Technical paper

Hydroxyl Radical Scavenging-based Method for Evaluation of TiO_2 Photocatalytic Activity

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Abstract

A novel hydroxyl radical scavenging method was developed to establish the photocatalytic activity of TiO_2 thin films. Transparent TiO_2 thin films were prepared on soda-lime glass substrates using the sol-gel method and characterized using X-ray diffraction.

During photoirradiation in aqueous buffered solutions, activity of the films was followed using the substituted nitrobenzene *N,N'*-(5-nitro-1,3-phenylene)bisglutaramide as a hydroxyl radical scavenger and its hydroxylated products were quantified using HPLC. The yield of hydroxyl radicals was evaluated at various pH of the reaction media, and reflected the dependence of the rate of the hydroxylation reaction on the experimental conditions and on the different qualities of the TiO_2 thin films. The proposed method allows for direct assessment of hydroxyl radical production, it is straightforward and is proposed for routine use.

Keywords: Titanium dioxide; Photocatalysis, *N,N'*-(5-nitro-1,3-phenylene)bisglutaramide, Radical scavenger, HPLC

1. Introduction

Nano-sized titanium oxide (TiO_2) is important in many applications and is a particularly promising photocatalytic material. Since the discovery of photocatalytic splitting of water on a TiO_2 electrode in 1972,[1] great efforts have been invested in promoting the activity of TiO_2. Nanosized TiO_2 in the anatase crystalline form prepared through different pathways is the usually used photocatalyst. Among all synthetic procedures, the sol–gel route remains one of the most attractive ones. The important advantage of this approach is the possibility of preparing powders or films of pure and mixed oxides in nanoparticulate form on a routine basis.[2–4]

The principle of photocatalysis involves photogeneration of pairs of electrons and holes as per reaction (1) below, by the absorption of light of energy greater or equal to the energy of the band gap. Photoreactions occur at the surface of the catalyst to promote an electron from the valence band to the conduction band, leaving a "hole" behind. Since the band gaps for rutile and anatase are 3.0 and 3.2 eV, respectively, corresponding to photons of wavelengths 410 and 385 nm, ultraviolet light is needed for photoexcitation. According to the reaction (2), upon oxidation of surface water, the hole is either converted to a hydroxyl radical, or is subject to recombination (3). Electrons are able to reduce oxygen to superoxide radical $O_2^{\bullet-}$, or to hydrogen peroxide H_2O_2 (4) and (5). Reaction (4) is slow and it is expected to be followed by reactions (5) and (6)[5].

$$\mathrm{TiO_2} \xrightarrow{hv} h^+ + e_{TiO_2}^- \tag{1}$$

$$h^+ + \mathrm{H_2O}_{ads} \longrightarrow \mathrm{HO}^{\bullet}_{ads} + \mathrm{H}^+ \tag{2}$$

$$h^+ + e_{TiO_2}^- \longrightarrow \mathrm{TiO_2} \tag{3}$$

$$e_{TiO_2}^- + \mathrm{O_2} \longrightarrow \mathrm{O_2}^{\bullet-} \tag{4}$$

$$\mathrm{O_2}^{\bullet-} + e_{TiO_2}^- + 2\mathrm{H}^+ \longrightarrow \mathrm{H_2O_2} \tag{5}$$

$$e_{TiO_2}^- + \mathrm{H_2O_2} \longrightarrow \mathrm{HO}^{\bullet} + \mathrm{OH}^- \tag{6}$$

It is evident that reactions (2), (5) and (6) are dependent on pH of the reaction medium. Since hydroxyl radicals are by far the most potent oxidants among the reactive oxygen-containing species in the series of reactions above, it is of interest to understand the reactions leading to their generation better.

There are many different methods for assessment of the photocatalytic activity of thin films. Many are based on the degradation of dyes and the quality of chemical information is rather poor, since absorbance is measured over time providing indication of the photocatalytic activity. A considerable number of studies have been published on this topic. In many cases[6–8] the authors used methylene blue where results are usually evaluated as a function of dye concentration, the amount of active substance (film) and pH. Furthermore, methyl red, congo red, indigo, indigo carmine and many other dyes have also been used for the purpose.[9] However, these methods are indirect, and only radical scavenging-based methods provide quantitative data on rates of free radical formation since hydroxyl radicals are trapped with suitable probes and the hydroxylated products are then determined.[10]

It has been assumed that the formation of $HO^•$ takes place through oxidation of OH^- ions or water molecules adsorbed on material surface. Due to the redox potential of $HO^•$, their generation is a very important parameter to be studied in the evaluation of photocatalysis. $HO^•$ generation has been studied using methanol,[11] coumarin,[12] and terephthalic acid. The latter is a fluorescence-based method and after irradiation, the highly fluorescent hydroxyterephthalic acid is formed and it can be determined by HPLC.[13] However, selectivity of many radical traps can be an issue.

