A facile method for the synthesis of MoS₂/g-C₃N₄ photocatalyst

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Abstract

MoS₂/g-C₃N₄ composite was synthesized by a significantly simpler method using Na₂MoO₄ and thiourea as precursors, without the need for a hydrothermal or an ultrasound step. The photocatalytic activity of the synthesized material was evaluated by the degradation of Rhodamine B (RhB) in aqueous solution under blue light, and the composites with low content of MoS₂ performed better than pure g-C₃N₄. Using a low-power LED light source, this study resulted in two orders-of-magnitude improvement in the photochemical space-time yield, proving improved energy efficiency and productivity, compared to earlier studies. The degradation pathway of organic pollutants was confirmed by the effects of selective scavengers.

Keywords: LED, MoS₂/g-C₃N₄, photocatalysis, visible light.

1. INTRODUCTION

Removal of organic pollutants in aqueous media by photodegradation using semiconductors as heterogeneous catalysts has drawn much attention, since this process uses solar radiation as a green energy source and oxygen in the air as an abundant oxidant [1]. However, many available oxide semiconductors can only absorb ultraviolet (UV) light. Therefore, the modifications of oxides that can work efficiently in visible light have been widely investigated [2, 3]. In addition to the oxides, recently, carbon nitride with graphite-like structure (g-C₃N₄), a metal-free organic semiconductor has allured significant attention as a potential photocatalyst due to its electronic structure with band gap of 2.7 eV and relatively high chemical stability [4]. However, photocatalytic performance of pure g-C₃N₄ is limited because of its poor absorption in visible region, fast recombination of photo-generated charge carriers and low specific surface area [5]. In order to overcome these disadvantages, various methods have been investigated such as co-polymerization [6, 7], altering different precursors [8, 9] and non-metal doping [10]. Therefore, coupling techniques with other co-catalysts is a promising way to enhance photocatalytic efficiency [11]. Molybdenum disulfide (MoS₂), a typical 2D nanomaterial, has received much attention in potential applications such as lithium ion batteries, electronics,

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optoelectronics, super-capacitors and sensors. Moreover, with a unique electron structure and band gap of 1.3 eV, it was also in focus as a co-photocatalyst in water splitting in the form of MoS₂/pyridine-modified g-C₃N₄ [12] and in the domain of degradation of organic pollutants in aqueous solutions in the form of MoS₂/Bi₂MoO₆, MoS₂/BiOBr, MoS₂/Ag₃PO₄ and MoS₂/C₃N₄ [13-16]. These reports showed that the presence of MoS₂ plays a beneficial role in improvement of light harvesting, electron transfer at interfaces and charge separation in the composite materials. These benefits are attributed to proper band gap edge positions and good lattice matching of MoS₂ and g-C₃N₄ [17].

So far, the synthesis of the MoS₂/g-C₃N₄ composite has been reported in only a few studies [18-20]. Generally, the reported methods consist of three steps in which, the two individual materials g-C₃N₄ and MoS₂ are produced separately, by heating precursors such as urea, melamine, cyanamide for the former and a hydrothermal method for the latter. Then, the mixture of g-C₃N₄ and MoS₂ is treated by ultrasound. However, both of the hydrothermal and ultrasound steps require high energy and the former occurs at hydrothermal conditions. Therefore, a facile method to synthesize a large amount of material without compromising photocatalytic activity is still in need.

In this paper, we show the successful synthesis of MoS₂/g-C₃N₄ composites using thiourea and sodium molybdate as precursors just by calcining through a two-step process in inert gas. Photocatalytic performance of the composites was evaluated by degradation of rhodamine B (RhB) using light from blue LEDs. The optimized composite MoS₂/g-C₃N₄ exhibited a photochemical space-time yield (PSTY) as high as $8.3 \times 10^{-3} \text{ day}^{-1} \cdot \text{kW}^{-1}$, which was two orders-of-magnitude greater than the values, calculated from the results of the previous reports [18, 19]. PSTY was previously used as a new benchmark measure to compare energy efficiency of photochemical system [21]. The effect of initial pH, catalyst loading and H₂O₂-RhB molar ratio on the catalyst activity was investigated. Furthermore, the photocatalytic mechanism and active species were also explored using triethanolamine (TEOA) and t-BuOH (TBA) as hole scavenger and hydroxyl radical scavenger, respectively.

