# Production of quantum-sized particles of $TiO_2$ in photohydrolysis of $Ti^{3+}$ ion in aqueous medium

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UV irradiation of an aqueous solution of  $Ti^{3+}$  ion generates the  $Ti^{4+}$  ion and hydrogen; the latter spontaneously hydrolyes to  $TiO_2$  giving ultra-fine colloidal particles which display size-quantization effects. Mechanisms that stabilize photogenerated  $TiO_2$  in the ultra-fine form are discussed.

### 1. Introduction

Over the past decade and half, a large number of reports have appeared on photocatalytic properties of semiconductor particles. More recently, attention has shifted to preparation and study of the physical properties of ultra-fine or quantum-size (Q) semiconductor particles [1-7]. Semiconductor Q-particles possess novel properties such as fluorescence. band blue-shifts, photoemission and non-linear optical effects [1]. There is also evidence that ultra-fine semiconductor particles have enhanced photocatalytic activity [2] as a result of (1) large effective surface area, (2) more efficient charge separation and transfer to the solution and (3) change in the band gap and band positions. The best characterized and easily prepared Q-semiconductor are chalcogenides (e.g. CdS, PbS, CdSe) [1-7]. Although zinc oxide Q-particles [8] can be readily made, the preparation of most oxide semiconductors in the Q-form is difficult. In the case of TiO2, standard techniques generally yield macrocrystallites, unless extreme precautions are taken [9]. We have found that Q-particles of  $TiO_2$  can be produced by photohydrolysis of  $Ti^{3+}$ ion in the aqueous medium. The UV irradiation of an aqueous solution of  $Ti^{3+}$  (i.e.  $TiCl_3$  in dilute HCl) generates hydrogen and Ti<sup>4+</sup> ion, the latter 'instantaneously' hydrolyses into  $TiO_2$ , producing a colloidal solution that shows quantum-size effects.

#### 2. Experimental

TiCl<sub>3</sub> solution was prepared by heating titanium metal in concentrated HCl. The solution was diluted to  $[Ti^{3+}]$  of 0.01 M and the pH was adjusted to  $\approx 1.6$ with HCl. In all experiments, atmospheric oxygen contamination was avoided (Ti<sup>3+</sup> solutions absorb  $O_2$  from the atmosphere and hydrolyse into TiO<sub>2</sub>; at very low pH (<2), oxidation is negligible). Photolysis of the Ti<sup>3+</sup> solution (300 ml) was carried out in a 500 ml photochemical reactor (Applied Photophysics) with a medium-pressure 400 W Hg lamp housed in a double-walled, water-cooled (26°C) quartz cylinder. The solution was kept continuously purged with Ar (99.99%) at a rate of  $11 \text{ cm}^3 \text{ min}^{-1}$ . Hydrogen in the out-going gas was monitored volumetrically at atmospheric pressure by gas chromatography (Shimadzu GC-9AM, gas chromatograph, carrier gas Ar, molecular sieve 5A column, thermal conductivity detector). The development of  $TiO_2$  in the solution during photolysis was observed by absorption (Shimadzu UV-3000 spectrophotometer) and fluorescence (Shimadzu spectrofluorophotometer RF-500) spectroscopy.

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## 3. Results and discussion

It is well known that several transition-metal cations, when photolysed in aqueous medium, liberate hydrogen with an increase in the oxidation state by one unit [11-13]. The primary photochemical reaction being generation of a solvated electron or hydrogen free radical, the latter process is favoured at low pH [14]. Irradiation of a solution of  $Ti^{3+}$  leads to formation of  $Ti^{4+}$ , i.e.

$$2\mathrm{Ti}^{3+} + 2\mathrm{H}_2\mathrm{O} \xrightarrow{h\nu} 2\mathrm{Ti}^{4+} + 2\mathrm{OH}^- + \mathrm{H}_2. \tag{1}$$

However, Ti<sup>4+</sup> is highly unstable and undergoes almost instantaneous hydrolysis,

 $Ti^{4+} + 2H_2O \rightarrow TiO_2 + 4H^+$ , (2)

the net reaction being

$$Ti^{3+} + 2H_2O \xrightarrow{h\nu} TiO_2 + \frac{1}{2}H_2 + 3H^+$$
. (3)

