Abstract

Nanosized TiO_2 exhibits great potential for use in many areas, such as air purification, water cleaning, photovoltaics, water splitting, and self-cleaning surfaces. However, its potential is reduced by the wide band gap, which limits the TiO_2 light-absorption capabilities, rendering it photocatalytically active only under UV and near-UV irradiation. Recently, research efforts have been put into developing TiO_2 featuring a narrower band gap, capable of absorbing visible light as well as UV light. To efficiently utilize TiO_2, we must know how the fundamental properties (morphological, surface, and optical properties) affect its functional properties. Furthermore, it is essential to research how the synthesis parameters define the fundamental and, in turn, the functional properties of TiO_2.

The goal of my work was to i) synthesize the most active photocatalyst for visible and/or UV irradiation, ii) to find out how the fundamental properties of TiO_2 affect its functional properties, and iii) to tailor the desired photocatalyst via selected synthesis parameters. In order to do this I chose two synthesis procedures: a) precipitation of hydrated TiO_2 from a $TiOSO_4$ solution and using a hydrothermal treatment for the crystallization, b) sol-gel synthesis via the hydrolization of titanium tetra-isopropoxide and heating at high temperature for crystallization. In order to promote the visible-light activity, I doped my samples with selected elements, i.e., N, Fe, Mn, Ce, La, Gd, Cu, and Cu+Zn. XRD was used to determine the structural properties of the samples, DRS for the optical properties, FTIR and Raman spectroscopy for the surface properties, electron microscopy (FE-SEM and HR-TEM) for the morphological analysis, XPS for the oxidation state of some elements of selected samples, and BET for the specific-surface-area determination. The photocatalytic activity was measured using three different methods: gas-solid isopropanol oxidation into acetone (VOC air purification simulation), NO_x abatement, and MB degradation in a liquid-solid system (water cleaning in a slurry reactor simulation). Furthermore, some of the samples were tested for their antibacterial properties against Gram-negative (*E.coli*) and Gram-positive (MRSA) bacteria.

Low pH values and the addition of isopropanol in an autoclave during the synthesis favoured rutile crystallization. Rutile showed the highest photocatalytic activity under simulated sunlight as well as under visible-light-only irradiation. The addition of some of the dopants (N, Fe, and Mn) had little to no effect on the structural properties of the synthesized products. Ce, La, and Gd, on the other hand, resulted in mixed-phase samples. Rutile crystallized in the form of elongated nanorods, while anatase and brookite formed smaller, spherical particles. Consequently, the specific surface area of the samples containing a larger proportion of rutile was smaller. Doping did not have the desired effect of promoting the photocatalytic activity. On the contrary, the most active sample was undoped, synthesized at low pH and with the addition of isopropanol, consisting of pure rutile.

The Cu+Zn-doped samples were prepared via sol-gel synthesis. In fact, the samples were not truly doped as the Cu and Zn formed respective oxides on the surface of the TiO_2, thus forming a hybrid material. Samples modified only with Zn exhibited a higher photocatalytic activity. Cu-modified samples, on the other hand, exhibited a strongly antimicrobial activity. The samples modified by both elements show no discernible trend, neither in their photocatalytic activity nor in their antimicrobial activity. The Cu-modified samples additionally exhibited a photochromic effect, caused by the transition between different copper oxidation states ($Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$). The photochromic effect was evaluated and quantified by DRS spectroscopy.

In the present work I managed to correlate the synthesis parameters with the fundamental properties of TiO_2 particles as well as the fundamental properties with the functional properties of the prepared photocatalyst. I was able to prepare an undoped photocatalyst that surpassed the performance of the industrial benchmark P25 under both simulated sunlight (1250 ppm/h vs. 900 ppm/h) and visible light (95 ppm/h vs. 40 ppm/h) irradiation.

Key words: TiO_2, synthesis, doping, photocatalysis, antibacterial activity, photochromism