VISIBLE-LIGHT-ACTIVE TITANIUM DIOXIDE PHOTOCATALYSTS PREPARED BY A MECHANOCHEMICAL APPROACH

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Abstract

The development of photocatalysts active under visible-light irradiation remains a major challenge due to the limited spectral response of titanium dioxide (TiO_2). In this work, a simple mechanochemical approach based on high-energy ball milling was employed to prepare visible-light-active TiO_2 photocatalysts from both synthesized and commercial anatase and rutile powders. The influence of milling conditions on phase composition, surface properties, optical characteristics, and photocatalytic performance was systematically investigated. Ball milling induced partial transformation of anatase to rutile, the formation of anatase/rutile interfaces, and the generation of oxygen vacancies. These structural modifications enhanced visible-light absorption and led to band-gap narrowing. Photocatalytic activity was evaluated through the degradation of 4-chlorophenol under blue-light irradiation. The milled anatase samples exhibited significantly higher activity than both the pristine materials and the commercial Evonik P25 reference photocatalyst. The highest degradation efficiency was achieved with ball-milled sol-gel-derived anatase, reaching up to 65% degradation after 5 h of irradiation. The prepared materials also performed well when deposited as stable coatings on glass substrates.

1 Introduction

Semiconductor photocatalysis has attracted considerable attention as an environmentally friendly technology for water purification, air treatment, and self-cleaning surfaces [1–3]. Titanium dioxide is one of the most extensively studied photocatalysts owing to its chemical stability, low toxicity, abundance, and low cost. However, its practical application is limited by its wide band gap, which restricts photoactivation primarily to ultraviolet radiation [2,3].

Numerous strategies have been explored to extend the photoresponse of TiO_2 into the visible-light region, including doping with metal and non-metal elements, coupling with narrow-band-gap semiconductors, and surface modification [2,3]. Although these approaches have shown promising results, many suffer from drawbacks such as poor long-term stability, complex synthesis procedures, or high production costs.

Mechanochemical treatment offers an attractive alternative, as it can modify the crystal structure and defect concentration without introducing foreign elements [3]. The aim of this work was to develop visible-light-active TiO_2 photocatalysts using a simple ball-milling approach and to investigate the relationship between their physicochemical properties and photocatalytic performance.

2 Work performed / Main Section (it could be several sections)

2.1 Preparation of photocatalysts

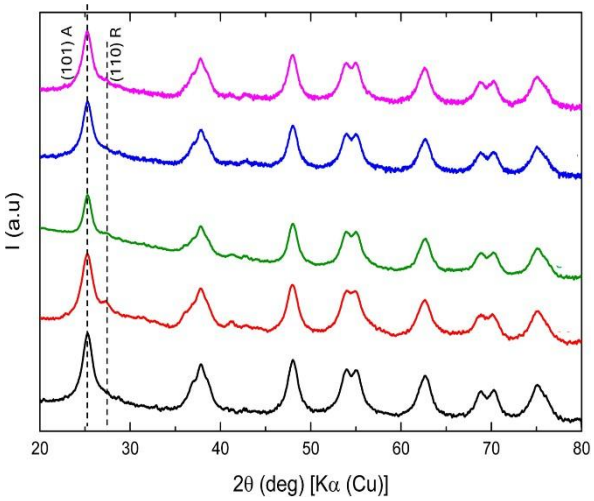


Titanium dioxide samples (**Figure 1.**) were prepared from different precursors. Anatase was synthesized by precipitating titanium hydroxide from $TiCl_4$, followed by calcination at 500 °C, while rutile was obtained by calcination at 900 °C. Additionally, anatase samples were produced via a sol–gel route using titanium butoxide. For comparison, commercial anatase TiO_2 was also included.

Figure 1. Illustration of TiO2 milled sample.

The powders were subjected to high-energy ball milling in air at rotational speeds of 300-600 rpm. The milling process required less than one hour and produced significant structural modifications.

