

**Photocatalytic properties of layered structures and
ultrathin films containing reactive nanoparticles**

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Introduction

Nowadays, nanotechnology is one of the most dynamically and most spectacularly developing field of the modern science which connects the fields of chemistry, physics and biology in many respect. As a result of the widespread research numerous chemical, physical, biological and medical problems can and could be solved. The main tendency of these research activities is the preparation and the characterization of nanostructured materials which requires wide colloid chemical skills. The so-called controlled colloid chemical synthesis methods like the sol-gel technique allow for preparing materials with well controlled particle size, high specific surface area and phases with various degree of crystallinity. Nanoparticles with small grain size and high surface energy can be prevented from spontaneous aggregation if they are immobilized on the inner and outer surfaces of the support material, furthermore, it is possible to prepare nanocomposite materials with high specific surface area. Due to their specific structure, nanoparticles and nanostructured materials have unusual electric, catalytic and optical properties which give them a great practical importance. The nanosized semiconductor materials can be applied efficiently in the conversion of solar energy to chemical energy; in addition they can oxidize organic molecules present in environmental pollutants. The heterogeneous photocatalysis as one of the highly efficient oxidizing techniques exploits the above mentioned properties of the semiconductor nanoparticles.

Many people in many ways have made an effort to solve the problem of the world-wide environmental pollution. The removal of the dissolved and non-biodegradable organic compounds from the wastewaters is impossible by using only the well-known industrial water purification procedures. These compounds can be mutagenous in the environment and sometimes bring about cancer in human. Researchers dealing with heterogeneous photocatalysis aim at removing the organic materials from the aqueous systems using the natural solar energy and the photocatalytically active materials prepared under optimized conditions. Titanium dioxide as one of the possible photocatalyst material is highlighted due to its advantageous physical and chemical properties. Other transition metal oxides (e.g. ZnO, SnO₂, ZrO₂) were also characterized in photocatalytic experiments.

Layered double hydroxides (LDHs) as possible adsorbent-photocatalyst materials have received greater attention only recently. In spite of the fact that the LDHs have been well known for a long time they were used only in therapeutics and in the industry.

The LDHs can be synthesized easily using cheap precursors and depending on their composition and on the preparation conditions they can be used as photocatalysts which makes them more important; in addition they are harmless for the environment. The industrial application of the photocatalytic water treatment is cumbersome and up to now it wasn't successful because the recuperation and the regeneration of the suspended catalyst from the purified liquid is very expensive and difficult.

Using thin layers of the photocatalyst material the above mentioned problems can be avoided and the water treatment in a flow system may be realized with minimal loss of the active catalyst.

One of the aims of this work was the preparation of nanoporous anatase TiO₂ nanoparticles with high specific surface area and the subsequent immobilization of these particles on the lamellae of a layered silicate followed by the structural and photocatalytic characterization of the prepared nanocomposite materials.

Another objective was to clarify the influence of the support material on the optical and the photocatalytic properties of the nanocomposites together with studying the influence on the photocatalytic efficiency of parameters such as the semiconductor content of the nanocomposite, the suspension concentration, and the ionic strength.

The next objective involved the preparation of photocatalytically active LDHs containing zinc oxide phase and the study of the morphological properties and chemical composition of the samples prepared under different circumstances such as different temperature and aging time.

I tried to make multilayers with different layer thicknesses from LDHs or Degussa P25 TiO₂ by means of layer-by-layer immersion method and to monitor the layer buildup and the structure by independent analytical methods.

I compared the photocatalytic efficiency of the ultrathin layers prepared from different photocatalyst materials of different thicknesses with that of the suspended materials.

The ultimate goal was the preparation ultrathin layers which are mechanically and chemically stable, easily regenerable and reusable for photocatalytic degradations.

Experimental

Titanium dioxide sols prepared by the sol-gel technique and Nanomontmorillonite suspensions were used to prepare photocatalytically active layered nanocomposites by means of the heterocoagulation method. Layered double hydroxide samples were prepared by the so-called co-precipitation method in which an aluminum- and zinc salt mixed solution and a nitrate containing alkali solution were used. The temperature of the co-precipitation process as well as the aging time was controlled carefully during the preparations.

