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Araştırma Makalesi / Research Article

Columnar TiO_2 Thin Films Decorated with Cu Nanoclusters Prepared by Photocatalytic Deposition for Enhanced Photocatalytic Performance under UV Illumination

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Abstract

TiO_2 photocatalyst is a promising material for different kinds of applications, including air and water purification, hydrogen production, and self-clean surfaces. It is usually combined with other materials to improve its charge separation as well as its activation under solar illumination. However, using such an approach is not suitable for practical photocatalytic applications because noble metals are too expensive. Therefore, cost-effective metals (e.g., copper, nickel, etc.) should be also considered instead of noble metals. In this study, we prepared photocatalytically active TiO_2 thin films decorated with copper (Cu) nanoclusters (NCs) to improve the charge separation. Here, the metallic Cu NCs were deposited on TiO_2 thin surface by a photocatalytic deposition process (under ultraviolet (UV) illumination). The morphology, size, and surface coverage of Cu NCs on TiO_2 were varied by controlling the UV illumination time. Results showed that the optimum surface coverage (3.04 %) leads to a remarkable increase in photocatalytic performance compared to bare TiO_2. However, depositing more Cu NCs with bigger sizes and higher surface coverage (7.08 %) decreased the overall photocatalytic activity. This might be due to the blocking of UV light incoming to the TiO_2 thin film by bigger Cu NCs on the surface. The presented Cu-TiO_2 hybrid system would be a good alternative to conventional co-catalyst systems which are composed of expensive metals (Au, Ag, Pt, etc.) and TiO_2 structures.

Keywords: photocatalyst, TiO_2, thin film, Cu, nanoclusters, photocatalytic deposition

UV Aydınlatma Altında Gelişmiş Fotokatalitik Performans için Fotokatalitik Biriktirme ile Hazırlanan Cu Nanokümelerle Süslenmiş Sütunlu TiO_2 İnce Filmler

Öz

Fotokatalizör TiO_2, hava ve su arıtma, hidrojen üretimi ve kendi kendini temizleyen yüzeyler dahil olmak üzere farklı uygulama türleri için umut verici bir malzemedir. Genellikle yük ayrımını ve güneş ışığı altında aktivasyonunu iyileştirmek için soy metaller ile birleştirilir. Ancak, bu yöntem kullanılan soy metallerin çok pahalı olmalarından dolayı pratik fotokatalitik uygulamalar için uygun değildir. Bu çalışmada, bakır (Cu) nanokümeleri (NK) ile süslenmiş fotokatalitik olarak aktif TiO_2 ince filmler hazırlanmıştır. Burada, metalik Cu NC'ler TiO_2 ince yüzeyi üzerine fotokatalitik biriktirme (ultraviyole (UV) aydınlatma altında) işlemi ile biriktirilmiştir. TiO_2 üzerindeki Cu NK'lerin morfolojisi ve yüzey kaplaması UV aydınlatma süresi değiştirilerek edilerek kontrol edilmiştir. Sonuçlar, optimum yüzey kaplamasının (%3,04) çıplak TiO_2'ye kıyasla fotokatalitik aktivitede önemli bir artışa yol açtığını göstermiştir. Bununla birlikte, daha büyük boyutlara ve daha yüksek yüzey kaplamasına (%7,08) sahip daha fazla Cu NK biriktirmek genel fotokatalitik aktiviteyi azaltmaktadır. Bunun nedeni, TiO_2 ince filmine gelen UV ışığının yüzeydeki daha büyük Cu NK'ler tarafından engellenmesi olabilir. Cu-TiO_2 hibrit sistemi, pahalı metaller (Au, Ag, Pt, vb.) ve TiO_2 yapılarından oluşan geleneksel eş katalizör sistemlerine iyi bir alternatif olabilir.

Anahtar Kelimeler: fotokatalizör, TiO_2, ince film, Cu, nanokümeler, fotokatalitik biriktirme

