

Article



Facile Synthesis of Various ZrO_2 Phases and ZrO_2 -MO₂ (M = Ti, Hf) by Thermal Decomposition of a Single UiO-66 Precursor for Photodegradation of Methyl Orange

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Abstract: A zirconia-based catalyst with controlled crystalline phases is synthesized through a simple thermal decomposition of a parent UiO-66 single precursor. The introduction of Ti(IV) and Hf(IV) cation into the Zr(IV) framework has been successfully obtained to tune the photocatalytic activity over methyl orange (MO) solution. Their resulting crystalline phases, morphologies, elemental analysis, band gap values, surface area, and photocatalytic degradation study over MO dye are presented and discussed. The tetragonal zirconia (*t*-ZrO₂) catalyst exhibits the highest photocatalytic activity with 89% decoloration efficiency under UV irradiation ($\lambda = 254$ nm) for 300 min compared to *m*-ZrO₂ (67%), the mixed phases (*t*-ZrO₂ and *m*-ZrO₂), as well as the synthesized mixed oxides ZrO₂-MO₂ (M = Ti or Hf), where the photocatalytic activities are 74% and 63%, respectively. This result is on par with commercially available anatase TiO₂ and other reported *t*-ZrO₂ catalysts.

Keywords: photodegradation; methyl orange; UiO-66; post-synthetic exchange; thermal decomposition

1. Introduction

Zirconium(IV) oxide (ZrO₂) is a very interesting semiconductor with a myriad of cutting-edge applications, such as a catalyst [1], a sensor of chemical species [2], corrosion-resistant coatings [3], and solid oxide fuel cells [4]. ZrO_2 exhibits three different phases: monoclinic (*m*-ZrO₂), tetragonal (*t*-ZrO₂), and cubic (*c*-ZrO₂). The crystalline phases of interest in catalysis are the crystalline phases of *m*-ZrO₂, low temperature stabilized *t*-ZrO₂, and a mix of monoclinic and tetragonal phases [5]. Having a wide band gap value and a high negative value of the conduction band potential, ZrO_2 has been widely studied as a photocatalyst in different chemical reactions [6]. The reported band gap energy of ZrO_2 ranges between 3.25 and 5.1 eV, depending on the preparation technique of the sample [7].

Methyl orange (MO), as one of the widespread carcinogenic water pollutants, is one of the very common water-soluble azo dyes that is extensively used in several industries such as textiles, paper, printing, and food [8–10]. One simple method to mitigate such water pollutants is photocatalytic degradation using photoactive catalysts, such as zirconia (ZrO₂). Based on the existing literature, we note that the photocatalytic degradation activity of zirconia depends on its adopted synthetic route and the resulting crystalline phase(s).



Citation: Jannah, I.N.A.; Sekarsari, H.F.; Mulijani, S.; Wijaya, K.; Wibowo, A.C.; Patah, A. Facile Synthesis of Various ZrO₂ Phases and ZrO₂-MO₂ (M = Ti, Hf) by Thermal Decomposition of a Single UiO-66 Precursor for Photodegradation of Methyl Orange. *Catalysts* **2022**, *12*, 609. https://doi.org/10.3390/catal12060609

Academic Editors: Jaime Carbajo, Patricia García-Muñoz and Vincenzo Vaiano

Received: 16 April 2022 Accepted: 30 May 2022 Published: 2 June 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Basahel et al. [11] reported nanosized ZrO_2 powders with near pure monoclinic (*m*-ZrO₂), tetragonal (*t*-ZrO₂), and cubic (*c*-ZrO₂) structures synthesized by varied methods, using different precursors. In their paper, MO photodegradation reached 99% within 110 min using *m*-ZrO₂ nanoparticles, while the *t*-ZrO₂ and *c*-ZrO₂ nanocatalysts showed 90% and 80% degradation, respectively. Reddy et al. [12] showcased that photodecomposition of MO decreased with increasing irradiation time using *t*-ZrO₂. On the other hand, a low percentage (37%) of MO removal was presented by Mansouri et al. [13], where the ZrO₂ nanoparticle was synthesized by the sol–gel method.

