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Title: Photocatalytic water purification with ZnO thin films in demineralised as well as natural waters

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Abstract

ZnO films prepared on glass plates using a water based coating solution are characterized and tested for methylene blue dye photocatalytic decolourisation in various types of waters (demineralised water, sea- and lake-water). The influence of various parameters such as wavelength and attenuation of incident radiation by dye and/or organic matter is studied. In demineralised water, up to 90% decoloration was achieved within 1h with 365 nm irradiation on a 10 ml. Although the ZnO films still show some activity when illuminated by standard visible light lamps, the efficiency of the photocatalytic process is greatly reduced. Natural waters result in a significant decrease of the photocatalytic activity, under both UV and visible light irradiation. The main factor is believed to be enhanced UV light absorption within the liquid. The influence of organic and mineral matter in natural waters is briefly discussed.

1. Introduction

The increasing contribution of emerging pollutants to water quality degradation is becoming a matter of serious concern. For example, the recent UNESCO report on the discharge of pharmaceutical products in the aquatic environment of the Baltic Sea region reveals the presence of more than 100 pharmaceuticals that are not efficiently removed from wastewater by municipal wastewater treatment plants.^[1] This results in an annual release of about 1.8 thousand tons of pharmaceuticals in the environment every year just in this restricted area of the world. Among several new treatments, which are under development in order to mitigate this worrisome situation, the mineralization of pollutant molecules by means of photocatalysis appears as a promising solution. In this type of processes, an electron-hole pair is created in a semiconducting material upon irradiation with ultraviolet (UV) or visible light. Both charge carriers can interact directly or indirectly with pollutant molecules adsorbed on the surface of the semiconductor, splitting these molecules into smaller fragments and hopefully ending with harmless compounds. Zinc oxide (ZnO) is an interesting semiconducting material for photocatalytic water purification and has been the subject of many studies.^[2-7] Although its large scale use still suffers from important limitations such as limited efficiency under visible light due to a band gap of about 3.2 - 3.4 eV and photocorrosion^[8-11], recent developments have demonstrated that ZnO nanoparticles have a tremendous potential for water purification applications using a photocatalytic approach, which is simpler than a photoelectrocatalytic process^[12-14]. Furthermore, ZnO has the benefits of being cheap and mechanically stable. For

environmental applications however, the use of nanoparticles is not the optimal solution, since the particles need to be reclaimed from the treated water after use and ZnO nanoparticles are not without dangers for ecological receptors^[15-18] although it is often claimed that ZnO is non-toxic. Thin films would be more appropriate, because the photocatalytic material remains fixed and can be removed by redrawing the film from the treated water. The photocatalytic activity of ZnO thin films has been less studied than that of nanoparticles, although some research teams have already reported results on the photocatalytic degradation of a variety of dyes such as malachite green, reactive black, orange II, rhodamine B, rose bengal and methylene blue on ZnO films [19-23]. These studies are usually performed using pure-water-based dye solutions. However, to tackle the problem of environmental pollution and its remediation, studies of photocatalytic degradation of dyes in natural waters are also needed. The purpose and novelty of the present work is to obtain preliminary data for assessing the influence of the latter on the efficiency of ZnO films, using the industrial dye methylene blue trihydrate as a case study.

2. Results and discussion

2.1 Films characterization

Figure 1 shows the thermogravimetric (TG) trace recorded upon heating a 9.3 mg sample of dried precursor solution consisting initially of a solution of zinc acetate and polyvinyl alcohol (PVA) in deionized water. It shows a first, sharp mass loss between 200°C and 250°C, which amounts to about 50% of the starting sample mass. It is followed by a slower mass loss that is finished at 480°C with a total mass loss of 72% (i.e. $\approx 22\%$ for the second mass loss). These two temperature ranges correspond well to those reported for the thermal decomposition of Zn-acetate^[24] and PVA^[25] respectively. Furthermore, the theoretical mass loss values are expected in the intervals 43% - 52% for Zn acetate and 20% - 23% for PVA depending on the degree of hydration of Zn-acetate in the powder. These values are in good agreement with the observed mass losses. The fact that ZnO forms within the PVA matrix prior to the disappearance of the latter at higher temperature is expected to be favorable for limiting the grain growth of ZnO.