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1. Introduction

The current energy crisis and environmental problems are of great concern to the world. In terms of sustainable solutions, photocatalysis has been proposed as a potential candidate for these critical problems (Bramhaiah and Bhattacharyya, 2022; Ng et al., 2021; Rajendran et al., 2020). Photocatalysis is a process whereby light energy is used to enable the oxidation-reduction of chemical compounds, such as those used in air and water purification, degradation of organic pollutants, production of hydrogen fuel, and other energy-producing or energy-storing compounds (Kundu et al., 2020; Mao et al., 2012). Numerous photocatalysts have been used for these applications, including TiO_2, ZnO, WO_3, CuO, g-C_3N_4, $BiPO_4$, etc. (Belver et al., 2019; Hong et al., 2016; Kuru, 2020). However, titanium (IV) oxide (TiO_2) is a widely used semiconductor due to its high activity, earth abundance, low cost, no toxicity, and high stability (Fujishima et al., 2008; Fujishima and Honda, 1972). Thus, incorporating TiO_2 into energy conversion, storage systems, and water remediations is an attractive and promising idea (Etacheri et al., 2015; Tsui and Zangari, 2014). However, TiO_2 has not been considered an efficient photocatalyst for practical applications due to its wide bandgap (rutile: 3.0 eV and anatase: 3.2 eV), which can be only activated by ultraviolet (UV) light and fast recombination of photoexcited charge carriers (electrons and holes) (Hanaor and Sorrell, 2011). In general, decreasing the size of TiO_2 particles from micro- to nanoscale generally increases the active surface area due to the high surface-to-volume ratio (Hoffmann et al., 1995). This also decreases the time needed for migration to surface sites, which leads to getting a high chance for further reactions without recombination. However, the cost-efficient and safe recovery of nano-sized TiO_2 nanoparticles from reaction media is still a difficult process (Tang et al., 2013). Furthermore, agglomeration of these nanoparticles decreases photocatalytic activity and light absorption of TiO_2 (Pellegrino et al., 2017; Qutub et al., 2022). Immobilized TiO_2 nanoparticles, such as thin films, would be a promising candidate for practical indoor and outdoor photocatalytic applications (Nalajala et al., 2019). However, thin film photocatalysts show a relatively low surface area compared to nanoparticle-based photocatalysts. Therefore, their surface properties need to be improved to eliminate this critical problem. Recently, we have developed a new way to improve the surface area of TiO_2 thin films through the creation of nano-crack networks in sputtered films (Ghori et al., 2018; Henkel et al., 2018; Vahl et al., 2019). Besides only improving the surface properties of TiO_2 thin films, an effective photogenerated charge separation (electrons and holes) can also promote the use of these films in various indoor and outdoor photocatalytic applications (Veziroglu et al., 2019).

To improve the effective electron and hole separation in TiO_2 thin films, researchers have turned to a variety of techniques such as doping of metal and non-metals (Chen et al., 2011; Kuru and Narsat, 2019), loading of metallic particles (Ghori et al., 2018; Meng et al., 2019), and coupling with other semiconductors (forming heterostructure) (Low et al., 2017; Veziroglu et al., 2020). The loading of metallic particles to TiO_2 thin film surface is one of the most common approaches due to not only increasing the light absorption properties from UV to visible region but also increasing the lifetime of photogenerated charge carriers by trapping the electrons (Yang et al., 2013). Well-controlled metallic particles on TiO_2 thin film surface can be achieved by various synthesis methods including chemical (Rubtsov et al., 2021), physical (Sriubas et al., 2021), and photochemical processes (Mendoza-Diaz et al., 2020). Among others, the photochemical process (e.g., photodeposition or photocatalytic deposition) gives proper control of the size, shape, and distribution of deposited metallic particles as well as strong chemical adhesion between TiO_2 thin film surfaces (Wenderich and Mul, 2016). Recently, we developed a technique to fabricate metallic (Au, Ag, etc.) micro (Shondo et al., 2021; Shondo et al., 2022; Veziroglu et al., 2018) and nanostructures (Shondo et al., 2022; Veziroglu et al., 2019; Veziroglu et al., 2020; Veziroglu et al., 2020) on TiO_2 thin film surface by using a photocatalytic deposition process. Initial results showed that there is a clear relationship between the size, shape, and distribution of metallic structures (e.g, Au, Ag, etc.) and achieving higher photocatalytic activity (Wenderich and Mul, 2016). In general, noble metal ions are easily reduced as metallic particles onto TiO_2 thin film surface by photocatalytic deposition process due to their low reduction potential (or activation energy), however, they are not suitable for practical indoor and outdoor applications due to low availability and their high price.

Among different metallic candidates for TiO_2 thin film modification, copper (Cu) is a highly promising material both under artificial (UV) and solar irradiation (Stucchi et al., 2016). For example, in comparison to other well-known noble metals (Au, Pt, and Ag) as extremely efficient co-catalysts of TiO_2, Cu, as a consequence of abundant transition metal, is an inexpensive material that is 100 times and 6000 times cheaper than Ag and Au, respectively (Bhanushali et al., 2015). In addition to this, Cu is in the same group of the periodic table as Au and Ag and shows similar properties due to its electronic configuration (Janczarek and Kowalska, 2017). Therefore, one can expect similar performance from Cu to increase the photocatalytic activity of TiO_2 photocatalysts with higher useability for practical applications. Recently, Li et. al. synthesized Cu/TiO_2 nanocomposites by a one-pot sol-gel method and reported that the optimal Cu loading (0.5 wt%) on the composite surface is crucial to achieving higher photocatalytic activity (Li et al., 2010). Similarly, Wu et al showed that photocatalytic activity can be enhanced up to 10-fold by optimum loading of % Cu (~1.2 wt%). They pointed out that Cu particles can be oxidized (CuO_x) during photocatalytic reactions, which might negatively affect the photocatalytic activity (Wu, 2004). Valentina et al prepared CuO nanoparticles embedded into TiO_2 by water-in-oil microemulsion process and reported that the combined presence of the Cu/CuO_x species influences the band gap and some of the positive aspects of the hybrid system that can account for the superior performance (Gombac et al., 2010). Similarly, Yu et al. showed that the quantum size effect of CuO clusters alters its energy levels in the CuO-TiO_2 hybrid system, which would be beneficial for electron transfer during the reaction and enhances the photocatalytic activity (Yu et al., 2011). Bandara et al. showed that higher catalytic activity and increased stability of CuO-TiO_2 also derive from an efficient charge transfer process between two components (Bandara et al., 2005). Various research studies have been reported on Cu-modified TiO_2, however, in most cases, Cu may co-exist in both forms (metallic - Cu^0 and oxides - Cu^{1+} or Cu^{2+}). The diversity of forms provides difficulty in clearly understanding the role of Cu in the Cu-TiO_2 hybrid structure during the photocatalytic reaction. Therefore, a statement that the nature of Cu species in TiO_2 photocatalysis is still not fully understood, which may need more investigation.

