The Complex Compound of Amino Acids With Titanium (III) as a Method to Control and Synthesis of Different Structures of TiO₂ Nanoparticles; Usage as Photocatalysts to Oxidize Alcohols to Aldehyde

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The complex compound of amino acids with Titanium (III) as a method to control and synthesis of different structures of TiO₂ nanoparticles; usage as photocatalysts to oxidize alcohols to aldehyde

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Graphical Abstract:

Highlights:

- Synthesizing complex compounds of titanium chloride (III) with different derivatives of amino acids for the first time
- Controlling and synthesizing TiO₂ in different structures with high purity and porosity
- Photocatalytic ability of TiO₂ for converting alcohols oxidize to corresponding aldehydes

Abstract

Different types of the amino acids (Glutamine, Glycine, Alanine) were used to coordinate TiCl_3 in order to investigating the best precursor for synthesis of TiO_2 . Also, a full investigation was carried out to synthesis four different structures of TiO_2 nanoparticles [TiO_2 ($\text{A}_{0.8}\text{R}_{0.2}$), TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$), TiO_2 (Anatase), and TiO_2 (Rutile)]. Oxidation of derivatives alcohol to their corresponding aldehyde through the obtained nanoparticles, as a photocatalyst, under UV light was considered to investigate the best structure of TiO_2 . Different physical-chemical analyses were applied to investigate the result. The result showed that the titanium dioxide nanoparticle, synthesized from glycine was obtained at the least temperature and was chosen as a precursor to synthesis of four different types of TiO_2 . All the synthesized TiO_2 were applied for oxidation of benzyl alcohols into benzaldehyde, as a test, and TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$) could give the best result (87% efficiency). Then it was used to oxidize benzyl alcohol, 4-cholorobenzyl alcohol, 4-nitrobenzyl alcohol and 4-methoxybenzyl alcohol to their corresponding aldehyde and efficiency were 74, 92, 87, and 65% respectively.

Keywords: acid amino; TiO_2 ; organometallic; nanoparticle; photocatalytic- oxidation; alcohol

1. Introduction

Titanium dioxide nanoparticles in different ratios have found their place among all types of nanoparticles and they are used in different applications such as painting, catalyst, photocatalyst, solar energy, food, beverages, and pharmaceutical industries etc [1–8].

Many methods have been created by scientists for the synthesis of titanium dioxide nanoparticles, including sol-gel, microwave, micelle, aerogel, hydrothermal, chemical vapour deposition, physical vapour deposition, electrochemical accumulation, sonochemical, and microwave. Organometallic complex compounds are also proper initial products for the synthesis of nanoparticles, with the advantages of low temperature, less time, purity, and environmentally friendly [9–16].

Amino acids are natural substances with a low-temperature melting point, soluble in water, and also they have an active side to make complex compounds with titanium ions, so they are active and effective ligands to synthesize complex compounds of titanium. Titanium

dioxide obtained from these types of complex compounds can be obtained at low temperature and less time with high purity [17].

Amino acids have different categories, specifying with their side chains, including amino acids with electrically charged side chains, amino acids with polar uncharged side chain, amino acids with hydrophobic side chain, and special case.

On the other hand, titanium dioxide nanoparticle has different phases and structures, including anatase, brookite, and rutile. There is also an artificial structure called Degussa, which is made by 80% anatase and 20% rutile, and it shows a high ability for different application such as photocatalyst. So they illustrate different abilities based on their molecular structure, and according to these properties, synthesizing TiO_2 with different ratio of phases can be very essential, especially when they are used as optical and photocatalyst. The photocatalytic oxidation of alcohols to their corresponding aldehydes has attracted a great deal of interest in several fields of chemistry [18–25]. This is because of the importance of aldehydes in various chemical usages, including drugs, dyes, resins and fragrances[26]. TiO_2 nanoparticles, as the most important semiconductor photocatalysts, were confirmed as an effective and selective agent in partial oxidation of benzyl alcohols to corresponding benzaldehydes [27–29]. It has been confirmed that the structure of TiO_2 and the adsorbed oxygen molecules on the surface of TiO_2 , as two essential factors, have strong influences on the selective physicochemical activity[30–32].

Generally, numerous studies have been demonstrated that the photocatalytic activity of bare anatase and rutile TiO_2 , is lower than that observed for their anatase/rutile composites[33–39]. One of the best examples is the P25 commercial material, containing 70–80% of anatase and 30–20% of rutile that produced by Evonik. Moreover, they reported the charge transfer between particles of different phases caused high photoactivity of P25 [40–42].

In this study, we focused on the photocatalytic application of titanium oxide nanoparticle in the oxidation reaction of benzyl alcohols into aldehydes, as an especial and important reaction in industries. To this aim, we synthesized nanoparticle of titanium oxide [TiO_2 with 20%anatase-80% rutile ($\text{A}_{0.8}\text{R}_{0.2}$), TiO_2 with 60% anatase-40%rutile ($\text{A}_{0.6}\text{R}_{0.4}$), TiO_2 with 100%anatase (A), and TiO_2 with 100%rutile (R)] through the complex compounds of amino acids of Glycine, L-Alanine, and glutamine, which belong to the special case, amino acid with hydrophobic side chain, and amino acids with a polar uncharged side chain respectively. For comparison purposes, the home-prepared nano- TiO_2 s have been applied in the photocatalytic oxidation of benzyl alcohols to the corresponding aldehydes in acetonitrile at

ambient temperature, under UV irradiation. The partial photocatalytic oxidation of benzyl alcohol, 4-chlorobenzyl alcohol, 4-nitrobenzyl alcohol and 4-methoxybenzyl alcohol to the corresponding aldehydes was investigated with home-prepared nano-TiO₂ samples. Also, the influence of the substituent group was studied in the photocatalytic oxidation reaction.