Figure 1. TG measurement of the dried precursor solution in air (heating rate: 5 °C/min).

The XRD pattern of a ZnO film deposited on a glass plate and after heat treatment at 600°C is shown in the inset of **Figure 2b**. There is an amorphous background coming from the glass substrate but diffraction peaks corresponding to ZnO (hexagonal, wurtzite form) are clearly seen. For random crystallite orientation, the peak appearing at $2\theta = 36.1^\circ$ (Miller indices (101)) would have about twice the intensity of those at 31.6° (100) and 34.3° (002). Therefore it can be concluded that some preferential orientation is present in the ZnO films, although only to a rather limited extent. The full width at half maximum of these three peaks can be used for estimating the ZnO grain size D based on the Scherrer equation:

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

Where λ is the wavelength of the incident CuK α radiation (1.54 Å), θ is the full width at half maximum of the diffraction peaks expressed in radians after subtraction of the instrumental line broadening determined using Si standard powders and ϑ is the Bragg angle of the diffraction peak. The average result

is 140 ± 20 nm. The films heated to 600°C indeed show a fine microstructure with particles around 100 – 300 nm size as revealed in the SEM picture presented in **Figure 2b**.

The UV-Vis absorption spectrum of a ZnO film deposited on glass (Figure 2a), shows an absorption threshold close to 400 nm, with an absorption peak around 370 nm, as usually reported for ZnO.^[26-32] Using a tauc plot (inset in Fig.2a), a band gap of 3.21 ± 0.05 eV was found, a value in agreement with previously published data for ZnO films.^[12,13]

Figure 2. (a) UV-Vis absorption spectrum of a ZnO film on glass (inset: tauc plot indicating a band gap of 3.21 eV). (b) SEM image (backscattering mode) of a ZnO film showing grains with diameters lower than 200 nm (inset: XRD pattern of the film. The reflections correspond to ZnO and reveal a partial texture).

2.2 Photocatalytic decolorization of methylene blue solutions

Figure 3a illustrates the decolorization of methylene blue solutions in deionized water versus time under UV irradiation with two different wavelengths, i.e. 311 nm and 365 nm and three different volumes of liquid while the surface area of the ZnO film was fixed at 19 cm^2 for all experiments. Whereas the wavelength of the incident radiation has no influence on the decolorization rate, decreasing the volume of the methylene blue solution results in a clear acceleration of the process. This is most likely a result of the increased ratio between film surface area and solution volume rather than an effect due to UV absorption by the solution itself. In fact, although the liquid height varies from 2.5 mm for 10 ml solution to 10 mm for 40 ml, no changes in the intensity of the incident UV radiation is taking place. The latter ($950 \pm 10\text{ }[\mu\text{Wcm}^{-2}]$) is estimated by placing the radiometer below the liquid holder and progressively adding more solution. No intensity decrease within the measuring accuracy of the measuring instrument is observed up to the maximum tested liquid height (12.5 mm, corresponding to 50 ml solution).

Figure 3. (a) Methylene blue decolorization in deionized water solutions under irradiation with two different UV wavelengths. (b) Methylene blue decolorization under two standard Philips TL/35 light bulbs (emission spectrum based on supplier's data in the inset – 2000 Lux intensity at liquid surface) as well as results of measurements in the dark.

Figure 3b shows the results of decolorization experiments conducted using a standard TL/35 Philips lamp, whose emission spectrum, redrawn from the supplier's data is shown in the inset of Figure 3b. The decolorization speed is obviously much reduced compared with irradiation with the UV source. Comparison with measurements performed without ZnO films but otherwise similar conditions (photolysis) shows a measurable albeit weak decolorization effect. Nevertheless, the ZnO films clearly accelerate the degradation effect. Contrary to the case of UV irradiation, the intensity of the visible light reaching the ZnO film is greatly reduced by absorption taking place in the methylene blue solution. The attenuation rate amounts to 85 Lux (4.2%) per mm of liquid lying above the film. There is however some measurable UV irradiation coming from the lamps corresponding to a power density of $3.5 \mu\text{W cm}^{-2}$ that is not affected by the presence of the methylene blue solution. It can be assumed that the observed decolorization of the solutions is mostly due to this weak UV contribution since the band gap of the ZnO films ($\approx 3.2 \text{ eV}$) corresponds to a wavelength of 387 nm so that only a tiny amount of the radiation can be harvested.

