



## RESEARCH PAPER

Highly highly photocatalytic performance of TiO<sub>2</sub> nanowires in the conversion of benzaldehydes to benzoic acidSudirman\*<sup>[a]</sup>, Lalu Dimas Pratama Atmaja<sup>[a]</sup>, Ari Jamhari Pratama<sup>[a]</sup>, Emmy Yuanita<sup>[a]</sup>, Ni Komang Tri Dharmayani<sup>[a]</sup>, Maria Ulfa<sup>[a]</sup>, Romel Hidayat<sup>[b]</sup>

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**Abstract:** The synthesis of environmentally friendly-based chemicals such as solvent-free continues to be developed. A critical precursor in chemical synthesis is benzoic acid. This research developed a synthesis method by utilizing TiO<sub>2</sub> nanomaterials with different morphologies as photocatalysts, namely nanoparticles (NPs) and nanowires (NWs). Titanium (IV) oxide with nanowires morphology was synthesized by hydrothermal method under alkaline conditions. SEM, XRD, and FT-IR images confirmed the morphologies of TiO<sub>2</sub> NPs and TiO<sub>2</sub> NWs. Photocatalytic performance in converting benzaldehyde to benzoic acid showed a significant difference of up to 38% using TiO<sub>2</sub> NPs and 94% using TiO<sub>2</sub> NWs.

Keywords: nanomaterials, photocatalyst, TiO<sub>2</sub> NPs, TiO<sub>2</sub> NWs, benzaldehydes, benzoic acid.

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## INTRODUCTION

The oxidation of carbonyl compounds plays an essential role in synthesizing organic compounds because carbonyl compounds are widely used as intermediates in the laboratory and industry. Benzoic acid is a chemical commonly used in various fields, not only as a precursor but also as an additive in multiple industries and manufacturers. Benzoic acid is generally obtained from the oxidation of benzene derivatives using permanganate and chromate. Another study using Na<sub>2</sub>WO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> got the highest yield value of 81%, and involving a surfactant in the form of beta-cyclodextrins obtained a yield value of 90% [1]. The use of a cyclo-[(s)-His-(s)-phe] complex catalyst has been used in oxidizing benzaldehyde to obtain a specific conformation of benzoic acid derivatives [2]. However, oxidation involving many oxidizers, activators, and surfactants resulted in an inefficient process of isolating the synthesized products. In addition, excessive use of supporting chemicals will cause waste that can pollute

the environment.

Experiments on organic synthesis for oxidation reactions using heterogeneous catalysts have begun to be developed to increase efficiency both in separation and yield value. Heterogeneous catalyst candidates were initially created using metals such as Gold (Au) [3], Osmium (Os) [4], Rhenium (Re) [5], Platinum (Pt) [6], and transition metals such as Cobalt (Co) and Copper (Cu) [4]. Even though the yield obtained is relatively high, the reaction using this noble metal is generally carried out under particular conditions related to the pressure and atmosphere used. Other heterogeneous catalysts developed are derived from synthetic and modified zeolite groups and metal oxides. Some of them, namely Fe/SBA-15 [7], Ce<sub>0.3</sub>Co<sub>0.7</sub>Fe<sub>2</sub>O<sub>4</sub>[8], Co<sub>3</sub>O<sub>4</sub>@ZSM-5 [9], Co-ZSM-5[10], and Co-ZSM-11 [11], have been successfully used in the synthesis of organic chemistry for oxidation reactions. But even so, the main weakness of using these catalysts is that almost all processes still require solvents, including acetone, acetonitrile, methanol, and 1,4 dioxane, which

can still be environmental pollutants. A similar catalytic reaction experiment without solvent using Co/ZSM-5 catalyst successfully converted styrene into benzoic acid with a yield of up to 100% under 2 MPa pressure under a saturated O<sub>2</sub> atmosphere [12]. However, the atmospheric conditions still need to be carried out on a large scale, and the Co/ZSM-5 catalyst type is still relatively expensive.

