper loading was determined by atomic absorption analysis.

The photocatalytic measurements were performed in the quartz cell under continuous magnetic stirring. As a light source, a high-pressure 120 W Hg lamp equipped with IR water filter was used. The light of wavelengths shorter than 300 nm was cut off using a glass filter. The radiant flux entering the photoreactor was 20 mW/cm^2 in the wavelength region between 300 and 380 nm which can be absorbed by TiO_2. The incident light was completely absorbed both in the photocatalyst-stabilized emulsion and in the suspension of photocatalyst. For urea photoproduction measurements, CO_2 was bubbled in the reaction solution (PFD:TiO_2 emulsion or TiO_2 suspension containing the same amount of the photocatalyst) for 1 h before illumination and the CO_2 bubbling was continued throughout the photocatalytic experiment. The concentration of photoproduced urea in the aquatic phase was measured colorimetrically with biacetyl oxime thiosemicarbazone in the presence of Fe^{3+} [12]. The formate concentration was determined photometrically using the procedure described by Higgs and Charles [13]. Photodegradation of $CHCl_3$ was investigated in the aerated PFD:TiO_2 emulsion and TiO_2 suspension under continuous air bubbling. For preparation of emulsion and suspension, the saturated aqueous solution of chloroform (62 mM) was used, with pH adjusted to 4.5 to prevent the photo-induced hydrolysis of chloroform [14]. The concentration of the released chloride ions was determined with the use of ion-selective electrode.

3. Results and discussion

3.1. Characterization and stability of emulsion-based photocatalytic system

In the absence of the stabilizing agents, the PFD-in-water emulsion exhibits very poor stability and complete coalescence occurs within several minutes. By contrast, the emulsion prepared in the presence of colloidal titania demonstrates much higher stability even at high concentrations (of up to 1 M) of nitrate and isopropanol. The effect of dispersed titania on the stability of PFD-in-water emulsion to coalescence was assessed by following the upward movement of the clear oil–emulsion boundary. The degradation of PFD:TiO_2 emulsion on standing occurred monotonically, without noticeable induced period, and no presence of emulsion fractions which differ as to their stability was observed. Coalescence was completed within 2 h and to ensure the emulsion stability all photocatalytic experiments were performed under continuous stirring. For PFD:TiO_2 emulsion exposed to UV light, the rate of coalescence decreased by 30% as compared to the unexposed one, i.e. the light-induced processes occurring at the surface of titania particles operating as the photocatalyst do not impair their ability to stabilize the emulsion.

The blank photocatalytic experiment with air-saturated PFD:TiO_2 emulsion containing no nitrate and isopropanol in aqueous phase evidenced that PFD exhibits high stability against titania-assisted photolysis: after 7-h illumination, the PFD photodegradation degree estimated from the data on the concentration of the released fluoride ions, measured with the use of ion-selective electrode (LaF_3), does not exceed 0.007%.

3.2. Photo-induced reduction of CO_2 with NO_3^- to urea in PFD:TiO_2 emulsion

It has been shown by Yoneyama and co-workers [15] that nanocrystalline titania-catalyzed simultaneous photoreduction of CO_2 and nitrate ions yields urea and formate as the major reduction products. Fig. 1, depicting the time course of the production of urea obtained by irradiation of CO_2-saturated PFD:TiO_2 emulsion and TiO_2 suspension in the presence of nitrate and isopropanol as the hole scavenging compound, evidences that in the case of emulsion the efficiency of urea photoproduction dramatically increases even at low concentrations of nitrate (a seven-fold build-up of initial rate of urea photoproduction, from 0.03 mM/h for suspension to 0.21 mM/h for emulsion, is observed at $[NO_3^-] = 0.06$ M). By contrast, the relative yield of formate exhibits some

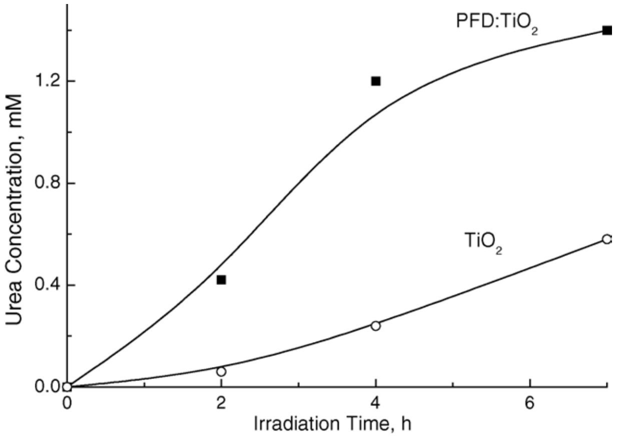

Fig. 1. Time profiles of urea photoproduction in CO_2-saturated titania-suspension and titania-stabilized perfluorodecalin-in-water emulsion. Aquatic phase initially contained 0.06 M $NaNO_3$ and 1 M isopropanol, pH 5.5.

decrease when going from suspension to emulsion; thus, at $[NO_3^-] = 0.06$ M the urea-to-formate photoproduction rate ratio amounts 2.4 for TiO_2 suspension and 2.6 for PFD:TiO_2 emulsion.