In the present study, we have proposed a method for the preparation of a highly active Cu-TiO_2 thin film photocatalyst. Photocatalytic deposition under (UV illumination) was used to deposit Cu nanoclusters (NCs) on columnar TiO_2 thin films. We used different UV irradiation time intervals (from 10 min to 30 min) to control the morphology and size of the deposited Cu NCs and their surface coverage. Here, a stable Cu-TiO_2 hybrid system allows us to better understand the role of Cu in the photocatalytic reaction. Our results showed that the optimum amount of Cu content (4.61 %) showed superior photocatalytic activity under UV illumination. This hybrid system would be a good alternative to conventional co-catalyst systems which are composed of expensive metals (Au, Ag, Pt, etc.) and TiO_2 structure.

2. Materials and Methods

2.1. The preparation of TiO_2 thin films

The TiO_2 thin films were deposited using reactive pulsed DC magnetron sputtering from metallic titanium (Ti) target (2 inch, Goodfellow, 99.99%) in the presence of argon (Ar) and oxygen (O_2) as process and reactive gas respectively (Ghori et al., 2018). Silicon wafer pieces (Si, 10 x 10 mm) were used as substrate. Before the TiO_2 deposition process, we basically achieved a base pressure of 10^{-5} Pa by using a rotary and a turbo molecular pump. Afterward, the Ti target surface was cleaned by pure Ar plasma (for 15 min) followed by a conditioning phase of 5 min with both Ar (250 sccm) and O_2 (10 sccm) flow. Here, a magnetron output power of 90W was fixed during the conditioning and deposition phases. To achieve a homogenous TiO_2 film (thickness: 900 nm), the sample holder was rotated with constant speed during the deposition process. After deposition, we heat-treated the TiO_2 thin film samples for 1 h at 650 °C in an oven before quenching them with air.

2.2. The synthesis of Cu NCs on TiO_2 thin films

As shown schematically in Figure 1, the photocatalytic deposition method was used to decorate TiO_2 thin films with Cu NCs. The starting material, Cu solution (in % HNO_3) was purchased from Carl Roth, Germany. An aqueous solution of copper precursor (0.8×10^{-3} mol/L) was filled into a quartz cell. The prepared TiO_2 thin films were then immersed in precursor solution and UV-illuminated (4.5 mW/cm^2, $\lambda = 365$ nm) for different time intervals (from 10 min to 30 min). Finally, to remove the solution remaining on the TiO_2 thin film surface, the samples were rinsed with deionized water (H_2O) and dried with air after UV irradiation.

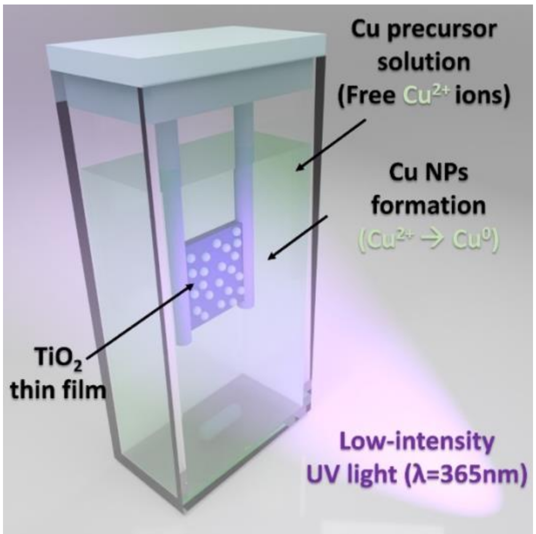

Figure 1. Schematic illustration of the photocatalytic deposition process to fabricate TiO_2 thin films decorated with Cu NCs.

2.3. Materials characterization

Scanning electron microscopy (SEM, Supra55VP-Carl Zeiss) was used to analyze the surface morphology and structure of the prepared Cu-TiO_2 thin films. The MATLAB-based MIPAR TM software was utilized to investigate the particle size and distribution on the thin film surface. The chemical composition and surface chemistry of the Cu-TiO_2 sample were examined by X-ray photoelectron spectroscopy (XPS, Omicron Nano-Technology GmbH). All binding energies (BE) were calibrated to the C1s peak at 285.0 eV based on the absorbed carbon over the sample surface.

