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The photocatalytic activity of g-C_3N_4/Ta_2O_5 composite under visible light irradiation

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Abstract

The g-C_3N_4/Ta_2O_5 composites were synthesized by heating mixtures of urea and Ta_2O_5 at 500 °C. The as-prepared samples were denoted as CN-500/TaO-W, where W is weight ratio of urea/Ta_2O_5 and equals to 3, 4 and 5. The materials were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, and Ultraviolet-visible diffuse reflectance spectroscopy. The photocatalytic activity of CN-500/TaO-W samples was assessed by degradation of methylene blue in aqueous solution under visible light. Among them, CN-500/TaO-4 exhibited the best performance. An enhancement in photocatalytic activity of the composites is believed to be the presence of g-C_3N_4.

Keywords. g-C_3N_4, Ta_2O_5, photocatalytic activity, methylene blue, g-C_3N_4/Ta_2O_5 composite.

1. INTRODUCTION

The study of materials that could absorb light from the sun to decompose organic pollutants in water and air is not only an opportunity but also a challenge for many researchers and attracts a lot of interest from society. The semiconductors that highly exhibit the catalytic performance under light have been known as potential photocatalysts. They possess many advantages including high efficiency in conversion of solar energy, strongly catalytic activity, highly capable decomposition of organic pollutants, reusability and especially environmental friend.

Among the semiconductors, in recent years, Ta_2O_5 has attracted much attention in photocatalysis. However, with the large band gap energy (about 3.8 to 5.3 eV), its photocatalytic activity only exhibits in ultraviolet region [1], leading to limit its application in practice. To solve this problem, many works have been done to modify Ta_2O_5 by doping with some other elements to improve optical absorbance in visible light [2, 3].

At the same time, g-C_3N_4 material, a polymer organic semiconductor with graphitic-like structure, can absorb visible light (the band gap energy of about 2.7 eV), taking a lot interest of researchers due to its wide range of applications. However, the fast recombination rate of photoinduced electron-hole pair for this material leads to its low photoefficiency. This is a drawback when using it in invidual status. Therefore, many attempts to enhance the photocatalytic performance of g-C_3N_4 by modifying it with other elements have been done [4, 5].

To improve the photocatalytic capability of each material when using them in separate systems, we synthesized g-C_3N_4/Ta_2O_5 composite as described in details in the previous works [6]. In this article, we focused on effect of the ratio (urea/Ta_2O_5) on properties of the products and evaluated their photocatalytic activity by photodegrading methylene blue in aqueous solution.

2. EXPERIMENTAL

2.1. Chemicals

Tantalum pentoxide (Ta_2O_5), urea (CH_4N_2O), and methylene blue ($C_{16}H_{18}N_3S$) were purchased from Merck. All chemicals were analytical grade and used without further treatment.

2.2. Synthesis

Urea and Ta_2O_5 were mixed with different weight ratios (urea/Ta_2O_5 in weight = 3, 4 and 5). The mixtures were put into a porcelain cup sealed with aluminum foil and then calcined at 500 °C with a heating rate 10 °C min^{-1} for 2 hours. The samples were denoted as CN-500/TaO-W, where W is weight ratio between urea and Ta_2O_5.

For comparison, pure g-C_3N_4 was also prepared by heating urea at 500 ^oC, and denoted as CN-500.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were conducted using a Bruker D8 Advance with Ni-filtered CuK_α radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) was performed using an ESCALab spectrometer (Thermo VG, UK) with monochromated AlK_α radiation. Ultraviolet-Visible Diffuse reflectance spectroscopy (UV-Vis DRS) was investigated on a GBC Instrument - 2885 spectrophotometer.

2.4. Photocatalytic Activity

To evaluate photocatalytic activity of the prepared materials, methylene blue (MB) was selected as an organic pollutant. To 200 mL of 50 mg/L MB solution, 0.1 g of the prepared sample was dispersed under stirring and the solution kept in dark condition for 3 h to reach equilibrium of adsorption-desorption process. Then, the solution was irradiated by visible light using a 75W-220V lamp with a filter cutting UV rays. MB degradation was monitored by taking suspension at irradiation time intervals of 1 h. Each suspension was centrifuged to separate the catalyst from the MB solution. The degradation rate was calculated as a function of irradiation time from the change in absorbance at wavelength of 663 nm as measured using a UV-Vis spectrophotometer (Jenway 6800).