2. Experiment

Characterizations. XRD pattern was obtained by GNR Explorer advance using 1.541 Å (Cu-Kα). Firefly 7.1.G software was used for quantum-chemical modelling of the molecule and complex. Synchronous thermal analysis (simultaneous recording of TG and DSC curves) was performed on a Netzsch STA 449 F3 Jupiter installation in air. BET analysis to measure the surface activity of the nanoparticles was carried out by capillary condensation of nitrogen at 77 K on a micrometric Belsorp-mini II. To estimate the mesoporosity and pore size distribution function, the Barrett-Joyner-Halenda method (BJH) was used. The microscopic images of the nanoparticles were detected by TESCAN BRNO-Mira3 LMU to study the morphology of the nanoparticles, which was accompanied by EDX analysis. TEM images were taken by LEO 912AB through dispersing by ethanol. Estimating the energy bandgap of the nanoparticles was carried out by UV-Vis spectroscopy varian 50. The melting points of the products were determined with an Electrothermal Type 9100 melting point apparatus. FT-IR spectra were recorded on pressed KBr pellets using an AVATAR 370 FT-IR spectrometer (Therma Nicolet spectrometer, USA) at room temperature in the range between 4000 and 400 cm⁻¹ with a resolution of 4 cm⁻¹. NMR spectra were recorded on an NMR Bruker Avance spectrometer at 300 MHz in CDCl₃. Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70 eV electron impact ionization, in m/z (rel %). All yields refer to the isolated products after purification by column chromatography. The photocatalytic oxidation experiments were performed in a capped-sealed test tube equipped with a 100 W Hg lamp (UVA, UVB Light). The system was cooled by water circulating and the temperature was about 20°C.

Material. All the main precursor, including ligands and solvents, were purchased from Merck and Sigma-Aldrich and were used as received without further purification. The purity determinations of the products and the progress of the reactions were accomplished by TLC on silica gel Polygram STL G/UV 254 plates.

2.1. Synthesis of complexes

General method. Using 100% natural-renewable amino acids as ligands, which decomposes at $<550^{\circ}\text{C}$ with high uniformity to synthesize titanium oxide make an advantage of using these types of ligands to use as ligands for making complexes as precursors for obtaining nanoparticle. All the procedure was carried out under a nitrogen atmosphere to avoid any oxidization. Due to using the derivatives of amino acid, as the ligand, the observation was almost the same with a difference in time of different step. Deionized water and methanol with 60 and 40% were used respectively, as solvents to solve the ligands. Then NaOH was added to make the environment of the reaction neutral. After that, TiCl_3 was added dropwise to make precipitate. The colour was changed from colourless to green and then it changed to blue. Then it stayed for days at room temperature and after some days the blue colour changed to white suspension. The mentioned method was repeated for Glutamine (L^1), Glycine (L^2), and L-Alanine (L^3).

2.2. Synthesizing nanoparticles of TiO_2

General method. The obtained complex compounds were used as a precursor to isolate titanium oxide nanoparticle of TiO_2 . Thermal decomposing was the method used to transfer complex compound to the nanoparticles. To test the proper temperature and time, a small amount of the complex compound was analyzed thermally. The following procedure was applied for the TGA analysis (Thermal Gravimetric Analysis).

For this purpose, each complex compound was placed in a closed aluminium crucible and the temperature was set between $25\text{--}900^{\circ}\text{C}$. The heating rate was 10 deg/min . According to the obtained result from the analysis and XRD pattern, the product, from the complex of glycine and TiCl_3 (ML^2), was obtained at a lower temperature (around 525°C), the obtaining titanium oxide nanoparticle from Glutamine+ TiCl_3 (ML^1) and L-Alanin+ TiCl_3 (ML^3) was resulted at around 860°C and 900°C respectively. So ML^1 was chosen, as the most proper precursor, for obtaining further products, including TiO_2 ($\text{A}_{0.8}\text{R}_{0.2}$), TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$), TiO_2 (A), and TiO_2 (R).

The mentioned products were obtained by controlling the temperature (Fig.1). TiO_2 (A), as the first phase of TiO_2 , was obtained at around 525°C , TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$) at around 650°C , TiO_2 ($\text{A}_{0.8}\text{R}_{0.2}$) at about 750°C , and finally, TiO_2 (R) was obtained at 800°C .

Fig. 1. TGA analysis from the obtained complexes; (a) ML^1 (b) ML^2 , and (c) ML^3

2.3. Photocatalytic degradation of some alcohol derivatives to their corresponding aldehydes.

Photo-oxidation reaction was carried out in a capped-sealed test tube containing home-prepared nano-TiO₂ (3mg) suspended in a solution consisting of 2 ml benzyl alcohol (1mmol) and acetonitrile as solvent. The mixture was stirred using constant magnetic stirring in different periods under UV light irradiation. The progress of the reaction was monitored by TLC (eluent: n-hexane/EtOAc 5:2). After completion of the photocatalytic reaction, the photocatalysts were separated by centrifugation at 10,000 rpm rate. The quantitative value of benzaldehyde was obtained by column chromatography.

3. Result and discussion

3.1. Complex compounds

Quantum chemical modelling of the complexes. To reveal the structure and electronic properties of the isolated complexes I to III, we performed a DFT calculation of the molecular structure of both organic molecules: HL^1 , HL^2 , HL^3 , and molecules that model the structure of the isolated complexes: $Ti(L^1)_2OH$ (I), $TiL^2(OH)_2$ (II), $TiL^3(OH)_2$ (III). The molecular structure of the calculated organic molecules and complexes is shown in Fig. 2

Fig. 2. The molecular structure of the molecules according to the calculation by the DFT method

Figure 2 shows the results of the calculation of organic molecules HL¹, HL², and HL³, which have an air force of N2 ... H (O1). Attempts to calculate the centre ion forms of HL² molecules with the BBC (O1) - ... H (NH₃⁺) showed less stability - during the calculation, the hydrogen atom passed from the nitrogen atom to the oxygen atom and we obtained the forms shown in Fig. 2. It should be noted that the organic molecules are stabilized by the BBC H(O1) ... N1 (R = 1,843 – 1,850 Å).

The disadvantage of the Ti (L¹)₂OH (a₂), TiL²(OH)₂ (b₂) and TiL³(OH)₂ (c₂) structures corresponding to the chemical analysis data is the low coordination numbers of titanium: five and four, instead of the expected coordination number six. It can be assumed that, in crystalline form, the titanium atom, being in forms (a₂), (b₂), and (c₂), can complete its coordination sphere due to the interaction with the oxygen atoms of neighbouring complex molecules, forming polymer structures. At the same time, the possibility of completing the coordination sphere of titanium in Ti(L¹)₂OH exists due to the additional interaction with the O3 atom of one of the ligand molecules, as in the Ti(L¹)₂OH (a₃) molecule (Fig. 2). It was found that the Ti(L¹)₂OH (a₃) form is 60 kJ/mol more stable than the Ti(L¹)₂OH (a₂) form.

