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Article

Facile and Economical Preparation Method of TiO₂/Activated Carbon for Photocatalytic Degradation of Methylene Blue

Phuoc Huu Le ^{1,2,3,*}, Tran Thi Thuy Vy ⁴, Vo Van Thanh ⁴, Duong Hoang Hieu ⁴,
Quang-Thinh Tran ⁴, Ngoc-Van Thi Nguyen ⁴, Ngo Ngoc Uyen ³, Nguyen Thi Thu Tram ³,
Nguyen Chi Toan ⁵, Ly Tho Xuan ⁶, Le Thi Cam Tuyen ⁷, Nguyen Trung Kien ⁸, Yu-Min Hu ⁹
and Sheng-Rui Jian ^{10,*}

- ¹ Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, New Taipei City 24301, Taiwan.
 - ² International Ph.D. Program in Plasma and Thin Film Technology, Ming Chi University of Technology, New Taipei City 24301, Taiwan
 - ³ Faculty of Basic Sciences, Can Tho University of Medicine and Pharmacy, 179 Nguyen Van Cu Street, Can Tho City 94000, Vietnam; lhuuphuoc@ctump.edu.vn (P.H.L); nnuyen@ctump.edu.vn (N.N.U); ntttram@ctump.edu.vn (N.T.T.T)
 - ⁴ Faculty of Pharmacy, Can Tho University of Medicine and Pharmacy, 179 Nguyen Van Cu Street, Can Tho City 900000, Vietnam; 1953030090@student.ctump.edu.vn (T.T.T.V); vovanthanhct2020@gmail.com (V.V.T); 1953030015@student.ctump.edu.vn (D.H.H); 2053030101@student.ctump.edu.vn (Q-T.T); ntnvan@ctump.edu.vn (N-V.T.N);
 - ⁵ Faculty of Pharmacy and Nursing, Tay Do University, 68 Tran Chien Street, Can Tho City 900000, Vietnam; nctoan@tdu.edu.vn
 - ⁶ Department of Materials Science and Engineering, National Taiwan University Science and Technology, Taipei City 106335, Taiwan; lyxuan.141@gmail.com
 - ⁷ Faculty of Chemical Engineering, Can Tho University-3/2 Street, Ninh Kieu District, Can Tho City 900000, Vietnam; lctuyen@ctu.edu.vn
 - ⁸ Faculty of Medicine, Can Tho University of Medicine and Pharmacy, 179 Nguyen Van Cu, Can Tho 900000, Vietnam; ntkien@ctump.edu.vn
 - ⁹ Department of Applied Physics, National University of Kaohsiung, Kaohsiung 81148, Taiwan; ymhu@nuk.edu.tw
 - ¹⁰ Department of Materials Science and Engineering, I-Shou University, Kaohsiung 84001, Taiwan
- * Correspondence: phle@mail.mcut.edu.tw (P.H.L) and srjian@gmail.com (S-R.J)

Abstract: Nanocomposites of TiO₂ Degussa P25 nanoparticles/activated carbon (TiO₂/AC) were prepared at various mass ratios of (4:1), (3:2), (2:3), and (1:4) by a facile process. The effects of TiO₂/AC mass ratios on the structural, morphological, and photocatalytic properties were systematically studied in comparison with bare TiO₂ and bare AC. TiO₂ nanoparticles exhibited dominant anatase and minor rutile phases, and a crystallite size of approximately 21 nm; while AC had XRD peaks of graphite and carbon, and a crystallite size of 49 nm. The composites exhibited tight decoration of TiO₂ nanoparticles on micron-/submicron AC particles, and uniform TiO₂/AC composites were obtained as evidenced by the uniform distribution of Ti, O, and C in an EDS mapping. Moreover, Raman spectra show the typical vibration modes of anatase TiO₂ (e.g., E_{1g}⁽¹⁾, B_{1g}⁽¹⁾, E_g⁽³⁾) and carbon materials with D and G bands. The TiO₂/AC with (4:1), (3:2), and (2:3) possessed higher reaction rate constants (*k*) in photocatalytic degradation of methylene blue (MB) than that of either TiO₂ or AC. Among the investigated materials, TiO₂/AC = 4:1 achieved the highest photocatalytic activity with a high *k* of 55.2×10⁻³ min⁻¹ and an MB removal efficiency of 96.6% after 30 min treatment under UV-Vis irradiation (120 mW/cm²). The enhanced photocatalytic activity for TiO₂/AC is due to the synergistic effect of the high adsorption capability of AC and the high photocatalytic activity of TiO₂. Furthermore, TiO₂/AC promotes the separation of photoexcited electron/hole (e⁻/h⁺) pairs to reduce their recombination rate and thus enhance photocatalytic activity. The optimal TiO₂/AC composite in this study can be used for treating industrial or household wastewater with organic pollutants.

