



Probing titanate nanowire surface acidity through methylene blue adsorption in colloidal suspension and on thin films



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ABSTRACT

The interaction of the cationic dye methylene blue (MB) with titanate nanowires (TiONWs) was investigated in different pH environments using visible spectroscopy and electrophoresis on thin films as well as in aqueous suspension. The surface charge of the TiONWs depends on the pH and ionic strength leading to positive charge under acidic and negative under alkaline conditions. The TiONWs have the same adsorption capacity on films and in suspensions at neutral pH while under alkaline conditions they are able to adsorb significantly more MB in suspension due to their higher surface area. Detailed adsorption studies in water revealed that dye cations form monomers, dimers and larger aggregates of H-type (face-to-face) on the TiONW films. The results indicate that below pH = 4.0 the TiONWs' external surface consists of Brønsted acid sites capable of protonating MB. It was suggested that reversible indicator role of MB molecule dimers probes the TiONW surface acidity (Brønsted sites).

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1. Introduction

Surface chemistry (e.g., acido-basicity) on various heterogeneous systems has actively been investigated because it determines fundamental chemical reactions in all types of catalysis including photocatalysis. Nowadays, in harmony with the aim to broaden the utilization of solar energy, a new class of hybrid organic–inorganic photofunctional materials was synthesized for environmental applications such as renewable energy and environmental purification. The main challenge when preparing these photofunctional materials is how to arrange molecular assemblies on multiphase media to optimize photochemical and photophysical processes, e.g., light harvesting and/or ROS (reactive oxygen species) formation in the system [1–5].

Methylene blue (MB) is a cationic phenothiazine compound widely used as a redox indicator in analytical chemistry. Additionally, it plays an important role as a sensitizer in solar energy conversion and as a test molecule in photocatalysis [6–10] as well as being used extensively as model substrate for adsorption studies on various surfaces [11–14]. In aqueous solutions the molecule has a deep blue color in its oxidized state (MB) with a maximum absorption at light wavelengths of 609 and 668 nm. Conversely, its reduced form (leucoMB) is colorless, hence does not absorb in the visible region. In equilibrium, these blue and colorless forms of the molecule form a reversible oxidation–reduction system

(electron donor–acceptor couple). Experimental observations pointed out that the visible absorption spectra of aqueous MB solutions do not obey the Beer's law. The violation of Beer's law has been ascribed to concentration dependent MB molecular aggregation [15]. Thus, in diluted aqueous solutions the dye forms face-to-face (H-type) dimers, while with increasing dye concentration higher aggregates appear. Ultimately, the shapes of MB absorption spectra are influenced by the concentration of the dye, the dielectric constant of the solvent, pH and ionic strength of its surroundings, etc. Many other concentrated dye solutions, e.g., proflavine, show a comparable shift of the most prominent absorption band. This color change with no chemical change in the dye itself is generally called metachromasy [15,16]. It has been observed on chromotropic polyelectrolytes and in the staining of biological tissues. In routine histology the preferentially adsorbed dye molecules are so closely packed, e.g., on DNA, that they show an aggregate like spectrum. Similar effects can also occur upon dye adsorption onto inorganic solids. The latter has been shown in our previous work. We reported on the reversible dimerization of methylene blue (MB) on titanate nanowires. The self-organizational properties of MB on the surface of this nanostructured material studied by spectroscopic means revealed that the light absorption properties of the MB molecules were humidity dependent. Based on the observed humidity dependent metachromasy, a MB-titanate nanowire coated optical fiber humidity sensor was fabricated which is adapted for medical, industrial or environmental applications [17]. We have also revealed that several other functional dye molecules adsorbed onto the titanate nanowire surface display similar

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aggregation dependent spectral changes. Thus, in order to develop favorable coatings for light harvesting, it is very important to identify the physical state of the adsorbed photosensitive molecules. The interactions of the oxide surface with organic molecules are often governed by acid–base interactions.

Interaction of MB with titanate derivatives such as nanotubes [12], nanobelts [18] and nanoflowers [14] as well as with other composite materials [7,8,19–21] has been extensively investigated due to the fact that the MB concentration can be easily followed spectrophotometrically and the adsorption properties can be quantified by measuring the MB concentration before and after the adsorption process. The aims of these investigations were testing either the photocatalytic activity of the titanate derivatives or the determination of the adsorption capacity [14,22,23]. Photocatalysis occurs upon radiation with light of an appropriate wavelength and the adsorption step is critical in this process. Numerous quantitative studies of MB adsorption have been released in the past to describe the mechanism, to determine the adsorbed amount and to suggest a relation between structural properties and interaction forces. In many cases, Langmuir and Freundlich type isotherms were assumed to describe the adsorption isotherms and the maximum adsorbed amount varied from 30 to 300 mg MB adsorbed on unit mass of the materials depending on the experimental conditions applied [12–14]. The majority of these studies assume electrostatic interactions between the materials and MB, but other secondary interactions were also assumed. Surprisingly, there is a lack of investigations dealing with the effect of MB speciation on the absorbance spectra during the experiments, nevertheless, this significantly affects the quantitative determination of the MB concentration spectrophotometrically by following the development of the characteristic bands in the region of 609–668 nm.

