A novel preparation of iron-doped TiO_2 nanoparticles with enhanced photocatalytic activity

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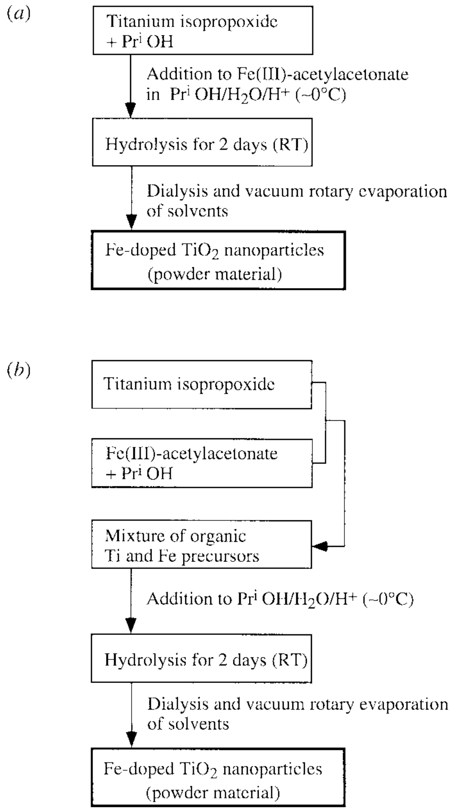
Fe^{III}-doped TiO_2 nanoparticles prepared from organic precursors (⩽2.5 atom% Fe) exhibit strongly enhanced photocatalytic activity as demonstrated by the quantum yields measured for the formation of formaldehyde by photocatalyzed oxidation of methanol in aqueous solution (Φ up to *ca.* 15%).

In recent years, considerable effort has been devoted to the study of Fe^{III}-doped titanium dioxide in order to improve the photocatalytic efficiency of TiO_2.[1–4] The generally accepted mechanism to explain this improved photocatalytic performance is the formation of shallow charge trapping sites within the TiO_2 matrix as well as on the particles' surface through the replacement of Ti^{IV} by Fe^{III} ions.[3] Thus, the undesirable recombination of electron/hole pairs generated upon ultra-bandgap irradiation can be partially prevented. In most cases such photocatalysts have been prepared by hydrolysis of a Ti-precursor in the presence of a Fe^{III}-containing aqueous solution (Scheme 1*a*). Since the reaction system is fed with the Ti and Fe precursors present as different solution phases, the Fe/Ti ratio is unavoidably changed on addition of the Ti precursor to the solution of the Fe precursor, particularly so in the initial stage of particle growth. There is little doubt that this effect influences the local distribution of iron in the particles formed and hence the photocatalytic efficiency. In view of this we have developed a novel preparation in which organic Ti and Fe precursors were employed and mixed prior to hydrolysis (Scheme 1*b*). To the best of our knowledge, such a preparation has not been reported previously.



Scheme 1 Preparation of iron-doped TiO_2 nanoparticles. Previous (*a*) and present novel method (*b*).

As seen from Scheme 1*b*, the fraction of iron in the mixture and, hence, the nominal iron content of the particles can be varied as desired. As-prepared samples come as yellowish powders which can be resuspended in water, methanol or in a mixture of both solvents to obtain a colloidal suspension transparent in the visible region.

Fig. 1 shows the absorbance spectra of as-prepared samples of neat TiO_2 and of TiO_2 doped with different amounts of Fe^{III}. From Fig. 1 and by use of the procedure given by Kormann *et al.*[5] the bandgap energy, E_g, of the colloidal particles was obtained as 3.32, 3.25, 3.22 and 3.07 eV for zero, 0.25, 0.5 and 2.5 atom% iron, respectively. Clearly, E_g decreases with increasing iron content. Compared with bulk anatase TiO_2 (E_g = 3.23 eV[6]) the bandgap of the undoped TiO_2 particles (3.32 eV) is larger by *ca.* 0.1 eV. This corresponds to a mean spherical particle diameter of *ca.* 2.7 nm when the Brus equation[7] is applied.