2.4. Photocatalytic activity analysis

The photocatalytic degradation of methylene blue (MB) solution, which is the most common material as a test dye, was used to measure the photocatalytic performance of bare TiO_2 and Cu-TiO_2 thin films. (Houas, 2001). Initially, the prepared thin film samples were dipped into 6.5 mL MB aqueous solution (10 μmol/L). Then, the MB solution was stirred (by magnetic pill) and illuminated by UV light (4.5 mW/cm^2, λ = 365 nm) for 6 hours (240 min). Finally, the change in the absorption at 664.5 nm was collected by using a UV-Vis spectrophotometer (StellarNet BLUE-Wave Miniature Spectrometer with SL5-DH light source).

3. Findings and Discussion

A cross-section and top-view SEM images of TiO_2 thin film are shown in Figure 2. It can be clearly seen, the TiO_2 thin film shows a typical sputter-deposited layer morphology with a columnar type of structure (Figure 2a). Here the most noticeable observation is the randomly distributed nanocrack network on the TiO_2 surface (represented with red arrows in Figure 2b), which has been reported earlier (Henkel et al., 2018). This well-distributed nano crack network enhances the active surface area, which significantly improves the photocatalytic activity of TiO_2 thin films (Vahl et al., 2019; Veziroglu et al., 2019).

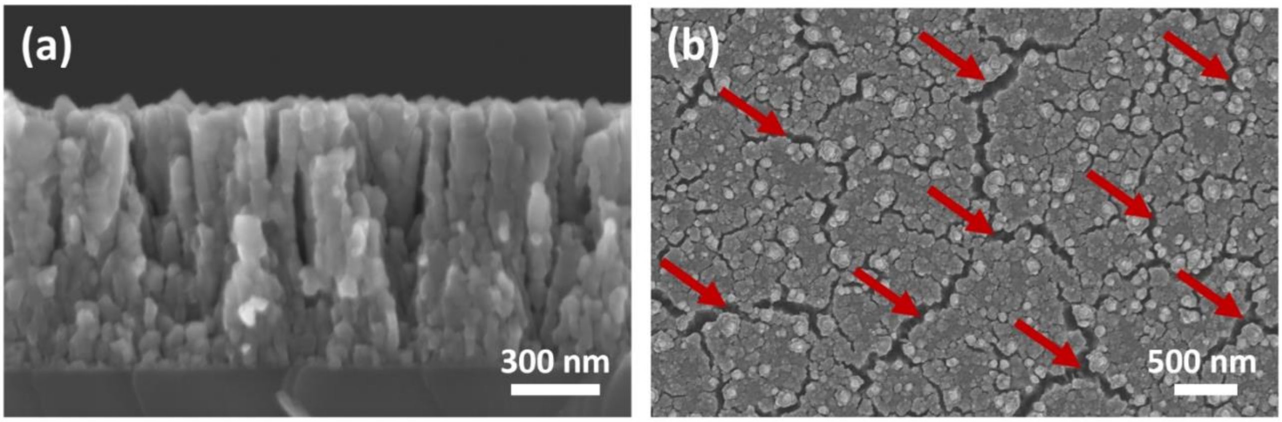

Figure 2. **(a)** Cross-section and **(b)** top-view SEM image of columnar TiO_2 thin film which is prepared by DC reactive magnetron sputtering.

After the photocatalytic deposition at different time intervals (10, 20, and 30 min), well-distributed Cu NCs were observed on the TiO_2 thin film surface (Figure 3). As one can easily see differences in the morphology (Figure 3a–d), the UV illumination time (called deposition time) clearly affects not only the shape and size but also the distribution density of the deposited Cu NCs.