A well-studied $HO^•$ scavenger, designed specifically to quantify $HO^•$ production, is *N,N'*-(5-nitro-1,3 phenylene)bisglutaramide (NPG), a substituted nitrobenzene (Fig. 1). Due to its structure, hydroxylation predominantly leads to generation of orto- and para-hydroxylated products [14]. It has been used both in spectrophotometric and chromatographic assays.[15,16] Due to the diffusion-controlled rate of hydroxyl radical addition onto NPG, the rate of hydroxylation is normally assumed to correspond to the rate of hydroxyl radical production. The dependence of hydroxyl radical production in a Fenton-reaction type system was examined and NPG was used to examine the dependence of the reaction yield on pH.[17] Since NPG is dissociated at pH > 7, the rate of its reaction with hydroxyl radicals should not be influenced by pH in the neutral and mildly alkaline region of interest.

2. Experimental

2. 1. Preparation of Sols and Deposition of Thin Films

The sol–gel method was employed to prepare TiO_2 thin films. According to the literature,[18] diffusion of Na^+ ions from the soda lime support during calcination reduces the activity of the catalyst. Therefore, TiO_2 films were deposited by dip-coating from TiO_2 sol ("TiO_2" and "TiO_2+P") onto SiO_2-precoated glass. The withdrawal speed was 100 mm/min in the case of TiO_2 sol and 50 mm/min in a case of SiO_2 sol. Coatings were dried at room temperature for 30 min and then they were calcined at 500 °C in a furnace for 30 min.

SiO_2 sol was prepared from tetraethoxysilane $Si(OEt)_4$ (J. T. Baker) by dissolving in ethanol (Riedel-de Haen) (n(ethanol)/n($Si(OEt)_4$) = 6.6). Separately, a 11.5% solution of nitric(V) acid was prepared by diluting of the concentrated (65%) HNO_3 (J. T. Baker) in water (n($Si(OEt)_4$)/n(HNO_3) = 3.2). After 10 min both solutions were mixed together and the resulting sol was used after 2h, at room temperatures.

Titania sol was prepared using titanium isopropoxide $Ti(OiPr)_4$ stabilized by adding ethyl acetoacetate EAA (n(EAA)/n($Ti(OiPr)_4$) = 1) during constant stirring. After 5 min, the prepared solution was dissolved in 2-methoxyethanol $MeOCH_2CH_2OH$ (n($MeOCH_2CH_2OH$)/n(Ti) =13.6). The alkoxide solution was stirred at room temperature for solvolysis and condensation reactions for at least 3 h. After use, the sol was kept in a refrigerator. It was conditioned at room temperature for at least 1 h before the next use (denoted as "TiO_2").

The procedure for preparation of the sols with added surfactants was the same as described above. Pluronic F-127 with structural formula $EO_{97}PO_{69}EO_{97}$, where EO represents the ethylene oxide block and PO represents the propylene oxide block (average molar mass = 126000 g mol^{-1}), was dissolved in the sol after the addition of $MeOCH_2CH_2OH$ (denoted as "TiO_2+P").[19]

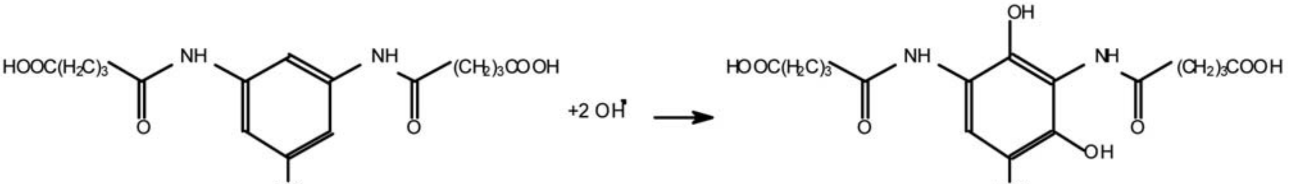

Figure 1: Hydroxylation of *N,N'*-(5-nitro-1,3 phenylene)bisglutaramide (NPG).