In the case of $\text{TiL}^2(\text{OH})_2$ and $\text{TiL}^3(\text{OH})_2$ complexes, the possibility of completing the coordination sphere of titanium is possible, for example, in the dimer molecules $\text{TiL}^2(\text{OH})_2$ (b_3) and $\text{TiL}^3(\text{OH})_2$ (c_3) (Fig. 2). It was found that for these molecules the energy of structures (b_3) and (c_3) are 134 and 135 kJ/moles lower than the doubled energies of structures (b_2) and (c_2), respectively. The results obtained for $\text{Ti}(\text{L}^1)_2\text{OH}$, $\text{TiL}^2(\text{OH})_2$, and $\text{TiL}^3(\text{OH})_2$ indicate higher stability of titanium octahedral complexes in comparison with tetragonal pyramidal or tetrahedral ones.

Some calculated bond lengths and bond angles for organic molecules and complexes are shown in Table 1.

Table 1. The lengths of some bonds R (Å) calculated by the DFT method and the bond angles ω (deg) in the molecules (The numbering of atoms is given in Fig. 2.)

Molecule	HL ¹	I(a)	I(b)	HL ²	II(a)	II(b)	HL ³	III(a)	III(b)
Bond	R (Å)								
Ti-O1	-	1,966	2,049	-	1,975	1,985	-	1,976	1,984
Ti-N1	-	2,221	2,247	-	2,223	2,228	-	2,214	2,223
Ti-O3	-	-	-	-	1,813	1,951	-	1,817	1,949
Ti-O3'	-	-	2,241	-	-	2,141	-	-	2,154
Ti-O4	-	1,812	1,832	-	1,817	2,017	-	1,813	2,019
Ti-O4'	-	-	-	-	-	2,202	-	-	2,199
O1-H	0,997	-	-	0,999	-	-	0,997	-	-
C1-O1	1,334	1,314	1,286	1,333	1,309	1,310	1,335	1,307	1,310
C1-O2	1,203	1,209	1,230	1,202	1,209	1,209	1,203	1,211	1,210
C1-C2	1,549	1,555	1,547	1,544	1,547	1,549	1,548	1,555	1,553
C2-N1	1,470	1,483	1,485	1,467	1,486	1,486	1,471	1,493	1,493
C3-O3	1,217	1,216	1,216	-	-	-	-	-	-
C3-N2	1,365	1,366	1,366	-	-	-	-	-	-
C3'-O3'			1,246	-	-	-	-	-	-
C3'-N2'			1,338	-	-	-	-	-	-
Angle	ω	(Degree)							
O1TiN1	-	77	75	-	77	78	-	77	78
TiO1C1	-	124	116	-	124	122	-	123	122
TiN1C2	-	110	109	-	107	106	-	107	107
O1C1C2	113	114	116	113	113	113	113	113	114
C1C2N1	110	109	110	111	110	110	108	108	109
O3TiO4	-	-	-	-	125	121	-	125	121

From the results given in table 1, it follows that the five-membered metal cycles in the complexes $\text{Ti}(\text{L}^1)_2\text{OH}$, $\text{TiL}^2(\text{OH})_2$, and $\text{TiL}^3(\text{OH})_2$ have a similar structure, and the bond lengths naturally change upon transition from organic molecules to complexes. Complex I (a_3) somewhat falls out of the range of bond lengths and bond angles, where the Ti-O1 and Ti-N1 bonds are longer than in other complexes, the angle O1TiN1 is smaller (Table 1). A

similar difference is associated with the restructuring of the coordination polyhedron. Besides, the C1 – O2 bond in this complex is slightly longer than in the other molecules, due to the participation of the O2 atom in the formation of the H(N2')...O2 air force (R=1.860 Å), which additionally stabilizes the molecule.

Dimeric molecules (a₃, b₃, and c₃) can be formed by the approach of molecules (a₂, b₂, and c₂), in which the planes of the metallocycles are approximately perpendicular and the oxygen atoms of the hydroxyl groups form a distorted square structure. However, complete alignment of Ti – O bonds do not occur. Thus, the bonds Ti-O3 and Ti-O4 are shorter than the bonds Ti-O3' and Ti-O4' (Table 1). Similarly, Ti'-O3' and Ti'-O4' bonds are shorter than Ti'-O3 and Ti'-O4 bonds. Note that the Ti – Ti' distances in the dimeric complexes II (b₃) and III (c₃) are 2.307 and 2.310 Å, respectively. The atomic charges calculated by the NBO method in the calculated molecules are shown in Table 2.

Table 2. The charges calculated by the NBO method on some atoms in the molecules (The numbering of atoms is given in Fig. 2.)

Atom	HL ¹	I (a ₂)	I (a ₃)	HL ²	II (b ₂)	II (b ₃)	HL ³	III (c ₂)	III (c ₃)
Ti	-	+1,543	+1,542	-	+1,564	+1,421	-	+1,563	+1,437
H(O1)	+0,491	-	-	+0,488	-	-	-0,491	-	-
O1	-0,698	-0,797	-0,777	-0,702	-0,795	-0,756	-0,700	-0,790	-0,762
O2	-0,605	-0,613	-0,702	-0,604	-0,614	-0,609	-0,604	-0,621	-0,613
O3	-0,636	-0,631	-0,634	-	-0,976	-0,925	-	-0,974	-0,927
O3'	-	-0,633	-0,729	-	-	-0,927	-	-	-0,928
O4	-	-0,956	-0,922	-	-0,974	-0,947	-	-0,976	-0,947
O4'	-	-	-	-	-	-0,957	-	-	-0,958
N1	-0,892	-0,884	-0,879	-0,894	-0,895	-0,884	-0,888	-0,892	-0,888
N2	-0,809	-0,811	-0,811	-	-	-	-	-	-
C1	+0,848	+0,852	+0,863	+0,833	+0,829	+0,826	+0,840	+0,838	+0,834
C2	-0,136	-0,130	-0,122	-0,318	-0,309	-0,307	-0,139	-0,135	-0,128
C3	+0,721	-0,721	+0,720	-	-	-	-	-	-