Titanium (IV) oxide is still the most popular semiconductor developed as a photocatalyst material. TiO<sub>2</sub> has various advantages over other semiconductor oxides, including a band gap that is easily modifiable, good chemical stability, and easy to synthesize with environmentally friendly methods such as hydrothermal. Previous research also explained that TiO<sub>2</sub>, with certain physical properties as a photocatalyst, can degrade and oxidize specifically organic materials such as benzyl alcohol [13]. TiO<sub>2</sub> films modified with sulfate also show spontaneous photocatalytic activity on the surface of TiO<sub>2</sub> films in oxidizing acetaldehyde to formic acid with significant yields [14]. In addition to doping on TiO<sub>2</sub>, morphological modifications also show differences in photocatalytic activity. TiO<sub>2</sub> NPs (nanoparticles) show a fast charge recombination process compared to TiO<sub>2</sub> NWs (nanowires)[15], which means that if the generated photoelectron is not immediately captured by the substrate, it will reduce the effectiveness of the TiO<sub>2</sub> NPs catalyst. On the other hand, under certain conditions, TiO<sub>2</sub> NWs have another potential due to the slow charge recombination. Therefore, this study studied the photocatalytic activity of TiO<sub>2</sub> NPs and TiO<sub>2</sub> NWs in oxidizing benzaldehyde at ambient conditions.

## MATERIALS AND METHODS

### Material

The materials used in this study are TiO<sub>2</sub> NPs (Merck Millipore), KOH (Merck Millipore), and Benzaldehyde (Sigma-Aldrich) with a purity of 98% and a density of 1.04 g/L (25 °C).

### Synthesis of TiO<sub>2</sub> NWs

The synthesis of TiO<sub>2</sub> NWs using the hydrothermal method was adopted from the process in Ref. [16], which was modified using a sonication device. First, TiO<sub>2</sub> NPs were mixed with KOH (10 M) in a ratio of 1:

10. The mixture was stirred for at least 30 minutes to obtain a homogeneous suspension. Next, the suspension obtained was sonicated for two hours and put into an autoclave at 200°C for 24 hours. Finally, the filtrate and substrate were separated using a centrifuge to obtain TiO<sub>2</sub> NWs.

### Performance test of TiO<sub>2</sub> as a photocatalyst.

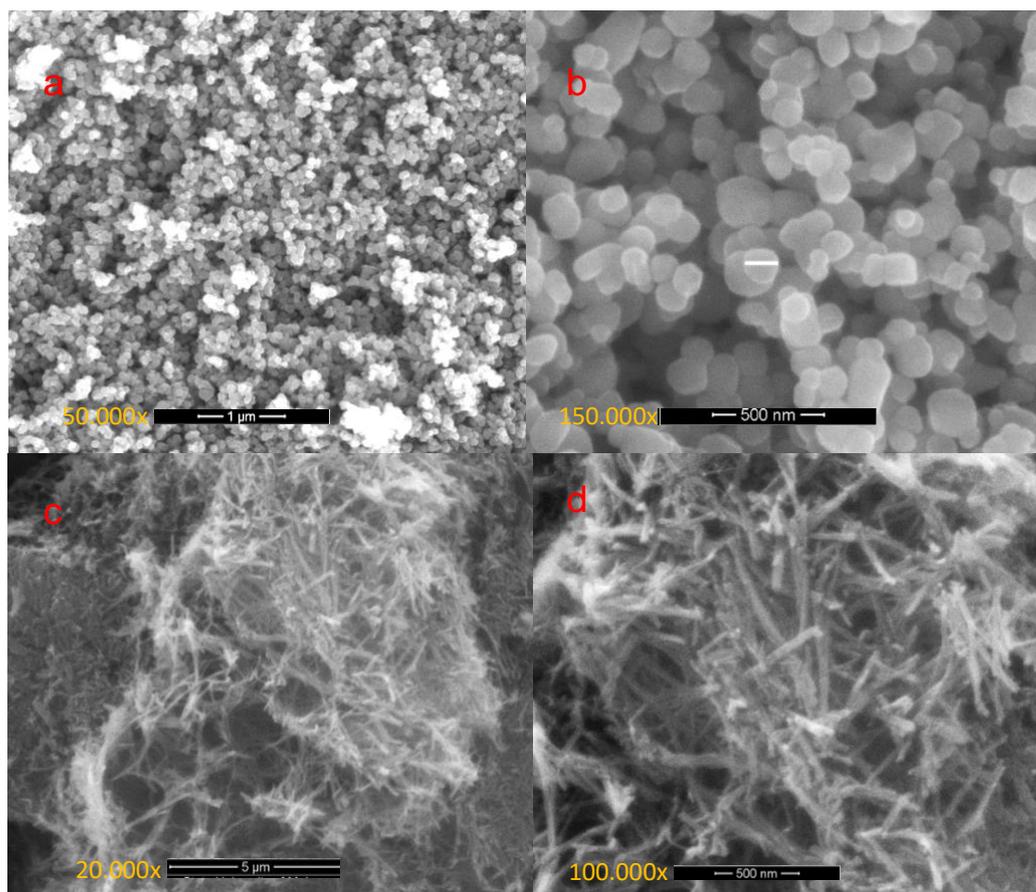
The performance of TiO<sub>2</sub> NPs and NWs (0.1 g) as photocatalysts were tested by oxidizing benzaldehyde (25 mL) under 360 nm UV light and oxygen atmosphere for 60 minutes, expected to become benzoic acid. Fourier Transform Infra-Red investigated the reaction products.