In the present work, the adsorption and aggregation behavior of a cationic dye (MB) onto acid and base surface pre-treated titanate nanowire (TiONW) based thin films as well as TiONWs in aqueous dispersions at different pHs were investigated by different methods. The formation of MB aggregates on the film surface was also considered and taken into account. Accordingly, this study aims to compare adsorption properties and surface charge characteristics of TiONWs deposited on a substrate and in their aqueous dispersion.

2. Materials and methods

2.1. Materials

Titanium dioxide (anatase, TiO_2), sodium hydroxide (NaOH), ammonium hydroxide (NH_4OH), methylene blue (MB) and hydrochloric acid (HCl) pure grade, were obtained from Sigma–Aldrich (Sigma–Aldrich, Steinheim, Germany) and were used without further purification. Standard pH buffer solutions were obtained from Metrohm (Herisau, Switzerland) for pH adjustments and for the calibration of the combined glass electrode purchased from the same company. Microscopic glass slides for film preparation were purchased from Menzel GmbH & Co KG (Braunschweig, Germany).

2.2. Preparation of protonated titanate nanowires and their suspension

Protonated titanate nanowires (TiONWs) were prepared by a two-step hydrothermal process. The details about the typical synthesis procedure are given elsewhere [24]. For the fabrication of the nanowire suspension, TiONW powder (2.4 g) is dispersed in 100 mL of 2-propanol (Merck, Darmstadt, Germany), and the mixture is homogenized with an ultrasonic tip (Bandelin Sonopuls,

Microtip MS73) purchased from Sigma–Aldrich (Steinheim, Germany) at 10% amplitude for 30 min. Identical procedure was used to prepare nanowire suspension in deionized water. The concentration of the stock solution was 10 mg mL^{-1} .

Thin films were fabricated on the microscopic glass substrates. The TiONW dispersion of 24 mg mL^{-1} in 2-propanol was doctor bladed using a $40 \mu\text{m}$ spacer (3 M) to obtain the desired film thickness of $2.5 \mu\text{m}$. Once deposited onto glass slides, the samples were heat treated at $150 \text{ }^\circ\text{C}$ in air for 2 h in order to evacuate the solvent.

2.3. Surface treatment

Acido-base properties of the protonated TiONW based thin films were modified by using NH_4OH ($\text{pH} = 12$) and HCl ($\text{pH} = 1$) solutions in water. The substrates were immersed into 10 mL solutions of the given pH for 1 h at room temperature. To eliminate the contribution of the weakly adsorbed and/or ion-exchanged protons, the films were rinsed five times with deionised water so that any unadsorbed labile protons were removed from the pores and from the surface of the nanowires.

2.4. Transmission and scanning electron microscopy

SEM secondary electron (SE) images were taken on a Philips XLF-30 FEG scanning electron microscope. Transmission electron microscope (TEM) images were taken on a Philips/FEI CM12 electron microscope.

2.5. UV–VIS spectroscopy

All adsorption spectra were recorded using a CARY 50 UV–VIS spectrophotometer in the wavelength range of 500–850 nm. Matched quartz cuvettes of 0.5 cm path length were used. The MB solution concentration was chosen such that the absorbance values did not exceed 1.5. All the measurements reported in this work were carried out at $25 \pm 1 \text{ }^\circ\text{C}$. The cationic dye (MB) was used without further purification, hence its spectrum in water had a similar shape to that reported in the literature with $\lambda_{\text{max}} = (664 \pm 1) \text{ nm}$. For the qualitative adsorption kinetics, $0.5 \times 2 \text{ cm}$ pieces of glass substrates holding $2.5 \mu\text{m}$ thick films of protonated TiONWs were placed into the cuvettes so that the light passed through the film. Subsequently 1.5 mL of 20 mg/L MB solution was added and the spectra were recorded at 60 min time intervals for 24 h. The residual MB concentrations in the supernatant solutions were determined. The amount of MB adsorbed onto TiONWs was calculated by the difference between the initial MB concentration and the residual concentration.

The obtained samples were first thoroughly rinsed with distilled water to remove non-adsorbed MB and then dried at $100 \text{ }^\circ\text{C}$ for 1 h to obtain the MB–TiONW nanocomposite. In order to determine the MB spectral changes as a function of the TiONW surface acidity, the MB–TiONW samples were subjected to solutions having pH of 1, 4, 7, 9 and 12, respectively. After rinsing the films carefully, the spectra were also recorded in deionised water.

2.6. Electrophoretic and size measurements

Electrophoretic mobility and hydrodynamic radius measurements were performed with a ZetaNano ZS (Malvern Instruments, Worcestershire, UK) instrument equipped with a He/Ne laser operating at 633 nm as a light source and an avalanche photodiode as a detector. The device applies an electric field strength of 4 kV/m in the electrophoretic mode. The size measurements were carried out at a scattering angle of 173° . In general, the hydrodynamic radii were calculated from the average of 5 individual measurements

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