2.2 Physicochemical characterization



X-ray diffraction analysis revealed that milling of the precipitated anatase (**Figure 2.**) induced partial transformation into rutile, resulting in anatase/rutile mixtures containing approximately 6–10 % rutile. In contrast, milling of commercial anatase and rutile led to the formation of small amounts of the high-pressure TiO_2-II (srilankite) phase [4].

Figure 2. XRD patterns of precipitated anatase.

Nitrogen adsorption measurements showed that the precipitated anatase retained a high specific surface area after milling, ranging from 84 to 105 $m^2 g^{-1}$. Such high surface areas are advantageous for photocatalytic processes because they provide more active adsorption sites.

UV–Vis spectroscopy confirmed enhanced visible-light absorption following mechanochemical treatment [4]. The absorption edge shifted from 382 nm for the initial anatase to 401 nm for the sample milled at 450 rpm. Correspondingly, the band gap decreased from approximately 3.25 eV to about 3.02–3.09 eV. Electron paramagnetic resonance measurements further verified the formation of oxygen vacancies and other structural defects generated during milling [4].

2.3 Photocatalytic activity

Photocatalytic degradation experiments were carried out using an aqueous solution of 4-chlorophenol (4-CP) with an initial concentration of 1×10^{-4} M. The reaction was performed in a 25 mL quartz cuvette equipped with an external cooling system that maintained the temperature at 20 °C. Irradiation was provided by three blue LEDs emitting at 440–445 nm, resulting in an irradiance of 20 mW cm^{-2} inside the cuvette, as measured with an ILT2400 radiometer (International Light Technologies) [5] (**Figure 3.**).

The initially precipitated anatase exhibited only 17% degradation after 5 h, whereas the milled samples showed markedly higher activity. The sample milled at 450 rpm achieved 59 % degradation, and the sol-gel-derived anatase milled at 600 rpm reached 65 % degradation [4].

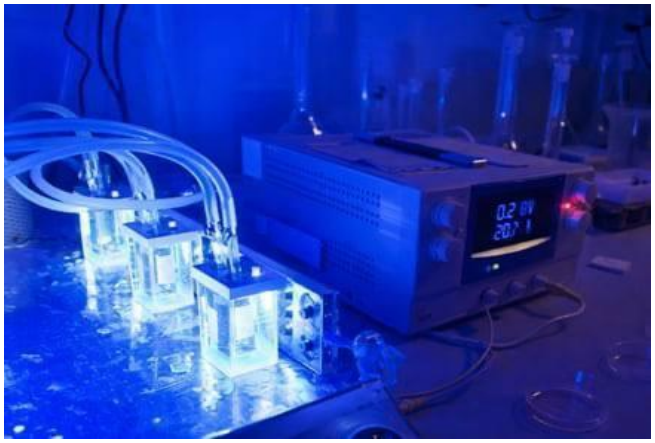


Figure 3. Experimental setup used for photocatalytic degradation of 4-chlorophenol under blue LED irradiation.

The degradation rate of constants increased substantially after mechanochemical treatment and exceeded those obtained for the commercial Evonik P25 photocatalyst (**Figure 4.**). The improved activity can be attributed to several synergistic effects, including the formation of anatase/rutile homojunctions, increased concentration of oxygen vacancies, enhanced visible-light absorption, and preservation of a high specific surface area [3,4].

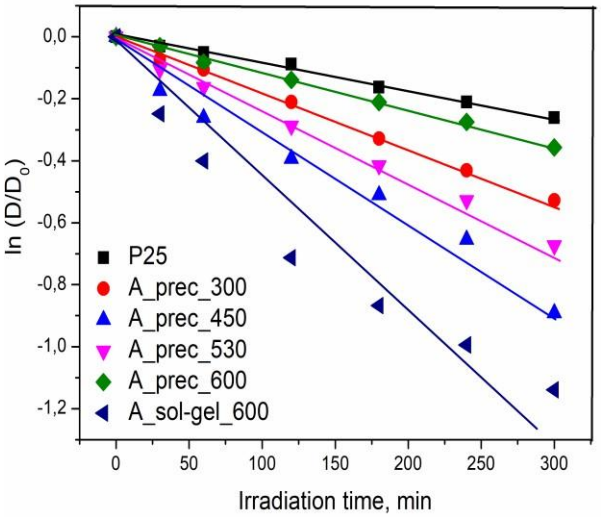


Figure 4. Kinetic curves of 4-chlorophenol degradation under blue-light irradiation for TiO_2 photocatalysts prepared by high-energy ball milling in powder form.