Keywords: TiO₂/activated carbon; mass mixing ratio; photocatalyst; methylene blue

1. Introduction

Water is an essential resource for the growth of the natural environment on the earth and people. Water pollution with organic dyes, heavy metals, and other contaminants (i.e. pesticides, steroid hormones, antibiotics) is a current environmental issue [1]. Synthetic organic dyes are omnipresent in many application areas of the textile, tannery, cosmetic and food industries, and medicine [1]. The dying process in the textile and tannery industries can release a vast majority of organic dyes due to the nature low efficiency of the dying process with approximately 15% of dye lost [1,2]. Organic dye pollution in the aquatic environment poses a threat to animal or human health and causes adverse effects on aquatic biota and water ecosystems [1,3]. Semiconductor photocatalysis for environmental applications was introduced [4], and the field has been greatly developed over the years [5,6].

Titanium dioxide (TiO_2) is well-known to be the most practical and prevalent photocatalyst owing to its high photocatalytic activity, cost-effectiveness, chemical stability, abundant, and nontoxic [5]. Commercial powder of TiO_2 Degussa P25 (a flame-made multiphasic TiO_2 nanoparticles) was developed, and it has been widely used as a benchmark material for studying photocatalytic mechanisms, materials, and processes [7]. TiO_2 P25 contains anatase, rutile, and a small amount of amorphous phase, which were reported to be 77.1% anatase, 15.9% rutile, and 7.0% amorphous TiO_2 [7]. However, TiO_2 is a wide band gap semiconductor with $E_g = 3.2$ eV for anatase and 3.0 for rutile [8], and consequently, TiO_2 only works in the ultraviolet region, which accounts for less than 5% of the total energy of the solar spectrum [9]. A drawback of TiO_2 nanoparticles is the fast recombination of photoexcited carriers (electrons and holes) [10], and low specific surface area that limits the contaminant adsorption capability and the photocatalytic activity.

TiO_2 P25 (a powder form photocatalyst) offers relatively high photocatalytic degradation of organic dyes [11] and pharmaceuticals [11–14] and a high possibility toward practical scale application. However, TiO_2 P25 use in the form of suspension (slurry) may pose an ecological risk to aquatic organisms [15], which should need an expensive filtration process to separate the suspension catalyst from the treated water. Therefore, many nanostructured TiO_2 films developed on rigid substrates (e.g. TiO_2 nanotubes [16], TiO_2 nanowires on TiO_2 nanotube arrays [17–19]) have been studied for photocatalyst, solar energy conversion, and other applications [16]. The film forms of TiO_2 nanomaterials face a big challenge in scaling up to the practical scale of water treatment. Another approach is that TiO_2 nanomaterial is loaded on/in another bigger nano/micro-scale structure to form a heterostructure or a composite. Heterostructure and composite photocatalysts can offer activity enhancement due to some mechanism related to manipulating the photoresponse region and the fate of the electron/hole pairs [9]. In this way, TiO_2 has been impregnated on several porous supports such as silica, alumina, zeolite, and carbon materials [e.g., activated carbon (AC)] [20–22]. TiO_2/AC has been found to possess higher photocatalytic activity than bare TiO_2 as it combines the good photocatalytic activity of TiO_2 and the high surface area of AC [21–28]. In addition, TiO_2 nanoparticles loaded in the AC immobilization can resolve the limitation of using TiO_2 suspension, while AC is a very economical–useful adsorbent, and it is characterized by high surface area, micro- to macro-pore structures, and a high degree of surface reactivity [29].

Many studies focused on developing TiO_2/AC with structural, compositional, and surface functional modification [21–28], which usually needs the use of chemicals and laboratory equipment. Noticeably, a complicated preparation process of TiO_2/AC can hinder the practical application at the household level, where non-specialized people will be the operator of their household water treatment tank or plant. In this study, we prepared TiO_2 P25/AC using the two commercial raw materials by a facile and low-cost method by mixing TiO_2/AC mechanically at different mass ratios. Differ from the previous studies, the compositional weight portions of TiO_2/AC were in some specific range such as $\text{TiO}_2/(1\text{--}15 \text{ wt.}\%)\text{-AC}$ [28], $\text{TiO}_2/(5\text{--}75 \text{ wt.}\%)\text{-AC}$ prepared by sol-gel method [21], while the weight ratios of TiO_2/AC in this study were $\text{TiO}_2/\text{AC} = 5:0$, $\text{TiO}_2/\text{AC} = 4:1$, $\text{TiO}_2/\text{AC} = 3:2$, $\text{TiO}_2/\text{AC} = 2:3$, $\text{TiO}_2/\text{AC} = 1:4$, $\text{TiO}_2/\text{AC} = 0:5$. It is worthy to mention that the use mass ratio unit for the composite should be easier and more convenient for normal people to apply in practice when they implement TiO_2/AC material into their household water treatment plant. Moreover, this study has two reference samples (i.e., TiO_2 , AC) to get insight into the role of either TiO_2 or AC in the

photocatalytic degradation of methylene blue, which is a typical organic dye and considered a good model for studying photocatalyst activity and process. This study provides the effect of mixing weight ratios of TiO_2/AC on the morphological, structural, compositional, and photocatalytic properties of the composite.