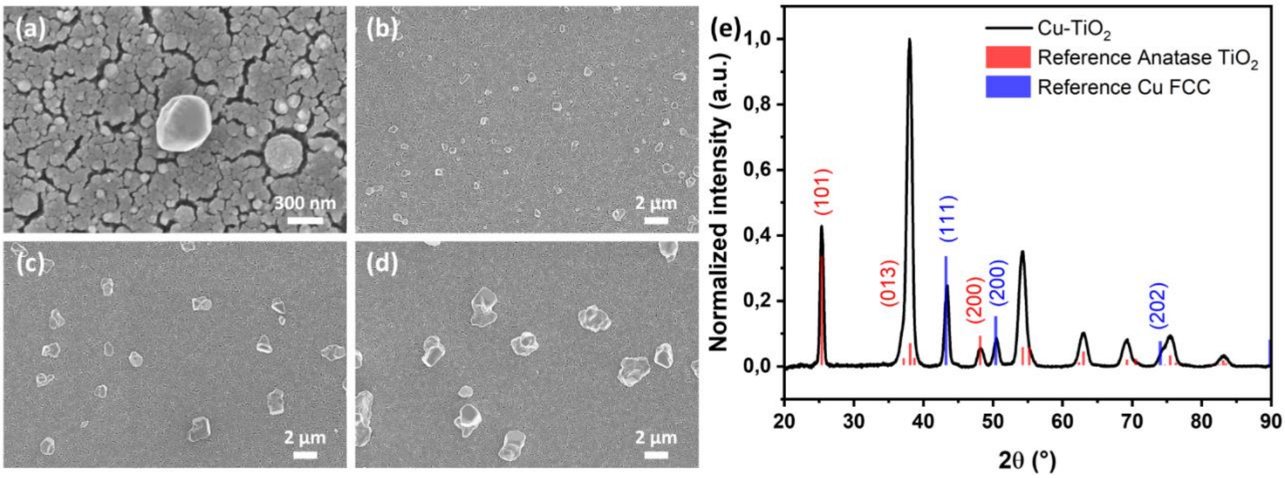

Figure 3. SEM images of Cu-TiO$_2$ thin film samples which are prepared by photocatalytic deposition process for **(a)**, **(b)** 10 min, **(c)** 20 min, and **(d)** 30 min. (e) XRD pattern of Cu-TiO$_2$ thin film sample with corresponding reference peaks for anatase TiO$_2$ and Cu fcc.

Figure 3e represents the XRD pattern of the prepared Cu–TiO$_2$ thin film. The XRD results showed that the main diffraction peaks at 25.4 (101), 38.2 (013), and 48.3 (200) are observed in the patterns corresponding anatase crystalline structure of TiO$_2$ (JCPDS 21-1272) (Antić et al., 2012). The other XRD diffraction peaks at 43.4 (111), 50.5 (200) and 74.2 (202) match well with the reference Cu-faced centered cubic (fcc) (JCPDS 851326) (Tian et al., 2014).

To better understand the changes in particle size distribution and surface coverage of deposited Cu NCs on thin film surfaces, MIPAR image analysis software was used to analyze the SEM images of samples, which were deposited at different time intervals (Figure 4). The results show that short deposition time (e.g., 10 min) leads to the creation of many nucleation points with relatively small Cu NCs (mean particle size: 539.3 nm). However further UV illumination (e.g., 30 min) can drastically increase the size of clusters from 539.3 nm to 1845.5 nm as well as mainly covering almost 7.83 % of the TiO$_2$ thin film surface.

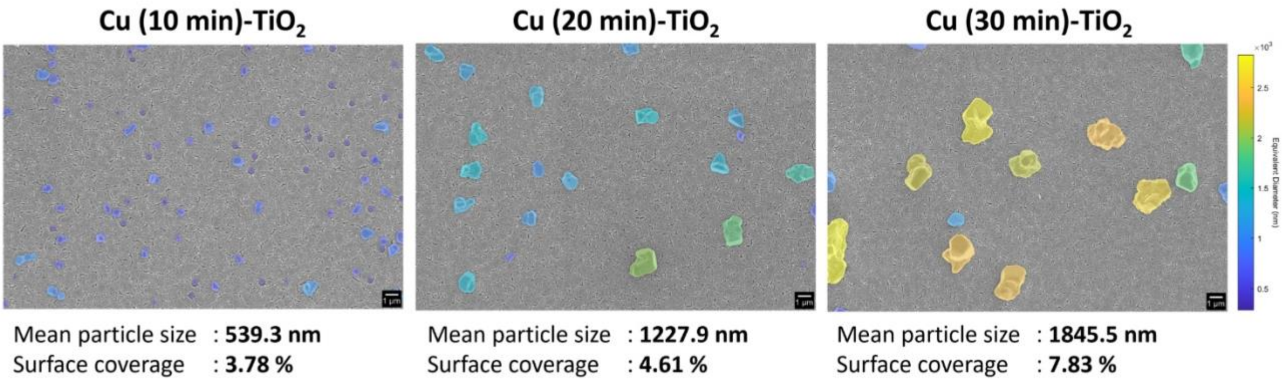

Figure 4. Particle size distribution and surface coverage analysis of Cu-TiO$_2$ samples prepared at different time durations.

As shown schematically in Figure 5, UV irradiation generates charge carriers (electrons and holes) on a columnar TiO_2 thin film. First, photo-excited electrons directly reduce Cu ions (Cu^{2+}) in an aqueous solution to stable Cu NCs. (nucleation). Extra UV irradiation produces more photo-excited electrons, which transfer to reduce more Cu^{2+} ions onto already growing Cu NCs (cluster formation) (Veziroglu et al., 2020; Veziroglu et al., 2020). However, further UV irradiation starts cluster-cluster interaction of Cu NCs, which might combine the individual Cu NCs as a big cluster (coalescence) on the surface. Here, the photocatalytic performance of the TiO_2 thin film and the duration of UV irradiation play a significant role in the size, morphology, and distribution of the deposited Cu NCs on the TiO_2 surface. (Wenderich and Mul, 2016).