The calculated charges of titanium atoms in the complexes range from +1.421 to +1.564 (Table 2). These values differ significantly from those assumed in the case of ionic bonding of charges on the titanium atom +3. The magnitude of the charge of the titanium atom indicates a significant contribution of the covalent component in the interaction of titanium with ligands and transfer of about 1.5 electrons from the ligands to each titanium ion. In this case, each organic molecule passes from 0.45 to 0.50 electrons, and each hydroxide ion from 0.50 to 0.54 electrons. The populations of titanium valence orbitals have the following meanings:

In $\text{Ti}(\text{L}^1)_2\text{OH}$ I(a₂) $3d^{2.23}4s^{0.19}4p^{0.01}4d^{0.04}$, In $\text{Ti}(\text{L}^1)_2\text{OH}$ I(a₃) $3d^{2.20}4s^{0.21}4p^{0.01}4d^{0.04}$,
 In $\text{TiL}^2(\text{OH})_2$ II(b₂) $3d^{2.21}4s^{0.19}4p^{0.03}4d^{0.03}$, In $\text{TiL}^2(\text{OH})_2$ II(b₃) $3d^{2.31}4s^{0.22}4p^{0.02}4d^{0.05}$,
 In $\text{TiL}^3(\text{OH})_2$ III(c₂) $3d^{2.21}4s^{0.19}4p^{0.03}4d^{0.03}$, In $\text{TiL}^3(\text{OH})_2$ III(c₃) $3d^{2.30}4s^{0.23}4p^{0.02}4d^{0.04}$.

It can be seen that mainly 3d orbitals are populated in the complexes at the titanium atom.

The transfer of electron density from ligands to titanium atoms occurs so that the electron density on the O1 and N1 atoms directly bonded to the titanium atom, as a rule, changes little and even increases, and on atoms that are not directly bonded to the titanium atom, decreases. In this case, the electron density on the O1 atom increases especially: charges on this atom lie in the range from -0.698 to -0.702 in organic molecules and -0.756 to -0.797 in complexes. Note that the released charge on the O2 atom in the $\text{Ti}(\text{L}^1)_2\text{OH}$ (I) (b) complex is due to the presence of the H (N2')... O2 air force.

FT-IR spectroscopy and elemental analysis. The FT-IR spectroscopy of the complex compounds of titanium (III) with Glutamine (L^1), Glycine (L^2), and L-Alanine (L^3) and their characterizations are illustrated in figures 3-5.

Initially, the ligands are investigated in the free mode. There are different peaks in the free amino acids' derivatives. However, some of them have been recognized as the main functional groups of the amino acids. There are small differences between β -amino acids (L-alanine and glutamine) and α -amino acid (Glycine). In both cases, there is a sharp peak at around 2130 cm^{-1} , which related to N-H stretching in NH^{3+} group[43]. The peaks between 1640 and 1610 cm^{-1} are related to the deformation of NH^{3+} . There is another peak related to the ionic carboxyl group (around 1410 cm^{-1}). However, this is hard to see compared to other peaks. Also, COO^- mode is observable near 1600 cm^{-1} . Furthermore and according to some kinds of literature, ammonium can be seen at 2600 cm^{-1} [44]. The main difference between glycine, as α -amino acid, and β -amino acids (L-alanine and glutamine) is a broad carboxyl peak in near 1600 cm^{-1} .

After coordination of the metal ion, there are some changes, which effected on the vibration energy of some of the mentioned peaks. In the case L^1+Ti (Glutamine complex) (Fig.3), both peaks corresponding to the stretching carboxylate group and stretching vibrations of ammonium reduced to around 1632 and 2038 cm^{-1} from 1638 and 2043 cm^{-1} respectively. Also, the peak related to the ionic carboxyl group was reduced from 1415 to

1410 cm^{-1} . Such this change may be justified by η -mode coordination of titanium ion to the resonance forms of the carboxylate group.

In the next case, $\text{L}^2 + \text{Ti}$ (Glycine complex) (Fig. 4), there is a huge reduction in ammonium peak, and it changed from 2213 to 2136 cm^{-1} . Also, the carboxylate peak was deformed after complexation. Also, a new peak at around 3440 cm^{-1} badges of intermolecular bond in O-H stretching.

In the last case, $\text{L}^3 + \text{Ti}$ (L-Alanine) had its unique effect on the metal ion (Fig. 5). The significant change occurred in the carboxylic acid (O-H stretching), which reduced the peak from the around 2742 to 2729 cm^{-1} . Also, the peak related to ammonium changed and raised to around 2615 cm^{-1} from around 2600 cm^{-1} .

Fig. 3. IR spectroscopy of (a) glutamine (L^1), and (b) glutamine with titanium chloride (III) ($\text{L}^1 + \text{Ti}$)

Fig. 4. IR spectroscopy of (a) glycine (L^2), and (b) glycine with titanium chloride (III) (L^2+Ti)

Fig. 5. IR spectroscopy of (a) L-Alanine (L^3), and (b) L-Alanine with titanium chloride (III)

Elemental analysis of the complexes was taken in table 3.

Table 3. Elemental analysis of the complexes compounds

Name	Formula	C [%]	H [%]	N [%]	O [%]	Ti [%]
		C/O	C/O	C/O	C/O	C/O
Ti (L ¹) ₂ OH	C ₁₀ H ₁₆ N ₄ O ₆ Ti	35.73/36.42	4.8/5.93	16.67/14.42	28.56/27.32	4.24/13.21
Ti L ² (OH) ₂	C ₄ H ₁₀ N ₂ O ₈ Ti ₂	15.50/15.99	3.25/3.61	9.04/8.96	41.31/40.32	0.90/29.38
Ti L ³ (OH) ₂	C ₆ H ₁₄ N ₂ O ₈ Ti ₂	21.33/22.18	4.18/4.52	8.29/7.42	37.88/36.98	8.33/27.87

C: Calculated

O: Obtained

3.2. Nanoparticles

The obtained nanoparticles were labelled as followings; TiO₂ (A), TiO₂ (R), TiO₂ (A_{0.2}R_{0.8}), and TiO₂ (A_{0.6}B_{0.4}).

XRD pattern. The XRD pattern of the obtained nanoparticles was carried out between 10 and 80 degrees ($10 < 2\theta < 80$).

