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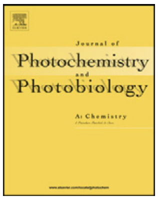

Short note

Reaction dynamics of the transfer of stored electrons on TiO_2 nanoparticles: A stopped flow study

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ABSTRACT

The dynamics of the transfer of electrons from TiO_2 nanoparticles to a variety of electron acceptors have been investigated employing a simple and facile stopped flow technique. Prior to the kinetic experiments nanosized TiO_2 particles are loaded with electrons by UV (A) photolysis in the presence of methanol as a hole scavenger. As a model for possible electron transfer reactions the reduction of dissolved O_2 and H_2O_2 by stored TiO_2 electrons has been successfully studied.

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1. Introduction

A fundamental understanding of the dynamics of the charge carrier transfer at TiO_2 nanoparticles is of crucial importance for the understanding and industrialization of the photocatalytic reactions as well as for the rational design of photocatalytic systems. During the last decades, much effort was devoted on the study of the kinetics and mechanistic details of the interfacial electron transfer processes at the TiO_2/water interface using the laser photolysis technique. Grätzel and Frank [1] dealt with the transfer of electron and hole from the conduction and valance band of ultrafine TiO_2 and CdS particles to reactants in solution. Bahnemann et al. [2] investigated the kinetics and mechanistic details of the processes occurring upon band gap irradiation in nanosized TiO_2 suspensions in the absence as well as in the presence of electron and hole scavengers. Recently Gao et al. [3] reported the kinetics of the reactions of excess electrons in TiO_2 produced by radiolysis employing steady state and pulse radiolysis techniques.

The present publication reports the results of an ongoing study concerning the kinetics and mechanism of a variety of reactions of the stored electrons in TiO_2 nanoparticles using the stopped flow technique. The basic concept of this work is rather simple; the electrons are generated on the TiO_2 nanoparticles by UV illumination in the presence of a hole scavenger, they remain stored on them in the absence of molecular oxygen and are subsequently used for the reduction of various oxidants such as O_2 and H_2O_2. The reduction kinetics have been studied following the decay of the transient absorbance of the stored electrons at 600 nm *vs.* time.

2. Experimental

Nanosized TiO_2 particles have been prepared following the recipe reported by Kormann et al. [4]. The XRD and TEM analysis evinces the formation of 100% anatase phase with 2–3 nm particle diameter. The resulting crystals were resuspended in pure water to obtain perfectly transparent colloidal solutions. The electrons were stored on the TiO_2 particles by illuminating a deaerated (argon purged) freshly prepared transparent colloidal solution of $3\,g\,l^{-1}$ (3.8×10^{-2} M) TiO_2 for 4 h in the presence of 0.02 M methanol. The illumination was performed using a high-pressure Xe-lamp (OSRAM HBO-500 W) placed inside a quartz jacket and equipped with a cooling tube. The employed UV (A) light intensity was $2.6 \times 10^{-3}\,J\,cm^{-2}\,s^{-1}$. Stopped flow experiments were performed using a SX.17MV-R Rapid Mixing Spectrophotometer (Applied Photophysics, United Kingdom) working in the UV–vis range (from 200 to 700 nm) with 0.2-cm optical path and 1 ms dead time. In a typical stopped flow experiment, the solution of nanosized TiO_2 particles loaded with electrons was carefully filled into one of the stopped flow syringes and an aqueous solution of the electron acceptor (O_2,

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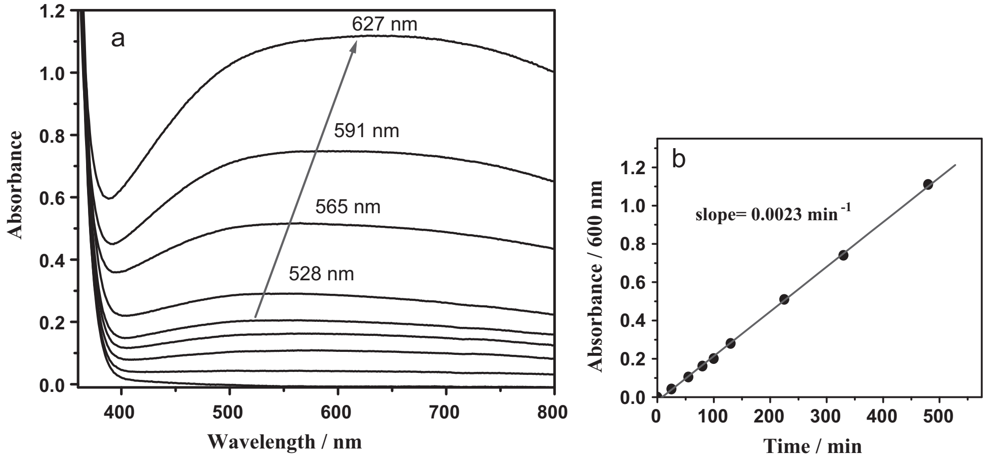

Fig. 1. (a) Build-up of the TiO_2 electron spectrum of 3.8×10^{-2} M deaerated TiO_2 suspension in 0.02 M methanol at pH 2.3 recorded following different periods of UV irradiation. (b) Change in absorbance at 600 nm as a function of the employed irradiation time.