3. RESULTS AND DISCUSSION

3.1. Characterization of catalysts

3.1.1. XRD

The XRD patterns of the samples in figure 1 show that the main diffraction peaks of all samples are from orthorhombic Ta_2O_5 [7], indicating that orthorhombic Ta_2O_5 phase still remains in the as-prepared samples under thermal treatment of the mixture of Ta_2O_5 and urea at 500 ^oC.

In addition, it is worth to note that an extra peak with 2θ value at about 13.2 and 27.3^o belonging to g-C_3N_4 [8] (figure 1) can be seen clearly for CN-500/TaO-4. This diffraction is indexed to (100) and (002) plane, respectively, for graphite-like layer structure of g-C_3N_4. This peak is very strong for the CN-500/TaO-5, proving a larger amount of g-C_3N_4 in this material.

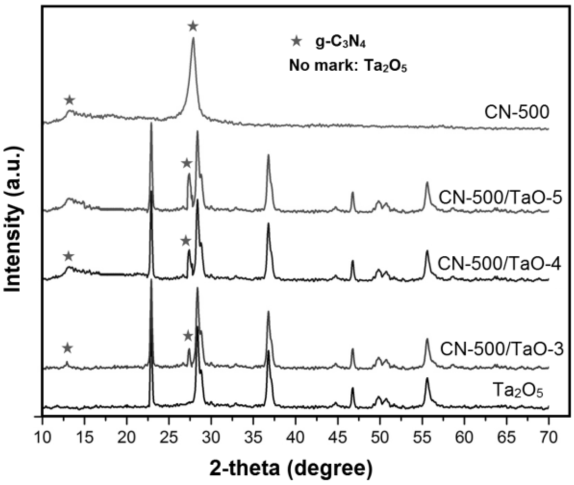


Figure 1: XRD patterns of Ta_2O_5, CN-500 and CN-500/TaO-3, CN-500/TaO-4 and CN-500/TaO-5

3.1.2. XPS

XPS was used to examine the surface composition and chemical state of C, N, O and Ta in the samples. Figure 2 and table 1 show XPS of C, N, O and Ta of a representative sample, CN-500/TaO-4.

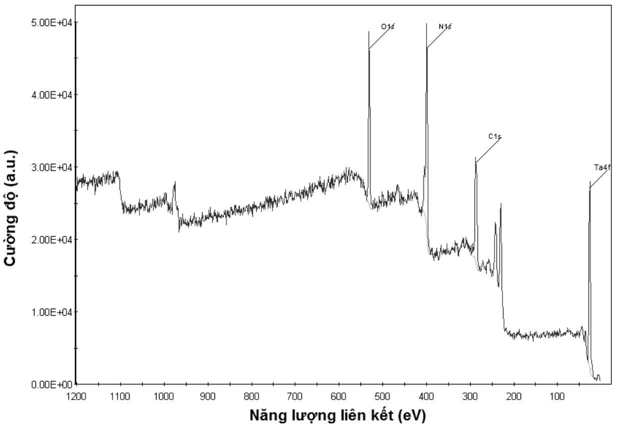


Figure 2: XPS spectrum of CN-500/TaO-4

Table 1: Binding energy of Ta4f, O1s, C1s, N1s

Orbital	Ta4f	O1s	C1s	N1s
$E_{binding}$ (eV)	25.5 27.3	530.6	287.7 284.5	398.6

For C1s XPS, in addition to the peak at 287.7 eV corresponding to the referenced C, a strong peak at 284.5 eV can be attributed to carbon in the C-N-C configurations of g-C_3N_4 [9, 10]. The presence of g-C_3N_4 in the sample can be further confirmed by N1s XPS in table 1. The intense pic at 398.6 eV may be assigned to sp^2 hybridized aromatic nitrogen atoms bonded to carbon atoms (N=C) [11]. The peak at 530.6 eV for O1s is usually reported as O in Ta_2O_5

[12]. Also shown in table 1, Ta 4f7/2, and Ta 4f5/2 peaks appeared at 25.5 eV and 27.3 eV, respectively, which correspond to Ta^{5+} in Ta_2O_5 [12]. However, compared to pure Ta_2O_5 (26.6 eV and 28.5 eV, respectively), a slight shift to lower energy has been obtained. Such a shift may be caused by presence of an interaction between Ta and g-C_3N_4 in the composite. These results rather demonstrated that CN-500/TaO-4 is a composite consisting of Ta_2O_5 and g-C_3N_4.