Another widely adopted route for synthesizing nano oxide catalysts is using Metal– Organic Frameworks (MOFs) as a sacrificial template. The morphology of the parent MOF can be retained after a certain degree of controlled calcination. Using the optimized condition, specific crystalline phase(s) can also be easily isolated [14]. MOFs can easily be modified in three different ways to achieve high photocatalytic activity and stability, such as (i) through the introduction of metal sites; (ii) through an indirect route (postsynthetic modification), e.g., as a sacrificial template to make nano oxide catalysts; and (iii) through the creation of defects [15]. There are some reports showing nano ZrO_2 -derived MOFs for photocatalytic degradation [8,10,16]. The 50% TiO₂- ZrO_2 binary oxide catalyst exhibited a high phenol degradation (99%) and a high reaction rate (0.73 mg L⁻¹ min⁻¹), as reported by Kambur et al. [17]. Gota and Suresh obtained the Zr/Ti ratio (6.3), which degraded 88.72% of reactive red dye after 70 min [18]. Porous TiO₂/ ZrO_2 obtained by calcining TiO₂/UiO-66 nanocomposites, reported by Abdi [8], displayed the excellent RhB photocatalytic degradation performance of 95% after 180 min.

Apart from the studies mentioned above, research on isolating crystalline phases of ZrO_2 and their effect on photocatalytic degradation of dyes is scarce. Herein, we report a simple route for isolating highly photoactive *t*- ZrO_2 , *m*- ZrO_2 , mixed *t*- and *m*- ZrO_2 with and without MO₂ (M = Ti or Hf) using UiO-66 as a single sacrificial template, without the use of additional precursors. All synthesized catalysts are photocatalytic active, and *t*- ZrO_2 showcases the highest photocatalytic degradation of MO, comparable to commercially available anatase TiO₂ and other reported *t*- ZrO_2 catalysts.

2. Results

A phase-pure, zirconium-based MOF, UiO-66, was obtained through the solvothermal method. The process of dissolving $ZrCl_4$ with DMF needs to be carried out under relatively inert conditions to avoid the form of irreversibly zirconyl chloride ($Zr(OH)_2(H_2O)_4Cl$). At the same time, DMF deprotonates H_2O , accelerating the formation of UiO-66 [19]. Apart from DMF, acetic acid was employed to increase the solubility of $ZrCl_4$ in DMF and functioned as a modulator [20]. The as-synthesized UiO-66 displays typical UiO-66 peaks at 7.32° and 8.46° 20 without any unidentified peak, confirming the successful formation of phase-pure UiO-66, Figure S1a. The expected morphology of UiO-66 is shown in Figure S1b with a particle size of 420 nm, as observed using ImageJ[®] software.

2.1. Tetragonal and Monoclinic ZrO₂

The synthesis of t-ZrO₂, m-ZrO₂, mixed phases (t- and m-ZrO₂), and ZrO₂-MO₂ (M = Ti or Hf) was successfully carried out through a facile optimized calcination process using UiO-66 as a sacrificial template. Overall, calcination at 500 °C for 2 h obtained the nearly pure tetragonal ZrO₂ phase (t-ZrO₂). Elevating the time (and temperature) of calcination increases monoclinic phase composition. The close-to-pure m-ZrO₂ is obtained at 800 °C for 24 h. Therefore, the mixed-phase of t- and m-ZrO₂ can be easily obtained by using conditions between the two aforementioned conditions.

