Modified TiO\textsubscript{2} for photocatalytic removal of organic pollutants in water

S Mergenbayeva\textsuperscript{1,2,3}, A Ashir\textsuperscript{1}, B Yergali\textsuperscript{1}, G Ulykbanova\textsuperscript{1} and S Poulopoulos\textsuperscript{1}

\textsuperscript{1}Department of Chemical and Materials Engineering, School of Engineering and Digital Sciences, Nazarbayev University, 010000, Nur-Sultan, Kazakhstan

\textsuperscript{2}Corresponding author’s e-mail: saule.mergenbayeva@nu.edu.kz

\textsuperscript{3}Corresponding author’s ORCID: https://orcid.org/0000-0002-3110-5396

Abstract. In this work, TiO\textsubscript{2}/Ti\textsubscript{2}O\textsubscript{3} composite catalysts were prepared by simple one-step thermal treatment method at various temperatures. The morphology and structure of as-prepared samples have been examined by XRD, TGA and SEM. The XRD characterization results revealed three-phase mixture in sample treated at 550°C, while at 650°C phase transformation from TiO\textsubscript{2} anatase to TiO\textsubscript{2} rutile and particle size growth was observed. Moreover, the effect of treatment temperature on the photocatalytic degradation of caffeine was evaluated under UV light irradiation. Results indicated that TiO\textsubscript{2}/Ti\textsubscript{2}O\textsubscript{3}-550 exhibited higher catalytic activity than others achieving complete caffeine removal in 60 min.

1. Introduction

Water pollution is one of the major environmental issues that the world community is facing in the twenty-first century [1]. The recent studies establish the newly found type of contaminants called «emerging pollutants». Among the detected EPs, the most well-known sources of them are personal care products, pharmaceuticals and endocrine-disrupting compounds [2]. Although the amount of these pollutants are relatively low in water, its continuous release may pose serious threat and toxic effects to entire living beings [3].

Caffeine belongs to the methylxanthine class of compounds and is extensively applied in the production of beverages, pharmaceuticals, personal care products, etc [4-5]. Consequently, all water impacted by human domestic emissions contains caffeine [6]. The frequency of caffeine absorption in high concentrated effluents is vast. Nevertheless, heavy caffeine use can lead to health problems, including anxiety, tremors and insomnia [7]. Occurrence of caffeine in water will produce adverse impacts due to its resistance to natural degradation and potential toxicity to aquatic organisms and human life [8]. Therefore appropriate treatment method should be utilized to overcome this problem.

Photocatalysis has emerged as a promising advanced oxidation process (AOP) that can oxidize nearly all organic compounds by reactive oxygen species without production of harmful end products [9]. The commercial TiO\textsubscript{2} - P25 is one of the best photocatalytic materials applied in the degradation of organic pollutants due to its high chemical and photostability, non-toxicity and low cost [10]. After the introduction of hydrogen production by photocatalysis through degradation of water [11], the interest in TiO\textsubscript{2} has been increasing in industrial and academic fields. TiO\textsubscript{2} photocatalysis is a photo-induced chemical reaction on the surface of TiO\textsubscript{2} that involves light absorption followed by the electrons shift from the valence to the conduction band which leads to the generation of a positive hole.
(h⁺) in the latter, thus causing charge separation. The resulting electron-hole pair participate in the redox reactions forming various highly reactive species (·OH, O₂⁻, HO₂⁻) which further react with organic pollutants and oxidize them [12].

Despite the all good properties, TiO₂ finds application only under UV light region due to the relatively high bandgap (3.0 - 3.2 eV). This part of the spectrum represents less than 5% of the solar energy, thus the overall solar activity of TiO₂ is limited [13]. Therefore, various approaches have been proposed to narrow intrinsic bandgap and augment photocatalytic efficiency of TiO₂, including doping with metals (Co, Ni, Mn, Fe, Cr, etc.) or non-metals (N, S, C, I, etc.), oxygen vacancies and dye-sensitization [14-17].