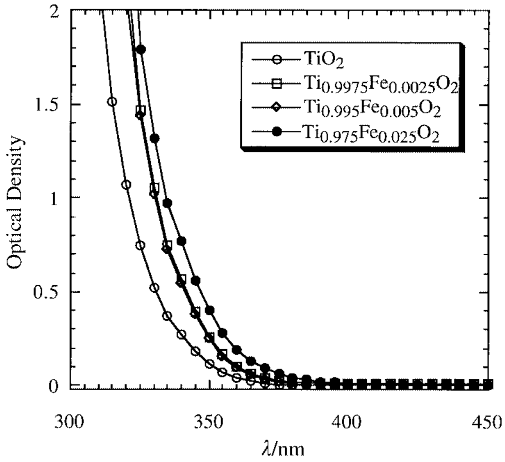


Fig. 1 Absorbance spectra of TiO_2 and iron-doped TiO_2 nanoparticles in colloidal aqueous solution (as-prepared according to Scheme 1*b*, pH ≈ 3, 1 cm cell, virtually no light scattering).

From the preparation procedures given in Scheme 1 it is expected that the distribution of iron in the TiO_2 matrix of the particles prepared by method (1*b*) is more uniform than by method (1*a*). Uniformity of doping was expected to result in enhanced photocatalytic activity. This was indeed verified by determination of the quantum yield of formaldehyde produced by photocatalytic oxidation of methanol in aerated aqueous solution[9] in the presence of the TiO_2 colloidal particles doped

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with iron by different methods. The photocatalytic reaction was carried out in a cylindrical cell under cw-illumination by filtered light from a xenon lamp (WG 320 + UV black filters, 60% transmission at 340 nm). The photon flux of this illumination set-up was determined by use of the Aberchrome-540 chemical actinometer.[8] The production rate of HCHO was measured by HPLC of samples taken at different time intervals[9] (total photolysis time *ca.* 30 min).

TiO_2-photocatalyzed oxidation of methanol proceeds as follows:[1,9,13]

$$\mathrm{TiO_2} + h\nu(\geq E_g) \xrightarrow{(\mathrm{fs})^1} \mathrm{h^+_{VB}} + \mathrm{e^-_{CB}} \tag{1}$$

$$\mathrm{h^+_{VB}} + \equiv \mathrm{Ti^{IV}OH} \xrightarrow{(\mathrm{fast})^1} \equiv \mathrm{Ti^{IV}OH^{\bullet +}} / \mathrm{OH^{\bullet}} \tag{2}$$

$$\mathrm{e^-_{CB}} + \equiv \mathrm{Ti^{IV}OH} \xrightarrow{(<100\ \mathrm{ps})^1} \equiv \mathrm{Ti^{III}OH} / \mathrm{e^-_{tr}} \tag{3}$$

$$\mathrm{e^-_{tr}} + \mathrm{O_2} \xrightarrow{k_4} \mathrm{O_2}^{\bullet -} \tag{4}$$

$$\mathrm{OH^{\bullet}} + \mathrm{CH_3OH} \xrightarrow{k_5} {}^{\bullet}\mathrm{CH_2OH} + \mathrm{H_2O} \tag{5}$$

$${}^{\bullet}\mathrm{CH_2OH} + \mathrm{O_2} \xrightarrow{k_6} \mathrm{HCHO} + \mathrm{HO_2}^{\bullet} \tag{6}$$

$${}^{\bullet}\mathrm{CH_2OH} + \equiv \mathrm{Ti^{IV}OH} \xrightarrow{(\mathrm{fast})^{13}} \mathrm{HCHO} + \equiv \mathrm{Ti^{III}OH} / \mathrm{e^-_{tr}} + \mathrm{H^+} \tag{7}$$

where $k_4 = 7.6 \times 10^7$ M^{-1} s^{-1} for trapped electrons,[10] $k_5 = 5 \times 10^8$ M^{-1} s^{-1}[11] and $k_6 \approx 5 \times 10^9$ M^{-1} s^{-1}.[12] As detailed by Sun and Bolton[9] the quantum yield of HCHO is proportional to that of $OH^{\bullet}$ which plays a vital role in TiO_2 based photocatalytic reactions.[1,15]

Table 1 shows the values of Φ_{HCHO} determined for the TiO_2 and iron-doped TiO_2 colloidal photocatalysts prepared here by different methods. A 15 min pre-illumination of the aqueous colloidal particles was applied in the absence of CH_3OH for removal of surface flaws. Note that without pre-photolysis the concentration of HCHO was not proportional to the photolysis time but rather showed an induction-type behavior characteristic for the oxidation of residual organic material originating from the catalyst preparation. No HCHO was formed in the dark or during illumination in the absence of methanol evincing that the process was truly photocatalytic. As seen from Table 1, iron-dopant concentrations of up to 0.5 atom% increase Φ_{HCHO} dramatically. Further, Φ_{HCHO} is strongly affected by the method of photocatalyst preparation in some cases. Comparison of Φ_{HCHO} demonstrates that the novel preparation, Scheme 1*b*, is superior to that of Scheme 1*a* for the optimum dopant concentration of 0.5 atom% iron, where Φ_{HCHO} exhibits a *ca.* sixfold increase over the quantum yield measured in the presence of 2.7 nm undoped TiO_2 particles. The optimum iron-dopant concentration depends on the method of catalyst preparation (0.5 atom% for methods 1*a* and 1*b*, 0.25 atom% for the preparation from $TiCl_4$, similar to ref. 2).