To find the optimum calcination condition referenced above for isolating near-pure *t*and *m*-ZrO₂, we conducted experiments at two calcination temperatures of 800 °C (for 2, 8, and 24 h) and 500 °C (for 2, 6, and 8 h). The synthesized ZrO₂ is denoted as ZrO₂-A-B, where A indicates the calcination temperature and B represents the calcination time. The patterns of *t*-ZrO₂ have many peaks at 30.2°, 34.6°, 35.3°, 50.2°, 50.7°, and 60.2°, which were assigned to the (101), (002), (110), (112), (200), and (211) planes; thus, t-ZrO₂ has three facets of $\{101\}$, $\{002\}$, and $\{112\}$. Meanwhile, *m*-ZrO₂ has typical peaks at 28.3°, 31.6°, 34.3°, 35.3°, 40.9°, and 44.8°, attributed to the (111), (111), (020), (200), (211), and (112) planes, with three crystal facets of {111}, {020}, and {112}. As shown in Figure 1, a mixture of monoclinic dominant phase (JCPDS 78-1807) and tetragonal (JCPDS 79-1769) ZrO_2 is already formed even in the shortest calcination time of 2 h when calcining at 800 °C. Elevating the calcination time at 8 and 24 h shifts the mixture of tetragonal and monoclinic phases to nearly pure monoclinic, as indicated by the disappearing $30.2^{\circ} 2\theta$ peak. Furthermore, increasing the calcination time increases the peak intensity, indicating an increase in crystallinity and particle size of ZrO₂. Thus, close-to-pure *m*-ZrO₂ is obtained at 800 °C calcination for 24 h. Therefore, the dominant tetragonal phase would be observed below 800 °C, as reported by Basahel et al. [11] and Li et al. [21]. Lowering the calcination temperature to 500 °C isolates more t-ZrO₂, with the near-pure pattern showing a 2 h calcination time. To obtain the ratio of the tetragonal-to-monoclinic phase, we use Toraya's method, which calculated the volume ratio by X-ray diffraction [22]. Table 1 showcases the yield of t-ZrO₂ and m-ZrO₂ for each sample obtained from the varying calcination temperatures and times above. The table shows that different calcination temperatures and time variations can gradually transform the ZrO₂ phase.



Figure 1. PXRD patterns of ZrO₂ at different calcination temperatures and times.

Semala 7rO	% Phase			
Sample $2rO_2$ –	t-ZrO ₂	<i>m</i> -ZrO ₂		
ZrO ₂ -800-24	3.90	96.1		
ZrO ₂ -800-8	6.90	93.1		
ZrO ₂ -800-2	15.7	84.3		
ZrO ₂ -500-8	60.0	40.0		
ZrO ₂ -500-6	71.1	28.9		
ZrO ₂ -500-2	84.4	15.6		

In general, the morphology of the UiO-66 particle after calcination did not differ from that of pristine UiO-66, yet appeared denser and agglomerated, with a lighter color due to the expected change in chemical composition, giving a solid ZrO_2 . It is observed that the ZrO_2 (the calcined UiO-66) size was much smaller than that of the UiO-66, Figure 2, as expected, due to organic linker decompositions. The approximate particle size of ZrO_2 was only about 116 nm, compared to parent UiO-66 420 nm in size.



Figure 2. SEM images of UiO-66 particle after calcination at 500 °C.

2.2. ZrO_2 - MO_2 (M = Ti or Hf) Composites

Aside from investigating ZrO_2 phases against MO photocatalytic degradation, we also studied the composite of ZrO_2 with other oxides of the same group (Ti and Hf). HfO₂ has not been reported as a photocatalytic active material due to having a wide band gap; however, mixing HfO₂ with ZrO_2 has mixed results in a favorable photocatalytic band gap. Further, tuning the ZrO_2 band gap can also be completed by adding notorious photoactive TiO₂ by making a ZrO_2 -TiO₂ composite. We have successfully synthesized these composites, ZrO_2 -MO₂ (M = Ti or Hf), by a simple thermal decomposition of Ti- or Hf-substituted Zr-UiO-66 as a single precursor.

The process of forming the composites starts with partially replacing the Zr(IV) cations with Ti(IV) in a post-synthetic exchange (PSE) reaction of UiO-66 with TiBr₄ at 85 °C for 1, 3, and 5 days. The post-synthetic cation exchange process of Ti⁴⁺ to UiO-66 generates a proportion of Ti⁴⁺ to Zr⁴⁺ of around 2:1. This process did not cause the changes, even for the structure in which Hf ⁴⁺ exists. There is no change in either PXRD patterns or morphology of UiO-66(Zr/Ti) compared to those of UiO-66, indicating a successful partial substitution of Zr(IV) by Ti(IV), Figures S2–S4. The Ti(IV) cation amount was 0.04, 0.05, and 2 % atom for 1, 3, and 5 days, respectively, as observed by SEM-EDS.