Black TiO₂ first introduced in 2011 has received widespread attention due to enhanced photocatalytic activity under the whole spectrum of light [18]. It represents self-structural modifications, including self-doped Ti³⁺/oxygen vacancy or the inclusion of H-doping. Moreover, a significant change in electronic and crystal structures is observed, and the most noticeable effect is the change of color. TiO₂ is white as it does not absorb visible irradiation, while self-structural modification of TiO₂ results in black or colorful appearances as it absorbs the whole or part of visible-light.

To prepare black titania, the synthetic approaches fall into two categories: partial reduction of TiO₂ and incomplete oxidation from low-valence-state of Ti species. The first approach includes chemical reduction, electrochemical reduction, or hydrogen thermal treatment. For instance, in order to obtain defective TiO₂, noble gases as reductants can shift the thermodynamic equilibrium of TiO₂ ↔ TiO₂ – x⁺, x/O₂ [13, 19]. Moreover, Ti³⁺ self-doped TiO₂ can be attained in the presence of a reductant in the hydrolysis of Ti species. Regarding the starting materials for oxidation approaches, Titanium of low valence state including Ti, TiO, TiH₂, TiCl₃ etc. was exploited. The addition of some reductants can prevent full oxidation of these species, and this approach is known as reductant-assisted oxidation [19].

In this study, a thermal treatment method was applied to prepare colorful titania at temperatures of 550-750°C. The effectiveness and feasibility of thermally modified TiO₂/Ti₂O₃ catalysts in the degradation of caffeine in water were evaluated under UV light irradiation.

2. Materials and methods

2.1. Chemicals
All chemical reagents, including titanium dioxide (TiO₂-P25 ≥ 99.5%), titanium (III) oxide (Ti₃O₅, 99.9%) and caffeine were supplied by Sigma-Aldrich and used without further purification.

2.2. Preparation of photocatalysts
In a typical method for achieving colourful TiO₂/Ti₂O₃, Ti₂O₃ mixed in a ratio of 1:1 with TiO₂ was crushed into a fine powder and then placed in a muffle furnace for 3 hours to calcine under different temperatures (550, 650, and 750°C with an increment of 5°C/min) in air. The prepared materials were denoted as TiO₂/Ti₂O₃-550, TiO₂/Ti₂O₃-650 and TiO₂/Ti₂O₃-750.

2.3. Characterization
The phase transformation of the prepared samples was analysed using X-ray diffraction system (XRD, Rigaku SmartLab®). The surface morphology of the thermally modified catalysts was examined by Scanning Electron Microscope (SEM, Auriga Crossbeam 540, Carl Zeiss). Meanwhile, to characterize changes that catalysts undergo during the heating thermal analysis (TGA-DTA-DSC, STA 6000) was applied.

2.4. Evaluation of photocatalytic activity
The efficiency of the as-prepared photocatalysts were determined for the photodegradation of caffeine in aqueous solution by means of batch operated photochemical reactor, supplied with an ultraviolet
lamp (365 nm). Typically, 0.2 g of the photocatalyst was added into a 500 mL of caffeine (30 mg/L) solution. The resultant mixture was stirred without UV irradiation for 30 min to reach adsorption/desorption equilibrium between the reactant and photocatalyst. At a regular interval (every 30 min), 20 mL were taken out from the solution and filtered (0.2 μm pore size syringe filters) to remove the catalyst powders from solutions before analysis. The caffeine degradation and total organic carbon (TOC) were measured by High-Pressure Liquid Chromatography (HPLC, Agilent 1290 Infinity II) and Multi N/C 3100 analyzer (Analytik Jena AG, Germany).

3. Results and discussion

3.1. Characterization

Figure 1 illustrates the representative SEM images of untreated TiO$_2$/Ti$_2$O$_3$ (blank) and its thermally treated modifications. The particles corresponding to the blank and TiO$_2$/Ti$_2$O$_3$-550 had nearly identical shapes (Figures 1a, 1b), which could be assumed to be spherical with the diameter range between 20 nm and 30 nm. More and more spherical particles became rare and bigger with the increase of treatment temperature (Figure 1c). This observation clearly indicated that the particles agglomerated on the surface when contacted with heat at high temperature.