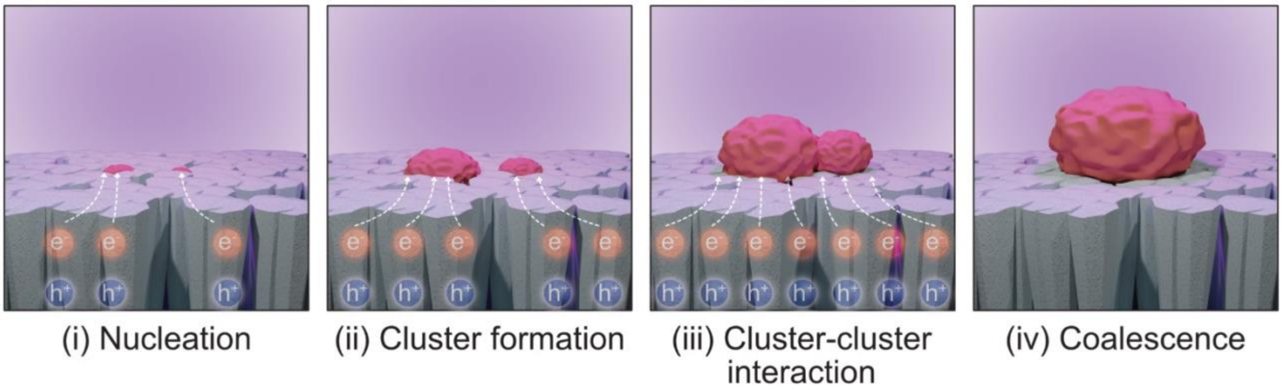

Figure 5. Schematic representation of step-by-step (from nucleation to coalescence) photocatalytic deposition process to fabricate Cu-TiO_2 thin film.

To distinguish the chemical state on the surface, XPS spectra of the Cu (10 min)-TiO_2 thin film were examined as given in Figure 6. Figure 6a shows the peak positions of the Ti $2p_{1/2}$ and the Ti $2p_{3/2}$ peak on the binding energy (BE) scale that can be extracted. The Ti $2p_{1/2}$ and the Ti $2p_{3/2}$ positions are found to be at 464.1 eV and 458.4 eV respectively (Du et al., 2021). The difference in the binding energy (5.7 eV) can be ascribed to Ti^{4+} which indicates TiO_2 (Sánchez-Zambrano et al., 2022). Combing this finding with the fact that the Ti 2p spectrum does not display any significant subpeaks, the XPS result indicates that the thin film surface is most likely consisting of fully oxidized TiO_2.

The peak position for the O 1s is at about 529.8 eV, which is due to the O_2 in the lattice structure of TiO_2. However, the peak, at 531.9 eV, can be described as adsorbed oxygen (hydroxy groups, etc.) on the sample surface (Figure 6b). Figure 6c shows that the two main peaks of Cu 2p (at 932.7 and 952.5 eV) can be assigned to the binding energy of Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively (Miller and Simmons, 1993; Zhang, 2017). In general, it is significantly challenging to identify the copper (I) oxide (Cu_2O) and metallic copper (Cu) by the XPS peaks of Cu $2p_{3/2}$ and Cu $2p_{1/2}$. Because the binding energies of these peaks are very close. However, there are no satellite peaks around 942 and

962 eV, which are assigned to Cu_2O or CuO structures (Vasquez, 1998b, 1998a; Wu et al., 2006; Zhang, 2017). Therefore, these XPS results validate that the Cu NCs on the TiO_2 surface are in metallic form (Cu^0) (Eskandarloo et al., 2015).

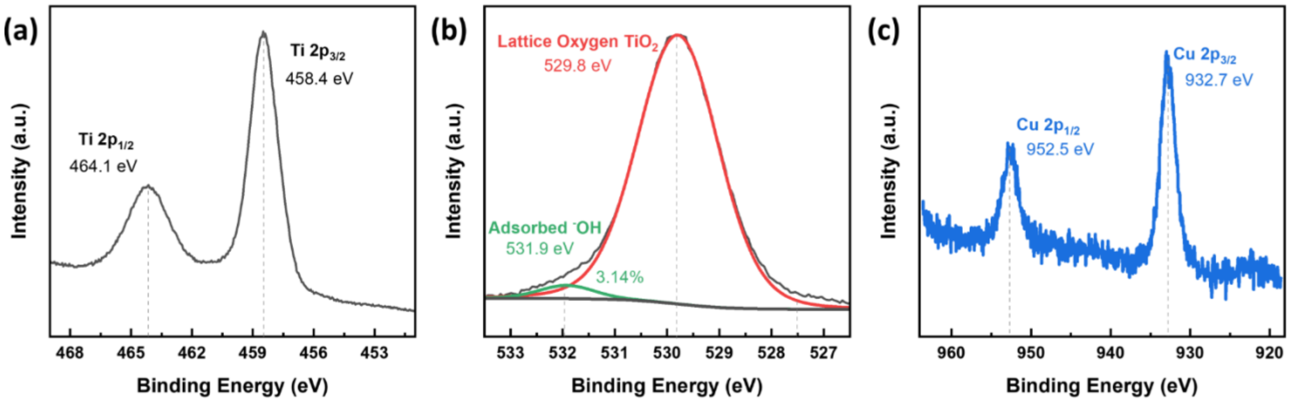

Figure 6. High-resolution XPS spectra of (a) Ti 2p, (b) O 1s, and (c) Cu 2p.

