



Short note

Reaction dynamics of the transfer of stored electrons on TiO₂ nanoparticles: A stopped flow study

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ABSTRACT

The dynamics of the transfer of electrons from TiO₂ nanoparticles to a variety of electron acceptors have been investigated employing a simple and facile stopped flow technique. Prior to the kinetic experiments nanosized TiO₂ 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 O₂ and H₂O₂ by stored TiO₂ electrons has been successfully studied.

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1. Introduction

A fundamental understanding of the dynamics of the charge carrier transfer at TiO₂ 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 TiO₂/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 TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ nanoparticles using the stopped flow

technique. The basic concept of this work is rather simple; the electrons are generated on the TiO₂ 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 O₂ and H₂O₂. 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 TiO₂ 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 TiO₂ particles by illuminating a deaerated (argon purged) freshly prepared transparent colloidal solution of 3 g l⁻¹ (3.8 × 10⁻² M) TiO₂ 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 × 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 TiO₂ particles loaded with electrons was carefully filled into one of the stopped flow syringes and an aqueous solution of the electron acceptor (O₂,

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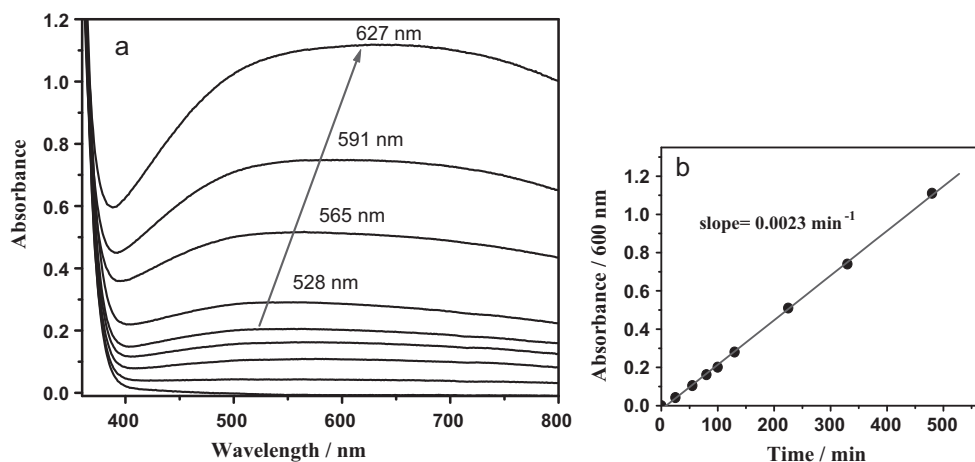


Fig. 1. (a) Build-up of the TiO₂ electron spectrum of 3.8×10^{-2} M deaerated TiO₂ suspension in 0.02 M methanol at pH 2.3 recorded following different periods of UV irradiation. (b) Change in absorbance at 600 nm as a function of the employed irradiation time.

H₂O₂) 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 TiO₂ electrons with time. All measurements were carried out at ambient temperature.

3. Results and discussion

The UV (A) photolysis of a system containing TiO₂ (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 TiO₂ 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 TiO₂ 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 TiO₂ electrons (e^-_{CB}) are trapped as

Ti³⁺ states, *i.e.*, that the conduction band electrons get trapped at Ti⁴⁺ sites. The shifting of the absorption maximum of the TiO₂ electrons to longer wavelengths upon extended illumination may be attributed to the storing of the excess electrons in the conduction band of TiO₂ 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 TiO₂ electrons can be determined from the absorbance measurements provided that the respective extinction coefficient is known. The extinction coefficient of the stored electrons in TiO₂ 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 ($\epsilon_{600\text{nm}} = 600 \pm 27$) 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 $(36\text{--}42) \times 10^{19}$ electrons l⁻¹, corresponding to an average of about 6–8 electrons/TiO₂ particle (see Ref. [10] for determining of the no. of TiO₂ particle/l).

As a blank experiment, the absorption spectrum of the stored electrons on TiO₂ was determined using the stopped flow instrument. The blue colloidal solution of the stored TiO₂ 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

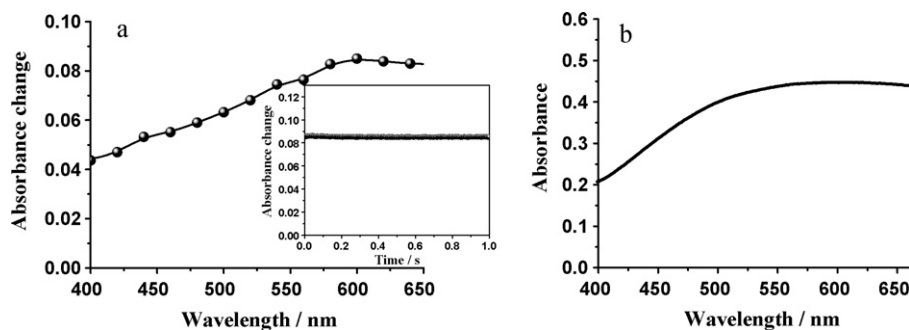


Fig. 2. (a) Transient absorption spectra measured after 5 ms of mixing a 3.8×10^{-2} M deaerated TiO₂ suspension at pH 2.3, inset shows transient absorbance vs. time after mixing of TiO₂ electrons with deaerated water at pH 2.3 (HCl), (b) steady state absorbance of TiO₂ electrons after 1:1 mixing with deaerated H₂O at pH 2.3 (HCl).

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