3.1.3. UV–Vis DRS

The optical absorption spectra and band gap energy of Ta_2O_5, CN-500/TaO-3, CN-500/TaO-4, and CN-500/TaO-5 are shown in figure 3.

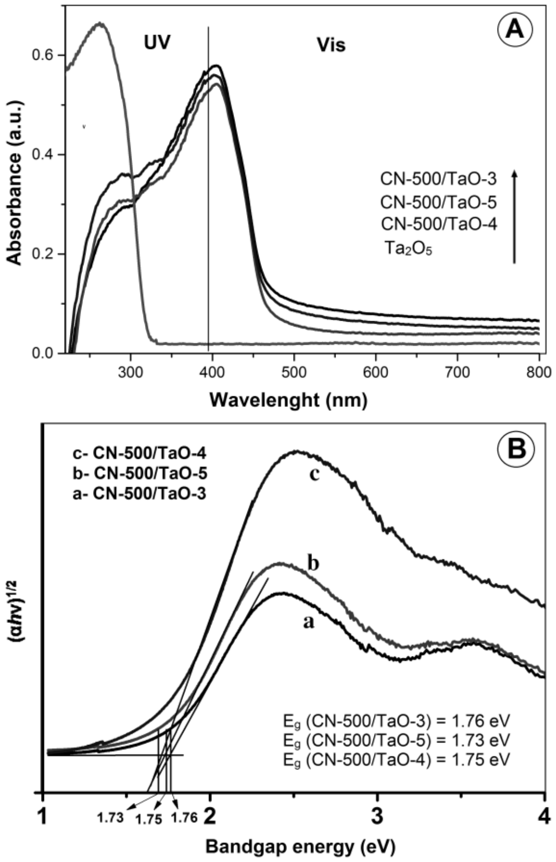
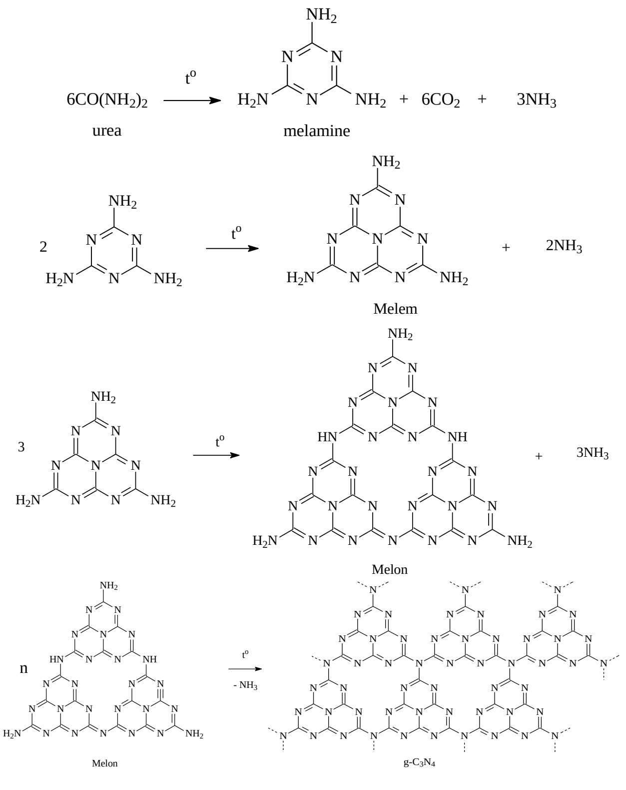


Figure 3: (A) UV–Vis DRS and (B) band gap energy of Ta_2O_5, CN-500/TaO-3, CN-500/TaO-4, CN-500/TaO-5

In figure 3A, Ta_2O_5 exhibits an absorption peak centered at approximately 275 nm which is assigned to the O2p to Ta5d charge transfer band of the Ta_2O_5 [13]. This peak can be observed in the composites, however their intensity strongly reduced. Compared to the pristine Ta_2O_5, a broad absorption band covering the range of 300-500 nm with a peak centered at about 380 nm for the composites has been obtained. This broad absorption in the visible light region may come from g-C_3N_4 in the composites. This indicates that the g-C_3N_4 may serve as a sensitizer to extend the absorption in visible light region for the composites and thus improve their photocatalytic activities under visible light irradiation.

