

Dual-Phase Titanate/Anatase with Nitrogen Doping for Enhanced Degradation of Organic Dye under Visible Light

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The need for environmental remediation processes on a large scale is becoming ever more urgent, especially in anticipation of the increasing demand (and potential shortage) of potable water supplies for a growing world population. Among the armory of advanced oxidation technologies (AOTs), photocatalytic (solar-light-driven) processes are particularly attractive, and photocatalysts have a well-demonstrated potential to mineralize harmful organic substances in air and water and even to act as regenerable adsorbents for toxic heavy metal ions, some of these being recovered as photodeposited metals.^[1] Although anatase TiO₂ remains the most popular photocatalyst due to high catalytic activity and chemical stability, there are some drawbacks associated with it. The activity is confined to UV-light stimulation, representing just a few percent of the solar-power spectrum. In this respect, much research has been done in modifying the bandgap of the material to extend the absorption into the visible-light region.^[2] In addition, the adsorptive properties of TiO₂ are not ideal either.^[3] Since photoreactions take place at or near the catalyst surface, surface adsorption is critical for efficient interfacial charge transfer to and from the target molecules. In contrast, titanate materials have recently been identified as superior adsorbents for, for example, organic dyes and heavy metal ions.^[4] The crystal structure consists of layers of TiO₆ octahedra in edge connectivity with protons or alkali metal ions localized between the layers.^[5] Various one-dimensional structures, including nanotubes, wires, ribbons, and fibers have been obtained through high-alkalinity treatment of TiO₂ powders and ion ex-

change.^[6] However, these titanates have bandgaps reported to be even larger than that of anatase and thus remain solely UV-light responsive.^[7] From the photocatalytic standpoint, it would be highly beneficial to combine the high catalytic activity of TiO₂ with the superior adsorptive properties of titanates, while sensitizing both to visible light. Herein, we report a novel dual-phase anatase/protonated titanate photocatalyst that synergistically adsorbs and degrades methylene blue (MB) dye under visible light. The crystal structure of this nanocomposite is studied in depth in this report. Visible-light sensitivity is imparted through nitrogen doping and the synthesis is a simple one-pot process at low temperature.

The as-synthesized powders have a cubic morphology with a mean particle size of 20 nm (Figure S1 in the Supporting Information) and consist of two distinct phases mutually interdispersed on the 5 nm scale, as confirmed by TEM and XRD studies. Figure 1 shows a high-resolution

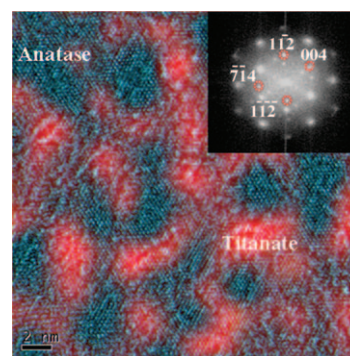


Figure 1. HRTEM image of the as-synthesized photocatalyst with two phases distinguishable by color. The inset shows the diffraction pattern obtained from the FFT study of the monoclinic titanate (weak spots) and tetragonal anatase phases (strong spots).

TEM (HRTEM) image of a single particle consisting of both anatase (cyan color) and titanate (red color) nanocrystallites that share intimate interfaces. A fast Fourier transformation (FFT) study of the entire area shows two sets of diffraction patterns (see inset of Figure 1). The strong spots are characteristic of tetragonal anatase TiO₂, whereas the weak spots are assumed to be derived from a protonated layered titanate phase. The structure has been predicted

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based on octahedral rearrangement of the related $A_2Ti_n(O)_{2n+1} \cdot xH_2O$ titanate structures ($A = Cs, H$) that were previously reported in conjunction with Rietveld refinement.^[5,8] We propose this titanate phase to have a monoclinic structure with water molecules intercalated between ribbons of edge- and corner-connected TiO_6 and TiO_5 polyhedra.