 ZrO_2-MO_2 composites are shown in Figure 3, denoted as (Zr/M)-Xd-A-B, where X represents the reaction time. From that figure, it is known that anatase TiO₂ starts to form under the decomposition process at 500 °C for 2 h, with a sharp anatase TiO₂ peak (JCPDS 21-1272) appearing at 25.4°, with 2 θ characteristics to {100} facet, observed for the sample with PSE reaction for 5 d. The amount of TiO₂ increases as we increase reaction times (1, 3, and 5 d) during UiO-66(Zr/Ti), Table 2. The highest t/m-ZrO₂ ratio with the highest percentage of TiO₂ is 1.58, observed in the (Zr/Ti)-5d-500-2 sample. It is noteworthy from our results that anatase TiO₂ can provide stability to the tetragonal structure of ZrO₂ as shown in Figure 4, which is susceptible to forming a monoclinic phase. We observe such a phase of pure *t*-ZrO₂ formation in the presence of anatase TiO₂ in our (Zr/Ti)-5d-500-2 sample, Table 2. Re-heating the sample further to 800 °C for 24 h did not transform the sample into pure *m*-ZrO₂, confirming our hypothesis above on the role of TiO₂ in stabilizing the tetragonal phase of ZrO₂.



Figure 3. PXRD patterns of ZrO_2 -Ti O_2 and ZrO_2 -Hf O_2 composites.

Table 2. The volume ratio of binary oxide catalysts.

7-0 MO -	% Phase			
$2rO_2-MO_2$	t-ZrO ₂	<i>m</i> -ZrO ₂	TiO ₂ Anatase	
(Zr/Hf)-7d-500-2	37.9	62.1	-	
(Zr/Hf)-5d-500-2	34.6	65.4	-	
(Zr/Ti)-5d-500-2-800-24	29.7	54.6	15.7	
(Zr/Ti)-5d-500-2	44.2	28.0	27.8	
(Zr/Ti)-3d-500-2	81.0	-	19.0	
(Zr/Ti)-1d-500-2	78.9	21.1	-	



Figure 4. SEM image of ZrO₂-TiO₂ composite for (Zr/Ti)-5d-500-2.

Like Ti(IV) substitutions, Hf(IV) doping does not significantly affect the diffraction pattern of UiO-66, as shown in Figure S5. The Hf(IV) cation exchange lasted for 5 and 7 days. The binary oxide ZrO_2 -HfO₂ composites were obtained by calcining UiO-66(Zr/Hf) at 500 °C for 2 h, featuring overlapping patterns between monoclinic and tetragonal phases for both ZrO_2 and HfO₂. The observed broad peaks resulted from mixing two metal oxides (ZrO_2 and HfO₂) with the same phases with similar diffraction patterns, Figure 3. In Table 2, the ratios of t/m-ZrO₂ are 0.53 and 0.61 in (Zr/Hf)-5d-500-2 and -7d-500-2, respectively.

Shifting peaks in PXRD patterns were observed for different metal dopants, Figure 3, as expected in accordance with the atomic radius of the dopant. With the same PSE reaction time for 5 days, a slight change of the {101} facet from 35.3° to 35.2° was observed for Ti(IV) doping. Hf(IV) doping showed a different character, where there was a left shift from 35.3° to 35.0° for {101} facet. According to Takeuchi and Inoue [23], due to a larger ionic radius, Hf(IV) doping tends to expand the crystallite size diameter of the {101} facet more significantly than Ti(IV) doping, as observed in our result.