2. Materials and Methods

2.1. Materials

Commercial Degussa TiO_2 P25 was purchased from Merck (Germany), and activated carbon (AC) was a product of Tra Bac company, Tra Vinh City, Vietnam, which was made from coconut shell. First, TiO_2 Degussa P25 was activated in NaOH 5 M solution at room temperature for 100 min, then it was filtered and cleaned with deionized water before drying in an oven at 100°C for 3 hrs. Then, AC (~5 g) was placed in a clean mortar, then crushed with a pestle for 30 minutes (Figure 1a). Next, AC was mixed with TiO_2 nanoparticles (P25) at different weight ratios, while the total weight of the material ($\text{TiO}_2 + \text{AC}$) was fix at 0.5 g. Six types of samples were prepared, including S1 (TiO_2), S2 ($\text{TiO}_2/\text{AC} = 4:1$), S3 ($\text{TiO}_2/\text{AC} = 3:2$), S4 ($\text{TiO}_2/\text{AC} = 2:3$), S5 ($\text{AC}/\text{TiO}_2 = 1:4$), and S6 (AC). Specifically, for example, we mixed 0.3 g TiO_2 with 0.2 g AC to prepare the S3 sample. To obtain a uniform mixture and surface functionalize for the TiO_2/AC composite, the 0.5 g powder was placed in a beaker filled with 10 ml ethanol 95% under sonication for 30 min (Figure 1b). Next, the powder mixture was filtered using a paper filter (Figure 1c). Finally, the material was annealed in an oven at 160°C for 3h. The powder products were stored in glass containers for later use.

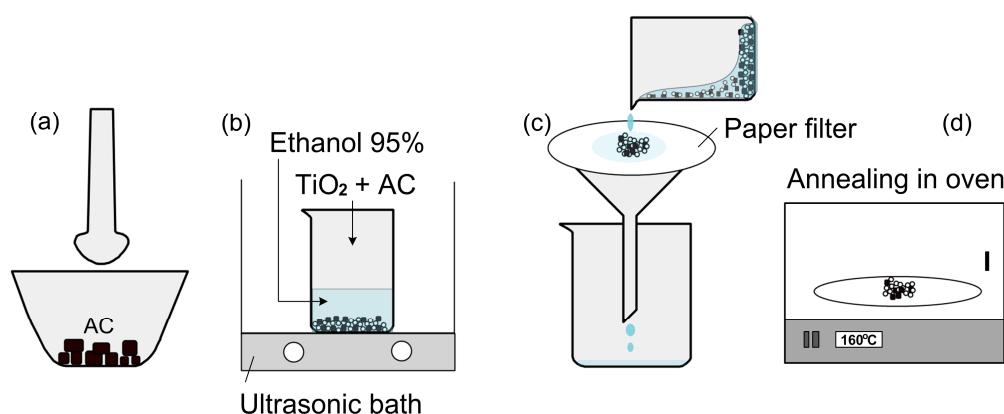


Figure 1. TiO_2/AC preparation process.

2.2. Photocatalytic activity in degradation MB of TiO_2/AC

Photocatalysis was carried out by placing 10 mg of the material powder in a 30 mL MB (at an initial concentration of 10 mg/L; the catalyst dosage of 333.3 mg/L) beaker and irradiating with ultraviolet-visible (UV-VIS) radiation from a Xenon lamp (power 100 W and power density of $120 \text{ mW}/\text{cm}^2$). The temperature of all QXT reaction beakers was kept at $32\text{--}33^\circ\text{C}$. After each given photocatalytic reaction time (15, 30, 45, or 60 min), 1 mL of MB solution was extracted for qualitative and quantitative study of the relative concentration of MB by UV-VIS spectrophotometer (Hitachi U-2900, Japan) through the characteristic absorption peak of MB at 655 nm.

2.3. Characterization Methods

The orientation and crystallinity of the materials were determined by X-ray diffraction (XRD, Bruker D2, Bruker, USA) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and θ - 2θ configuration. The morphology of the samples was determined by scanning electron microscope (SEM, Hitachi S-4800, Japan). The chemical composition was analyzed by X-ray energy dispersive spectroscopy (EDS, Oxford probe) integrated SEM (JEOL JSM-IT700HR). Raman spectrum of a selected TiO_2/AC was

obtained using a Horiba Evolution (Labram HR model) spectrometer operated with an excitation wavelength of 514 nm.