2. MATERIALS AND METHODS

2.1. Reagents

Sodium molybdate dihydrate (Na₂MoO₄·2H₂O, 99.5%), thiourea (CN₂H₄S, 99.0%), rhodamine B (RhB, C₂₈H₃₁ClN₂O₃, 95%) were purchased from Sigma-Aldrich. Triethanolamine (TEOA, C₆H₁₅NO₃, 99+%, Acros Organics), tert-butyl alcohol (TBA, C₄H₁₀O, 99.5%, Merck), H₂O₂ (30%, Merck), 0.1 M HCl and 0.1 M NaOH (Reagecon) were used as received without further purification. Deionised water was used to prepare all of the aqueous solutions.

2.2. Preparation of catalysts

The thin layered MoS₂ (M) was synthesized by calcination of Na₂MoO₄ and thiourea. Specifically, 1.0 g of sodium molybdate (VI) dihydrate and 3.0 g of thiourea were ground in a mortar before transferring the resulting mixture into a ceramic crucible (30 mL). This crucible was covered by its lid to prevent the loss of product from sublimation. The mixture was then heated to 550°C at a heating rate of 10°C/min under N₂ gas atmosphere and then was kept at constant temperature for 2 h prior to cooling. The composites MoS₂/g-C₃N₄ were fabricated by heating the mixture of M and thiourea with different weight ratios. Typically, m₀ gram of M (m₀ = 0.06, 0.12, 0.18 and 0.30 for MCN1, MCN2, MCN3 and MCN5, respectively), was well-mixed with 24.0 g of thiourea by a shaker before grinding thoroughly by pestle and mortar, then the mixture powder was transferred to four separate 30-mL ceramic crucibles and were heated as per the same conditions described for synthesis of M above (heating rate 10°C/min, 550°C under N₂ gas for 2h).

For comparison, g-C₃N₄ was also prepared by heating thiourea in the same conditions with a final mass yield of 15%. The pure g-C₃N₄ was denoted as CN. All the obtained samples were washed by distilled water and ethanol before being heated at 60°C for 10h. The MoS₂ contents in the MCN1, MCN2, MCN3, and MCN5 were calculated to be 1.6, 3.2, 4.8 and 8.0 w.t. %, respectively.

2.3. Catalyst Characterization

X-ray diffraction (XRD) analysis was carried using a D8 Advanced Bruker anode X-ray Diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation. The morphology and size of the synthesized samples were characterized by scanning electron microscopy (SEM, JEOL JSM-600F) equipped with an energy dispersion X-ray spectrum (EDS). Infrared (IR) spectra of the samples were recorded using an IR Prestige-21 spectrophotometer (Shimadzu). Thermogravimetric analyses were carried out on the SETRAM LABSYS TG system under argon flow with heating rate of 10°C/min. The optical properties were examined on a Jasco V-650 Spectrophotometer (No. UV-1800) using BaSO₄ as reference. The surface area of samples were determined with TriStar 3000 V6.07 A. X-ray photoelectron spectroscopic (XPS) measurements were made on an Escalab 250Xi system.

2.4. Photocatalytic experiments

The photocatalytic activity of the as-prepared samples was evaluated in batch, by using RhB as a pollutant molecule. At low concentration pollutants, the Langmuir-Hinshelwood model would become pseudo-first-order, as below [22].

$$\ln(C_0/C) = kt \quad (1)$$

where C is the concentration of RhB (mg.L^{-1}), C_0 is the adsorption equilibrium concentration of RhB before irradiation (mg.L^{-1}), t is the reaction time (min), and k is the reaction rate constant (min^{-1}). Accounting for the lamp power and the treated solution volume, a new benchmark could be used to compare the photocatalytic activity of different reactor and catalyst combinations. This benchmark measure is the photochemical space-time yield (*PSTY*), which can be calculated by the following equation [21].

$$PSTY = STY/LP \quad (2)$$

Where, STY is space-time yield (day^{-1}) and LP (kW) is the standardized lamp power. The detailed calculation of these parameters are explained among the Supporting Information. This benchmark was used as described by Leblebici et al. [21].

