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ORIGINAL ARTICLE

Exploiting stored TiO_2 electrons for multi-electron reduction of an azo dye methyl orange in aqueous suspension

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Abstract The mechanism of multi-electron reduction of methyl orange (MO) azo dye on TiO_2 nanoparticles has been studied performing stopped flow technique. A multi-electron reduction of azo dye has been investigated. It was found that a multistep reduction of the dye takes place: the stored electrons reduce the conjugative system of the azo group resulting in the decolorization of the dye and leading to the formation of hydrazine derivative followed by further 2 electron transfer step leading to the cleavage of the N–N bond and the formation of aromatic amines. The FTIR analysis of the products confirms the proposed mechanism of the dye reduction. The kinetic parameters and of the multi-electrons reduction of the MO have been determined. The rate of MO reduction was found to be dependent on both the TiO_2 electrons and the dye concentrations.

1. Introduction

Heterogeneous photocatalysis has been widely employed for the decomposition of toxic substances present in waste-water [1–4]. Under band-gap excitation electron hole (e^-–h^+) pairs produced, which initiate the oxidation and reduction processes of the adsorbed substrates. Among environmental water pollutants, azo dyes have drawn much attention due to their undesirable consequences on the eco-system and human health as they are carcinogenic and mutagenic [5–8]. Several advanced oxidation/reduction processes have been investigated employing UV irradiated TiO_2 nanoparticles for treatment of hazardous azo dyes in wastewater [9–15]. Aromatic dyes as adsorbed species on suitable sites on the surface of semiconductors undergo photooxidation or photoreduction under ultraviolet and visible light irradiation. Recently, Ultrasonic wave induced mechanoluminescence (USML) has been investigated to drive photocatalysis [16]. The photodecomposition of the azo dye by TiO_2 nanoparticles can be expressed according to the following mechanism:

$$TiO_2 + h\nu \rightarrow TiO_2(e^-_{CB} + h^+_{VB}) \quad (1)$$

$$OH^- + h^+_{VB} \rightarrow OH^{\cdot} \quad (2)$$

$$H_2O + h^+_{VB} \rightarrow H^+ + OH^{\cdot} \quad (3)$$

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$$O_2 + e^-_{CB} \rightarrow O_2^{\bullet -} \quad (4)$$

$$Dye + O_2(\text{or } O_2^{\bullet -} \text{ or } OH^{\cdot}) \rightarrow \text{Degraded or mineralized products} \quad (5)$$

$$Dye + h^+_{VB} \rightarrow \text{Oxidation products} \quad (6)$$

$$Dye + e^-_{CB} \rightarrow Reductionproducts \quad (7)$$

The radicals (*i.e.*,$OH^{\cdot}$ or $O_2^{\bullet -}$) formed in the above equations are found to be the powerful oxidation agents which can mineralize the dye to carbon dioxide. On the other hand, a comparative ease with which a simple azo dye can be reductively decolorized by photogenerated electrons in colloidal semiconductors suspensions has been also demonstrated [17,18]. The advantage of the photocatalytic reduction pathway is that the reduction products are amenable for conventional photocatalytic oxidation using the same photocatalytic system responsible for carrying out the reduction [18]. However, little attention has been paid to the study of the kinetics and the mechanisms of the reduction pathway process. This knowledge is very important for improving the reductive decomposition efficiency and rate for industrial applications.

The stopped flow spectrophotometric technique was found to be a very powerful tool for such comprehensive and detailed study of the kinetics and mechanisms for electron transfer reaction with half lives in the millisecond scale. Inside the stopped flow apparatus, the rapid mixing of the reactants takes place and the resulting reactant mixture travels to the optical cell, which is provided with photometric detection, usually by UV/Vis, IR, fluorescence and/or chemiluminescence [19,20] or less common, detection by dichroism, refractive index, EPR or NMR [21,22]. The kinetic analysis of different types of reactions such as complexation, polymerization and electron transfer reactions can be studied utilizing the stopped flow technique [20,22].

