

Selective Photoreduction of Carbon Dioxide to Methanol on Titanium Dioxide Photocatalysts in Propylene Carbonate Solution

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Methanol is selectively photosynthesised from carbon dioxide using TiO₂ photocatalysts in propylene carbonate containing propan-2-ol as a hole scavenger.

Photoinduced reduction of carbon dioxide has been fairly intensively investigated using semiconductor particles suspended in solutions as photocatalysts.^{1–9} However, the major product obtained so far is formate which is a two-electron reduction product; no selective production of methanol which requires six electrons has been reported yet. There seems to be no established technique in electrochemistry fields to obtain methanol, though electrochemical synthesis of methanol from carbon dioxide is interesting as a means for regeneration of carbon dioxide to a fuel. We have succeeded in selectively reducing carbon dioxide to methanol using quantized TiO₂ and commercially available P-25 TiO₂ as photocatalysts in propylene carbonate solutions.

The quantized TiO₂ photocatalyst (67 mmol dm⁻³) was prepared by adding titanium tetraisopropoxide dropwise to a propan-2-ol solution containing 0.8 mmol dm⁻³ HCl, 0.6 mol dm⁻³ H₂O and 0.5 mass% poly(vinylpyrrolidone) (PVPD) under vigorous agitation. The resulting solution was further agitated for 2 h, resulting in a size quantized TiO₂ (Q-TiO₂) sol. The Q-TiO₂ was immobilized in a PVPD film using electrophoretic deposition, the details of which will be published elsewhere. The Q-TiO₂ sol (20 cm³) was put into a Pyrex cell equipped with a 2.5 × 1 cm Pt mesh (80 mesh) and a Pt plate electrode of 1 cm². The electrophoresis of the TiO₂ sol under application of 30 V cm⁻¹ resulted in a Q-TiO₂-PVPD film on the Pt mesh cathode. The amount of Q-TiO₂ in the film prepared by electrophoresis for 1 h was determined to be 7 × 10⁻⁶ mol and accounted for 63 mass% of the film, as determined by absorption analysis using disodium catechol-3,5-disulfonate (Tiron) as a complex agent for a solution prepared by dissolving the immobilized TiO₂ in boiled mixture of ammonium sulfate and sulfuric acid. It was found that the deposition occurred in proportion to the electrophoresis time. The Q-TiO₂ particles were mostly anatase and ranged from 2 to 4 nm, as determined by TEM. Reflecting the small size of the particles size quantization effects were operative and the absorption threshold was 350 nm. For comparative purposes, P-25 TiO₂-PVPD films were prepared by applying the same electrophoresis conditions as those mentioned above to 67 mmol dm⁻³ P-25 TiO₂ instead of the Q-TiO₂.

The photoreduction experiments were carried out using a quartz cell (1 × 1 × 5 cm) the top of which was capped by an air-tight glass cap with a ground joint. CO₂-saturated propylene carbonate (3 cm³) containing 1 mol dm⁻³ propan-2-ol as a hole scavenger was used as a reaction solution and the photocatalyst film was hung in the cell through a septum fitted in the glass cap. The experiments were carried out using the following four settings of the photocatalysts: (a) TiO₂ was suspended in the solution without immobilizing in the PVPD films; (b) the photocatalyst film was completely immersed in the solution; (c) lower one-half of the photocatalyst film was immersed in the

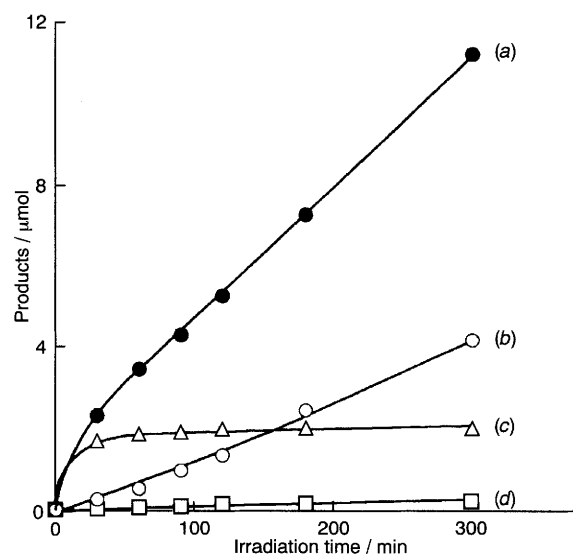


Fig. 1 Time course of (a) acetone, (b) methanol, (c) Ti³⁺ and (d) H₂ productions obtained by irradiation with a 500 W high pressure mercury arc lamp of Q-TiO₂-PVPD film, one face of which was in contact with CO₂ gas and the other face with 3 cm³ of CO₂-saturated propylene carbonate containing 1 mol dm⁻³ propan-2-ol as a hole scavenger