H_2O_2) was filled into the other syringe. The solutions were injected into the stopped flow mixing chamber (1:1 v/v) and the resulting reactant mixture was subsequently forced into the optical cell where the change of the optical absorbance with time was measured. The kinetics of the electron transfer reactions were studied by following the decay of the absorbance of the TiO_2 electrons with time. All measurements were carried out at ambient temperature.

3. Results and discussion

The UV (A) photolysis of a system containing TiO_2 (3.8×10^{-2} M) and methanol in the absence of molecular oxygen results in the formation of a transparent blue colloidal suspension indicating the generation of the stored electrons in the TiO_2 particles. The blue coloration is characterized by a broad absorption band in the visible region (400–800 nm) with a maximum observed after 25 min of illumination at 523 nm, which is then slightly shifted to longer wavelengths with increasing irradiation time to finally reach 627 nm after 480 min of illumination. Fig. 1(a) shows the absorption spectra of the aqueous TiO_2 suspension observed after different UV irradiation periods. Fig. 1(b) shows the change of the absorption of the stored electrons at 600 nm with irradiation time. It is important to notice that the holes have been completely scavenged in our system by the employed alcohol (methanol). Tamaki et al. [5] have directly prove fast and efficient hole scavenging by methanol employing femtosecond and nanosecond transient absorption measurements. The authors obtained a reaction time of sub-ns and a yield of ~100%.

In accordance with the mechanisms proposed in the literature [6] it is concluded that the TiO_2 electrons (e^-_{CB}) are trapped as Ti^{3+} states, *i.e.*, that the conduction band electrons get trapped at Ti^{4+} sites. The shifting of the absorption maximum of the TiO_2 electrons to longer wavelengths upon extended illumination may be attributed to the storing of the excess electrons in the conduction band of TiO_2 after the available surface traps have been filled [7] or rather by the trapping of the electrons in bulk rather than in surface traps, *i.e.*, assuming that bulk electron traps exhibit slightly red shifted absorption spectra.

The concentration of the stored TiO_2 electrons can be determined from the absorbance measurements provided that the respective extinction coefficient is known. The extinction coefficient of the stored electrons in TiO_2 at 600 nm has been determined through their titration with the Thionine dye or Benzoquinone [BQ], respectively, in the strict absence of oxygen yielding an average value of ($\varepsilon_{600\,nm} = 600 \pm 27$) $M^{-1}\,cm^{-1}$. This value agrees rather well with the value of 470 $M^{-1}\,cm^{-1}$ [8] determined in acidic solution or with 800 $M^{-1}\,cm^{-1}$ determined in alkaline solution [9]. According to the determined value of 600 $M^{-1}\,cm^{-1}$, the concentration of stored electrons in the reported experiments was calculated ranging from 5.9×10^{-4} to 6.9×10^{-4} M which is equivalent to $(36–42) \times 10^{19}$ electrons l^{-1}, corresponding to an average of about 6–8 electrons/TiO_2 particle (see Ref. [10] for determining of the no. of TiO_2 particle/l).

As a blank experiment, the absorption spectrum of the stored electrons on TiO_2 was determined using the stopped flow instrument. The blue colloidal solution of the stored TiO_2 electrons at pH 2.3 was mixed with a deaerated aqueous HCl solution at the same pH in the stopped flow apparatus and the change of absorption with time was recorded. Fig. 2(a) shows the transient absorbance spectrum (400–640 nm) that is recorded 5 ms after the mixing. A broad

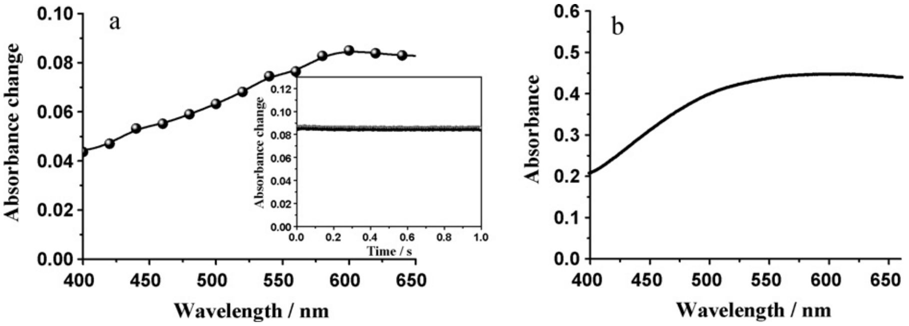

Fig. 2. (a) Transient absorption spectra measured after 5 ms of mixing a 3.8×10^{-2} M deaerated TiO_2 suspension at pH 2.3, inset shows transient absorbance *vs.* time after mixing of TiO_2 electrons with deaerated water at pH 2.3 (HCl), (b) steady state absorbance of TiO_2 electrons after 1:1 mixing with deaerated H_2O at pH 2.3 (HCl).