2.3. Band Gap Characterization

The estimated band gap values for different catalysts and anatase TiO₂ are shown in Figure 5. The pristine TiO₂ anatase has a band gap of 3.16 eV. The ZrO₂-TiO₂ composite derived from UiO-66 (Zr/Ti) reduces the band gap of ZrO₂ from 4.81-5.01 eV to 3.01-3.14 eV, Figure 5 (purple line). Despite having a more significant concentration of electron density on oxygen atoms than that of ZrO₂, which would be advantageous for photocatalysis purposes because such defect levels would serve as electron-trapping sites for accelerated transfer of photogenerated electrons, the band gap of HfO₂ is generally too wide, 5.68 eV, to be an excellent photocatalyst [24]. Alloying with a lower band gap could lower the composite band gap to become photoactive. However, the introduction of Hf to form the ZrO₂-HfO₂ composite did not change the band gap of ZrO₂ significantly (from 5.68 eV to 5.01 eV). We conclude from the above band gap values that all catalysts are photoactive in the UV region. Therefore, we proceed with their measurements in the photocatalytic degradation of MO. The band absorption of all *t*-ZrO₂-containing compounds is less sharp than those of *m*-ZrO₂-containing compounds. This may indicate the existence of an indirect band gap within all *t*-ZrO₂-containing combinations.



Figure 5. The plot of the Jacobian corrected Kubelka-Munk function for all catalysts.

2.4. Photocatalysis Activity of ZrO₂, ZrO₂-TiO₂, and ZrO₂-HfO₂

The performance of different catalysts in the photocatalytic degradation of MO is summarized in Figure 6. MO has two characteristics of the UV-visible absorption spectrum, i.e., the peaks at 464 nm and 272 nm. The first maximum peak of 464 nm indicates the azo groups (-N=N-), while the lower-intensity peak at 272 nm represents aromatic substances from benzene rings, Figure 6a. Typical catalysts are more likely to destroy the azo groups than benzene rings. TiO₂ and *t*-ZrO₂ catalysts can simultaneously break both the azo and aromatic rings [25].



Figure 6. UV-vis spectra (**a**) and decoloration efficiency (**b**) of photocatalytic degradation MO with different catalysts.

The decoloration efficiency observed in Figure 6b is divided into two regions, i.e., before the UV light is on (dark condition) and after the UV light is on. Each catalyst has a different decoloration value during dark conditions due to different catalyst adsorption capacities. The highest adsorption percentage, above 20%, occurred for $(t-\text{ZrO}_2 + m-\text{ZrO}_2 + \text{HfO}_2)$ and $t-\text{ZrO}_2$. This may be due to a larger surface area and pore volume, as observed for $t-\text{ZrO}_2$, than for $m-\text{ZrO}_2$ and pristine TiO₂ [26], as summarized in Table 3. After the first photocatalytic test, the $t-\text{ZrO}_2$ catalyst was re-characterized by PXRD to investigate its phase stability and reusability, Figure S6. The PXRD pattern remained unchanged with no additional peak, which supports the stability of the $t-\text{ZrO}_2$ catalyst.

Sample	$S_{BET} (m^2 g^{-1})$	Pore Radius (nm)	Pore Volume (cm ³ g ⁻¹)
TiO ₂	6.40	-	-
t-ZrO ₂	57.388	152.45	0.0942
<i>m</i> -ZrO ₂	3.656	154.32	0.0623

Table 3. Surface area, pore radius, and pore volume of ZrO₂.

3. Discussion

The photoactivity of t-ZrO₂ in degrading MO is eminently higher than other catalysts, reaching a maximum decoloration efficiency of 89% within 300 min. The concentration of MO decreases rapidly with the reaction rate constant of 0.0063 min⁻¹ for t-ZrO₂. Other catalysts exhibit moderate MO decoloration efficiency (63–74%), with reaction rate constants ranging from 0.031 to 0.042 min⁻¹, Figures 6 and 7 and Table 4. The photocatalytic degradation reactions of all catalysts follow pseudo-first-order kinetics, as pointed out in Figure 7b.



Figure 7. The concentration changes over measuring time (**a**) and the kinetics of photocatalytic degradation MO with different catalysts (**b**).