3. Results and Discussion

Figure 2a presents the XRD pattern of TiO₂ P25 nanoparticles (S1), TiO₂/AC composites prepared at various mass ratios (S2 – S5), and AC (S6). Generally, TiO₂ had dominant anatase phase characterized by diffraction peaks of A(101) at 25.3°, A(004) at 37.9°, A(200) at 48.2°, A(204) at 62.8°, and minor rutile phase with the observed peaks of R(110) at 27.5° and R(211) at 54.1°. Meanwhile, the AC exhibited the diffraction peaks of graphite [e.g., G(002) at 26.6°, G(020) at 45.5°], carbon C(100) at 20.9°, and 3D carbon structures with peaks G_{3D}(002) at 30.0°. The intensity of TiO₂ and AC peaks varied reasonably with the evolution of TiO₂/AC content (see Figure 2a). The dominant anatase phase over the rutile one for TiO₂ Degussa P25 in this study is consistent well with results reported in ref. [30].

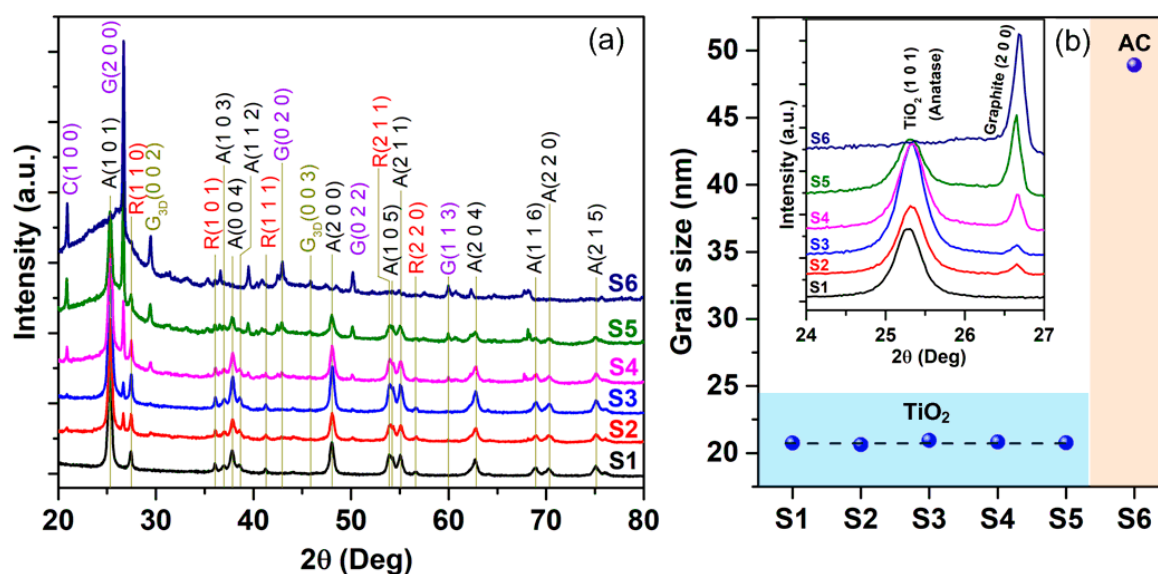


Figure 2. (a) X-ray diffraction patterns of TiO₂, TiO₂/AC composites, and AC. The symbol C (hkl) is the spectral peak of carbon (IMCSD #0013020); the symbol G (hkl) and G_{3D} (hkl) are the peaks of graphite (IMCSD #0000049) and graphite 3D structures (IMCSD #0013980), respectively; A (hkl) and R (hkl) indicate the patterns of TiO₂ anatase and TiO₂ rutile phases, respectively. (b) The crystallite size of the materials; the inset is the zoom-in-view of high-intensity characteristic peaks for TiO₂ and AC.

The crystallite size (D) in TiO₂ P25 and AC were estimated using the Scherrer equation and TiO₂ (101) and G(200) peaks, respectively. The Scherrer equation is given as, $D = 0.9\lambda/\beta\cos\theta$, where λ , β , and θ are the X-ray wavelength, full width at half maximum of the diffraction peak, and Bragg diffraction angle, respectively [19,21,31]. The D value for TiO₂ P25 in S1–S5 samples was a range of 20.6 – 21.0 nm, while the D of AC was 48.9 nm. The D of TiO₂ in this study is comparable with that of pristine TiO₂ synthesized by the sol-gel method ($D = 17.5$ nm), smaller than the D values of 43.4 – 109.0 nm for the TiO₂ annealed thermally at 200 – 500°C for 120 min [26]. Noticeably, the crystallite size (48.9 nm) for the present AC is very close to the D of 50 nm for the commercial AC used in ref. [26].