The results show that all the nanoparticles are in good crystallinity with their strong and tiny diffraction peaks and different phases and structures related to TiO₂ nanoparticle were obtained at different temperatures.

According to the result, the sample with the XRD pattern provided in figure 6a (A_{0.2}R_{0.8}) has been obtained as a mix of anatase (JCPDS No.21e1272) and rutile (JCPDS NO. 21e1276) phases, and the main peaks were placed at 25.2558, 27.4214, 37.7254, 41.2115, 47.9888 and 53.7981.

TiO₂ (A_{0.6}B_{0.4}) is illustrated by figure 6b. The main peaks were located at 25.2558, 27.4214, 32.84, 36.13, 47.89, 54.37, and 62.8. According to the result, it is matched with JCPDS 76-1934.

Anatase phase, as the first phase of TiO₂, was obtained at around 525°C (Fig. 6 c). The main peaks are observable at 25.3192, 37.87, 48.16, 54.01, 55.20, 62.87, 68.92, and 70.48. JCPDS No. 21e1272 is the best match with the obtained sample, which proved 100% Anatase phase.

Finally, the rutile phase, as the most stable and last phase of TiO₂, is illustrated by figure 6d. This phase, the same as other structures, was obtained at high purity. The main peaks are located at 27.49, 36.13, 39.24, 41.28, 44.09, 54.37, 56.67, 62.08, 64.08. According to the result, the obtained sample is a 100% rutile phase with JCPDS NO. 21e1276.

The average crystallite diameter (D) of the obtained nanoparticles and their lattice strain calculated in the diffraction pattern. Scherer equation (1) was used to calculate the mentioned parameters and the data are taken in table 4.

$$D_c = k\lambda/\beta\cos\theta \quad (1)$$

Where, K is shape factor (about 0.9), λ is the wavelength of the X-ray source (1.5406Å), β is the breadth of the observed diffraction line at its half intensity maximum (400).

Table 4. Chemical-physical features of TiO₂

Sample	Crystallite size (nm)
TiO ₂ (A _{0.2} R _{0.8})	25,51
TiO ₂ (A _{0.6} R _{0.4})	17,87
TiO ₂ (A)	31,95
TiO ₂ (R)	34,54

Fig. 6. XRD pattern of (a) TiO₂ (A_{0.2}R_{0.8}), (b) TiO₂ (A_{0.6}R_{0.4}), (c) TiO₂ (A), and (d) TiO₂ (R)

FT-IR spectroscopy. Investigation of the surface state of prepared nanoparticle was carried out by FT-IR spectrum, adjusted between 400- 4000 cm⁻¹ (Fig. 7).

There is a broad absorption band between 3400 and 3500 cm⁻¹, which related to the absorption of the H₂O molecules' stretch on the surface of the TiO₂ samples. It is clear in the cases A_{0.6}R_{0.4} and R [45]. Besides, some components band gap illustrates various kind of

interaction of water molecules with TiO_2 , containing their absorption into the mesoporous [46]. The broad absorption band between 400 and 800 cm^{-1} and the maximum at around 1000 cm^{-1} corresponding to Ti-O stretches in TiO_6 octahedral of different types of distortion. Some adsorptions with very low intensity, around 1300 cm^{-1} , show the presence of CO_2 which exist in the air and absorbed by the surface of the TiO_2 nanoparticles.

Fig. 7. FT-IR spectroscopy of the nanoparticles; (a) $\text{TiO}_2 (\text{A}_{0.2}\text{R}_{0.8})$, (b) $\text{TiO}_2 (\text{A}_{0.6}\text{R}_{0.4})$ (c) $\text{TiO}_2 (\text{A})$, and (d) $\text{TiO}_2 (\text{R})$

FESEM and EDX analysis. Because each crystal facet provides especial properties so the morphology of the obtained nanoparticles was investigated by FESEM image (Fig.8). All the nanoparticles were obtained in very high purity, as they are seen in the figures. This is one of the most important properties of the oxide nanoparticles, which synthesized through organometallic complex compounds[47].

There are very uniform in their surface and the shapes of the nanoparticles have been investigated by TEM image. There is no accumulation and tendency, which almost always is due to the high temperature and stability of the nanoparticles. Also, the high porosity on the surface of the samples made them be used as good photocatalysts for radicalism reactions.

The obtained size for all the nanoparticles was calculated; mean size for $\text{TiO}_2 (\text{A}_{0.2}\text{R}_{0.8})$

structure was around 25nm, and for TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$), anatase, and rutile was around 20nm, 29nm and 31nm respectively. The results obtained from the FESEM were well equal to what obtained from the XRD analysis.

Fig. 8. FESEM image of (a) TiO_2 ($\text{A}_{0.2}\text{R}_{0.8}$), (b) TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$), (c) TiO_2 (A), and (d) TiO_2 (R)

Besides, EDX of the nanoparticles, to investigate the amount of the elements was carried out (Fig. 9). According to the analysis, all the nanoparticles were synthesized with high purity (Table 5).

Table 5. Elemental analysis of the samples

Sample	Ti [%]	O [%]
TiO_2 ($\text{A}_{0.2}\text{R}_{0.8}$)	54.45	45.55
TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$)	50.10	49.90
TiO_2 (A)	51.31	48.69
TiO_2 (R)	50.03	49.97

Fig. 9. EDX pattern of (a) TiO_2 ($\text{A}_{0.2}\text{R}_{0.8}$), (b) TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$), (c) TiO_2 (A), and (d) TiO_2 (R)

TEM analysis. To further investigation of the obtained nanoparticle TEM image analysis was carried out (Fig.10).

Figure 10a shows the TEM image of the TiO_2 ($\text{A}_{0.2}\text{R}_{0.8}$) structure. According to the analysis, the anatase and rutile phases grew on different nuclei during the process. Indeed, the anatase and rutile phases appeared nearby. During the process of the formation of TiO_2 ($\text{A}_{0.2}\text{R}_{0.8}$) structure, rutile phase forms an over-layer on the anatase surface.

TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$) structure is illustrated in figure 10b. Controlling conditions to TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$) structure is more difficult than anatase and rutile, even TiO_2 ($\text{A}_{0.2}\text{R}_{0.8}$) structure, if it is expected just to synthesis a single structure of TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$) because it is a phase between anatase and rutile phases. However, based on the data extracted from XRD and TEM, using a complex compound of glycine with titanium chloride made this possible to have a product with the structure in high purity. The obtained structure has a pseudo-cubed shape.