Figure 4 demonstrates the effect of changing from deionized water to natural sea water on the decolorization speed of methylene blue solutions under UV irradiation. Obviously, the decrease of methylene blue absorbance level takes place at a remarkably slower pace in the present case. Using lake water instead of sea water yields similar results, which are therefore not shown here. Measurements conducted without ZnO films even show a monotonic increase of the absorbance during the 6.5 h runs. This effect can be attributed to slow evaporation H_2O under the effect of UV irradiation, which results in a progressive increase of the methylene blue concentration in the solutions. Considering the fact that the pH of natural waters (8.2 in the present cases) is much higher than that of deionized water (5.5), the significantly slower decolorization rate may appear surprising. Indeed, previous reports demonstrated that increasing the pH of methylene blue solutions by addition of NaOH results in an increased decolorization rate with optimum around 8-11.^[23,31,32] This effect is related to the fact that methylene blue

is a cationic dye so that its adsorption on the surface of ZnO (point of zero charge between 8.9 and 10.2)^[34-36] is favored at high pH where the surface of ZnO becomes less positively or even negatively charged.

Figure 4. Methylene blue decolorization under irradiation with a 365 nm UV source. The solvent consisted of sea water collected in the Baltic Sea near the city of Roskilde in Denmark (pH = 8.2). The water was used either as collected or after boiling. Data for experiments with fresh sea water without ZnO films (photolysis) are also included. Inset: intensity of the UV irradiation (365 nm) reaching the film, versus the distance between the film and the water surface.

However, an additional effect plays an important role in natural waters: the absorbance in the near UV range is much higher than for deionized water. This is illustrated in **Figure 5**, where the UV-Vis absorption spectrum of deionized H₂O is compared to the absorption of natural water samples of two different origins, i.e. collected in the Baltic Sea and in the Avnsø lake. This enhanced absorption, which results in a yellowish color, reduces the intensity of the UV irradiation reaching the ZnO film and thereby decreases the efficiency of the photocatalytic decolorization process.

Figure 5. UV-Vis absorbance of the three kinds of waters used for the photocatalytic decomposition of methylene blue trihydrate. For the natural waters (sea and lake), the dotted line represents the measurements performed after boiling. Inset: intensity of the UV irradiation (365 nm) reaching the film, versus the distance between the film and the water surface.

A sterilization treatment was applied by boiling the natural waters during one hour under reflux. This resulted in the decantation of at least a part of the microorganisms that deposited on the bottom of the glass beaker during cooling. Nevertheless, the yellowish color subsisted, with limited changes in the UV absorption of the waters under study and only a slight improvement of the decolorization rate of the methylene blue solution can be observed for the 10 ml and 20 ml solution volumes. For the 40 ml sample, a worsening is even observed. A possible explanation for this difference might be that sedimentation of dead microorganisms continues at a decreasing rate during several hours after boiling so that the ZnO films are progressively partially covered with inert matter that absorbs UV radiation and/or prevents methylene blue molecules of adsorbing on the surface of ZnO particles. This effect is expected to be enhanced with a larger solution volume or more specifically with an increase of the height of liquid lying above the ZnO film. This hypothesis however needs to be confirmed by further experiments. Other phenomena due to e.g. dissolved ionic species, Na^+ or Cl^- ions present in sea water, formation of a biofilm on the surface of the ZnO film, etc. may also be at play in natural waters and result in effects that are significantly different from those taking place in deionized water. These observations underscore the

importance of not restricting the study of photocatalytic pollutant degradation to solutions made with pure water, because natural water can result in significantly different effects.