Figure 3 shows the surface morphology of the studied materials. TiO₂ P25 exhibited uniform spherical nanoparticles (NPs) with a size of 25 – 35 nm, while AC was micron- and sub-micron particles. For TiO₂/AC composites, TiO₂ nanoparticles were well dispersed and decorated tightly on AC particles (Figure 3). The SEM images also reflect the contents of TiO₂ and AC in the composites, e.g., TiO₂ content decreases while AC content increases when we observe the SEM images from S2 to S5 (Figure 3). The elemental composition and distribution were illustrated by the EDS result (S4) in

Figure 4. This composite has 18.04 at.% C, 52.18 at.% O, 19.00 at.% Ti, which indicates a composition of AC/TiO₂. Notably, small contents of Na (5.5 at.%), Si (5.25 at.%), and Pt (0.03 at.%) were observed due to the remaining after the surface activation process for P25 using NaOH 5 M, the Si substrate, and Pt coating for taking SEM images, respectively. In addition, the EDS mapping in Figure 4 suggests a uniform elemental distribution, uniform decoration of TiO₂ on AC, and possibly loading of TiO₂ NPs inside the micro-pores and micro-channels of AC. The SEM and EDS results indicate the tight binding between TiO₂ and AC that should support the carrier transport for enhancing photocatalytic activity.

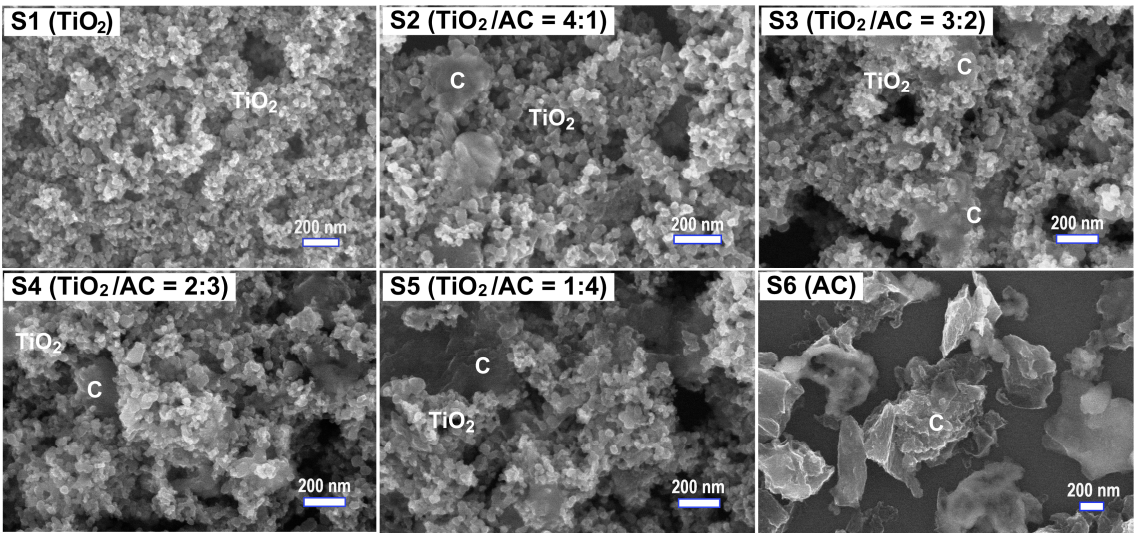


Figure 3. Scanning electron microscopy (SEM) images of TiO₂ P25 (S1), TiO₂/activated carbon (AC) composites prepared at various mass ratios (S2-S5), and AC (S6).