absorption spectrum is observed with an absorption maximum around 600 nm. Inset of Fig. 2(a) shows the transient absorption *vs.* time signal at 600 nm (mixing occurred at $t = 0$ s), it is obvious that the signal remains unchanged during the entire measurement time of 1 s. Fig. 2(b) shows the typical absorption spectrum of stored TiO_2 electrons prepared under the same conditions, *i.e.*, after 1:1 dilution of the stored TiO_2 electron suspension with deaerated aqueous HCl solution. It is important to clarify that the absorption spectrum obtained from the stopped flow measurements is measured in a cuvette with an optical path length of 0.2 cm, while that obtained from the steady state UV–vis spectrophotometer is measured with an optical path length of 1.0 cm. As can be seen from Fig. 2, the absorbance of the electrons is 5 times higher (using 1 cm cuvette) in comparison with the stopped flow measurements reflecting the difference in the optical path length (10 mm *vs.* 2 mm).

The reduction of dissolved O_2 and H_2O_2, respectively, by the stored TiO_2 electron has been chosen as model reactions in the present study. Fig. 3 shows the transient absorption *vs.* time signals observed upon mixing aqueous stored TiO_2 electron suspensions ($[e^-_{TiO_2}] = 5.7 \times 10^{-4}$ M) at pH 2.3 with aqueous solutions containing different concentrations of O_2 (0.65×10^{-4} M, air-saturated (1.25×10^{-4} M), O_2-saturated (6.25×10^{-4} M), and argon saturated H_2O). A similar kinetic experiment for the reduction of hydrogen peroxide by the stored TiO_2 electrons was also performed. Fig. 4 shows the transient absorption *vs.* time signals observed upon mixing the blue suspension of TiO_2 electrons ($[e^-_{TiO_2}] = 6.9 \times 10^{-4}$ M) at pH 2.3 with different concentrations of aqueous H_2O_2 solutions ((1.56–$6.25) \times 10^{-4}$ M). It is observed that in argon-flushed solution the absorbance signal is decreasing very slowly with a rate of 8.9×10^{-7} mol l^{-1} s^{-1}, while in solutions containing an electron acceptor (O_2 or H_2O_2) the electron absorbance is fading rapidly, depending on the concentration of the electron acceptor. The kinetic curves were analyzed according to double exponential decay fitting. The observed first order rate constants were found to increase linearly with increasing the concentration of the electron acceptors (O_2, H_2O_2) and the respective second order rate constants were obtained from the slope of the linear dependencies. The values of the resulting second order rate constants are summarized in Table 1. The rate constant of the first initial decay ($k_I^{obs} = 2.0 \times 10^4$ M^{-1} s^{-1}) and that of the second decay ($k_{II}^{obs} = 5.7 \times 10^3$ M^{-1} s^{-1}) for the reaction of stored TiO_2 electrons with molecular oxygen were found to be similar to the values of the rate constants of the two slower processes k_{III} ($7.3 \pm 1.5 \times 10^3$ M^{-1} s^{-1}) and k_{IV} ($1.0 \pm 0.2 \times 10^3$ M^{-1} s^{-1}) as reported by Gao et al. [3] who studied the reaction of electrons formed by radiation chemical processes in small TiO_2 particles and who suggested these slow processes to be due to the reaction of excess TiO_2 electrons with molecular oxygen in the bulk.

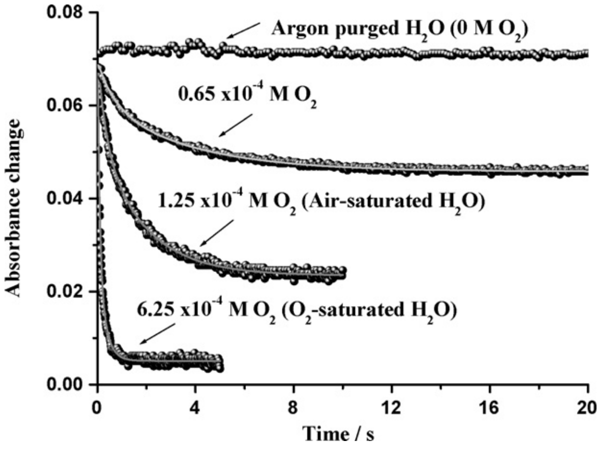

Fig. 3. Time profile of the decay of the $e^-_{TiO_2}$ absorbance at 600 nm ($[e^-_{TiO_2}] = 5.7 \times 10^{-4}$ M) upon mixing with different concentrations of dissolved O_2 saturated aqueous solutions at pH 2.3 (HCl). Solid lines show the double exponential fits.