For the investigation of the photocatalytic performance, the bare TiO_2 and Cu-TiO_2 samples were tested for their degradation ability of the methylene blue (MB) solution under UV illumination for 6 hours (240 minutes) (Figure 7a). It can be clearly seen that MB concentration decreases over time due to a fast photocatalytic reaction. Here, all Cu-TiO_2 samples showed significantly higher activities in comparison to bare TiO_2. However, Cu (20 min)-TiO_2 exhibited superior photocatalytic activity compared to the rest of the samples, which were decorated with Cu NCs at different photodeposition times. We observed that Cu (20min)-TiO_2 achieved about 2.15 times higher activity (90 % degradation for 240 min) in comparison to bare TiO_2 (42 % degradation for 240 min).

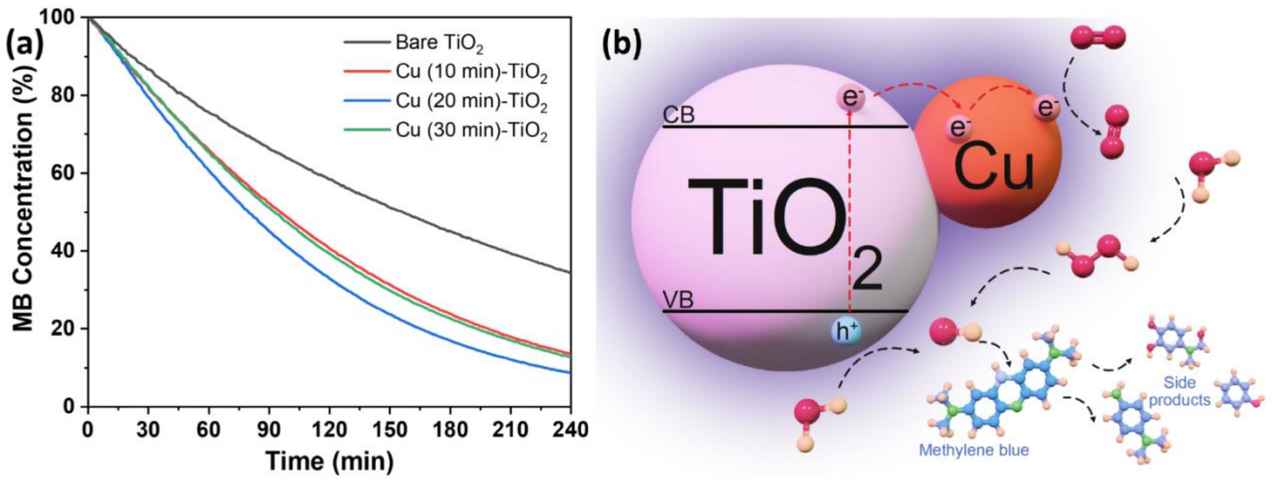

Figure 7. **(a)** Comparison of photocatalytic MB degradation by using bare TiO_2 and Cu-TiO_2 (with varied photodeposition times) photocatalysts **(b)** Schematic representation of the photocatalytic degradation mechanism of MB by Cu-TiO_2 photocatalyst under UV illumination.

Here, the positive effect of Cu NCs on the overall photocatalytic activity of TiO_2 can be explained by the optimal amount of Cu NCs (after 20 min of photodeposition), which can effectively separate the photo-excited electrons and holes pairs and reduce the recombination of these charge carriers for higher efficiency (Eskandarloo et al., 2015). However, a further increase in the content of Cu NCs causes a reduction of overall photocatalytic acidity. Especially, at 30 min photodeposition, the photocatalytic activity of the sample has a slight decrease. This might be due to an increase in the opacity and light scattering of the sample which was reported by Yu et al. earlier (Yu et al., 2002, 2011). Another possible explanation might be also (i) partial blocking of the TiO_2 thin film surface due to an excessive amount of Cu NCs and (ii) deterioration of the photocatalytic properties of Cu NCs due to their particle size enlargement (Veziroglu et al., 2020; Yu et al., 2011). As discussed before, the photocatalytic performance of the Cu-TiO_2 sample on the degradation of MB is mainly affected by the enhanced separation and transportation of photogenerated charge carriers. Here, Cu NCs on the TiO_2 surface act as promoters for trapping of photogenerated electrons, as a consequence, the lifetime of photogenerated holes of TiO_2 is prolonged (Eskandarloo et al., 2015; Heciak et al., 2013; Wang et al., 2012). Based on our observation, we propose a potential mechanism for photocatalytic degradation of MB by TiO_2 structure decorated Cu NCs (Figure 7b). When UV illumination starts the photogenerated electrons are transferred rapidly from the valance band (VB) to the conduction band (CB) of TiO_2. Subsequently, they create holes behind (at VB). These electrons, at CB, are transferred from TiO_2 to Cu NCs due to the Schottky barrier between two structures (Zhang, 2017). Here, adsorbed oxygen (O_2) on the Cu NCs can react with these electrons to form superoxide radicals, which significantly improve the degradation of MB. At the same time, the holes left in the VB of TiO_2 also react with water (H_2O) molecules to form hydroxyl radicals ($*OH^-$). These hydroxyl radicals attract and degrade the MB molecules to small and harmless organic molecules (side products).