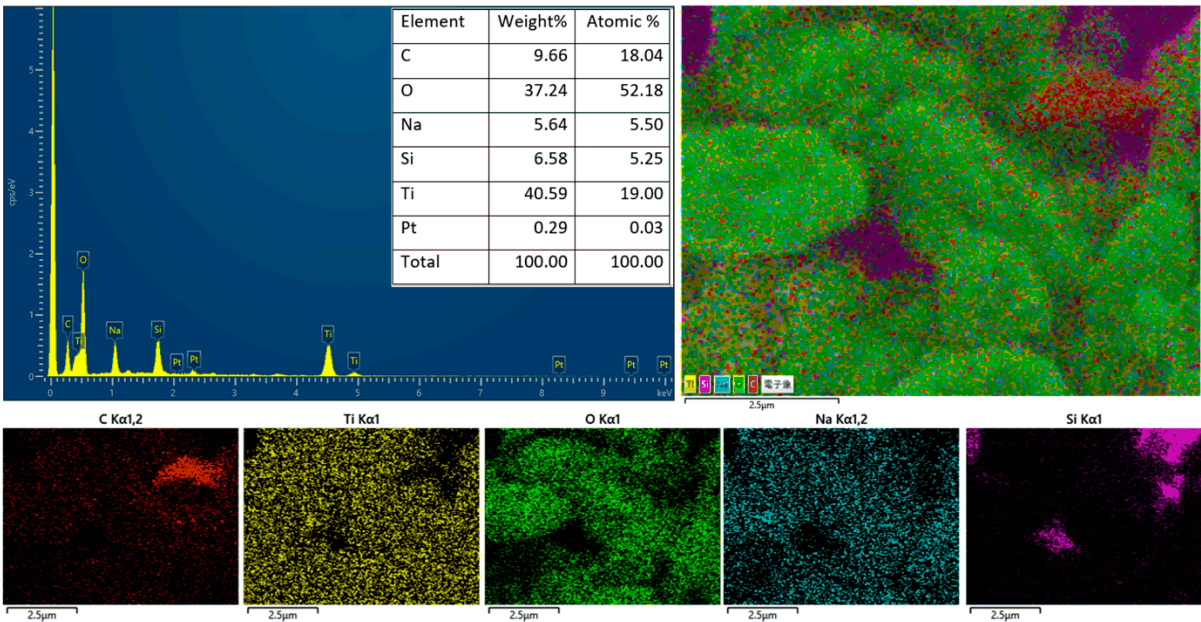


Figure 4. An EDS spectrum of a TiO₂/AC prepared by dropping a DI water solution containing S4 powder on a clean Si substrate; and an EDS mapping of the S4 powder sample.

To gain insight into the crystalline structure of TiO₂/AC composites, a typical Raman spectrum of TiO₂/AC was examined. In Figure 5, the spectrum exhibited characteristic peaks of TiO₂ predominant anatase phase at 146 cm⁻¹ (E_g⁽¹⁾), 200 cm⁻¹ (E_g⁽²⁾), 396 cm⁻¹ (B_{1g}), 516 cm⁻¹ (A_{1g}), and 635 cm⁻¹

¹ (E_g) as well as two graphite carbon peaks at 1327 cm^{-1} (D-band) and 1588 cm^{-1} (G-band) (Figure 5). The D-band is associated with asymmetric lattices and bond-angle disorders in graphitic structures [25], while G-band comes from the doubly-degenerate iTO and LO phonon with E_{2g} symmetry at the Brillouin zone center [32]. This Raman results for TiO_2/AC agreed well with the Raman results for the TiO_2/AC in ref. [25].

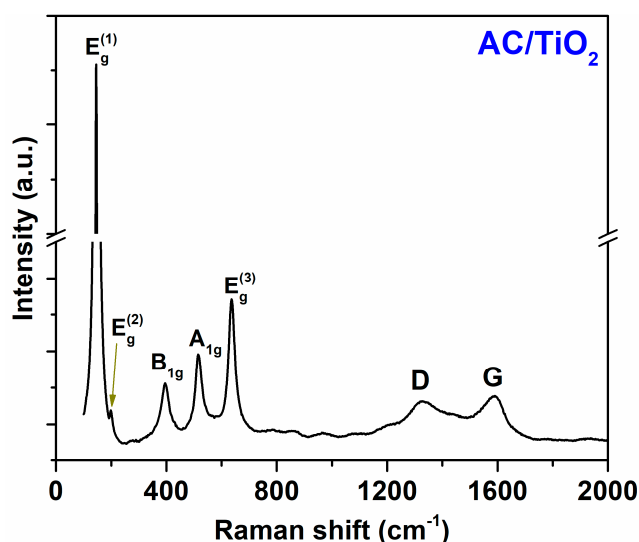


Figure 5. A typical Raman spectrum of AC/TiO₂.

The photocatalytic activities of TiO_2 , AC, and TiO_2/AC with different mixing mass ratios were studied by monitoring the photodegradation kinetics of MB (an organic substance, and popular use as an organic pollutant model) under UV-Vis irradiation (120 mW/cm^2). Figure 6a shows the evolution of the MB absorption peak (at $\sim 655\text{ nm}$) over the photocatalytic reaction time (t) using the TiO_2/AC (S2). The peak intensity (associated with MB concentration) decreased with t , and this behavior is true for the other photocatalysts in this study (S1, S3, S4, S5, S6). The photodegradation kinetics by photolysis and photocatalytic processes using the materials are shown in Figure 6b, which obeys the Langmuir–Hinshelwood kinetic model with the first-order reaction rate constant (k), $C_t = C_0 \times e^{-kt}$, where C_t is the concentration of MB at time t (mg/L), C_0 is the initial MB concentration (mg/L).