Table 1 Quantum yields of formaldehyde formation by the photocatalytic oxidation of methanol in the presence of TiO_2 and iron-doped TiO_2 colloidal nanoparticles[a]

Fe/atom%	Φ_{HCHO}[b]/%	Precursor(s)	Photocatalyst preparation
0	2.3	$TiCl_4$	ref. 2
	2.8	$TiPr^iO$[c]	Scheme 1*a*
0.25	12.0	$TiCl_4 + FeCl_3$	ref. 2
	12.0	$TiPr^iO$[c] + Fe-acac[d]	Scheme 1*a*
	12.5	$TiPr^iO$ + Fe-acac	Scheme 1*b*[e]
0.50	7.2	$TiCl_4 + FeCl_3$	ref. 2
	12.7	$TiPr^iO$ + Fe-acac	Scheme 1*a*
	15.3	$TiPr^iO$ + Fe-acac	Scheme 1*b*[e]
2.50	5.2	$TiCl_4 + FeCl_3$	ref. 2
	9.2	$TiPr^iO$ + Fe-acac	Scheme 1*a*
	9.5	$TiPr^iO$ + Fe-acac	Scheme 1*b*[e]

[a] 100 mM methanol, O_2-saturated aqueous solution at pH ≈ 3, catalyst loading 0.5 g L^{-1}, reaction volume 23 mL, $I_o = 1.43 \times 10^{-6}$ Einstein L^{-1} s^{-1}, room temperature. See text for further details. [b] ±0.2. [c] Titanium tetraisopropoxide. [d] Fe^{III}-acetylacetonate. [e] Present method.

In conclusion, it has been shown that the novel preparation, Scheme 1*b*, of iron-doped TiO_2 nanoparticles yields a highly active photocatalyst for the oxidation of methanol in aqueous solution. This is tentatively attributed to conditions of particle growth more favorable than with method 1*a*. Further work on photocatalytic properties of related as-prepared materials, including structure characterization and studies by time-resolved techniques,[10,14] is under way.

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Notes and references

1 M. R. Hoffmann, S. T. Martin, W. Choi and D. Bahnemann, *Chem. Rev.*, 1995, **95**, 69.
2 D. Bockelmann, M. Lindner and D. Bahnemann, in *Fine Particles Science and Technology*, ed. E. Pelizzetti, Kluwer Academic Publishers, The Netherlands, 1996, p. 675.
3 M. I. Litter and J. A. Navio, *J. Photochem. Photobiol. A: Chem.*, 1996, **98**, 171.
4 R. I. Bickley, J. S. Lees, R. J. D. Tilley, L. Palmisano and M. Schiavello, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 377.
5 C. Kormann, D. W. Bahnemann and M. R. Hoffmann, *J. Phys. Chem.*, 1988, **92**, 5196.
6 J. B. Goodenough and A. Hamnett, in *Landolt-Börnstein*, New Series, Group III, Vol. 17g, ed. O. Madelung, Springer Verlag, Berlin, Heidelberg, New York, Tokyo, 1984, p. 147.
7 L. E. Brus, *J. Phys. Chem.*, 1986, **90**, 2555.
8 H. G. Heller and J. R. Langan, *EPA Newsletter*, 1981, 71.
9 L. Sun and J. R. Bolton, *J. Phys. Chem.*, 1996, **100**, 4127.
10 D. W. Bahnemann, M. Hilgendorff and R. Memming, *J. Phys. Chem. B*, 1997, **101**, 4265.
11 G. E. Adams, J. W. Boag and B. D. Michael, *Trans. Faraday Soc.*, 1965, **61**, 1417.
12 G. E. Adams and R. L. Willson, *Trans. Faraday Soc.*, 1969, **65**, 2981.
13 R. Memming, *Top. Curr. Chem.*, 1994, **169**, 106.
14 K. Stopper and J. K. Dohrmann, *Z. Phys. Chem.*, 2000, **214**, 555.
15 P. A. Christensen, J. Eameaim and A. Hamnett, *Phys. Chem. Chem. Phys.*, 1999, **1**, 5315.