Sample	t/m-ZrO ₂ Ratio	Crystallite Size (nm)	Band Gap (eV)	Photo-degradation (%)	Rate Constant (min ⁻¹)
TiO ₂	-	41.7	3.16	96.14	0.0074
t-ZrO ₂	5.42	7.60	4.81	89.42	0.0063
<i>m</i> -ZrO ₂	0.04	32.9	5.03	67.23	0.0035
t/m-ZrO ₂	1.50	20.2	4.83	67.72	0.0037
t-ZrO ₂ + TiO ₂	1.58	8.40	3.01	71.42	0.0039
$t-ZrO_2 + m-ZrO_2 + TiO_2$	0.54	23.7	3.14	74.62	0.0042
t-ZrO ₂ + m -ZrO ₂ + HfO ₂	0.53	6.60	5.01	63.29	0.0031

Table 4. Properties of catalysts and their photocatalytic degradation of MO.

Table 4 summarizes the properties of each catalyst and their MO photodegradation performance. The catalyst with the largest-to-smallest rate constant is $TiO_2 > t-ZrO_2 > t-ZrO_2 + m-ZrO_2 + TiO_2 > t-ZrO_2 + m-ZrO_2 + m-ZrO_2 + HfO_2$. Basahel et al. [11] reported that a photocatalyst with a high surface area, pore volume, and pore size enhances dye adsorption and subsequent photocatalytic activity. This may partly explain the highest MO photocatalytic degradation observed for *t*-ZrO₂. We further observe that within the same t/m ratio, the substitutions of Ti(IV) to Zr(IV) to form ZrO_2 +TiO₂ composites improve, in general, the photodegradation activity of t/m-ZrO₂. Moderate photocatalytic degradation activity is observed for the ZrO_2 -HfO₂ composite, following its relatively wide band gap (5.1 eV).

Sakfali et al. [27], Kumar and Ojha [28], and Yu et al. [29] reported the correlation between calcination temperature, the resulting ZrO₂ phases, and their corresponding midgap states and oxygen vacancies, as well as their photocatalytic properties in the degradation of various compounds under UV irradiation. Such studies stressed the significance of ZrO₂ phases to photodegrade a compound under UV irradiation, similar to our study. They used the photoluminescence (PL) technique to determine the charge carrier separation and recombination efficiency correlated to the photodegradation activity of ZrO₂ phases. More investigations for the PL spectrum analysis will be conducted in the near future to gain a deeper insight into the recombined efficiency contribution of conduction band electrons and valence band holes to the photocatalytic degradation activity of our ZrO₂ phases and ZrO₂-MO₂ composites.

We further compared our highest photocatalytic-active t-ZrO₂ with other studies for MO photodegradation and found that our result is on par with other reported t-ZrO₂ and other catalysts, Table 5. Because we only completed a simple thermal decomposition of a bulk UiO-66, we believe that we can further enhance the photocatalytic activity by using

a variety of nano UiO-66 shapes as sacrificial templates. Such investigation of resulting nano oxides morphologies vs. photocatalytic activity will be conducted in the near future in our lab.

Catalyst	[MO] (mg L ⁻¹)	Catalyst Dosage (g/L)	UV Source (nm)	Time (min)	Photo-Degradation (%)	Ref.
Cu/ZnO	20	1.0	UV light	240	88	[30]
t-ZrO ₂ m-ZrO ₂ c-ZrO ₂	10	1.0	350-400	120	92 95 85	[11]
TiO ₂ -ZrO ₂ hollow spheres	50	1.0	313.2	60	8	[31]
VS ₄ /CP	10	1.0	Xe lamp	30	67	[32]
Cu-BDC UiO-66	20	0.5	UV light	40	3.3 36.4	[33]
TiO ₂ nanocellulose	40	1.0	365	30	99.7	[34]
t-ZrO ₂	10	0.1	Florescent lamp (20 W)	60	18 (pH 7) 28 (pH 3)	[35]
t-ZrO ₂	5	1.0	254	120	53	this work

Table 5. Comparison of the present study with other reported photodegradations of methyl orange.