The obtained TGA-DTA-DSC thermograms for the blank and thermally treated photocatalysts are illustrated in Figure 2. As seen from the Figure 2 (a and b), in the blank and TiO$_2$/Ti$_2$O$_3$-550 samples slight weight gain was observed due to the inclusion of oxygen from the air. Also, small exothermic
peaks at approximately 850°C in the DSC curves for both of the samples showed that two different phases of TiO$_2$ (anatase and rutile) were present. For TiO$_2$/Ti$_2$O$_3$-650 sharp exothermic peak occurred at 850°C which corresponded to the change of the TiO$_2$ anatase into TiO$_2$ rutile. Moreover, the glass transition temperature at 750°C was detected in the DSC curve for TiO$_2$/Ti$_2$O$_3$-750.

![Figure 2](image)

Figure 2. TGA-DTA-DSC thermograms of blank (a), TiO$_2$/Ti$_2$O$_3$-550 (b), TiO$_2$/Ti$_2$O$_3$-650 (c) and TiO$_2$/Ti$_2$O$_3$-750 (d).

The XRD patterns of the blank and modified samples are shown in Figure 3. The phase composition of the blank consist of peaks TiO$_2$ anatase and Ti$_2$O$_3$. In TiO$_2$/Ti$_2$O$_3$ -550, besides the peaks corresponding to the TiO$_2$ anatase and Ti$_2$O$_3$, the peaks of TiO$_2$ were observed indicating the start of Ti$_2$O$_3$ – TiO$_2$ rutile transformation. Upon increasing heating to 650°C more rutile peaks were identified, whereas at 750°C almost complete transformation to TiO$_2$ rutile could be observed.
Figure 3. XRD pattern of blank (a), TiO$_2$/Ti$_2$O$_3$-550 (b), TiO$_2$/Ti$_2$O$_3$-650 (c) and TiO$_2$/Ti$_2$O$_3$-750 (d).

3.2. Photocatalytic activity
The photocatalytic activity of the as-prepared photocatalysts was evaluated by degradation of caffeine in the presence of UV light for 120 min. Before light irradiation, the reaction solution was kept in a dark for 30 min with constant stirring to determine adsorption performance of each catalyst. The amount of caffeine adsorbed on the catalyst found to be low revealing that the catalyst requires a light for activation to degrade organic pollutants (Figure 4 a). Besides, caffeine self-degradation in the absence of photocatalyst under UV light exposure was ~ 28% after 60 min of reaction. It suggests, that caffeine molecules can absorb UV light in the region of lamp emission. However, the pollutant removal is increased at least to ~ 93% after 60 min when the catalyst was added. For all the composites, the caffeine degradation efficiency increased with the extension of illumination time because of the effective charge separation and redox reaction on the surface of the photocatalyst. Clearly, treatment temperature influence the photocatalytic activity of the catalyst. The treatment temperature increase led to decrease in efficiency. As shown in Figure 4 (a and b), TiO$_2$/Ti$_2$O$_3$-550 proved to be better at caffeine and TOC removal among all prepared materials.

Figure 4. Caffeine (a) and TOC (b) removal under UV light irradiation.

4. Conclusion
In summary, TiO$_2$/Ti$_2$O$_3$ samples were thermally treated in air at different temperatures, and characterized using XRD, SEM and TGA-DTA-DSC measurements. The change in phases, morphology and crystallite size was observed with the increase of treatment temperature. Besides, the effect of treatment temperature on the photocatalytic activity has been investigated. The experimental
results showed that complete caffeine degradation could be achieved after 2 hours of irradiation (UV) by all synthesized photocatalysts. The photocatalytic performance decreased with increasing thermal treatment temperature due to the effect of particle size increase. TiO\textsubscript{2}/Ti\textsubscript{3}O\textsubscript{4} treated at 550 exhibited the highest photocatalytic activity which could be attributed to the presence of three phases.

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