The aim of this work is to investigate the kinetics and the mechanism of the multi-electron reduction of methyl orange dye (MO) as a model for water soluble azo dye with photo generated electrons in TiO_2 nanoparticles. In the present work, the photo generated TiO_2 electrons are stored on the surfaces of TiO_2 nanoparticles as trapped Ti (III) species and have been exploited for the multi-electrons reduction of the MO. The kinetics of the multi-electron reduction of MO has been studied utilizing stopped flow method. The effect of the dye concentration as well as stored TiO_2 electrons concentrations on the rate of the reduction has been studied and the underline reaction mechanism has been discussed.

2. Experimental

2.1. Preparation of TiO_2 nanoparticles

TiO_2 nanoarticles were prepared from organic precursor based on previous method with some modifications [23] (Titanium (IV)-isopropoxide (Sigma–Aldrich, 99.999%). 6 ml of titanium tetraisopropoxide dissolved in 10 ml Ethylene glycol (Sigma–Aldrich, 99.99%) as size limiting agent followed by drop-wise addition to a solution of Ethylene glycol at pH 1.5 (perchloric acid). This mixture was stirred over night until it was virtually clear. The pH was changed to 2.3 by dialyses against distilled water using a double dialysis membrane. After vacuum drying of the solvent at 25 °C, white shiny crystals were produced and re-suspended perfectly in water. The as prepared TiO_2 particles were characterized by XRD, Raman spectroscopy and TEM.

2.2. Storage of electrons on TiO_2 nanoparticles

The photogenerating and storing of electrons on the TiO_2 nanoparticles were performed according to the previous work [24,25]. The deaerated transparent suspension of 3 g l^{-} of the nanoparticles has been irradiated for 4 h in the presence of 0.02 M methanol as a hole scavenger. The irradiation of the TiO_2 particles was performed using a glass reactor (100 ml) sealed with silicon cap irradiated from the top by UVA 365 UV lamp. The illuminated TiO_2 suspension was found to have a significant broad absorption band in the range 400–700 nm which is corresponding to the absorbance of trapped electrons on the TiO_2 surface (i. e., Ti (III)) (Eqs. (8) and (9)) [23–26]:

$$TiO_2 + hv \rightarrow TiO_2(e^-_{CB} + h^+_{VB}) \quad (8)$$

$$e^-_{CB} + Ti^{IV} \rightarrow Ti^{III} \quad (9)$$

The number of TiO_2 particles per liter can be determined by assuming that the particle has a spherical shape with an average diameter of 3 nm. Its volume can be determined to be 1.41×10^{-20} cm^3. The average weight of anatase TiO_2 particle can be calculated assuming its mass density of 3.894 g cm^{-3} to be 5.43×10^{-20} g. In the present system of 3 g l^{-1}, the number of TiO_2 particles will be consequently be 5.53×10^{19} particle/l.

The initial concentration of stored electrons on TiO_2 was determined using the molar extinction coefficient $\varepsilon = 600$ M^{-1} - cm^{-1} that has been reported in our previous work. [24–26] Assuming the determined ε value of TiO_2 electrons and that the particles of spherical shape of 3 nm size, the concentration of the TiO_2 electrons in the performed experiments is found to range from 3×10^{-4} to 6×10^{-4} M corresponding to an average of 2–6 electrons per particle. It is important to clarify that the absorption spectrum obtained from the stopped flow is measured in a cuvette with 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. So that the absorbance of electrons is 5 time higher in the steady state measurements in comparison with the stopped flow measurements.

2.3. Kinetic measurements

The kinetics of the photocatalytic reduction of MO dye was studied by exploiting the trapped TiO_2 electrons which are pre-stored on the TiO_2 nanoparticles surfaces and utilizing the stopped flow technique (SF-3 rapid mixing stopped flow spectrophotometer (200–700 nm) with 2 mm optical path cell and 0.5 ms dead time mixing). In a typical experiment a pre-illuminated TiO_2 aqueous suspension was injected in one of the stopped flow syringes and a deaerated aqueous dye solution was injected in the other syringe. A 1:1 mixing of the two reactants takes place in 0.5 ms and the resulting mixture travels to the optical cell were the change in the absorbance with time is measured. The bleaching of the dye was monitored over the wavelength range 400–580 nm and the kinetics of the electron transfer reactions was studied by following the decay of the absorbance of TiO_2 electrons at 600 nm as well as the bleaching of the dye at 510 nm.

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