### Material Characterization

The morphology of TiO<sub>2</sub> NPs and TiO<sub>2</sub> NWs was confirmed using a scanning electron microscope (SEM). At the same time, the crystal systems of both samples were characterized by powder X-ray diffraction (XRD). The photocatalytic performance of TiO<sub>2</sub> in converting benzaldehyde to benzoic acid was performed by Fourier Transform Infra-Red (FTIR).

## RESULTS AND DISCUSSION

The change in morphology of TiO<sub>2</sub> from nano spherical to nanowires was clearly observed through SEM images. The precursor used is a nano spherical (Fig. 1a and 1b) with a fairly uniform distribution of particle size and shape with an average diameter of 54.35 nm. The size of the TiO<sub>2</sub> precursor used is somewhat larger than generally used, which is in the range of 25-30 nm, but the size of the diameter of these TiO<sub>2</sub> NPs is smaller than the results of the synthesis carried out by the bottom-up method with titanium isopropoxide precursor [17]. Morphological transformations carried out by the hydrothermal method showed the shape of nanowires with a fairly uniform distribution (Fig. 1c and 1d) with an average diameter of 35.80 nm. However, it was clearly observed that the threads of TiO<sub>2</sub> began to agglomerate so that the TiO<sub>2</sub> strands looked chaotic, and the surface morphology still looked rough. It is likely due to a relatively lower temperature that causes a decrease in the crystallinity of TiO<sub>2</sub> NWs [18].

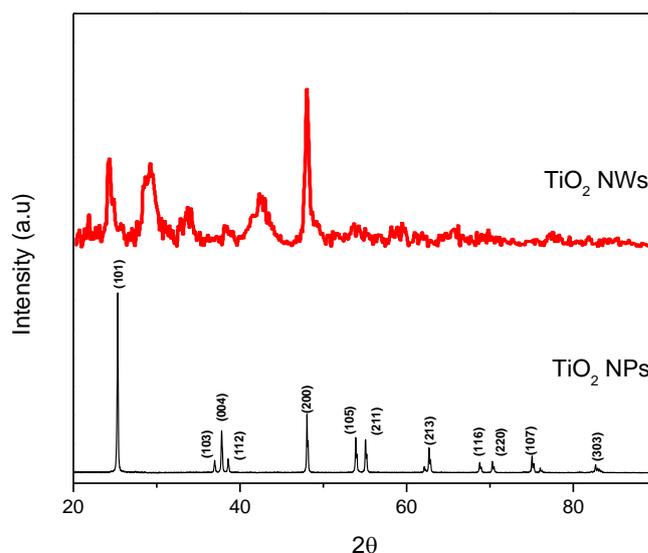


**Figure 1.** SEM images of TiO<sub>2</sub> NPs (a and b) and TiO<sub>2</sub> NWs (c and d).

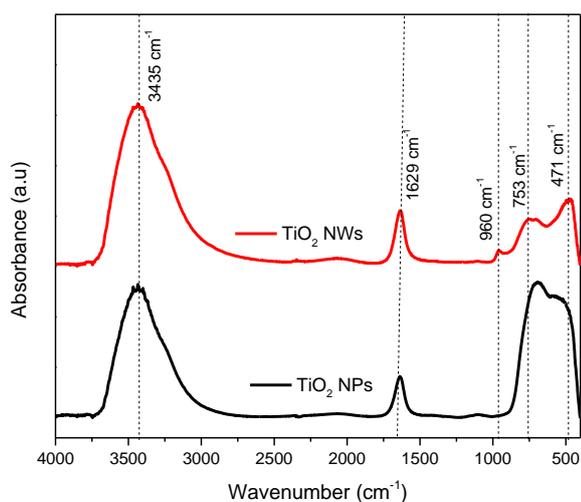
The decrease in crystallinity from TiO<sub>2</sub> NPs to TiO<sub>2</sub> NWs was confirmed through x-ray diffractograms (Fig. 2). Diffractogram TiO<sub>2</sub> NPs confirmed through JCPDS No. 01-084-1285 in the form of anatase crystals synthetic indicated from the peak with the highest intensity at 25.3 which is the distance of the spacing d<sub>101</sub>, where it is by the standard precursor used [19]. Whereas in the diffractogram pattern of TiO<sub>2</sub> NWs, it is still clearly confirmed anatase shape, corresponding to TiO<sub>2</sub> NPs. However, a clear difference is seen in the pattern diffractogram TiO<sub>2</sub> NWs crystalline peaks have a large-half peak width and tend to shift towards a smaller angle. It is due to a decrease in the level of crystallinity that is quite contrasting [20].