The photocatalytic efficiency of the nanocomposites and of the layered double hydroxides was tested by photooxidation of dichloroacetic acid and acridine orange dye, respectively. All of the starting materials of the experiments were analytical or reagent grade used without any further purification. High purity MilliPore MilliQ water was used as solvent and as medium in all experiments.

The crystal structure of the prepared samples was determined by XRD measurement and the nanostructure analysis was done by small angle X-ray scattering (SAXS).

For the morphological characterization of the samples transmission and scanning electron microscopy were applied.

The structure and the composition of the layered double hydroxides were determined by thermoanalytical (TG/DTA) measurements.

The real TiO_2 content of the TiO_2 /layered silicate nanocomposites was analyzed by ICP-OES measurements.

The optical properties of the catalysts were characterized by means of UV-Vis spectrometry.

The layer buildup of the ultrathin films made by the layer-by-layer immersion method from layered double hydroxides or the reference Degussa P25 TiO_2 was monitored using UV-Vis spectrometry and in some cases by AFM measurements.

Density determination in solid phase, streaming potential measurements and dynamic light scattering were used also for the characterization of the samples.

For the photocatalytical experiments a home made reactor equipped with a high-pressure Hg-arc lamp ($P = 400 \text{ W}$) and thermostatic pyrex glassware were used. UV-Vis spectroscopic measurements were carried out to monitor the change in the concentration of the dye molecules during the photooxidation.

The photocatalytic oxidation of dichloroacetic acid (DCA) using TiO_2 containing nanocomposites was followed by pH-stat titration technique. The pH of the irradiated catalyst suspension was monitored real-time in the flow system using an external measurement cell equipped with a combined pH-electrode. Due to the photooxidation of the model pollutant the amount of the evolved protons was measured by pH-metry and the compensation of the pH decrease. The constant pH was sustained by a home built pH-stat system.

Summary of the novel scientific results

I. Novel scientific results regarding the TiO_2 /layered silicate nanocomposites

1) Structural properties of the TiO_2 nanoparticles prepared by the sol-gel method

The TiO_2 nanoparticles with diameter of 80-90 nm prepared by the hydrothermal sol-gel method are built up from the aggregates of small (4-5 nm) nanoparticles. The titanium dioxide is present exclusively as the anatase polymorph which was demonstrated by XRD measurement. The mean primary particle diameter calculated by the Scherrer equation was 4.7 nm. The sample is porous which was proven by XRD studies, small angle X-ray scattering and nitrogen adsorption. The specific surface area of this sample was found to be $260 \text{ m}^2/\text{g}$ and the mean pore diameter in the sample aggregates is 3.4 nm. It can be concluded that the nanoparticles prepared by the sol-gel method are aggregates and its constituents are responsible for the optical property of the TiO_2 . The adsorption threshold determined by UV-Vis spectrometry of the nanoporous TiO_2 with high surface area is $\lambda_g = 397 \text{ nm}$ which is equivalent with $E_g = 3.12 \text{ eV}$.

2) Statements concerning about the structure of the TiO₂/layered silicate nanocomposites

During the heterocoagulation process between the montmorillonite and TiO₂ particles the bigger particle aggregates in the sol are disaggregating on the exfoliated silicate lamellae due to its electrostatic field as a result of the formation of the pillared clay in which the average pillar height is about 3 nm. The low temperature nitrogen adsorption measurement showed the composite samples are porous and the calculated specific surface areas fall into the 120-290 m²/g range. Each isotherm showed capillary condensation which is characteristic of the porous adsorbent. It was proved that more and more pores with the same size are forming with increasing the TiO₂ content in the nanocomposites. The results showed also the strong acidic (pH = 1) synthesis medium changes the chemical composition and the crystallinity of the layered silicate support resulting in the nanocomposite samples with higher specific surface area and more microporous structure.