4. Materials and Methods

Methyl orange solutions 100 ppm were made by mixing 25 mg of powdered methyl orange with demineralized aqua in a 250 mL volumetric flask. The MO solutions of 2, 4, 5, 6, 8, and 10 ppm were diluted from 100 ppm. The 10% acetic acid solution was also made by diluting 10 mL of acetic acid glacial in a 100 mL volumetric flask. Other substances were zirconium(IV) chloride, titanium(IV) bromide, and hafnium(IV) chloride, bought from the Aldrich company. At the same time, terephthalic (1,4-benzene dicarboxylate) acid 98%, titanium(IV) oxide, dimethylformamide, chloroform, acetic acid glacial, and methyl orange were purchased from the Merck company.

Synthesis of ZrO_2 was carried out through UiO-66 as a sacrificial template. The synthesis of UiO-66 was conducted according to Cavka et al. with some modifications [36]. A total of 7 mmol of $ZrCl_4$ was dissolved in 70 mL of DMF inside a Glove Box. Then, 7 mmol of H₂BDC (terephthalic acid) and 0.7 mL of acetic acid were added. The mixture was dispersed by sonication for 45 min, then heated at 120 °C for 24 h under a solvothermal setup. The resulting solids were washed with chloroform. The white powders then dried to produce UiO-66. The *m*-ZrO₂ was obtained by calcination of UiO-66 at 800 °C for 24 h, labeled as UiO-66-800-24. At the same time, *t*-ZrO₂ was obtained by calcination at 500 °C for 2 h, named UiO-66-500-2. The mixed phases were obtained within the time variations above.

The binary oxide was obtained from UiO-66, doped by Ti(IV) and Hf(IV). UiO-66(Zr/Ti) was synthesized by dissolving 0.3 mmol of TiBr₄ salts with 6 mL of DMF in a Glove Box. The dispersion process was assisted through sonication, and UiO-66 was added to the solution and then heated at 85 °C for 1, 3, and 5 days. The mixture was centrifuged and washed with 3×10 mL of DMF and 10 mL of methanol. The solids were left to immerse in methanol for 3 days and exchanged with fresh methanol [37]. The solids were then dried under a vacuum at 50 °C for 2 h. The UiO-66(Zr/Hf) was produced like UiO-66(Zr/Ti) but using HfCl₄ and different reaction times of 5 and 7 days. The powder of UiO-66(Zr/Ti) and UiO-66(Zr/Hf) was then calcined at the optimum temperature to obtain photocatalyst ZrO₂-TiO₂ and ZrO₂-HfO₂ composites. Labeling examples of UiO-66 underwent PSE with TiBr₄ for 1 d, followed by calcination at 500 °C for 2 h; (Zr/Hf)-5d-500-2 indicates UiO-66 underwent PSE with HfCl₄ for 5 d, followed by calcination at 500 °C for 2 h.

The crystalline phase identification of as-synthesized materials of UiO-66 (Zr), UiO-66 (Zr/Ti), UiO-66 (Zr/Hf), ZrO_2 , ZrO_2 -TiO₂, and ZrO_2 -HfO₂ was carried out using

powder X-ray diffractometer, a Rigaku Miniflex 600 instrument with $Cu-K_{\alpha}$ radiation ($\lambda = 0.1540593$ nm). The morphological analysis of the product was observed using Scanning Electron Microscopy (SEM) measurement SU3500 JEOL/EO version 1.0, and the element composition analysis was observed using EDS mapping. Band gap measurements of photocatalyst materials were completed using a Thermo Scientific Evolution 220 UV-vis spectrophotometer. The nitrogen sorption method performed surface area and pore size measurements using a Quantachrome Instruments Nova 3200e. The multipoint Brunauer–Emmett–Teller (BET) method was employed to analyze the surface area of samples.