Anatase phase is illustrated by figure 10 c. Anatase as the first phase of TiO_2 was obtained

as a truncated bipyramidal shape constructed by eight $\{101\}$ and two $\{001\}$, which is observable by TEM and FESEM image (inserted in figure 10c). According to the databases [48], this type of shape is obtained with hydrated surfaces.

Figure 10d provides information about the rutile phase. Rutile generally obtained with no regular shape and this is the most stable phase. However, here, the rutile phase was obtained with truncated bipyramidal shape, and the same as the anatase phase, with hydrate surface. All the samples' properties have been taken in the figure.

Fig. 10. TEM image of (a) $\text{TiO}_2 (\text{A}_{0.2}\text{R}_{0.8})$, (b) $\text{TiO}_2 (\text{A}_{0.6}\text{R}_{0.4})$, (c) $\text{TiO}_2 (\text{A})$, and (d) $\text{TiO}_2 (\text{R})$

Surface analysis. The typical N_2 adsorption-desorption isotherms (BET method) and the pore distribution curve of samples showed in Fig. 11. The micropores volume has been calculated in the P/P_0 range of 0-0.990 to collect information about the genesis of porosity (Fig. 11a). BET analysis has been used to investigate the surface activity of the samples (Fig. 11b), in addition, to determine pore diameter, volume and distribution BJH method have been carried out (Fig. 11c). Furthermore, Langmuir plot, which provides a mean of determining surface area according to monolayer coverage of the solid surface through the adsorptive, has been considered (Fig. 11d). DeBoer t-plot has also been done to determine the external surface area and micropore volume of microporous materials. This plot is according to standard isotherm and thickness curves that describe the statistical thickness of the of adsorptive on a non-porous reference surface (Fig. 11e). The relationship between the

pore shape and the adsorption-desorption isotherm is H₃. These materials have slit-shaped pores. Because of the tensile strength effect, which probably happens for N₂ at 77K in the pressure between 0.4 and 0.45, the desorption curve of H₃ hysteresis contains a slope related to the force on the hysteresis loop. Also, according to the IUPAC classification, they seem to belong to the type III, which they should be characteristic of macroporous adsorbents, having pore sizes exceeding 50.0 nm. However, the result provided much less than 50.0 nm (Table 6), and according to the data, they are characteristic of adsorbents that are mesoporous [49], which classified as IV or V. Classification as model V is more logical due to the appearance schematic and it is more logical than the model IV. There is also another study on the classification of the pore size, which recently provided by Mays[50], and according to his accurate investigation, the obtained nanoparticles can be also classified as super-nanopore (10-100nm).

The specific surface activity of the samples has been also determined separately by BET analysis (Table 6).

Adsorption is a phenomenon, which depends on the adsorbate on the adsorbent. Langmuir is one of the methods, which can describe the distribution of metal ion such as titanium between two phases of liquid and solid. According to this method, monolayer adsorption on the surface holding a limit number of adsorption site of identical strategies with no transmigration of adsorbate in the plane surface [51]. After filling the site, adsorption will not happen to the site. It illustrates that the surface has no more volume and it is saturated. The data obtained from this analysis can be seen in table 6.

Fig.11. Chemical physical properties of rutile sample; (a) micropores volume, (b) BET analysis, (c) BJH method, (d) Langmuir plot, and (e) DeBoer t-plot

Table 6. Physical-chemical properties of the samples

BET Analysis				
Parameters	TiO₂ (A_{0.2}R_{0.8})	TiO₂ (A_{0.6}R_{0.4})	TiO₂ (A)	TiO₂ (R)
V _m (cm ³ (STP) g ⁻¹)	7,0373	2,5958	4,1705	3,3219
a _{s,BET} (m ² g ⁻¹)	30,63	11,298	18,152	14,458
C	9,8457	26,352	10,938	16,18
Total pore volume (cm ³ g ⁻¹)	0,1433	0,070965	0,064058	0,059361
Mean pore diameter (nm)	18,709	25,124	14,116	16,423
BJH Analysis				
Parameters	TiO₂ (A_{0.2}R_{0.8})	TiO₂ (A_{0.6}R_{0.4})	TiO₂ (A)	TiO₂ (R)
V _p (cm ³ g ⁻¹)	0,1512	0,072623	0,066315	0,060265
r _{p,peak(Area)} (nm)	1,22	1,22	1,22	1,22
a _p (m ² g ⁻¹)	49,364	16,94	21,813	16,279
Langmuir Analysis				
Parameters	TiO₂ (A_{0.2}R_{0.8})	TiO₂ (A_{0.6}R_{0.4})	TiO₂ (A)	TiO₂ (R)
V _m (cm ³ (STP) g ⁻¹)	4,4766	2,3251	2,7007	2,8225
a _{s,Lang} (m ² g ⁻¹)	19,484	10,12	11,755	12,285
B	0,4004	0,6896	0,7635	0,5136
DeBoer t plot Analysis				
Parameters	TiO₂ (A_{0.2}R_{0.8})	TiO₂ (A_{0.6}R_{0.4})	TiO₂ (A)	TiO₂ (R)
a ₁ (m ² g ⁻¹)	144,47	7,3396	7,6368	8,0244
V ₁ (cm ³ g ⁻¹)	0	0	0	0
a ₂ (m ² g ⁻¹)	17,869	-	6,3449	-
V ₂ (cm ³ g ⁻¹)	0,127	-	0,015247	-
2t (nm)	1,9945	-	23,458	-

UV-Vis absorption. To calculate the energy bandgap of the samples, UV-Vis spectroscopy, between 200 and 800 nm, was carried out (Fig. 12). According to the results, maximum absorption was different for each sample; TiO₂ (A_{0.2}R_{0.8}), anatase, rutile (240nm), and TiO₂ (A_{0.6}R_{0.4}) (390nm), which illustrate the absorption, occurred in the UV region (200-400nm) and based on the nature of titanium dioxide, this is a common result.

The energy bandgap of the samples was calculated by the Tauc plot (2);

$$\alpha = \alpha_0(h\nu - E_g)^n/h\nu \quad (2)$$

Where α is Absorption coefficient, $h\nu$ is the photon energy, α_0 , h is the constants, E_g is the optical bandgap of the material and n is between 0.5 and 3 (it depends on the electronic transition).