3) Relation between the structure and the optical properties of the nanocomposites

In the case of 20, 33, 50% TiO₂ containing nanocomposites which were prepared from pH = 4 TiO₂ sol the excitation band gap energy determined from the UV-Vis absorbance spectra are higher than that of the nanocomposites prepared from the pH = 1 sol. Presumably the valence band and the conduction band in the intercalated particle between lamellae with negative charge excess are going to be perturbed therefore the recombination of the exciton (electron-hole pair) is hindered. In highly acidic medium (pH = 1) the aluminum(III) containing octahedron layer dissolves therefore the chemical composition and the crystallinity of the lamellae decrease, so the above mentioned recombination hindering phenomenon can not occur dominantly and therefore the composite samples containing less TiO₂ from the latter series are more excitable. In the case of 66 and 75 % TiO₂-containing composites the so-called quantum size effect is more dominant than the recombination hindering effect of the lamellae. It means increasing the particle size the band gap energy is decreasing so the magnitude of the E_g is going to be determined by the size of the intercalated TiO₂ particles. Since the calculated particle size in the case of TiO₂ /MA series is smaller than that of the TiO₂ /M series, the determined band gap energy is smaller in the latter case.

4) Photodegradation of dichloroacetic acid (DCA) using TiO₂/montmorillonite composites

It was found that the amount of the produced protons specified to 1g of the catalyst after one hour irradiation period increases – in accordance with the literature – with the TiO₂ content of the nanocomposites. The amount of produced proton specified to the pure TiO₂ content of the nanocomposites is higher in the case of TiO₂ 66/M and TiO₂ 75/M than that of the sol-gel TiO₂ although the values are lower in the case of TiO₂ 20/M and TiO₂ 33/M. The photocatalytic efficiency of the TiO₂ /MA series is lower than that of the TiO₂ /M series in all cases although the latter series has lower specific surface area. It means that the original montmorillonite support qualifies as a recombination hindering agent in the particles and not as an adsorbent because it was not possible to determine the adsorption of the DCA⁻ anions on the negatively charged silicate lamellae within the analytical accuracy.

5a) Effect of dichloroacetic acid adsorption and the electrolyte concentration on the photocatalysis

Increasing the concentration of the inert (KNO₃) electrolyte the photocatalytic efficiency decreases. The reason for this is the competition between the DCA⁻ species and the NO₃⁻ ions in the adsorption layer of the particle surface. The KNO₃ electrolyte influences the colloid stability as well as the adsorption process of the TiO₂ particles.

5b) Effect of the suspension concentration on the photocatalytic efficiency

To demonstrate that the light scattering decreases the photocatalytic efficiency, independent photodegradation experiments were preformed using the sol-gel TiO₂ of different suspension concentrations. This concentration was optimized. According to my experiments the turbidity and the light transmission of the suspension affect together the photocatalytic efficiency. In the region of low suspension concentrations (0.005%-0.047%) the turbidity is low and the light transmission is relatively high and increasing the concentration of the suspension the efficiency increases. In the region of higher suspension concentrations (0.057-0.072%) the turbidity increases and the light transmission dramatically decreases (~ 5-7%, thus the catalytic efficiency gradually decreases because less photons can effectively excite the suspended particles.

6) Effect of the support on the photocatalytic efficiency

It was shown in the case of the TiO_2 /M series that the support has a disadvantageous effect in case of lower TiO_2 content but it has a synergic effect if the TiO_2 content is higher. The photocatalytic efficiency of the support and the pure TiO_2 was determined and the theoretical degradation results were calculated related to the different TiO_2 containing nanocomposites. The comparison of the theoretical values with the measured data showed that the 20 and 33 % TiO_2 containing nanocomposites were less effective because of the shielding effect of the lamellae and the higher E_g values of these nanocomposites. In the region of higher TiO_2 content in the composites the relative amount of the montmorillonite is less. Therefore, the shading effect could be smaller and presumably the quantum size effect and the recombination hindering effect of the lamellae become dominant. It can be stated in the case of TiO_2 50/M sample that the two effects (shading and recombination hindering) equalize each other and the same photodegradation efficiency was determined as the theoretical value. In the case of the TiO_2 /MA series the support lamellae become amorphous resulting in the decrease in its charge density and ion exchange capacity so they can not influence the recombination hindering. Of course these lamellae also exhibit the shading effect therefore the TiO_2 /MA series provide lower photocatalytic efficiency than the TiO_2 /M series.