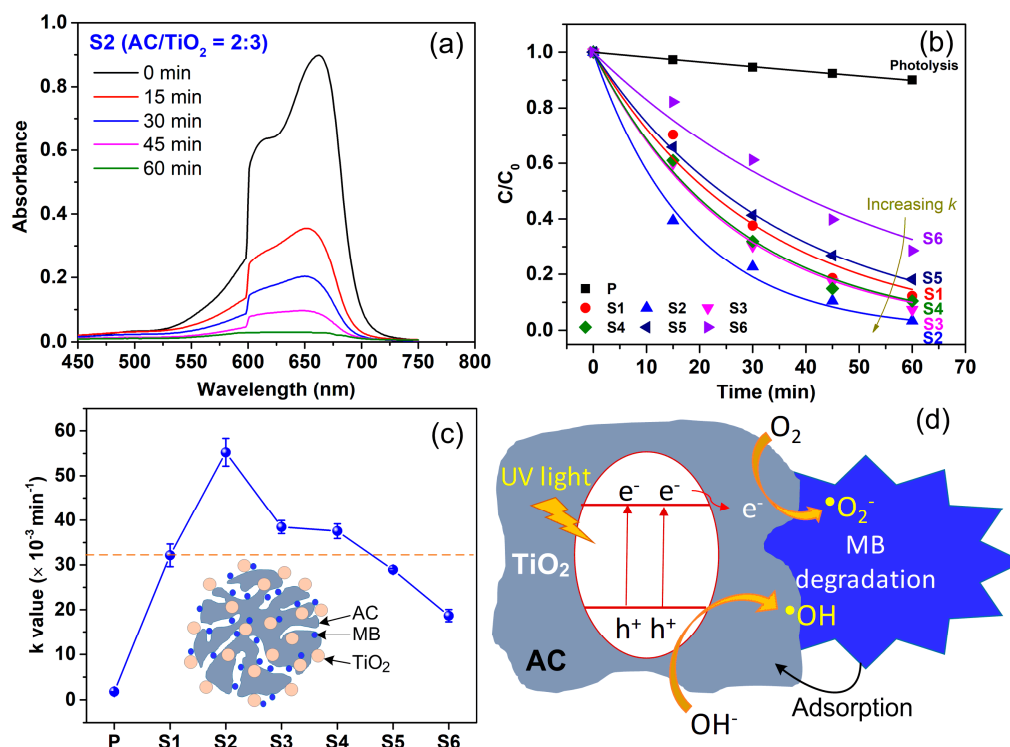


Figure 6. (a) Typical photodegradation of methylene blue (MB) using AC/TiO₂ materials (e.g., S2 sample case). (b) Photocatalytic degradation of MB by AC/TiO₂ materials prepared at various mass ratios under the UV-Vis irradiation of Xenon lamp (120 mW/cm²). (c) The pseudo-first-order kinetics constant *k* of photolysis (P) and photocatalytic reaction using AC/TiO₂ (S1 – S6); Inset in (c) shows a schematic of porous AC/TiO₂ in MB solution. (d) A schematic diagram for the photocatalytic degradation mechanism of MB using AC/TiO₂ composite. .

The solid lines in Figure 6b are the fitting curves using the kinetic model. The fittings yield the *k* values of the photolysis (P) and photocatalytic processes using the S1–S6 materials (see Figure 6c). The *k* of the photolysis reaction was a small value of $1.8 \times 10^{-3} \text{ min}^{-1}$, while the *k* values were $32.1 \times 10^{-3} \text{ min}^{-1}$ (S1), $55.2 \times 10^{-3} \text{ min}^{-1}$ (S2), $38.5 \times 10^{-3} \text{ min}^{-1}$ (S3), $37.5 \times 10^{-3} \text{ min}^{-1}$ (S4), $28.9 \times 10^{-3} \text{ min}^{-1}$ (S5), $18.7 \times 10^{-3} \text{ min}^{-1}$ (S6). This indicates that MB degradation is much faster and more effective by using the photocatalysts as compared to the photolysis process. In addition, the composites of TiO₂/AC (S2, S3, S4) exhibited an enhancement in the photocatalyst activity over either the pristine TiO₂ (S1) or AC (S6). Among the investigated TiO₂/AC composites with various mass mixing ratios (S2 – S5), the S2 possessed the highest photocatalyst activity, suggesting that TiO₂/AC = 4:1 is the optimal mass mixing ratio between TiO₂ P25 and micron- and sub-micron AC. Further increased AC and decreased TiO₂ contents to TiO₂/AC = 3:2 and TiO₂/AC = 2:3 also exhibited higher photocatalytic activities than that for TiO₂. Meanwhile, the sufficient low TiO₂ and high AC contents for the TiO₂/AC = 1:4 (S5) lead to the decrease of activity as compared to pristine TiO₂ (see the dashed line in Figure 6c). Noticeably, the observed decrease in MB concentration over *t* for AC (S6) material is attributed to the excellent adsorption characteristic of porous carbon materials (Figure 6c inset) [27,33,34].