Figure 2A shows the XRD pattern of the as-synthesized material. The broad peaks are characteristic of nanosized crystallites, consistent with the TEM observation. The first

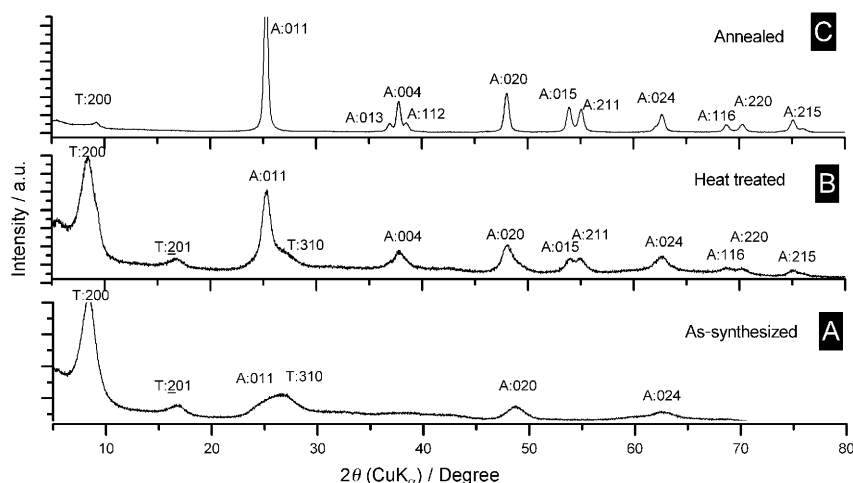


Figure 2. XRD profile of A) the as-synthesized dual-phase photocatalyst B) after vacuum-heat treatment and C) transformation into anatase after annealing. T denotes the titanate phase whereas A denotes the anatase phase.

two low-angle signals may be assigned as reflections from the (200) and (201) planes in the titanate structure. Because most titanates exhibit strong diffraction features for $2\theta = 8\text{--}16^\circ$, assignment of the crystal structure remains somewhat inconclusive. To the best of our knowledge, no other previously reported layered material exhibits the same low-angle reflections as those seen in Figure 2A. The remaining broad peaks belong to the nanocrystalline anatase phase. To validate this, the as-synthesized powders were pressed into pellets and vacuum sealed in a quartz tube. The pellets were then heated to 120°C for a week and ground into a powder. The XRD result of the heat-treated powder in Figure 2B shows the emergence of strong crystalline peaks from $2\theta = 25.28^\circ$ onwards; this matches known data of anatase titanium oxide well (PDF Card #21-1272). This indicates a growth in crystallinity of the anatase in the presence of a relatively unaffected titanate phase. Rietveld refinement was performed on the heat-treated sample by using the predicted crystal structure of titanate together with the known anatase data. After a series of refinements, we determined the titanate structure to be monoclinic ($C12/m1$ or $C2/m$) with the following lattice parameters: $a = 2.493(3)$ nm, $b = 0.3708(6)$ nm, $c = 1.026(1)$ nm, and $\beta = 123.1(1)^\circ$. The number of water molecules was determined by using moisture-loss calculations from a thermogravimetric analysis

(TGA). The final unit formula is proposed to be $H_2Ti_3O_7 \cdot xH_2O$. Figure 2C shows that calcination at 500°C eventually causes the layered titanate to transform into anatase TiO_2 .

A doping level of ≈ 3 at% nitrogen was typically found in the surface regions of the sample by X-ray photoelectron spectroscopy (Figure S2 in the Supporting Information). This imparted a distinct brownish tinge suggestive of absorption across the entire visible range. The UV/Vis diffuse reflectance spectrum (Figure 3) confirms that N-doping results in a broad absorption extending from the UV well into the near IR region. This seems generally consistent with independent reports of similar coloration attributed to N doping in either titanate or titania samples.^[9] Chen et al. reports O–Ti–N bonding with similar N 1s binding energy at 401.3 eV.^[2b] Our DFT calculations (not shown) also indicate bandgap narrowing by replacing O sites of Ti–O polyhedra in a titanate structure with N atoms. The exact N species found in TiO_2 remains debatable according to numerous reports. It is worth mentioning that the nature of nitrogen varies with the technique