Fig. 1 illustrates photogeneration of hydrogen from  $Ti^{3+}$  in aqueous HCl solution at different pH. The hydrogen generation rate is higher at lower pH. This can be understood because the rate-determining step is reaction (1), which is favoured at low pH. With



Fig. 1. Plot of rate of H<sub>2</sub> production  $(R_{H_2})$  versus time in photolysis of Ti<sup>3+</sup> solutions in HCl at different pH (number indicated near each curve).

the progress of reaction (3), the pH decreases, and consequently the hydrogen evolution rate  $(R_{H_2})$  initially increases with time. However, as  $R_{H2}$  also depends on [Ti<sup>3+</sup>], the curves of fig. 1 exhibit a maximum. Reaction (1) is initiated by charge-transfer excitation of the hydrated and/or chlorocomplexes of the  $Ti^{3+}$  ion [15] which is sensitive only to light of wavelengths  $\leq 300$  nm. On irradiation the solution develops an absorption edge characteristic of TiO<sub>2</sub> Q-particles. The absorption edge becomes only slightly red-shifted with the progress of the reaction. During photolysis, the absorption edge appeared at  $\approx$  350 nm (fig. 2a) in 2 h; after 5 h the position was shifted to  $\approx 352$  nm. Due to interference of the Ti<sup>3+</sup> absorption, exact location of the TiO<sub>2</sub> absorption edge was not possible at times earlier than  $\approx 2$  h. Undoubtedly, its position at earlier times would be lower by several nanometer. When the lamp is shut-off after 5 h of irradiation the red-shift of the absorption edge increased at a faster and easily detectable rate. Solution irradiated for 5 h remained transparent and visible opalescence was noticed only after 18 h. The same solution acquired absorption characteristics similar to polycrystalline anatase (absorption edge  $\approx$  378 nm) after nearly 75 h. The Q-particle effects were more vividly displayed in the fluorescence spectrum. Fluorescence in semiconductor particles originate from recombination of trapped carriers. Ti<sup>3+</sup> solutions shows no fluorescence; however, within minutes of irradiation, the aliquots drawn from the reactor show a fluorescence peaked at 360 nm. During 5 h of irradiation, the position of the fluorescence peak red-shifted very slightly (barely detectable) but became progressively more and more intense (fig. 2b). However, when irradiation was stopped, a marked increase in the wavelength (a saturation value of 375 nm was reached in  $\approx$  75 h) of the fluorescence peak was noted (fig. 2c). Both fluorescence and absorption measurements indicate that during irradiation, the rate of agglomeration of particles is suppressed. The explanation is that the irradiated particles are highly charged due to injection of one type of carriers into the solution. The mutual repulsion of highly charged particles prevents coagulation.

Photohydrolysis is favourable for generation of Qparticles for yet another reason. When two solutions are mixed to prepare a colloidal solution in a pre-



Fig. 2. (a) Absorption spectrum of  $Ti^{3+}$  solution initially irradiated for 5 h and left in dark for (1) 0 h, (2) 2 h, (3) 8 h, (4) absorption spectrum of TiO<sub>2</sub> (anatase) suspension in water. (b) Variation of fluorescence peak height with time during irradiation. Insert: Fluorescence spectrum after (a) 1 h, (b) 2 h of irradiation. (c) Red-shift of the fluorescence peak with time after irradiation.

cipitating reaction, even under carefully controlled conditions, the agglomerates that act as nuclei for coagulation are formed, because instantaneous mixing that avoids concentration gradients is impossible. In the light reaction, the precipitating product is formed at widely spaced points where the photons are absorbed. The shift absorption edge of Q-particles of TiO<sub>2</sub> made by the above method is  $\approx 28$  nm. Other methods of preparation have also given similar shifts [9,10]. Because of the higher effective masses of the carriers in high band gap materials, band shifts in the O-states are smaller. We have not succeeded in making an experimental assessment of the size of TiO<sub>2</sub> Q-particles made by our method. It is known that in the case of TiO<sub>2</sub>, the size-quantization effects are seen when the diameter is less than  $\approx 3 \text{ nm}$  [9,10].

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