The energy band gap is received from the plot made by the curves of $(\alpha h\nu)^2$ versus $h\nu$. The $h\nu$ value at the intersection point of the tangent and the x-axis is the bandgap. Based on the mentioned method, the result was 5.1, 3.1, 5, and 5 eV for TiO₂ (A_{0.2}R_{0.8}), TiO₂ (A_{0.6}R_{0.4}), anatase, and rutile respectively (Fig. 13).

Fig. 12. UV-Vis spectroscopy of (a) TiO_2 ($\text{A}_{0.2}\text{R}_{0.8}$), (b) TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$), (c) anatase, and (d) rutile

Fig. 13. Energy-band gap of (a) TiO_2 ($\text{A}_{0.2}\text{R}_{0.8}$), (b) TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$), (c) anatase, and (d) rutile

4. Photocatalytic activity of various forms of TiO_2 catalysts

To evaluate and compare the photocatalytic efficiency of the various forms of home-prepared TiO_2 s, the photo-oxidation reaction of 4-chlorobenzyl alcohol is carried out as a model reaction. Acetonitrile and water have been tested as solvents for the partial photo-oxidation reaction of 4-colours-benzyl alcohol under 8 h of UV light irradiation. Among solvents, acetonitrile behaves as the best medium for 99% selective yield of 4-choloro-benzaldehyde, which no significant over oxidation to the corresponding carboxylic acids,

were detected. Whereas, in the case of water, a small amount of 4-choloro-benzoic acid formation was formed.

To confirm the photocatalytic nature of TiO_2 , the reaction was carried out without the catalyst and after 20 h the result showed that no such oxidation occurred in the absence of TiO_2 catalyst under UV light irradiation. We have also verified that in the presence of catalyst no reactions occurred in the dark. Therefore, these results confirmed the photocatalytic nature of TiO_2 and reveal that both UV irradiation and catalyst needed for the carrying out the photo-oxidation reaction.

Also, the selectivity and conversion of the synthesized nano- TiO_2 s on photo-oxidation reaction of benzyl alcohols into benzaldehyde are investigated. Clearly, by extending the irradiation time up to 8h the yields of benzaldehyde gradually increased. However, the reaction yield was not changed after 8 h irradiation.

As mentioned above, the variation of the structure of the TiO_2 causes different surface properties and also different photocatalytic activity. Studies on partial photo-oxidation of 4-choloro-benzyl alcohol to 4-choloro-benzaldehyde in the presence of home-prepared nano- TiO_2 s indicate a significant difference of the selectivity and conversion for bare rutile, anatase and their composites. Results showed that the efficiency of $\text{TiO}_2(\text{R})$ in the aldehyde formation was higher than $\text{TiO}_2(\text{A})$. Moreover, in the case of $\text{TiO}_2(\text{R})$ and $\text{TiO}_2(\text{A})$, the rate of the reaction was lower than their composites form. However, the best and highest photocatalytic activity and conversion were observed by the $\text{TiO}_2(\text{A}_{0.2}\text{R}_{0.8})$ sample while the lowest one by $\text{TiO}_2(\text{A})$. Therefore, $\text{TiO}_2(\text{A}_{0.6}\text{R}_{0.4})$ obtained the highest transformation of 4-choloro-benzyl alcohol to 4-choloro-benzaldehyde after 6 h irradiation (Table 7).

Table 7. Oxidation of 4-chlorobenzylalcohol using home-prepared TiO_2 s

Sample	Time of irradiation (h)	The yield of aldehyde generation (%)
TiO_2 ($\text{A}_{0.2}\text{R}_{0.8}$)	8	80
TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$)	6	87
$\text{TiO}_2(\text{A})$	8	68
$\text{TiO}_2(\text{R})$	8	75

To evaluate the generality and applicability of this method, we have examined the photo-oxidation reaction of substituent-benzyl alcohols in acetonitrile at room temperature under UV irradiation by employing nanocomposite- $\text{TiO}_2(\text{A}_{0.6}\text{R}_{0.4})$ (Table 8). The results illustrated that the substituent group on the benzyl ring have a significant role in the photo-oxidation

reaction. The electron-withdrawing groups that caused low electron density on the OH group showed a rapid transformation on the OH into the CHO group. In contrary, the methoxy substitute in the para position has undesirable effects on the alcohol to aldehyde transformation. Hence, only after 6 h UV irradiation in the presence of nanocomposite TiO₂ (A_{0.6}R_{0.4}), 1mmol 4-Nitro-benzyl alcohol was oxidized to 92% 4-Nitro-benzaldehyde (0.92 mmol). Also, the obtained yield for the oxidation of 1mmol 4-choloro-benzyl alcohol to 4-choloro-benzaldehyde was 87%. Whereas, in the case of p-Methoxy-benzyl alcohol only 65% aldehyde formation was observed. It is probably because of the electron-donating nature of the Methoxy group and low electron-withdrawing nature of -Cl in comparison with the -NO₂ moiety.

Table 8. Oxidation of various alcohols using nanocomposite-TiO₂ (A_{0.6}R_{0.4}) in acetonitrile.

Entry	Substrate	Product	Time (h)	Yield (%) ^a
1			7	74
2			6	92
3			6	87
4			8	65

^a Yield refers to isolated products by column chromatography; all products were identified by comparing IR, Mass, and TLC with those of authentic samples.

5. Why is the nanocomposite-TiO₂ (A_{0.6}R_{0.4}) the best?

The process of the photocatalytic reaction is explained in detail in many types of research and our previous work [15,45,52].

First, it should be explained what properties could affect the photocatalytic and oxidation reactions. Everything comes from the physical properties such as surface activity, total pore volume and pore diameter, besides, the molecular structure of the samples can be also regarded as an important parameter. Furthermore, energy bandgap is also very important; less energy bandgap makes less distance for transferring an electron from the valence to conduct the band to make the photocatalytic reaction.

The larger surface activity provides a better condition for absorbing light to react. According to the BET surface activity, the highest surface activity is related to TiO₂ (A_{0.8}R_{0.2})

(30.63 m²g⁻¹), while the least is related to TiO₂ (A_{0.6}R_{0.4}) (11.29 m²g⁻¹). In another word, although the average pore diameter of the TiO₂ (A_{0.6}R_{0.4}) has the largest amount, pore volume and surface activity is almost the smallest, which shows almost the lowest porosity is related to this sample and it means one of the most effective parameters in the photocatalytic reaction has not been very efficient. It is also confirmed by BJH, Langmuir, and DeBoer t-plot analyses. The next parameter is the molecular structure.