Based on the document [14] and Kubelka-Munk equation [15], the band gap energy of the materials was determined and shown in Figure 3B. With a reduced band gap energy, CN-500/TaO-3, CN-500/TaO-4, CN-500/TaO-5 materials might possess good catalyst activity in visible light region.

The formation of the composites can be explained by that when heating the mixture of urea and Ta_2O_5, first, polymerization of urea can occur via some following steps [16, 17]:



The g-C_3N_4 was then formed on surface of the Ta_2O_5 particles to yield the composites.

3.2. Photocatalytic Activity

The photocatalytic activity of the samples was determined by degradation of MB in water under visible light. For comparison, photocatalytic activity of the pristine Ta_2O_5 and g-C_3N_4 (CN-500) was also presented. Figure 4 shows the variation of MB concentration (C/C_0) versus irradiation time on the five samples.

Ta_2O_5 exhibited a low photocatalytic activity in visible light which may be due to its large band gap energy. For g-C_3N_4 (CN-500), although relatively small band gap energy, about 2.70 eV [1], its photocatalytic activity is still low. This is explained by that the high recombination rate of electron-hole pair in pure g-C_3N_4 [18] leads to reduced photocatalytic activity.

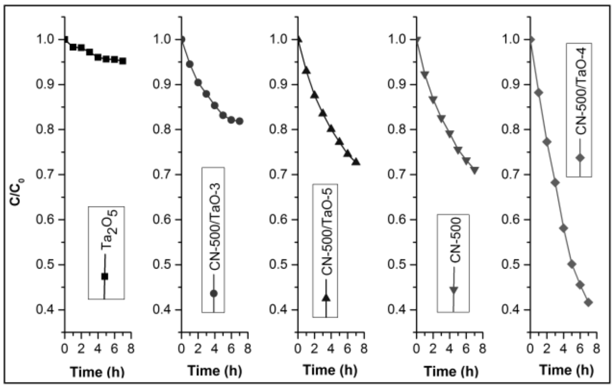


Figure 4: Photocatalytic activity of Ta_2O_5, CN-500, CN-500/TaO-3 and CN-500/TaO-4, CN-500/TaO-5 toward the degradation of MB

For g-C_3N_4/Ta_2O_5 composits, a difference in catalytic performance of the materials can be observed. On the CN-500/TaO-4 sample, the decrease in C/C_0 is much faster than for the others. For the CN-500/TaO-3 and CN-500/TaO-5, the decrease in C/C_0 is slower compared to CN-500/TaO-4. This may be attributed to a reduced recombination rate of electron-hole in CN-500/TaO-4. The photocatalytic activity of CN-500/TaO-4 is better than that of Ta_2O_5 and g-C_3N_4, indicating that a synergistic effect occurs in the composite during the photocatalytic reaction. Graphitic g-C_3N_4 playing a key role in enhancement of photocatalytic activity for composites was discussed in several reports [19]. On the basis of a number of works published [20, 21], decomposition mechanism of MB on the g-C_3N_4/Ta_2O_5 composites is proposed in figure 5A. In these composites, the photogenerated electrons on the conduction band of the g-C_3N_4 can directly inject into the conduction band of Ta_2O_5. This phenomenon can lead to a significant decrease in the electron–hole recombination for the pure g-C_3N_4. Hence, this may contribute to the enhancement of photocatalytic reactivity.

However, for CN-500/TaO-3 and CN-500/TaO-5 in this work, the photocatalytic activity is lower than that of the pure g-C_3N_4. This may be explained by that a small or too large amount of g-C_3N_4 in the two materials as shown in the characterizations does not form the synergistic effect mentioned above. In CN-500/TaO-5, when covered with a quite thick layer of g-C_3N_4, this material will show photocatalyst closing to that of pure g-C_3N_4. In contrast, with a smaller amount of g-C_3N_4, the activity of CN-500/TaO-3 is close to Ta_2O_5. This shows that a proper amount of g-C_3N_4 in composite is very important.

