Tailoring preparation, structure and photocatalytic activity of layer-by-layer films for degradation of different target molecules

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ABSTRACT

Photocatalytic thin films composed of titanium dioxide and poly(styrene sulfonate) with hierarchical porosity and high transparency were prepared by the layer-by-layer self-assembly method. The influence of preparation conditions on the structure and photocatalytic activity of the films was investigated. It was found there is no need to reach adsorption equilibrium during layer deposition. Using very short deposition times, films with better transparency and higher activity for methylene blue photo-oxidation were obtained. Diffusion limitations due to strong adsorption of dye molecules and ammonia to the polyelectrolyte were revealed. These results indicate that films could be devised to selectively degrade specific target molecules in a mixture. The films were deposited on a three-dimensional carbon substrate and successfully demonstrated in a photoelectrochemical water splitting experiment.

1. Introduction

Photocatalysis is a very popular strategy for remediation of air and water pollution. In photocatalysis generally a semiconductor breaks down pollutants using solar energy, which is essentially free. Usually nanosized semiconductor particles are investigated for their high surface area and efficient charge transport [1]. However, for easier handling, recycling and safety, it is advisable to immobilize these nanoparticles on a solid surface. Such a nanoparticle film ideally maintains high porosity and surface area, is robust and depending on the application, may be optically transparent (*e.g.* photocatalytic glass) [2,3].

Layer-by-layer (LbL) assembly is a versatile and low-cost technique to fabricate well-defined thin films. Contrary to most conventional techniques, it can be performed at low temperature and mild conditions, making it compatible with numerous substrates and components. LbL assembly consists of alternately dipping a substrate in solutions containing *e.g.* positively and negatively charged species [4]. The electrostatic interactions result

in gradual film buildup, while intermediate rinsing steps remove excess material so that only a monolayer of material is deposited in each step. Originally LbL was only applied to polymers [5], but quickly expanded to include deposition of nanoparticles as well [6]. Kotov et al. [7] were the first to introduce positively charged titanium dioxide (TiO_2) nanoparticles in a LbL assembly using poly(diallylmethylammonium chloride) counter-anions. Shortly after, Liu et al. [8] prepared transparent TiO_2 films using poly(styrene sulfonate) (PSS) as the anion, a method that was adopted by several other groups [2,3,9]. For TiO_2/polymer composites, Kim and Shiratori [9] showed that the use of weak polyelectrolytes results in thick films with high surface roughness whereas strong polyelectrolytes such as PSS give rise to dense films. Sohn et al. [10] highlighted the difference between spin-coated and dip-coated TiO_2/polymer films. Dip-coated films have a fuzzy, accessible structure, while spin-coated films are layered and have low permeability, which restricts their photocatalytic activity to a single layer of catalytic material. LbL films containing TiO_2 are optically transparent, robust and photocatalytically active. They have a tunable thickness and composition, and can be tailored to contain many more components. LbL assembly has proven itself as an interesting technique to prepare photocatalytic films on various surfaces.

Although some work exists examining the structure of such films and few investigate the influence of preparation conditions

on film structure, a relationship between film structure and photocatalytic activity has not been established. In this work, we describe the influence of LbL deposition parameters on resulting film structure, and its corresponding photocatalytic activity. We show that certain dyes can better penetrate in films with appropriate structure, whereas ammonia oxidation benefits more from increased photocatalyst loading. The same film structure was found useful for photoelectrochemical water splitting.

2. Materials and methods

2.1. Layer-by-layer deposition

Glass substrates with a surface area of $5\,cm \times 3\,cm$ were successively cleaned with detergent, ethanol and deionized water and then immersed in pure H_2SO_4 for 30 min. Finally, they were sonicated in pure acetone for 1 h to remove all dust particles and dried. Silicon substrates ($5\,cm \times 3\,cm$) were cleaned with compressed air and subsequently treated in H_2SO_4 and acetone in the same manner. Carbon fiber electrodes ($5\,cm \times 3\,cm$, Toray paper E030, Quintech) were only rinsed with acetone prior to LbL deposition.

LbL deposition was performed by manual dip-coating using an established procedure [2]. Dipping solutions were prepared using MilliQ water and kept in polypropylene bottles. Substrates were first treated with poly(ethylene imine) (Lupasol WF, $M_W \sim 25,000\,g/mol$, BASF) by dipping in a $3\,g\,l^{-1}$ solution for 20 min. Subsequently, substrates were alternatingly dipped, first in $1\,g\,l^{-1}$ poly(styrene sulfonate) ($M_W \sim 70,000\,g/mol$, Sigma Aldrich) solution and then in $\sim 1\,g\,l^{-1}$ TiO_2 (Aeroxide P25, Evonik Degussa Corporation) suspension, both adjusted to pH 2.5 using concentrated HNO_3. Between deposition steps, the substrates were first dipped in three different baths of MilliQ water (adjusted to pH 2.5) followed by rinsing with copious amounts of MilliQ water (pH 2.5) using a rinsing bottle. For some films, the dipping solutions were stirred at 500 rpm using a magnetic stirring bar. After deposition, films were annealed at $60\,°C$ in air for 1.5 h.