2. 2. Characterization of Thin Films Using XRD

Samples were characterized as thin films on the glass support. They were of a high optical and mechanical quality (mechanical scratching to prepare powders for XRD characterization would be extremely difficult since the adherence to the support was very high). XRD measurements were obtained using a PANalytical X'Pert PRO diffractometer with Cu-K_α ($\lambda = 0.1542$ nm) radiation from 20 to 60 2θ in steps of 0.034 and a time per step of 500 s.

2. 3. Photocatalytic Experiments

The photocatalytic activity was evaluated by measuring the increase in the concentration of *o*- and *p*-NPG during photoirradiation of films in solutions of NPG. Film deposited on ca. 1 cm^2 of glass substrate was inserted into a 10 mL glass reactor cell. We then introduced 2 mL 0.5 mM NPG dissolved in a 0,1 M phosphate buffer with the desired pH. *N*,*N*'-(5-nitro,1,3-phenylene)bisglutaramide was synthesized according to the literature[14] . The buffers were prepared from the corresponding mixtures of Na3PO4, Na2HPO4, and NaH2PO4 (Fluka), with pH 6.5, 7.5, 8.5, 9.5 and 10.5. All solutions were prepared with additionally purified deionised water (Millipore).

Irradiation experiments were carried out in the Heraeus Suntest CPS+ with a Xe lamp as the light source equipped with glass and quartz glass filters. The lamp power was 700 W/m^2, wavelengths below 370 nm were filtered.

The reaction medium (200 µL) was collected at different reaction times and analyzed using a HP 1100 Series high-performance liquid chromatograph coupled with a diode array detector. A Hypersil ODS chromatographic column was used (HP, 250 mm × 4 mm, 5 µm particle size) and 100 µL of the sample was injected. Gradient elution of 1.5 mL min^{-1} was used and consisted of 3–8% acetonitrile and of 97–92% phosphate buffer (20 mmol/L, pH 7) in 5 min, after which the unreacted NPG was flushed out of the column with a 30% acetonitrile/70% phosphate buffer eluent.

Hydroxylated derivates were isolated by preparative HPLC (HP ODS Hyperprep). The resulting eluates were acidified with sulphuric acid and extracted with ethyl acetate (for spectroscopy, Carlo Erba, Milano). The solvent was removed and the derivates were dried over P_4O_{10}. The remaining inorganic impurities (PO_4^{3-}, SO_4^{2-}) were determined using a Merck–Hitachi HPLC ion chromatographic system with a Dionex IonPac AS4A-SC column, carbonate buffer eluent, and conductometric detection with anion suppressor and H_2SO_4 as the regenerant. The unreacted NPG and inorganic impurities amounted to 1% (w/w) of the isolated products. The isolated derivatives were used for HPLC calibration.

3. Results and Discussion

It is known that the photocatalytic activity of TiO_2 films varies and depends on a number of parameters, such as film thickness, substrate, crystallite size.[20] In order to examine the structure of thin films prepared with and without surfactants, we investigated XRD patterns of thin films (Figure 2). The major peak at $2\theta = 25.4°$ corresponds to (101) diffractions of the anatase phase and is also supposed to be the most active in photocatalytic reactions. In the case of the TiO_2 + P thin film another peak is visible at $2\theta = 48.1°$ which corresponds to anatase (200) reflections. As expected, there is a significant difference between the films prepared with and without the surfactant. Its addition leads to formation of highly orientated anatase crystals and smaller grain size. The grain size was calculated from the (101) peak of anatase using the Scherrer's equation [21], and were 18 nm for TiO_2+P film and 32 nm for TiO_2 film.

The hydroxylation reaction of NPG is pH dependent and exhibit absorption properties in the region between 200 and 600 nm. The absorption maximum for o- hydroxylated NPG (o- HNPG) 421 nm and for p- hydroxyla-

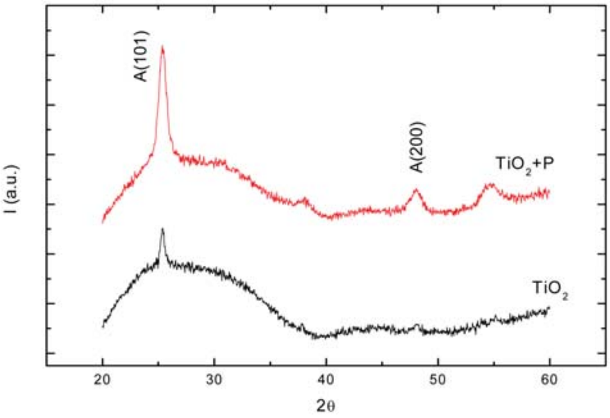

Figure 2: XRD pattern of TiO_2 thin films (A:anatase).