The rate of urea photoproduction increases with nitrate concentration for both TiO_2 suspension and PFD:TiO_2 emulsion and almost saturates at nitrate concentrations higher than 1 M (Fig. 2). In the concentrated nitrate solutions, the effect of emulsion medium on the urea generation efficiency is somewhat less pronounced (Fig. 3): at $[NO_3^-] = 1$ M the rate of urea photoproduction is 2.1 times higher for PFD:TiO_2 emulsion than for TiO_2 suspension. On the other hand, as can be seen from Fig. 3, at high nitrate concentrations the titania-stabilized PFD-in-water emulsion suppresses formate formation more effectively (at $[NO_3^-] = 1$ M the urea-to-formate photoproduction rate ratio amounts 3.9).

Modification of titania photocatalyst with copper, which is known to be a highly efficient catalyst towards CO_2 reduction in photocatalytic [16,17] and photo-electrochemical [18] systems, leads to further enhancement of urea photoproduction efficiency for both TiO_2 suspension and PFD:TiO_2 emulsion (Fig. 3), with the urea photoproduction rate reaching its maximum at copper loading of ca. 3 wt.%. Copper deposition not only contributes to the enhanced activity of the resulted photocatalyst but also increases dramatically the urea-to-formate photoproduction rate ratio, which amounts 10.9 for Cu-loaded titania. The employment of Cu-modified TiO_2 particles as the stabilizer of PFD-in-water emulsion leads to a ca. two-fold increase of initial rate of urea photoproduction as compared to suspension of Cu-loaded TiO_2 photocatalyst, i.e. the urea generation efficiency increases to the extent similar to that observed in the case of PFD-in-water emulsion stabilized with bare titania (Fig. 3). On the other hand, the formate photoproduction in the PFD-in-water emulsion stabilized with Cu-modified titania appears to be almost completely suppressed (the urea-to-formate photoproduction rate ratio is as great as 36.6).

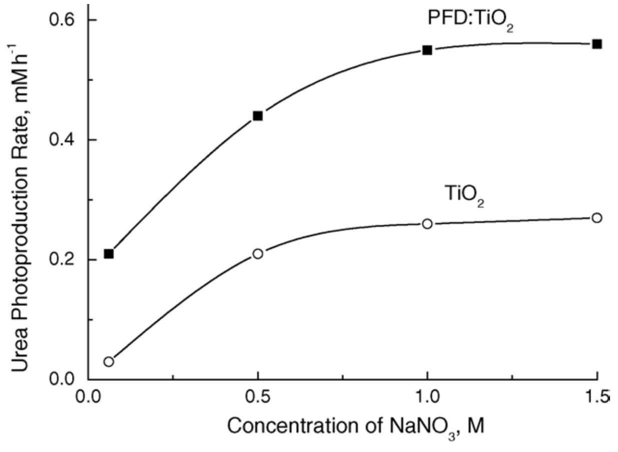

Fig. 2. Effect of the concentration of $NaNO_3$ on the initial rate of urea photoproduction in CO_2-saturated TiO_2 suspension and PFD:TiO_2 emulsion. Concentration of isopropanol is 1 M, pH 5.5.

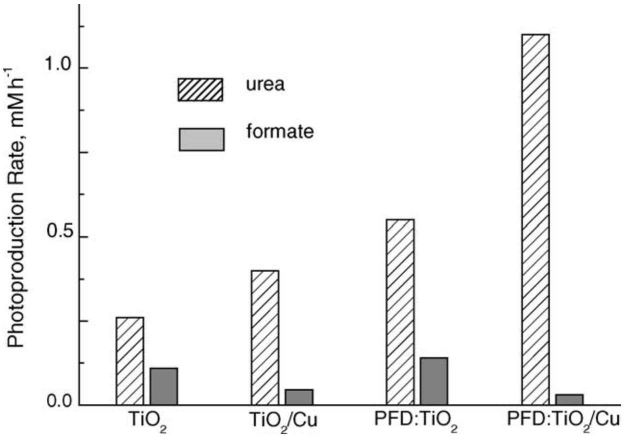

Fig. 3. Initial rate of urea and formate photoproduction in CO_2-saturated TiO_2 suspension, suspension of Cu-modified TiO_2, PFD-in-water emulsion stabilized with TiO_2, and PFD-in-water emulsion stabilized with Cu-modified TiO_2. Aquatic phase initially contained 1 M $NaNO_3$ and 1 M isopropanol, pH 5.5.