The molecular structures of anatase and rutile phases have been already reported (Fig.14). However, about the two others [TiO₂ (A_{0.8}R_{0.2}), TiO₂ (A_{0.6}R_{0.4})], as they are a composition of anatase and rutile phase, the same as Degussa p25, still nobody could find the exact crystalline structure[53], which is due to the lack of enough knowledge and proper methodology for finding the crystalline contents. So due to being both anatase and rutile phases in TiO₂ (A_{0.8}R_{0.2}) and TiO₂ (A_{0.6}R_{0.4}), we consider them as Degussa p25, as the nearest structure can be purposed so probably the properties will be the same. In both anatase and rutile phases, while the irradiation is occurring O-2p and some of Ti-3d are exist in the valence band, which make a powerful hybridization between the orbitals of p and d from O-2p and Ti-3d respectively, and indeed, they make the bonding state in the valence band region and provide a bed to transfer of photogenerated holes. In the opposite band, conduct band is composed by Ti 3d state, which makes interaction with some O-2p and Ti-3d states. In this band, the main hybridization occurs between Ti-3d and O-2p states, as the antibonding state. However, in the cases TiO₂ (A_{0.8}R_{0.2}) and TiO₂ (A_{0.6}R_{0.4}), there is no knowledge about the exact hybridization and standpoints of the atoms and structures.

Fig. 14. The molecular structures of rutile and anatase

Energy bandgap is another key factor, which has to be considered. According to the Uv-Vis spectroscopy of the samples and Tauc's plot, the smallest energy bandgap is related to TiO₂ (A_{0.6}R_{0.4}) with around 3eV, while others were obtained around the same amount of 5eV (Fig.

15). It means the electrons in the valence band of TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$) need to take less energy (almost half compare to other samples) to get the conducting band, so more electron have this possibility to get the conducting band to continue the photocatalytic process, in this case, oxidation reaction. And as a result, more holes are created in the valence band. Even the problem, which is too fast recombination in TiO_2 when used as photocatalyst [54], will not effective because the process can be continued as fast as it is possible.

Fig. 15. Comparison of energy bandgap between different samples

Conclusion

Different derivatives of acid amino in different groups were used to coordinate titanium chloride (III) as a method to control and synthesis TiO_2 in different phases and structures. Complex compounds of glycine with titanium chloride (III) gives the TiO_2 at the least temperature. TiO_2 ($\text{A}_{0.8}\text{R}_{0.2}$), TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$), anatase, and rutile were obtained through thermal decomposing the mentioned complex. The partial selective photocatalytic- oxidation of benzyl alcohols oxidation into corresponding benzaldehyde was investigated. The reaction carried out under UV irradiation in the present of home-prepared-nano- TiO_2 s. The use of UV-visible light to drive oxidation transformations provides a sustainable pathway for green synthesis. The results indicate that the selective photocatalytic oxidation of benzyl alcohols into corresponding aldehydes under UV light irradiation proceeded at high conversion and selectivity. It was found that the efficiency of the obtained TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$) in photo-oxidation of benzyl alcohols into benzaldehydes show high selectivity. These results confirm that the

oxidation properties of TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$), TiO_2 ($\text{A}_{0.2}\text{R}_{0.8}$) are better than of bare rutile and anatase TiO_2 . Moreover, the photocatalyst can be reused without any loss in selectivity and efficiency. Finally, it can be recommended that TiO_2 ($\text{A}_{0.6}\text{R}_{0.4}$) is a selective photocatalyst for the partial photo-oxidation reaction of benzyl alcohols into corresponding aldehydes. Also, it should be mentioned that although surface activity and porosity are two important factors in photocatalytic reactions, reducing energy bandgap can be more effective, which is obtained by controlling the condition to obtain a sample with the almost the same phases of anatase and rutile.

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Conflict of interest statement

The authors declare that they have no conflict of interest.

Research involving human participants and/ or animals

This chapter does not contain any studies with human participants or animals performed by any of the authors.

Informed consent

Informed consent was obtained from all individual participants included in the study.

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Figures

Figure 1

TGA analysis from the obtained complexes; (a) ML1 (b) ML2, and (c) ML3

Figure 2

The molecular structure of the molecules according to the calculation by the DFT method

Figure 3

IR spectroscopy of (a) glutamine (L1), and (b) glutamine with titanium chloride (III) (L1+Ti)

Figure 4

IR spectroscopy of (a) glycine (L2), and (b) glycine with titanium chloride (III) (L2+Ti)

Figure 5

IR spectroscopy of (a) L-Alanine (L3), and (b) L-Alanine with titanium chloride (III)

Figure 6

XRD pattern of (a) TiO₂ (A0.2R0.8), (b) TiO₂ (A0.6R0.4), (c) TiO₂ (A), and (d) TiO₂ (R)

Figure 7

FT-IR spectroscopy of the nanoparticles; (a) TiO₂ (A0.2R0.8), (b) TiO₂ (A0.6R0.4) (c) TiO₂ (A), and (d) TiO₂ (R)

Figure 8

FESEM image of (a) TiO_2 (A0.2R0.8), (b) TiO_2 (A0.6R0.4), (c) TiO_2 (A), and (d) TiO_2 (R)

Figure 9

EDX pattern of (a) TiO₂ (A0.2R0.8), (b) TiO₂ (A0.6R0.4), (c) TiO₂ (A), and (d) TiO₂ (R)

Figure 11

Chemical physical properties of rutile sample; (a) micropores volume, (b) BET analysis, (c) BJH method, (d) Langmuir plot, and (e) DeBoer t-plot

Figure 12

UV-Vis spectroscopy of (a) TiO_2 (A0.2R0.8), (b) TiO_2 (A0.6R0.4), (c) anatase, and (d) rutile

Figure 13

Energy-band gap of (a) TiO₂ (A_{0.2}R_{0.8}), (b) TiO₂ (A_{0.6}R_{0.4}), (c) anatase, and (d) rutile

Figure 15

Comparison of energy bandgap between different samples

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