Reference films were prepared by conventional dip-coating in a 5 wt% TiO_2 suspension, adjusted to pH 3.5 using concentrated HNO_3. Substrates were submerged in the suspension for 10 min, followed by gentle drying under an air stream and annealing at $60\,°C$ for 1.5 h. After annealing, the films were rinsed with MilliQ water. This process was repeated one more time to obtain the final film.

2.2. Film characterization

Transmission UV–vis spectroscopy was carried out using an Infinite M200 Pro instrument (Tecan). Absorbance of the glass substrate was subtracted from the measurements. Since a film was deposited on both sides of the glass substrates, the obtained number was divided by two. For ellipsometric porosimetry the films (prepared on silicon substrates) were introduced to a vacuum chamber in which the spectroscopic ellipsometer (Sentech SE801) was mounted and a system for dosing adsorbates is connected. The adsorbate used was toluene. For determination of adsorption isotherms, the adsorbate pressure was slowly increased until the saturation pressure was reached. The desorption was performed by slowly evacuating the chamber. The ellipsometric angles Ψ and Δ over the spectral range of 400–800 nm, the pressure, and the time were continuously recorded. These data were used for calculation of porosity and pore size distribution as described in reference [11]. High-resolution scanning electron microscopy (HR-SEM) was performed on a Nova NanoSEM 450 (FEI). Films deposited on silicon were mounted on aluminum stubs using carbon tape. Through-plane resistance measurements were performed using a home built

Teflon cell. A stainless steel sheet of $1\,cm \times 3\,cm$ with deposited LbL film was pressed perpendicular onto a stainless steel counter electrode ($2.65\,cm \times 3\,cm$). Linear scan voltammetry was used at potentials between $-0.1\,V$ and $+0.1\,V$.

2.3. Photocatalytic testing

2.3.1. Methylene blue degradation

LbL films were cut into pieces of $0.8\,cm \times 3\,cm$ and put in quartz reaction tubes containing 5 ml of a methylene blue solution (0.01 mM). The solutions containing LbL films were kept in the dark for 20 min to achieve equilibrium of adsorption in the film. They were then placed in a Luzchem LZC-ICH2 photoreactor (UVA, 385 nm, $5\,mW\,cm^{-2}$) with rotating sample carrousel, at a temperature of $35\,°C$. Every 15 min a $200\,\mu L$ sample was taken from the solution and analyzed by UV–vis spectroscopy at 664 nm. Afterwards it was returned to the solution.

2.3.2. NH_3 degradation

LbL films of $28\,cm \times 3\,cm$ were placed inside a home-built continuous flow gas phase reactor described elsewhere [12]. Nitrogen gas containing 1000 ppm NH_3, 5% O_2 and 3% H_2O was sent over the reactor at different flow rates. The sample was illuminated at room temperature using a UVA lamp (365 nm, $1.1\,mW\,cm^{-2}$).

2.3.3. Photoelectrochemical water splitting

Films deposited on carbon fiber electrodes were cut into pieces of $3\,cm \times 3\,cm$ and used as the photoanode in a membrane electrode assembly. For the cathode, Pd on activated carbon (3 wt%, Sigma Aldrich) was deposited on carbon fiber electrode ($2.5\,cm \times 2.5\,cm$) and a final loading of $40\,\mu g\,cm^{-2}$ was obtained. The electrodes were positioned on both sides of a Nafion® XL membrane (Quintech) and hot-pressed at $60\,°C$ and 10 bar for 3 min. The assembly was mounted in a home-built two-compartment photoelectrochemical cell described in earlier work [13]. The anode and cathode were fed with a water-saturated nitrogen gas stream at $20\,ml\,min^{-1}$. Before measurement, the cell was equilibrated overnight with both compartments fed with saturated nitrogen at $20\,ml\,min^{-1}$. The cell was illuminated by a Xe lamp with IR filter ($100\,mW\,cm^{-2}$, Oriel 66984, Newport) and currents were recorded using a potentiostat (Versastat 4, Princeton Applied Research).

3. Results and discussion

3.1. Film characterization

Film buildup was monitored by transmission spectroscopy at 300 nm (Fig. 1). At this wavelength, PSS does not absorb radiation so only the amount of TiO_2 is measured [2]. Film thickness was measured for some samples using ellipsometry. A linear trend is indicative of proper LbL deposition. In Fig. 1, film growth is shown for deposition times of 6 min and 9 min for PSS and TiO_2, respectively (referred to as $(6/9)_x$, x being the number of layer pairs). The inset shows the absorbance increase per layer pair for films with different deposition times. After an initial, fast adsorption step of species from solution, film growth decelerates limited by diffusion from the solution to the film surface. During the second phase, the adsorbed components may arrange into a more ordered structure, until saturation of the surface is reached [14–16].

The LbL films' microstructure was "fuzzy" instead of layered (Figs. 2 and 3). Similar observations were reported by other authors [2,9,10]. Interestingly, Fig. 3 shows island growth at short deposition times. This indicates that PSS and consequently TiO_2 are not homogeneously distributed over the surface. Considering only the first layer pair, island growth is also observed at longer deposition times (Fig. S2). This is believed to be responsible for a hierarchical