The difference in the photocatalytic behaviour of TiO_2 suspension and PFD:TiO_2 emulsion cannot be attributed to the difference in the efficiency of assimilation of incident photons (in both cases the photocatalytic experiments were performed under conditions of complete absorption of incident light flux); likewise, the photolysis of perfluorocarbon is unlikely to affect the urea photogeneration since the efficiency of the latter process, according to the blank experiment, is higher than that of the former one by at least three orders of magnitude. The increase of efficiency and selectivity of urea photoproduction observed for titania-stabilized perfluorocarbon-in-water emulsion can be attributed to high concentration of CO_2 in the oleic phase contacting with photocatalyst and favourable conditions for stabilizing of the reaction intermediates (CO-like and ammonia-like precursors capable of forming C–N bonds yielding urea [19]) in the case of two-phase reaction medium.

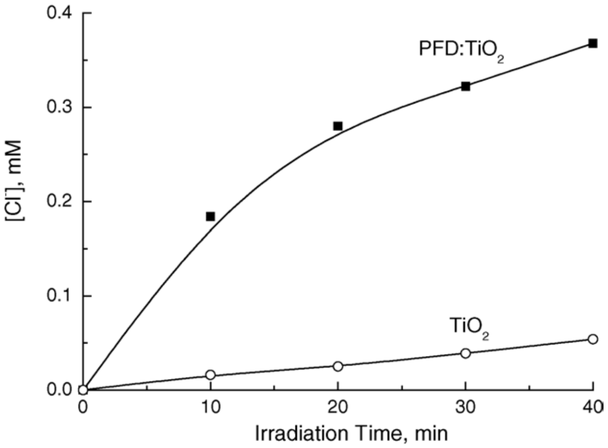

Fig. 4. Photocatalytic degradation of chloroform in aerated TiO_2 suspension and PFD:TiO_2 emulsion at pH 4.5 shown in terms of the release of Cl^- as function of time.

3.3. Photolysis of chloroform in PFD:TiO_2 emulsion

The characteristic feature of titania-stabilized PFD-in-water emulsion as the reaction medium is that $CHCl_3$ tends to concentrate in the perfluorocarbon phase. It is seen from Fig. 4 that the photocatalytic destruction of chloroform in the PFD:TiO_2 emulsion occurs much more efficiently as compared to TiO_2 suspension; in these experiments, the concentration of chloride produced as the result of TiO_2-catalyzed photodehalogenation (which accompanies the photodegradation of $CHCl_3$ [20]) was measured to trace the chloroform removal. Taking into account that the rate-determining step of chloroform photodegradation at TiO_2 is the reaction of surface-bound photoproduced hydroxyl radicals with $CHCl_3$ [21] one can attribute the enhanced efficiency of chloroform oxidation in the case of PFD:TiO_2 emulsion to the ability of perfluorocarbons to dissolve both molecular oxygen and organics that results in higher acting concentration of organic substrate and higher efficiency of $^{\bullet}OH$ production occurring under conditions favourable for capturing of photo-electrons from TiO_2 particles residing at the surface of emulsion drops. On the other hand, the running of catalytic photolysis of chloroform at high oxygen concentrations which are readily attainable in the case of PFD:TiO_2 emulsion additionally facilitate the destruction of organic substrate since the most efficient pathway of TiO_2-catalyzed chloroform photodegradation involves reaction of photoproduced trichloromethyl radicals with molecular oxygen [14].

4. Conclusions

This study shows that perfluorocarbon-in-water emulsions stabilized with titania particles can be used to intensify different photocatalytic processes by enhancing the reactions of TiO_2-catalyzed photo-induced reduction of CO_2 or O_2 which proceed, in the case of emulsion, at high concentrations of the dissolved gaseous substrates normally attainable only at very high pressures. This two-phase environment not only provides favourable conditions for colloidal titania to operate as a photocatalyst but also opens the possibility of combining photocatalytic decontamination with extraction of organic substrate from aqueous medium and facilitate separation of fine particles of semiconductor photocatalyst from the treated solution.

Acknowledgements

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