The characteristics of TiO<sub>2</sub> NPs and TiO<sub>2</sub> NWs are also seen based on the FT-IR spectra (Fig 3.), where it can be seen that there are no contrasting features between the two samples, namely in the range of wave numbers 2800-3600 cm<sup>-1</sup>, which is a vibrational feature of stretching O-H due to water molecules adsorbed on the surface of TiO<sub>2</sub> and at wave numbers around 1629 cm<sup>-1</sup> which is Ti-OH [21]. The differences that arise from the two samples are observed in the range of 500-900 cm<sup>-1</sup>, which is characteristic of rigid ionic bonds, where TiO<sub>2</sub> NPs show

a stronger absorbance than TiO<sub>2</sub> NWs due to an increasingly less ordered structure [22].



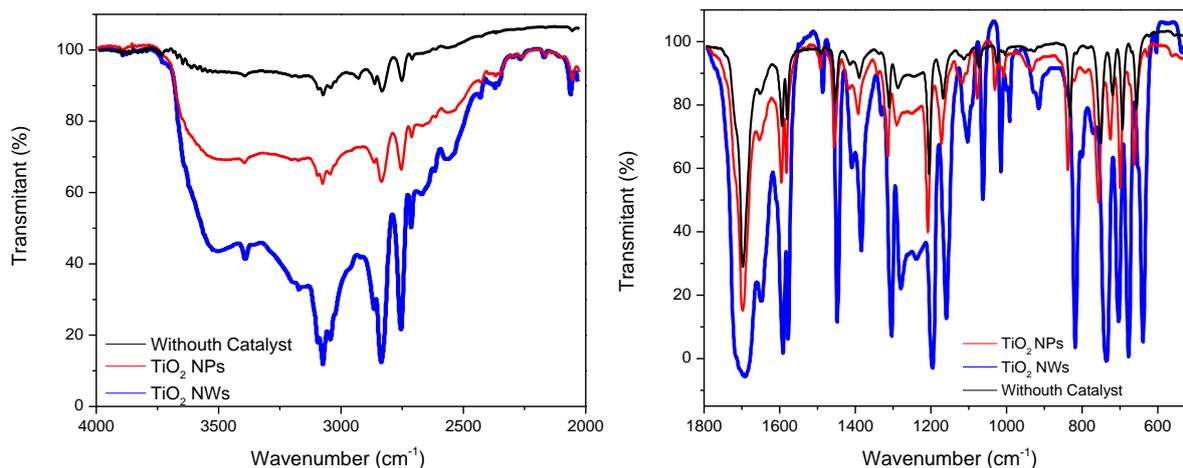
**Figure 2.** Powder XRD pattern of TiO<sub>2</sub> NPs (black line) and TiO<sub>2</sub> NWs (red line).



**Figure 3.** FT-IR Spectra of TiO<sub>2</sub> NPs (black line) and TiO<sub>2</sub> NWs (red line).

The photocatalytic performance of TiO<sub>2</sub> NPs and TiO<sub>2</sub> NWs in oxidizing benzaldehyde to benzoic acid was investigated by FT-IR (Fig 4.). All three samples showed major absorption regions in the range of 4000-2000 cm<sup>-1</sup> and 1800-500 cm<sup>-1</sup>. In the low-frequency region, the three samples showed the same features: absorption due to the vibrations of C=O (1720 cm<sup>-1</sup>), C=C aromatic (1589 cm<sup>-1</sup>), and C-H aromatic bonds. Contrasting feature changes appear in the 3850-2250 cm<sup>-1</sup> region of the three samples, where the absorption in this region is due to O-H vibrations. It strongly indicates the transformation of aldehyde functional groups into carboxylate groups. By considering the Beer-Lambert law (Eq 1), where the absorbance (A) is proportional to the logarithmic 1/Transmittance (T) and proportional to the concentration of the molar attenuation coefficient ( $\epsilon$ ) and the distance of the light source (b) which is identical because it is done on an identical system.

$$A = \log \frac{1}{T} = \epsilon b C \quad \dots\dots\dots \text{Eq 1}$$



**Figure 4.** FT-IR Spectra of Benzaldehydes after UV (360 nm) irradiation without catalyst (black line), with TiO<sub>2</sub> NPs (red line) and TiO<sub>2</sub> NWs (blue line) catalyst.