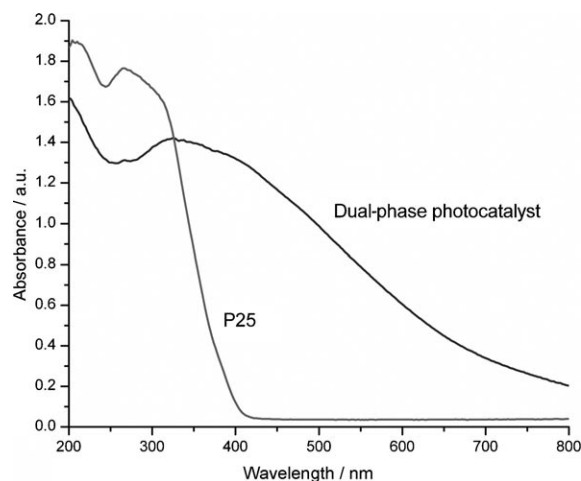


Figure 3. Diffuse reflectance UV/Vis absorption spectra of the as-synthesized dual-phase photocatalyst and the commercial P25 dye.

and precursors used. Herein, the unusually large interlayer spacing of the titanate phase does hint at retention of species somewhat bulkier than protons and associated water molecules. Since no clear evidence was seen by diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) for ammonium cations, the immediate bonding environment of

the N atoms remains uncertain at this stage. Nonetheless, the strong visible-light absorption is a powerful motivation for our ongoing investigations.

BET measurements reveal that the as-synthesized dual-phase material has a relatively high surface area of $\approx 180 \text{ m}^2 \text{ g}^{-1}$. This compares to a value of $\approx 50 \text{ m}^2 \text{ g}^{-1}$ for the commercial control sample (P25). Ostensibly, a high surface area should enhance the mass-specific adsorption properties of the dual-phase sample. However, the effect of surface area on photoactivity per se is not so predictable. There is a known trade-off between increasing dispersion and the associated increase in surface-defect density. Defects are known to promote electron/hole recombination.^[10]

The as-synthesized dual-phase material was found to be an active photocatalyst for degradation of MB under visible light. Figure 4 illustrates the change in concentration (C) of MB (normalized to the initial concentration (C_0)) with re-

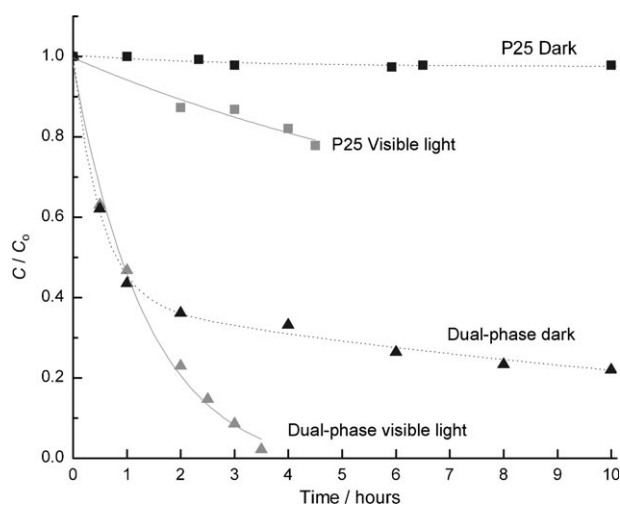


Figure 4. Change in concentration C/C_0 of MB (initial concentration $C_0 = 20$ ppm) over the dual-phase photocatalyst (compared with Degussa P25). The characteristic MB absorbance peak at 664 nm decreased with time. Solutions were tested both in the dark (dotted lines) and under visible-light irradiation by using a filter cutting wavelengths below 420 nm (solid lines).