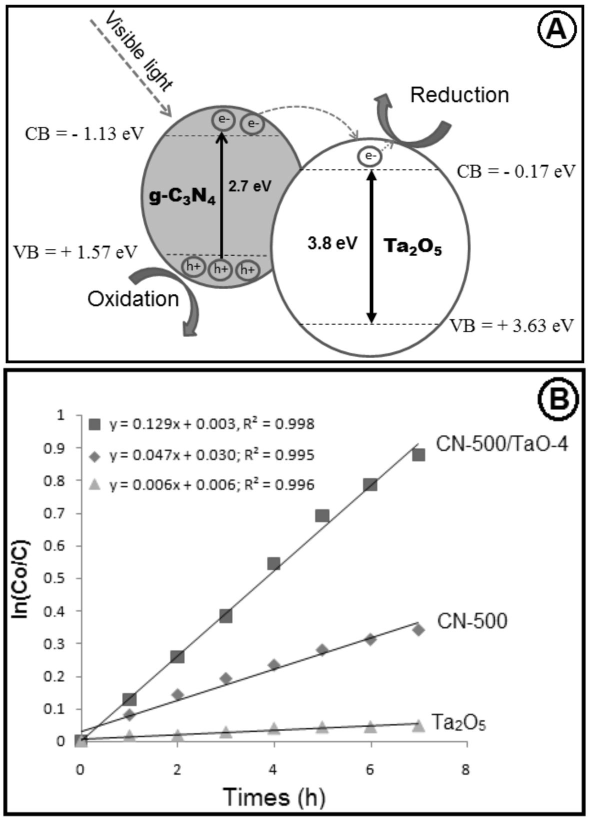


Figure 5: (A) Proposed mechanism for the photodegradation of MB on the g-C_3N_4/Ta_2O_5 composites; (B) linear plots of $\ln(C_0/C_t)$ *vs.* time for degradation of MB in aqueous solution under visible light

In order to investigate kinetics of the photocatalytic reactions, the Langmuir-Hinshelwood model has been usually employed. For solid-liquid reactions, the Langmuir–Hinshelwood equation can be expressed:

$$r = k\cdot\theta = k\cdot KC/(1 + KC) \qquad (1)$$

where r and k are the reaction rate and rate constant, respectively, θ is the surface coverage, K is the adsorption coefficient of the reactant, and C is the equilibrium concentration of the reactant. When C is at low concentration, $K\cdot C << 1$, hence $r = k\cdot KC/(1 + KC) \approx k\cdot K\cdot C = k_{app}\cdot C$. Therefore, the pseudo first-order kinetics equation (Eq. (2)) is applied:

$$\ln(C_0/C_t) = k_{app}\cdot t \qquad (2)$$

where C_0 and C_t are the reactant concentrations at reaction times, t = 0 and t = t, respectively, k_{app} is the apparent reaction rate constant.

A relationship between $\ln(C_0/C_t)$ and t was plotted in figure 5B. It can been clearly seen that the plots of $\ln(C_0/C_t)$ versus reaction time (t) are well fitted with the pseudo first-order rate model with high correlation coefficients ($R \geq 0.995$). From the plots, the k_{app} values were calculated for CN-500/TaO-4, CN-500 và Ta_2O_5 to be 0.129 và 0.047 và 0.006 h^{-1}, respectively. These results show that the reaction rate on the catalyst CN-500/TaO-4 is much stronger than CN-500 and Ta_2O_5.

The above obtained results show that weight ratio of urea and Ta_2O_5 in reaction mixture for the synthesis of g-C_3N_4/Ta_2O_5 composites plays an important role to determine their band gap energy and photocatalytic properties.

4. CONCLUSIONS

1. Composites of Ta_2O_5 and g-C_3N_4 with different weight ratios of the precursors (urea/Ta_2O_5 = 3, 4 và 5) have been successfully synthesized with a new method by calcining ure with Ta_2O_5 at temperature of 500 °C.

2. The composites demonstrate photocatalytic activity for degradation of methylene blue in aqueous solution under visible light irradiation. Among the composites, the sample derived from thermal treatment at 500 ^oC, weight ratio of urea/Ta_2O_5 = 4 exhibits the best photocatalytic activity.

3. Decomposition rate of methylene blue on CN-500/TaO-4 composite is more than 2.7 times the g-C_3N_4 and 21.5 times higher than Ta_2O_5.

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