Into a 25 mL of RhB solution at 5.0 mg.L^{-1} , the catalyst is dispersed at concentrations varying from 0.3 g.L^{-1} to 1.1 g.L^{-1} under stirring and the solution was kept in dark for 1 h to achieve adsorption equilibrium. The obtained optimal catalyst loading was used for other investigations. Irradiation was performed by 20 LEDs of blue light (Winger) with the emission wavelength of 450-495 nm (Fig. S1), the applied voltage and current values were 3V and 0.1 A, respectively. The spectrum of the blue light was recorded by Ocean Optics QE 65 Pro spectrophotometer. At a given time interval, the concentration of RhB in the collected solution was determined by measuring the absorbance at 553 nm after removing the catalyst by centrifuge. In order to investigate the active species for the photodegradation of RhB, the different quenchers were used. In this work, the used trapper reagents are triethanolamine (TEOA, h^+ scavenger) and t-BuOH (TBA, $\cdot\text{OH}$ scavenger). Their concentration was studied at 100 and 1000 times of RhB. Prior to the photocatalytic activity experiments, solution pH was adjusted by adding HCl and

NaOH solutions. The effect of oxidant concentration on photodegradation rate was also studied with the molar ratio H_2O_2 -pollutant in the range of 50 to 400 (see Supporting Information).

3. RESULTS AND DISCUSSION

3.1. Characterization of the materials

As shown in Fig. 1a, the XRD pattern of CN are indexed to $\text{g-C}_3\text{N}_4$ (JCPDS 87-1526). The two peaks located at 27.4° and 13° corresponds to the (002) stacking layered structure and the (100) in-plane repeated units, respectively [18, 19]. The XRD pattern of M could be ascribed to hexagonal phase of MoS_2 (JCPDS 37-1492) with two peaks located at 32.6° and 58.3° corresponding to the (100) and (110) of M. The disappearance of interlayer (002) peak of M indicates the formation of MoS_2 nanosheet [18]. The XRD patterns for MCN_x ($x = 1, 2, 3, 5$) are nearly the same as that for CN and there is no recognizable diffraction peaks corresponding to MoS_2 . This may be attributed to the low content of MoS_2 and its high dispersion in $\text{g-C}_3\text{N}_4$ [20].

Figure 1. (a) XRD patterns of M, CN, and MCN_x ($x = 1, 2, 3, 5$); (b) FT-IR spectra of CN, and MCN_x ($x = 1, 2, 3, 5$); XPS spectra of Mo3d (c) and S2p (d).

As shown in Fig. 1b, the absorption bands of CN from 1650 to 1240 cm^{-1} are attributed to the typical C=N stretching mode and out-of-plane bending vibrations of the C–N bonds in heterocycles of $\text{g-C}_3\text{N}_4$ [20], while the sharp absorption peak centered at 807 cm^{-1} is assigned to

the characteristic breathing mode of tri-s-triazine cycles. Moreover, the weak peak at 883 cm^{-1} can be assigned to the deformation mode of N-H in amino groups. Meanwhile, the broad peaks between 3000 and 3500 cm^{-1} are ascribed to the stretching vibration of residual free N-H in the bridging C-NH-C units and O-H from the physically adsorbed water on the surface of samples [23, 24]. Similar to the case of XRD, due to the small amount of M contents in the composites there is no difference between the IR spectra of composite samples MCNx and CN. The absence of MoS₂ characteristic peaks in XRD patterns and FT-IR spectra of the composites is consistent with the previous reports [18, 19, 25]. The presence of MoS₂ in the composite samples can be confirmed by XPS, and MCN5 sample was chosen as a representative. As shown in Fig. 1c, the Mo 3d spectrum exhibits two peaks at 228.9 eV (Mo 3d_{5/2}) and 232.5 eV (Mo 3d_{3/2}), and in Fig. 1d the two peaks at 161.7 eV and 162.8 eV, correspond to the S 2p_{3/2} and S 2p_{1/2}, respectively. This indicates the existence of Mo⁴⁺ and S²⁻ in the composite [26]. The appearance of two more weak peaks at 226.2 eV and 235.2 eV in Fig. 1c can be assigned to S 2s and Mo⁶⁺, respectively. The latter species may come from the formation of a small amount of MoO₃ on the surface of the composite [27].