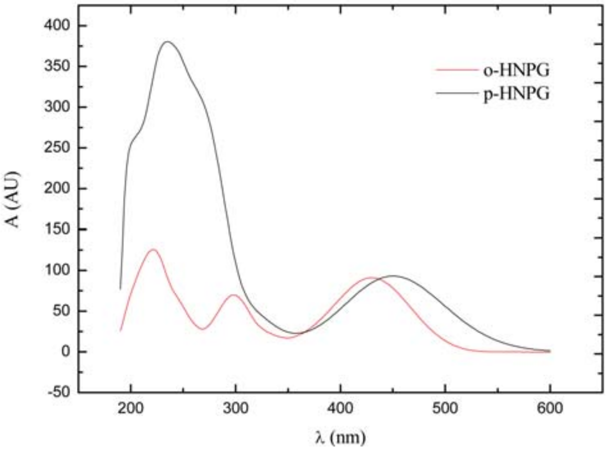

Figure 3: Absorbance spectra of o-HNPH and p-HNPG.

ted (p- HNPG) NPG 448 nm (Fig. 3) was achieved at pH 9 (Fig. 5), therefore reaction media should be adjusted to pH 9. Results are a sum of absorbance (concentration) of both components at 431 nm at which wavelength no chemical interferences appears.

In Fig. 4, we present the activity of the film in comparison with the blank experiment (no film), demonstrating the potential of the radical trapping method. Even in the blank, some hydroxylated derivatives are formed during irradiation of the NPG solution itself. However, it is evident that the rate of production of hydroxylated products is 4 times higher in the case of TiO_2 being present in the reaction solution than in the case where it was absent.

However, the overall photocatalytic activity of TiO_2 films should be, according to the reactions (2), (5) and (6), dependent on pH of the reaction medium. In order to investigate this, we controlled the reaction medium pH during the irradiation experiments. It turns out that the reaction is a first order process and the first order rate constants depend on pH, as shown in Fig. 5. The calculation was performed from the peak areas taking in an account the linear slopes of chromatographic calibration curves and mass of the thin film sample. From all the values obtained, the blank experiments have been subtracted.

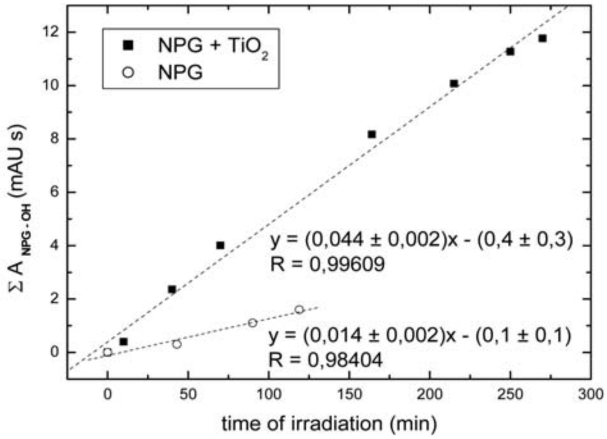

Figure 4: Relative relationship between the amount of hydroxylated products (expressed as sum of chromatographic peak areas) and time of irradiation in the absence and presence of TiO_2 thin films at pH 9.

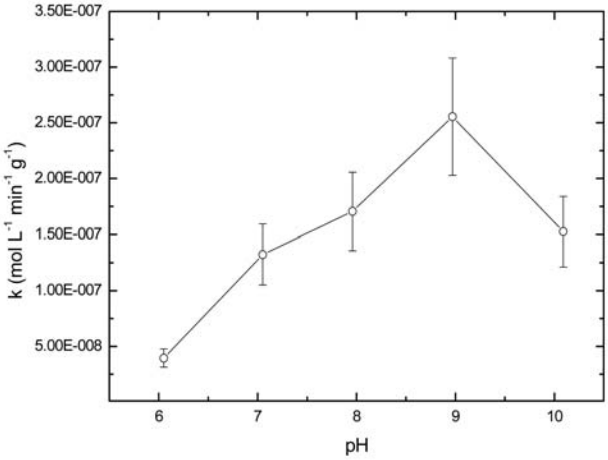

Figure 5: The influence of the pH of reaction media on the first-order reaction rate constants during irradiation of the thin film TiO_2 + P. The error bars represent uncertainties in the slopes of regression lines describing the concentration of hydroxylated derivatives vs. time, i.e. in rate constants. The values are corrected per sample mass which corresponds to film area.