II. Results related to the ultrathin films

7. Self-assembled, nanostructured films: preparation and structure

The build-up of ultrathin self-assembled films consisting of alternating nanoparticulate multilayers of 3:1 ZnAl LDH (permanent surface charge) and TiO_2 and SiO_2 (conditional surface charge) by X-ray diffraction, UV-visible spectrometry and atomic force microscopy. It was found that the amount of material accumulated over the surface of the substrate (microscope slide) owing to electrostatic attractions was proportional to the number of immersion cycles. In case of the films built up from layer double hydroxides, an evidence was found for the island-like deposition of the LDH lamellae. In the course of the successive immersion steps both the surface coverage and the thickness of the deposited layer increase. The surface concentration of the film-forming materials and the layer thicknesses have been determined by indirect (UV-visible) and direct (AFM) methods and they were found to be in good agreement in case of 100% coverage.

The same conclusions have been established for the TiO_2 and $\text{TiO}_2/\text{SiO}_2$ films, but in this case the data of surface concentration and layer thickness were only determined by the indirect method of spectrometry.

8. Photocatalytic degradations with TiO_2 films

a) Photocatalytic results of TiO_2 layers and suspensions

Photocatalytic experiments applying ultrathin films consisting of bare titanium dioxide ($d = 20\text{-}80$ nm) have shown that these films can be efficiently applied for the photooxidative decomposition of organic dyes. The catalytic efficiency increases with the number of layers (thus, the amount of particles) deposited on the glass surface by electrostatic forces. Based on data of mass measurements of three catalyst films prepared by ten immersion cycles with otherwise identical conditions and it was evidenced that, by fixation of the same amount of TiO_2 in thin films, a 15-20% higher photocatalytic activity could be achieved as compared to the case when the solid is suspended in the reactor. The reason for this is that the amount of photons adsorbed by the TiO_2 particles is small in the suspension-type photocatalytic system due to the high dilution (0.0054 mg/cm^3) compared to the extinction of titanium dioxide deposited with surface concentration of 0.0222 mg/cm^2 (for films prepared with 10 immersion cycles). The particles adhere in the film forming thus a uniform layer structure, via which, according to the experimental results, the effectiveness of the light penetrating in the reaction chamber is greater resulting in a concomitant higher efficiency for the decomposition of dyes.

b) Photocatalytic results of combined $\text{TiO}_2/\text{SiO}_2$ layers

Films of bare TiO_2 and mixed $\text{TiO}_2/\text{SiO}_2$ films containing the same amount of TiO_2 layers showed the same catalytic activity. Application of silica particles as sticking material opens a way towards the fabrication of UV resistant films since the binding component does not suffer photochemical degradation upon irradiation. Silica particles do not alter significantly the optical properties of the films, but they improve the adsorption of the model compound due to electrostatic reasons: the adsorption of positively charged dye molecules is preferred on the negative SiO_2 surfaces at the pH of the solutions used for the photocatalytic experiments

9. Photocatalytic investigations of nanofilms containing 3:1 ZnAl layer double hydroxides

My goal was to synthesize a ZnAl LDH sample which exhibits photocatalytic activity owing to the presence of a ZnO phase. According to the UV-visible spectra of the suspensions prepared from such samples, a radiation of $\lambda_g = 405$ nm is capable of exciting the semiconductor particles. The photocatalytic efficiency of the ultrathin layers prepared from the LDH of 3:1 Zn:Al molar ratio and the reference Degussa P25 titanium dioxide was tested via degradation of an organic dye, acridine orange. It was established that the catalytic activity of the layer double hydroxides after the three hours illumination time was higher than those of the ultrathin Degussa P25 TiO₂ films.

Potential practical applications of the results

10. Regenerability and reusability of the films

The regenerability and reusability of the ultrathin films self-assembled from Degussa P25 TiO₂ were investigated as well. The experiments showed that the catalyst films containing titanium dioxide could be simply and efficiently regenerated because the multilayers did not exhibit a significant loss of photocatalytic activity. This increases the importance of the application of film catalysts as a higher photocatalytic efficiency can be achieved by immobilization on a substrate surface as compared to that in dispersed state. Furthermore, the films are reusable and can be easily separated from the reaction vessel while it is rather hard and, in industrial dimensions, very expensive to recover the catalyst materials in their original state from suspensions.

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