Table 1 Products obtained by photoinduced reduction experiments of CO₂ using two kinds of TiO₂ photocatalysts with four different settings in a cell containing propylene carbonate^a

Catalyst	Setting ^b	Amount/μmol					
		Acetone	Ti ³⁺	Methanol	H ₂	Holes ^c	Electrons ^c
P-25 TiO ₂ ^d	A	0.55	— ^e	0.05	0.06	1.10	0.42
Q-TiO ₂	A	2.86	0.74	0.87	0.07	5.72	6.10
P-25 film	B	1.15	— ^e	0.12	0.05	2.30	0.82
Q-TiO ₂ film	B	5.50	2.11	1.30	0.12	11.0	10.2
Q-TiO ₂ film	C	9.40	2.82	2.82	0.66	18.8	21.0
P-25 TiO ₂	D	2.01	— ^e	0.40	0.10	4.02	2.60
Q-TiO ₂ film	D	11.28	1.97	4.22	0.24	22.6	27.8

^a 1 mol dm⁻³ Propan-2-ol was employed as a hole scavenger. Irradiation time: 300 min. ^b A: Dispersed in solution; B: Completely immersed in solution; C: Half immersed in solution; D: One face immersed. ^c The amount was evaluated based on the oxidation product and the reduction products. ^d Commercially available Degussa P-25 TiO₂. ^e Not determined due to light scattering.

solution; and (d) one face of the photocatalyst film was in contact with the solution and the other face with CO₂ gas. The last setting was made by laying the cell after mounting the photocatalyst film in the cell. Irradiation of the cell was carried out using a 500 W high pressure mercury arc lamp as a light source, wavelengths shorter than 300 nm were cut off by a coloured glass filter. The irradiation intensity was 0.36 W cm⁻².

Fig. 1 shows the progress with time of the production of photoinduced reaction products for the setting with one face of the Q-TiO₂-PVPD film in contact with the solution and the other with CO₂ gas. Acetone was produced as the oxidation product and the reduction products were Ti³⁺ in the film and methanol in the liquid phase plus a very small amount of hydrogen in the gas phase. Similar time courses for the production of these products were obtained for all cases investigated in the present study, though the amounts of products were different depending on the kind of photocatalysts used and the photocatalyst setting. Table 1 summarizes the results obtained for the two kinds of TiO₂ particles in four different settings in the reaction cell. On comparing the results obtained with the two kinds of TiO₂ but the same photocatalyst setting, it is noticed that Q-TiO₂ had remarkably higher activities than P-25 TiO₂. The apparent activities were also influenced by the photocatalyst setting. The highest activity was observed with the Q-TiO₂-PVPD photocatalyst in contact with both the solution and CO₂ gas. If the amount of electrons and holes involved in the photoinduced reaction is evaluated from the amount of all the products obtained, fairly good agreements are seen, suggesting that the major reaction products are those given in Table 1. Interestingly, only methanol was obtained as the reduction product of CO₂ for all cases. No other reduction product of CO₂, such as formate or oxalate, was detected. Labelling experiments confirmed that methanol was produced from carbon dioxide. MS of the products showed that when ¹³CO₂ was used, a signal appeared at *m/z* = 32, while *m/z* = 31 was observed when ¹²CO₂ was used. These signals are

attributed to one hydrogen-abstracted species of methanol (CH₂=OH⁺) which is the major signal in the MS of methanol. As reported previously,⁹ quantized TiO₂ prepared in SiO₂ matrices does not show activities for selective reduction of CO₂ to methanol in aqueous solutions. Based on that finding, it is suggested that the solvent used plays an important role in the selective reduction of CO₂ to methanol. Investigations on the role of the solution as well as the photocatalysts in the selective production of methanol are under way.

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