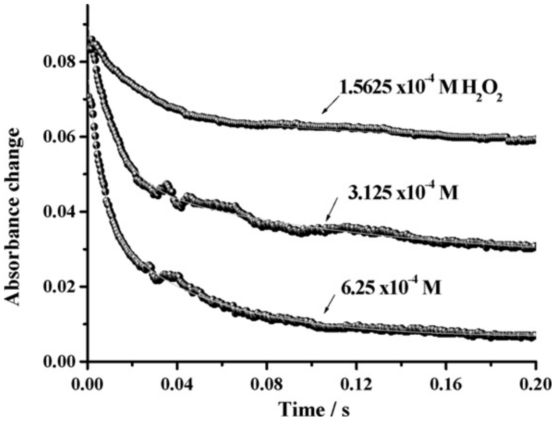

Fig. 4. Time profiles of the decay of the $e^-_{TiO_2}$ absorbance at 600 nm ($[e^-_{TiO_2}] = 6.9 \times 10^{-4}$ M) upon mixing with Ar-purged H_2O_2 solutions at pH 2.3 (HCl). Solid lines show the double exponential fits.

Table 1
Summary of rate constants of the reaction of TiO_2 electrons with O_2 and H_2O_2.

Electron acceptors	$e^-_{TiO_2}$ (M)	Number of transferred electrons	K (M^{-1} s^{-1})
O_2	5.7×10^{-4}	1.1	2×10^4
		2	5.6×10^3
		Total (3.1)	
H_2O_2	6.9×10^{-4}	1.1	2.7×10^5
		0.5	3.2×10^4
		Total (1.6)	

Bahnemann et al. [2] estimated a reaction rate constant of 7.6×10^7 l mol^{-1} s^{-1} for the reaction of trapped electrons produced by flash photolysis of platinized TiO_2 nanoparticles with molecular oxygen producing the superoxide radical which is considerably higher than the present value. This can be attributed to the multi-electron transfer process that is supposed to occur in the present system of excess electrons and may also be affected by the platinum metal employed in the previous work.

The rate constant of the first initial decay ($k_I^{obs} = 2.7 \times 10^5$ M^{-1} s^{-1}) and that of the second decay ($k_{II}^{obs} = 3.2 \times 10^4$ M^{-1} s^{-1}) for the reaction of the stored TiO_2 electrons with hydrogen peroxide are found to be in very good agreement with the respective k_I and k_{II} values obtained by Gao et al. [3] for small TiO_2 particles. In the latter study, the fast and slow decay rate constants, respectively, were suggested to be due to the reaction of stored electrons with the adsorbed H_2O_2 molecules and H_2O_2 molecules in the bulk, respectively. The number of consumed electrons can also be determined from the kinetic curves shown in Figs. 3 and 4 for the case that the initial concentration of the electron acceptor is lower than the initial concentration of the stored electrons. Thereby, it is found that in the presence of molecular oxygen an average of 3.1 electrons are transferred per O_2 molecule while in the presence of hydrogen peroxide an average of 1.6 electrons are transferred per H_2O_2 molecule. Safrany et al. [8] estimated a similar value of 3.3 electrons consumed in the reduction of one oxygen molecule using radiation induced TiO_2 electrons. The authors attributed this to the occurrence of two parallel pathways, *i.e.*, the two and the four electron reduction of O_2 to water (*cf.* Reactions

(1)–(5)).

$$2O_2 + 2e^-_{TiO_2} \rightarrow 2O_2^{\bullet -} \xrightarrow{-2H^+} 2HO_2^{\bullet} \rightarrow O_2 + H_2O_2 \qquad (1)$$

$$H_2O_2 + e^-_{TiO_2} \rightarrow HO^- + HO^{\bullet} \qquad (2)$$

$$HO^{\bullet} + CH_3OH \rightarrow {}^{\bullet}CH_2OH \qquad (3)$$

$${}^{\bullet}CH_2OH + TiO_2 \rightarrow TiO_2(e^-) + H^+ \qquad (4)$$

$$H_2O_2 + 2e^-_{TiO_2} \rightarrow 2HO^- \qquad (5)$$

4. Conclusions

The findings of this study clearly reveal that the stopped flow method represents a new facile method to study the dynamics of electron transfer reactions at TiO_2 nanoparticles using the stored electrons. As model reactions the reduction of O_2 and H_2O_2 was successfully investigated and their kinetic constants reported here were found to be in good agreement with published values determined by other techniques.

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