The photocatalytic degradation pathway was further investigated by identifying intermediate products, including benzoquinone, hydroquinone, and chlorocatechol [4]. Significant mineralization of organic compounds was confirmed by total organic carbon measurements.

2.4 Photocatalytic coatings

For practical applications, selected photocatalysts were deposited onto glass substrates. The resulting coatings exhibited photocatalytic activity (**Figure 5.**) comparable to that of the powder samples while maintaining good stability and reusability [4]. These findings highlight the potential of the developed materials for use in self-cleaning surfaces and environmental remediation technologies.

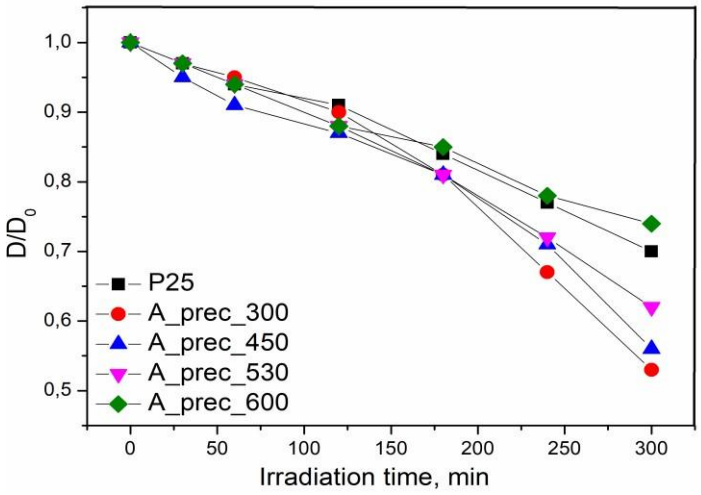


Figure 5. Kinetic curves of 4-chlorophenol degradation under blue-light irradiation for TiO_2 photocatalysts prepared by high-energy ball milling as layers.

3 Conclusions / Further Research / Summary / Discussion

A simple mechanochemical method based on high-energy ball milling was successfully employed to prepare TiO_2 photocatalysts active under visible light. Ball milling induced partial transformation of anatase to rutile, generated oxygen vacancies, and enhanced visible-light absorption. These structural modifications led to a significant improvement in photocatalytic activity during the degradation of 4-chlorophenol under blue-light irradiation.

Among the investigated materials, the ball-milled sol-gel-derived anatase exhibited the highest photocatalytic performance, surpassing both the initial TiO_2 powders and the commercial Evonik P25 reference. The prepared photocatalysts also demonstrated promising performance when applied as stable coatings on glass substrates.

Overall, the proposed approach provides a rapid, scalable, and economically viable route for producing advanced TiO_2-based photocatalysts for visible-light-driven environmental applications.

4 Acknowledgement

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5 References

[1] Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. Nature, 1972, 238, 37–38.

[2] Chen, X.; Mao, S.S. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications and Applications. Chemical Reviews, 2007, 107, 2891–2959.

[3] Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiuchi, Y.; Anpo, M.; Bahnemann, D.W. Understanding TiO_2 Photocatalysis: Mechanisms and Materials. Chemical Reviews, 2014, 114, 9919– 9986.

[4] Zin, O.; Sydorchuk, V.; Brabec, L.; Rathouský, J.; Belháčová, L.; Olszówka, J.E. Development of Visible-Light-Active Titanium Oxide Photocatalysts Prepared by Mechanochemical Approach. AMULET GEM Task Forum, 2026.

[5] L. Brabec, Supported g C3N4/WO3 mixed layers for photocatalytic water remediation, Chemical Papers, 78 (2024) 8749–8757.