The BET surface area and pore volume of pure g-C₃N₄ and MoS₂/g-C₃N₄ composites were determined by nitrogen adsorption-desorption isotherms (see Fig. S2). The CN sample has a surface area of $34.5\text{ m}^2\cdot\text{g}^{-1}$ and a pore volume of $0.176\text{ cm}^3\cdot\text{g}^{-1}$. Meanwhile, the corresponding values of MCNx samples are similar to that of pure g-C₃N₄ as shown in Table 1. In general, the variation in surface area of the materials is not significant.

Table 1 BET specific surface area and pore volume of the g-C₃N₄ and MCNx samples

Samples	CN	MCN1	MCN2	MCN3	MCN5
BET ($\text{m}^2\cdot\text{g}^{-1}$)	34.5	46.7	36.2	36.8	35.4
Pore volume ($\text{cm}^3\cdot\text{g}^{-1}$)	0.176	0.215	0.220	0.235	0.241

The thermal properties of materials were characterized by thermogravimetric analysis (TGA) in Ar atmosphere. Fig. 2a shows that there are two steps of weight loss for all of the samples: (1) from room temperature to $\sim 150^\circ\text{C}$ and (2) from ~ 400 to 625°C . The former step may be attributed to evaporation of physically adsorbed water and the latter was the decomposition of the materials, in which the CN's decomposition temperature meets the literature for the pure g-C₃N₄ [28]. Interestingly, the decomposition of the composites come at the lower temperature compared to CN, and this trend of decreasing the decomposition temperature when increasing the MoS₂ content of the composites can be observed in all the samples. This phenomenon was observed in some reports [28, 29] and it is explained by the catalytic role of MoS₂ or the disturbing effect of MoS₂ to the interlayer stacking structure of g-C₃N₄.

Figure 2. (a) TGA curves of samples M, CN, and MCNx in Ar atmosphere and (b) UV-Vis absorption spectra of CN, and MCNx ($x = 1, 2, 3, 5$).

To investigate the light harvesting properties of the samples, UV-vis diffuse reflectance spectroscopy (DRS) was performed and the spectra are shown in Fig. 2b. The CN sample shows absorption from UV through the visible range up to 450 nm which can be assigned to the intrinsic band gap of g-C₃N₄ (2.76 eV). For the composites, although there are not significant changes in the band gap values (see Fig. S3), the absorption intensity increases from MCN1 to MCN5 in the visible light region as compared to g-C₃N₄, which can be attributed to the presence of MoS₂ in the composite, resulting in high visible light photocatalytic performance.

In order to confirm the distribution and uniformity of MoS₂ and g-C₃N₄ in the composites, EDS elemental mapping was applied, and MCN2 was chosen as a representative. Fig. S4 shows that expected presence of C, N, S and Mo elements in uniform distribution can be observed. This result indicates that MoS₂ and g-C₃N₄ are combined uniformly throughout the composite. This shows that the composite possesses heterostructures and close contact between the components, g-C₃N₄ and MoS₂, which favours the transfer of photogenerated charge carriers, therefore enhancing the charge separation and the photocatalytic activity of the composites.

3.2. Photocatalytic activities

3.2.1. Photocatalytic comparison and proposed mechanism

As shown in Fig. 3, there was an improvement in the photocatalytic activity of MCNx samples compared to CN, except for MCN5. Applying Eq. (2) to calculate PSTY (see Supporting Information) for reactors in this work and the mentioned reports with values shown in Table 2.

Table 2 PSTY data of the reactors

	k (min ⁻¹)	STY (day ⁻¹)	LP (kW)	$PSTY$ (day ⁻¹ kW ⁻¹)
Ref. [18]	0.301	0.432	6.0×10^3	7.2×10^{-5}
Ref. [19]	0.036	5.2×10^{-2}	3.0×10^3	1.7×10^{-5}
This work	0.070	0.10	12.0	8.3×10^{-3}

Table 2 shows that the reaction rate constant of this study is higher than one but smaller than the other reference. However, the PSTY of this study is 2 orders of magnitude higher than those of the all references. This was particularly interesting since the power of the used light source was significantly lower (0.3 W vs. 300 W) [18]. The result indicates that not only is the synthesized catalyst equally or more efficient in light utilization compared to the literature but also are the LEDs more effective than the light sources used by the earlier studies.