The peak of activity is observed at pH 9, showing that the production of hydroxyl radicals is not dependent only on reaction (2), but must also be dependent on reaction(s), in which protons are reactants, such as (5) and (6).

We further tested the applicability of the new method for evaluation of TiO_2 thin films prepared with and without surfactants (Fig. 6). The catalytic activity increases with an increasing number of deposited layers on the substrate. The viscosity of the sol containing the surfactant is higher than without it, which leads to an increase in the TiO_2 film thickness. A thicker film may contain a bigger surface area of the catalyst, and hence more catalytic centres.

The addition of surfactants into the sol has a pronounced positive effect on the photocatalytic activity. The rate of production of hydroxylated derivatives of NPG, for the film prepared using the surfactant is three times higher than for the film deposited without the surfactant, for the same number of layers. Multiplication of layers has a further positive effect on the activity.

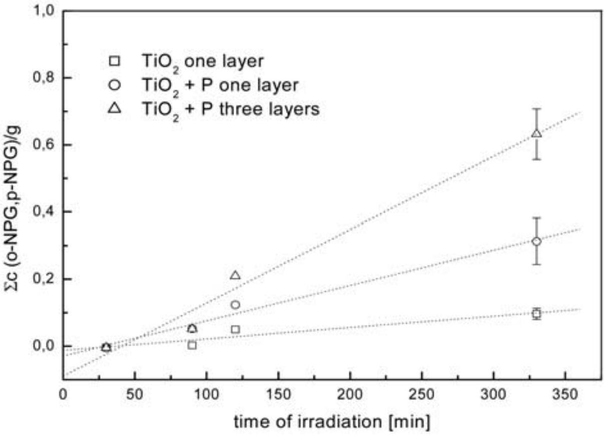

Figure 6: Relative photocatalytic activity of TiO_2 films deposited from two different sols on glass substrates with one and three dipping/heating cycles, measured by the production of hydroxyl radicals (i.e. rate of hydroxylation of NPG) as expressed by the sum of chromatographic peak areas of hydroxylated products and normalized to sample mass at pH 9.

4. Conclusions

An HPLC method for the selective quantitative determination of $HO^{\bullet}$ produced during irradiation of catalytically active TiO_2 thin films was obtained. The use the

N,N'-(5-nitro,1,3-phenylene)bisglutaramide is proposed as a radical scavenger during thin film irradiation experiments, as its hydroxylated products can be easily determined and as it reacts with hydroxyl radicals selectively, at a diffusion controlled rate.

We observed a peak of the rate constant of hydroxyl radical formation at pH 9 and have shown that the use of surfactants during preparation of thin films has a positive effect on the catalytic activity of the films during irradiation in aqueous media.

The technique is very straightforward and permits the calculation of the rate of hydroxyl radical formation, which is not the case of most spectrophotometric methods utilizing the bleaching of dyes as an indication of catalytic activity of thin films.

5. Acknowledgements

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6. References

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Povzetek

Razvili smo metodo za določanje fotokatalitske aktivnosti TiO2 tankih plasti. V ta namen smo uporabili tanke plasti TiO_2 pripravljene na steklenih nosilcih in jih predhodno okarakterizirali s pomočjo rentgenske difrakcije. Za določanje fotokatalitske aktivnosti TiO_2 smo uporabili substituiran nitrobenzen *N,N*'-(5-nitro-1,3-fenil)bisglutaramid, ki je deloval kot lovilec hidroksilnih radikalov. Hidroksilirane produkte smo kvantificirali s HPLC. Hitrost hidroksilacije je odvisna od eksperimentalnih pogojev in vrste tankih plasti TiO_2, nastanek hidroksiliranih radikalov smo vrednotili pri različnih pH vrednostih reakcijske mešanice.

Predlagana metoda omogoča neposredno določitev nastalih hidroksilnih radikalov, je relativno enostavna in primerna za rutinsko uporabo.