3. Conclusion

Using nanostructured ZnO films deposited on glass substrates using a green chemical solution deposition technique, it is shown that decolorization of methylene blue solutions upon 365 nm UV irradiation is more efficient in deionized than natural water under similar conditions. Visible light only results in slow decolorization but using an incident wavelength shorter than 365 nm does not accelerate the process. The ratio of the film surface to liquid volume plays a critical role in the decolorization kinetics. With visible light irradiation, this is partly due to light attenuation by absorption in the solution, an effect that is not significant for 365 nm irradiation in deionized water. Natural waters instead show an enhanced absorption in the UV range. The significant difference of decolorization kinetics taking place when natural water is used can have various origins, which deserve further studies. This effect can have very important implications for the potential use of ZnO photocatalyst films if they are intended to be used for remediation actions in case of accidental spillage of emerging pollutants in the environment.

4. Experimental Section

4.1. Film preparation

For manufacturing the ZnO films 10 g Zn-acetate dihydrate (BDH Chemicals Ltd) are dissolved in 50 ml demineralized H₂O, followed by the addition of 2.5 g polyvinyl alcohol (PVA – Alfa Aesar, 98-99%, hydrolyzed, low molecular weight). The substrates consist of microscope glass slides (Brand GmbH) that are cleaned with ethanol and methanol prior to coating. Spin coating is performed with a VTC-100 instrument from MTI Corporation at a spinning rate of 2000 rpm during 30 s. The films (single coating) are first dried at 50°C on a hot plate for 10 min. Conversion to ZnO is conducted under oxygen flow in a tube furnace at 600±5°C during 0.5 h, with 2 °C/min heating rate and furnace cooling. After heat treatment, the amount of deposited ZnO amounts to 70 µg/cm².

4.2. Characterization

The precursor decomposition is investigated by simultaneous thermogravimetry and differential thermal analysis (TG-DTA) using a Netzsch 449 STA instrument at a heating rate of 2°C min⁻¹ under oxygen flow. The sample consists of powders obtained by slowly evaporating H₂O from a few ml of coating solution and drying it on a hot plate at 50 °C. The microstructure of the film is studied by scanning electron microscopy (Hitachi TM3000). It is further characterized by UV-Vis spectroscopy (VWR UV-3100PC) and X-ray diffraction (Bruker D8 with Cu Kα radiation).

4.3. Photocatalysis experiments

The dye solution is made using methylene blue trihydrate (C₁₆H₁₈ClN₃S·3H₂O from Alfa Aesar, assay 100.4% - anhydrous basis). The concentration of the solutions is 5 ppm, in either deionized water or surface water collected from the Baltic Sea in the Roskilde Fjord (55.69° North, 12.09° East) or in a lake (Avnsø) situated on the Sjælland island (55.57° North, 11.89° East). The irradiation source consists of either a UV lamp

(UVP, 8W from Analytic Jena, $\lambda = 365$ or 311 nm), or a pair of standard Philips TL/35 light tubes. The volume of the tested solution varies from 10 ml to 40 ml depending on the experimental protocol. It is placed in a polyethylene box with rectangular shape (50×70 mm² internal surface area dimensions) with the ZnO films (19 cm² area) placed in the bottom of the boxes. The surface of the liquid is located about 12 cm below the UV lamp or 70 cm below the TL/35 light tubes resulting in a power density at the liquid surface of 950 ± 10 $\mu\text{W cm}^{-2}$ for the UV lamp (as measured with a UVX radiometer from Analytik-Jena AG) and an illuminance of 2000 Lux (Traceable® Light meter) for the visible light irradiation. Magnetic stirring is applied during the experiments. The 1.5 ml of the solution are redrawn for UV-Vis absorption during the course of the experiments and poured back in their respective holders after measurements in order to avoid decreasing the volume of liquid. The decolorization of the solution is followed by plotting the intensity of the absorbance at 664 nm (maximum absorbance of methylene blue) versus irradiation time after normalizing with the intensity at $t = 0$. Prior to switching the lamps on, the solution is left in contact with the films in the holders during 1h to reduce the influence of adsorption effects on the solution decolorization. The experiments performed with the methylene blue solution in deionized water and UV irradiation were conducted 3 times in a row with the same films merely rinsed with deionized water in between. The results were reproducible within 5%.

Conflict of Interest

The author has no financial/commercial Conflict of Interest.

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