Figure 3. (a) First-order kinetic plots for the photodegradation of RhB, (b) The rate constants for RhB photodegradation over various composites and photocatalytic degradation of RhB with different trapping agents (a) TBA and (b) TEOA under blue light over MCN1. Conditions of process: initial RhB concentration: 5.0 ppm, pH 3.0, catalyst loading: 0.7 g.L⁻¹, 25°C, under blue light.

Both of these factors had significant contributions to the RhB photodegradation under experimentally studied conditions. The efficiency of the LED can be due to its monochromatic behaviour. This way, all of the emitted photons fall within the excitation band of the catalyst. Meanwhile, when using Xe lamp as a light source [18, 19], the number of photons that have enough energy for the excitation only account for a small part of the total emitted photons [30]. This may justify the dramatically lower PSTY values of the state of the art.

The photocatalytic enhancement of the composites can be attributed to the charge separation. Due to the lower conduction band positions, MoS₂ in the composite is able to receive photoexcited electron from g-C₃N₄ [19], which favours the separation of electron-hole pairs. The separated electrons on the surface of M reduces present oxidants in the solution. For the case of dissolved oxygen this reduction step can be given as,

The formed superoxide radical anion continuously undergoes three more steps to release hydroxyl radical $\text{OH}^\cdot$ which are described as follows [31]:

Hydroxyl radical is a strong oxidizing species which would degrade the organic pollutants in the solution. Meanwhile, the accumulated holes on the surface of CN, are not only producing hydroxyl radical according to,

but also directly oxidizing the adsorbed dye molecule on the surface.

However, when further increasing the content of MoS_2 , the photocatalytic performance of MCN_x decreased, which might be explained by the light blocking effect [32]. This effect was observed most significantly for the highest content of MoS_2 as in MCN_5 (8.0 wt.% $\text{MoS}_2/\text{g-C}_3\text{N}_4$) sample. The photocatalytic activity of this sample was even lower than that of pure $\text{g-C}_3\text{N}_4$.

The effect of the scavengers were shown in Fig. 3c and 3d. The changes in RhB photodegradation rate indicated that both of TBA and TEOA had negative effects on the photocatalytic activity of the catalyst. However, TEOA scavenger exhibited much stronger inhibition showing that hole was the dominant reactive species in the photodegradation process of RhB under studied conditions.

3.2.2. Effect of pH

The experimental value of isoelectric point (IEP) of MCN_1 sample using solid addition method [33] (see Supporting Information), as shown in Fig. 4a had the value of 3.6. The pH of the solution affects not only the surface charge of the particles, but also the forms of pollutant molecule and consequently the adsorption ability of the molecule on the surface.

Figure 4. (a) Dependence of surface charge of MCN1 sample and the RhB structure on pH of reaction mixture and (b) Effect of initial pH on RhB degradation in the conditions of process: initial RhB concentration: 5.0 ppm, catalyst loading: 0.7 g.L⁻¹, 25°C, under blue light.

The pK_a of RhB in the aqueous solution is 3.22 [34] indicating that it is in the zwitterionic form in solutions with pH > pK_a, but in the cationic form with pH < pK_a, as shown in Fig. 4a. The effect of pH on photocatalytic activity of the catalyst was investigated within wide range of pH values, which were adjusted before irradiation. As shown in Fig. 4b, without adjusting medium (pH = 6.4), very low removal of RhB was observed. Increasing this value to 12.0, the degradation kinetics further slowed down. However, at pH 3.0, the RhB photodegradation increases dramatically, due to the strong hydrogen bonds between carboxylic acid groups and remaining lone pairs of electron on nitrogen atoms resulting in the increase of substrate adsorption [35]. However, at pH 1.5, the surface of the catalyst become more positive resulting in rising of the repulsive force, affecting the reaction rate negatively.