To check the stability of Cu NCs on the TiO_2 surface, we performed the photocatalytic MB degradation process for 16 hours and then we investigated the chemical composition of the sample surface by XPS analysis. Figure 8a shows that (like before the MB test) two main peaks of the Cu 2p (at 933.2 and 953.0 eV) can be assigned to the binding energy of Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. There is only a 0.7 eV shift in the binding energy after long UV illumination, which might be resulted from additional carbon leftover on the surface after the photodegradation of MB to carbon-based products. However, we haven’t observed any additional XPS peak around 940 eV which might be assigned as oxide form. Additionally, O 1s XPS spectra show there is no significant change in the oxygen content of the sample. Only the amount of the absorbed O_2 groups on the sample surface increased from 3.14 % to 4.08 % (Figure 8b). These results show that Cu NCs are highly stable over the TiO_2 surface after a long photocatalytic degradation process.

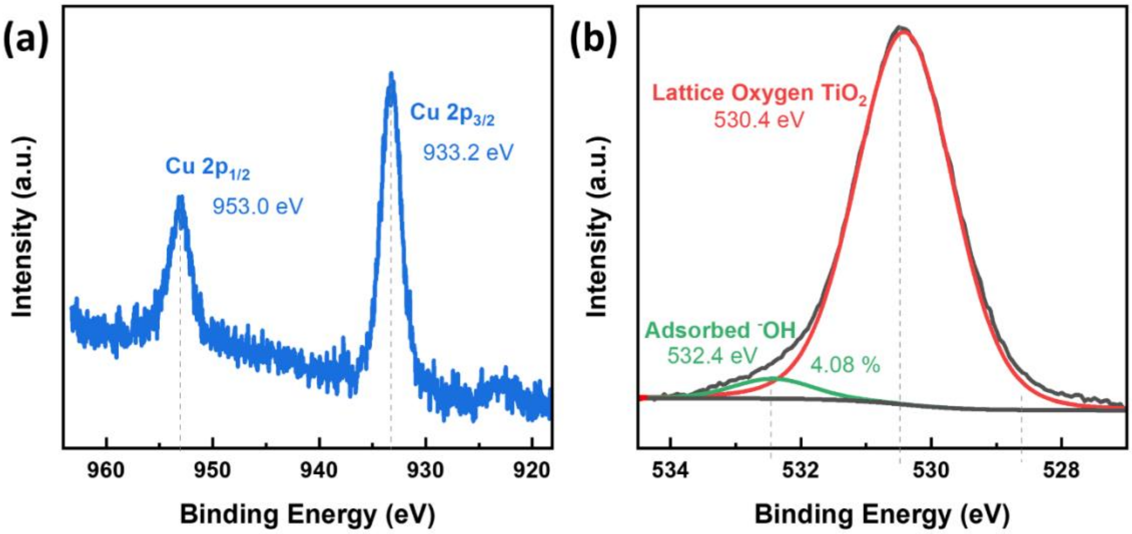

Figure 8. High-resolution XPS spectra of (a) Cu 2p and (b) O 1s after photocatalytic reaction for 16 hours.

4. Conclusions and Recommendations

In conclusion, we have fabricated a highly active Cu-TiO_2 hybrid photocatalyst (stable Cu NCs on columnar TiO_2 thin film) by photocatalytic deposition (under UV illumination) of Cu $^{2+}$ions. Our results showed that decorating columnar TiO_2 thin film with Cu NCs with an optimum surface coverage (4.6 %) significantly improved the photocatalytic performance, due to trapping the electrons on TiO_2, which reduces the recombination of photogenerated electrons and holes. However, an excessive amount of Cu NCs (7.83%) on the TiO_2 surface reduces the overall photocatalytic performance. These clusters might act as a recombination center as well as block the UV light which is exposed to the surface of the TiO_2 thin film. Additionally, the deposited Cu NCs showed good stability after a long photocatalytic degradation process. The Cu-TiO_2 hybrid system would be a good alternative to conventional co-catalyst systems which compose of expensive metals (Au, Ag, Pt, etc.) and TiO_2 structure. Such a concept can be easily extended for various photocatalytic applications including photocatalytic solar water splitting (production of hydrogen as fuel) due to its high efficiency (compared to induvial components) and cost-effectiveness (compared to noble metal-based co-catalysts). Besides such benefits, the photodeposition of Cu NC’s can be easily combined in preparation of bimetallic structures (Au-Cu or Au-Pt) as well as the fabrication of a Z-scheme photocatalytic systems (called artificial photosynthesis) for better photocatalytic performance in energy and environmental issues.

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Authors' Contributions

Salih Veziroglu: Experimental, Investigation, Formal analysis, Visualization, Writing - review and editing.

Statement of Conflicts of Interest

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

The author declares that this study complies with Research and Publication Ethics.

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