In other words, the absorption value in this region will be proportional to the concentration of benzoic acid formed. It can be seen that the oxidation of benzaldehyde without using a catalyst does not show significant absorption (~8%) in this region, which means that benzaldehyde cannot be oxidized using only UV irradiation (360 nm). In contrast, benzaldehyde oxidized with the addition of TiO<sub>2</sub> NPs catalyst gives a maximum absorption value of up to ~38%. Most interestingly, benzaldehyde oxidized using TiO<sub>2</sub> NWs catalyst gave a significant maximum uptake value of ~94%.

Based on experiments and considering the existing theory, a mechanism of oxidation of benzaldehyde molecules can be proposed, as seen in Fig. 5. The

proposed mechanism is a radical oxidation reaction, including the initiation, propagation, and termination stages (Fig 5). The initiation stage begins with the excitation of electrons from the valence band to the conduction band of TiO<sub>2</sub>. The active electrons are expected to collide with the chemisorbed benzaldehyde molecules on the surface of TiO<sub>2</sub> [23]. Then, the molecules would be converted into benzaldehyde radical molecules, which are expected to associate with oxygen molecules to form benzaldehyde-oxygen radicals [24], [25].

The propagation stage starts from the benzaldehyde-oxygen radical complex that collides with other benzaldehyde molecules, producing benzoic acid and

benzoate radicals. Then ends with the termination stage, namely, the benzoate radical is stabilized on the hole state of  $\text{TiO}_2$  to produce benzoate ions. The contrasting difference in photocatalytic activity values between  $\text{TiO}_2$  NPs and  $\text{TiO}_2$  NWs occurs because morphological differences affect the lifetime of active species in the reaction. The nano spherical shape of  $\text{TiO}_2$  allows charge recombinant towards the particle

center faster than the morphology of the nanowire [15]. Nanowires' shape does not reduce the surface area significantly and allows charge recombinant slower so that the oxidation process by the active species is more optimal.