AC/TiO₂ composites with mass mixing ratios of (4:1), (3:2), and (2:3) have higher MB removal performance than either TiO₂ or AC, which is attributed to the synergistic effect of the high adsorption capability of AC and the high photocatalytic activity of TiO₂. As illustrated in Figure 6d, under UV-VIS irradiation, electron/hole (e⁻/h⁺) pairs are generated, which lead subsequently to oxidation and reduction reactions in the treated solution to generate highly active free radicals, primarily •OH and •O₂⁻ (Figure 6d) [27,33,34], which in turn degrade MB dye. It is well-known that the recombination rate of e⁻/h⁺ in TiO₂ is fast. Meanwhile, in TiO₂/AC composites, the photogenerated carriers can be transferred between TiO₂ and AC, allowing to increase in e⁻/h⁺ separation and reducing the e⁻/h⁺ recombination rate, and consequently enhancing the photocatalytic activity. The AC (S6)

removes MB with k of $18.7 \times 10^{-3} \text{ min}^{-1}$ (58.3% of k for TiO_2), suggesting the AC has high adsorption capacity with many sufficient active adsorption sites and a large surface area [27,33,34]. The lower k value of S5 than S1 indicates that a composite with too little TiO_2 and too much AC contents ($\text{TiO}_2/\text{AC} = 1:4$ for the present case) will not give an enhancement of the photocatalytic activity. An advantage of a combination of a good photocatalyst with a good adsorption material (i.e., TiO_2/AC) is that TiO_2 degrades MB to create renewable active adsorption sites on the AC to adsorb more MB molecules as evidenced by the higher adsorption efficiency of pollutants near TiO_2 positions on the composite surfaces [27,35]. Also, TiO_2 plays the role of photocatalytic regeneration of AC, and this allows minimizing operational costs and product waste. The optimal TiO_2/AC (S2) obtained a high MB removal efficiency of 96.6% after 60 min treatment at the initial MB concentration of 10 mg/L and a composite dosage of 333.3 mg/L. This efficiency is comparable to that for the TiO_2/AC (i.e., 86.5%, 97.1%, and 99.4%, depending on the type of AC) under similar experimental conditions (i.e., reaction time of 60 min, UV light source, catalyst dosage of 400 mg/L, and MB initial concentration of 20 mg/L) [27].

4. Conclusions

In this study, TiO_2/AC composites with various mass mixing ratios were prepared through a facile and cost-effective process. The composites exhibited tight decoration of TiO_2 nanoparticles on micron-/submicron AC particles. TiO_2 had crystal phases of dominant anatase and minor rutile, and the crystallite size of TiO_2 was ~ 21 nm. Meanwhile, AC presented the XRD peaks of graphite and carbon, and it had a crystallite size of ~ 49 nm. TiO_2/AC composites are reasonably composed of main elements (O, Ti, C). The EDS mapping confirmed the uniform distribution of elements, indicating the formation of uniform TiO_2/AC composites. Among the TiO_2/AC composites prepared at different mixing ratios of (4:1), (3:2), (2:3), (1:4), bare TiO_2 , and bare AC, the $\text{TiO}_2/\text{AC} = 4:1$ possessed the highest photocatalytic activity in degradation of MB under UV-Vis irradiation, which yielded a high MB removal efficiency of 96.6% after 60 min treatment. The enhanced photocatalytic activity of TiO_2/AC composites is attributed to the synergistic effect of the high adsorption capability of AC and the high photocatalytic activity of TiO_2 . In addition, TiO_2/AC composites allow charge transfer for enhancing e^-/h^+ separation to reduce their recombination rate and enhance their photocatalytic activity. Thus, TiO_2/AC composite with a weight ratio of 4/1 possibly be used for treating industrial or household wastewater with organic pollutants.

Author Contributions: P.H.L: Conceptualization, Methodology, Investigation, Writing – original draft, Project administration; S.R.J: Resources, Writing – Review & editing, Supervision; T.T.T.V, Q-T.T; V.V.T, D.H.H, N.C.T, L.T.X: Data curation, Investigation, Data Analysis, Writing – original draft; L.T.C.T, N.N.U: Data curation, Data analysis; N-V.T.N, N.T.T.T, T.T.K, Y-M.H: Resources, Review & editing.

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

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