3.2.3. Effect of catalyst loading

To find out the optimum mass of catalyst, the photodegradation of RhB with various MCN1 loadings were carried out, as shown in Fig. 5a. When the catalyst loading increased from 0.3 g.L⁻¹ to 0.7 g.L⁻¹, the RhB degradation rate increased due to an increase in the photogenerated electron-hole pairs. However, there is not a significant change in the degradation rate when the catalyst loading is increased from 0.7 to 0.9 g.L⁻¹. Further increase in MCN1 loading results in a slight decrease in the RhB removal. This trend can be attributed to the negative effects of shielding by the suspended catalyst when the loading increased [36, 37]. This is proven in Fig. 5b, as the increase of catalyst loading results in the decrease of transmitted light irradiance from the solution. Owing to this effect, the rate of photodegradation is reduced after a threshold MCN1 catalyst loading. Furthermore, Fig. 5b shows that added catalyst creates a darkzone in the reactor after 13 mm depth.

Figure 5. (a) Effect of MCN1 catalyst loading on RhB degradation in the conditions of process: initial RhB concentration: 5.0 ppm, pH: 3.0, 25°C, under blue light, and (b) Irradiance of transmitted blue light of different RhB solution heights with different catalyst loadings from the solution.

3.2.4. Effect of H₂O₂-RhB molar ratio

In order to prevent the electron-hole recombination, and to improve the photocatalytic activity of a photocatalyst, a suitable electron acceptor can be added to the system. Some inorganic oxidants could be used for this purpose such as H₂O₂ and peroxodisulphate [37]. The former was chosen for this study. In the photocatalytic reactions, hydrogen peroxide does not only act as electron acceptor which promoting charge separation but also produces hydroxyl radical through the reaction with superoxide radical anion [36] according to the following equations:

As a result, the degradation of RhB after 10 minutes of irradiation increased from 37.1% in the absence of H₂O₂ to 41.5% and 49.9% when the H₂O₂-RhB molar ratio was 50 and 100, respectively, as shown in Fig. 6.

Figure 6. Effect of H₂O₂-RhB molar ratio. Process conditions: catalyst loading: 0.7 g.L⁻¹, initial RhB concentration: 5.0 ppm, pH: 3.0, 25°C, under blue light.

However, the degradation rate decreased again when the ratio was greater than 200. This negative effect was due to hole and OH[·] scavenger function of H₂O₂ at high concentrations. This can be expressed as follows [38]:

Therefore, at too high concentration of H₂O₂, the degradation reaction was inhibited.

4. CONCLUSIONS

In this work, the MoS₂/g-C₃N₄ composites were synthesized by a facile method from sodium molybdate and thiourea precursors just by calcination, without the need for hydrothermal-condition and ultrasound process steps. The synthesized composites were proven to be efficient and active photocatalysts by benchmarking them with prior works. An optimum MoS₂ content in the composite increased the interfacial charge transfer and thus reduced electron-hole recombination, improving the photocatalytic activity. The photodegradation of RhB was shown to be mainly due to the direct oxidation by photogenerated hole of the composite under visible light. The low pH values of the reaction solutions were proven to be beneficial for the photocatalytic degradation of the rhodamine B. An optimum pH of 3.0 and a catalyst loading of 0.7 g.L⁻¹ the photocatalyst showed the best activity. The blue LEDs was proven effective in efficient photodegradation of organic pollutant over MoS₂/g-C₃N₄ photocatalyst. PSTY, a benchmark for different reactor designs was also used to compare the catalysts studied in this work with the previous published ones. The simple method of synthesis of the photocatalyst MoS₂/g-C₃N₄ in combination with the use of efficient LEDs opens a new door to transfer it into various practical applications including wastewater treatment using visible light.

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Symbols used

C_o	[mg.L ⁻¹]	adsorption equilibrium concentration of RhB
C	[mg.L ⁻¹]	concentration of RhB
k	[min ⁻¹]	reaction rate constant
t	[min]	reaction time
$PSTY$	[day ⁻¹ .kW ⁻¹]	photochemical space-time yield
STY	[day ⁻¹]	space-time yield
LP	[kW]	standardized lamp power

Author Contributions

Duy Huong Truong carried out the experiment and wrote the manuscript with support and supervision from Mumin Enis Leblebici, Tom Van Gerven and Vien Vo.

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In this study, a significantly quicker and lower cost method was introduced for the synthesis of $\text{MoS}_2/\text{g-C}_3\text{N}_4$ composites. Using only two calcination steps and without any other high pressure or ultrasonic processes, a highly efficient visible-range photocatalyst was produced. Its activity was proven using the degradation of rhodamine B. At optimal conditions the reaction system showed a high energy efficiency and a performant apparent degradation rate.