spect to time. Experiments in the dark and under visible light were performed to distinguish the effects of adsorption from complete degradation. Whereas P25 shows little or no dark response, the MB level over the titanate/anatase nanocomposite dropped rapidly under the same conditions, eventually leveling out, suggestive of an adsorption isotherm (to saturation). Under direct visible-light irradiation, the initial adsorption process appears to dominate the kinetics for the first hour, after which the MB level drops quite rapidly to zero. The comparison between the dark and light experiment suggests genuine degradation of MB by the dual-phase material under visible light, enhanced by simultaneous adsorption, a clear pre-requisite for efficient charge transfer during photodegradation. To further elaborate on the mode(s) of MB breakdown, UV/Vis spectroscopy curves of

a dark-to-light experiment are included (Figure S5 in the Supporting Information). Following full adsorption to equilibrium over 16 h in the dark, the solution was then irradiated with visible light until MB completely disappeared. The MB absorption-band maximum at 664 nm clearly shifted to shorter wavelengths. This hypsochromic effect of irradiation on the MB supernatant in the presence of photocatalysts is well-known and has been attributed to N-demethylation upon dye breakdown.^[11] During the dark adsorption stage, no blue shift was evident. In contrast, the MB level dropped only slightly using P25 under the same irradiation conditions. This weak visible photoactivity is likely to be a consequence of direct photolytic breakdown of MB.^[12] Because no significant blue shift was observed in the MB absorption bands using P25 (UV/Vis spectroscopy curves are provided in Figure S6 in the Supplementary Information), the mechanism of degradation is evidently different. To highlight the visible-light activity, the dual-phase photocatalyst can also degrade phenol under visible light (Figure S7 in the Supporting Information).

In the case of Degussa P25 TiO_2 , in which anatase and rutile interfaces coexist, interesting synergies are seen, both in terms of cooperative surface-adsorptive properties in the thermal catalysis as well as enhanced spatial-charge separation in photocatalysis.^[13] These features underpin its value as a de facto standard. Similar effects may also be present in the novel dual-phase formulation studied herein, but such a statement remains mere speculation in the absence of suitable single-phase controls of corresponding texture. This will form the subject of a future investigation.

In conclusion, a N-doped dual-phase photocatalyst, consisting of interdispersed protonated titanate and anatase nanocrystallites, has been successfully synthesized in a simple one-pot process. We report the new titanate phase to be monoclinic ($C12/m1$ or $C2/m$) with the empirical formula: $\text{H}_2\text{Ti}_3\text{O}_7 \cdot x\text{H}_2\text{O}$. Our study has clearly highlighted the cooperative functioning between surface adsorption and photodegradation, which has not been paid much attention in previously reported dye-degradation studies. The newly synthesized dual-phase-photocatalyst surface shows unique affinity for dye adsorption, thereby facilitating efficient mineralization under UV and visible light due to sensitization by nitrogen doping. Based on these findings, other heterojunction semiconductor photocatalysts expressing such synergies can be designed and synthesized for improved visible-light activity in the future.

Experimental Section

Synthesis: Ethanol, acetylacetone (99.5%, Fluka), titanium isopropoxide (99.5%, Aldrich), triethylamine (99.5%, Aldrich), and deionized water were mixed thoroughly in molar proportions of 20:1:1:4:3. The solution was stirred for 30 min. The resulting clear yellow solution (50 mL) was measured into a 125 mL capacity stainless-steel autoclave. The autoclave was heated to 160 °C for 3 h and cooled to RT. The products were dried in an oven at 80 °C. The recovered powder was washed repeatedly with

ethanol and deionized water through centrifugation, to remove traces of organic waste, and finally redried at 80 °C.

Photoactivity measurements: Solutions of the MB dye (20 ppm) were prepared in deionized water. Photocatalyst powder (10 mg) was dispersed in the MB solution (100 mL). Reference-photocatalyst-powder Degussa P25 TiO₂ was tested under the same conditions, for comparison. During the experiment, the suspension was under constant stirring to ensure an aerobic environment for complete dye mineralization.^[2] Solutions were kept in the dark and under light irradiation to distinguish between adsorption and degradation. The pH of the MB solutions was around 4.9 before and after reactions. A 450 W xenon lamp (Newport) was used for irradiation with a cooling-water filter to block IR rays. Visible light was simulated by using a filter that allowed wavelengths from 420 nm onwards to pass through. Samples of MB were taken at regular time intervals and centrifuged. Absorbance measurements were performed on a Shimadzu 2500 UV/Vis spectrometer at 664 nm, the characteristic absorption maximum for MB.

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the depository number CSD-422026.

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