The diffraction pattern of different samples was measured using Toraya's method [22]. The integrated intensity ratio X_m can be expressed by Equation (1) as

$$X_m = \frac{I_m(\bar{1}11) + I_m(111)}{I_m(\bar{1}11) + I_m(111) + I_t(101)}$$
(1)

where I_m and I_t represent the intensity of monoclinic and tetragonal phases on each plane. Intensity was measured using OriginLab software. The volume fraction, V_m , can be obtained by Equation (2) [38]. The volume fraction of TiO₂ and HfO₂ was calculated on the plane with the highest diffraction pattern.

$$V_m = \frac{1.311X_m}{1 + 0.311X_m} \tag{2}$$

Each photocatalyst was dissolved in 90 mL methyl orange solution using ultrasonication for 10 min with a 1:1 (m/v) ratio and then stirred for 30 min before the UV light was turned on. This procedure was according to Zhang et al. [31]. The degradation experiment was recorded with a UV lamp ($\lambda_{max} = 254$ nm). At 0, 30, 60, 90, 120, 180, 240, and 300 min, the solution was taken out, centrifuged, and analyzed further using a Thermo Scientific Genesys 10S UV-Vis spectrophotometer to see how the photocatalyst performed either on UV or visible light. The measured samples are TiO₂ pristine, *t*-ZrO₂ (UiO-66-500-2), *m*-ZrO₂ (UiO-66-800-24), *t/m*-ZrO₂ (UiO-66-500-8), the binary oxide *t*-ZrO₂+TiO₂ ((Zr/Ti)-5d-500-2), and the mixing phase of binary oxide from *t*-ZrO₂+m-ZrO₂+TiO₂ ((Zr/Ti)-5d-500-24) and *t*-ZrO₂+m-ZrO₂+HfO₂ ((Zr/Hf)-5d-500-2).

5. Conclusions

A simple synthetic route for making a ZrO_2 catalyst comprising nearly phase-pure, tetragonal, monoclinic, mixed t/m- ZrO_2 , and ZrO_2 - MO_2 (M = Ti or Hf) composites has been effectively prepared by using only a single precursor, namely UiO-66, as a sacrificial template. All the synthesized catalysts are photoactive against MO dye degradation, with t- ZrO_2 showcasing the highest photodegradation activity, with 89% decoloration efficiency under UV irradiation for 300 min with a reaction rate constant of 0.0063 min⁻¹. Decoloration efficiencies for the m- ZrO_2 phase and ZrO_2 - MO_2 (M = Ti or Hf) are 67%, 74%, and 63%, respectively. This result places this catalyst among the best photocatalysts for photocatalytic degradation activity.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/catal12060609/s1, Figure S1: PXRD pattern (a) and SEM images (b) of UiO-66; Figure S2: PXRD patterns of UiO-66(Zr/Ti) 1, 3, and 5d; Figure S3: SEM images of UiO-66(Zr/Ti) 1, 3, and 5d; Figure S4: Elemental mapping and EDS spectrum of UiO-66(Zr/Ti) 1, 3, and 5d; Figure S5: PXRD patterns of UiO-66 (Zr/Hf) 5 and 7d; Figure S6: PXRD patterns of t-ZrO2 before and after successive catalytic cycle; Table S1: SEM-EDS analysis of % atomic of UiO-66(Zr/Ti).

Author Contributions: Writing—original draft preparation, formal analysis, investigation, visualization, validation, I.N.A.J. and H.F.S.; supervision, project administration, S.M. and K.W.; conceptualization, methodology, resources, supervision, writing—review and editing, funding acquisition, project administration, A.P. and A.C.W. All authors have read and agreed to the published version of the manuscript. **Funding:** This research was funded by Institut Teknologi Bandung and Universitas Airlangga, grant number 165/UN3.15/PT/2021.

Acknowledgments: The authors acknowledge Riset Kolaborasi Indonesia 2021 (Institut Teknologi Bandung, Universitas Airlangga, Institut Pertanian Bogor, and Universitas Gadjah Mada) for supporting this research. A.P. acknowledges P2MI FMIPA ITB FY 2022 for financial support. The authors are grateful to Yessi Permana and Laela Mukaromah for PXRD measurements.

Conflicts of Interest: The authors declare no conflict of interest.

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