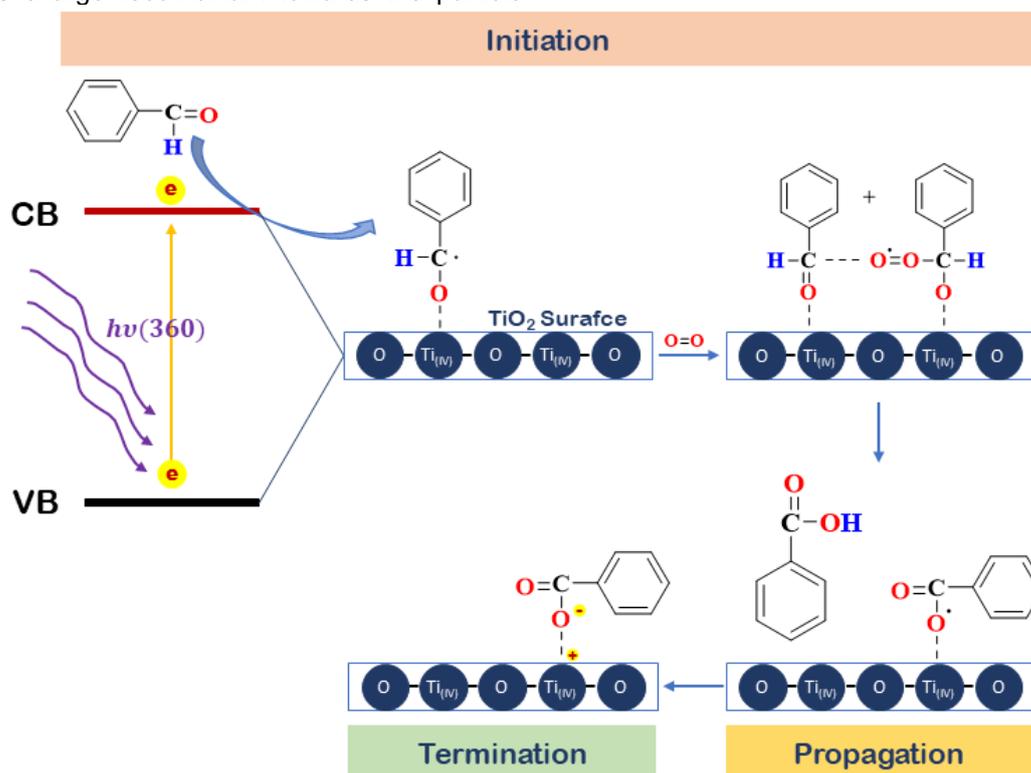


Figure 5. Proposed mechanism of oxidation of benzaldehyde to benzoic acid

## CONCLUSION

$\text{TiO}_2$ -derived nanowires (NWs) were successfully synthesized by a simple hydrothermal method under alkaline conditions. The success of this morphological transformation is confirmed by SEM images that show  $\text{TiO}_2$  NPs in nano spherical form with an average diameter of around 54.35 nm transformed into  $\text{TiO}_2$  NWs with an average diameter of around 35.80 nm. The analysis of XRD powder diffractogram patterns also showed the d-spacing peaks of anatase  $\text{TiO}_2$  crystals in both samples, where  $\text{TiO}_2$  NWs decreased crystallinity. While characterization conducted through FT-IR on  $\text{TiO}_2$  NPs and  $\text{TiO}_2$  NWs showed no significant difference in spectra features. The most interesting result is that the conversion value of benzaldehyde to benzoic acid through photocatalytic reactions shows a significant difference, namely 38% for using  $\text{TiO}_2$  NPs catalyst and 94% for using  $\text{TiO}_2$  NWs. It confirms the

indication of charge-recombinant slowing down in NWs morphology compared to NPs.

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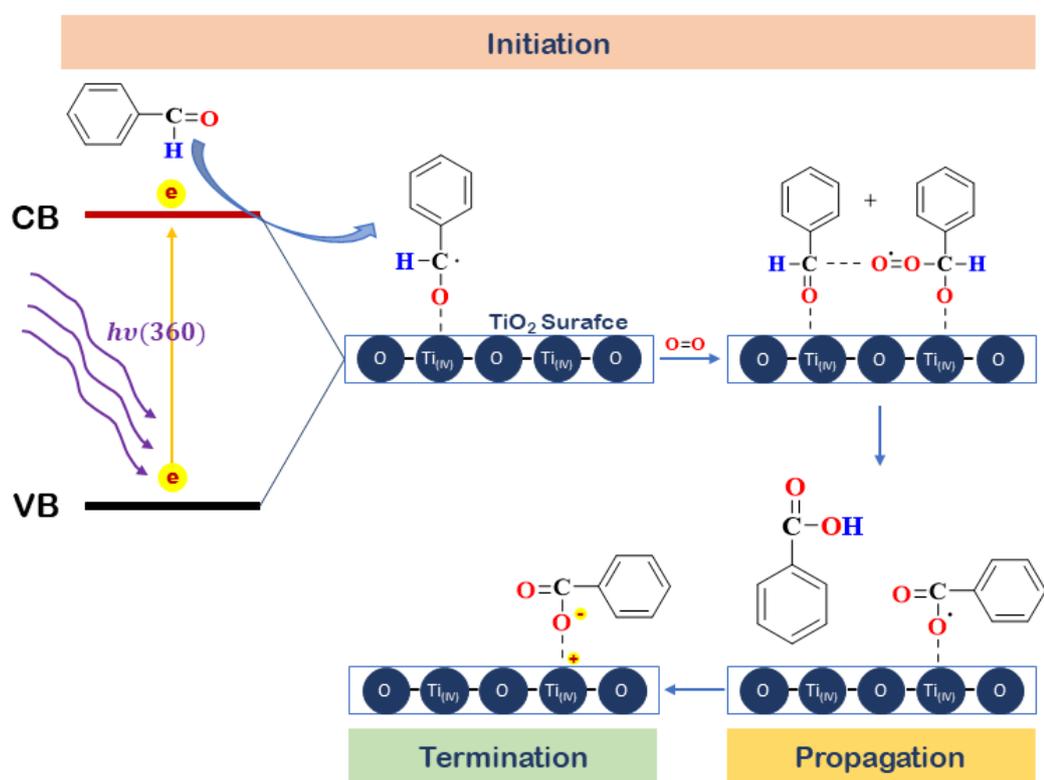
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