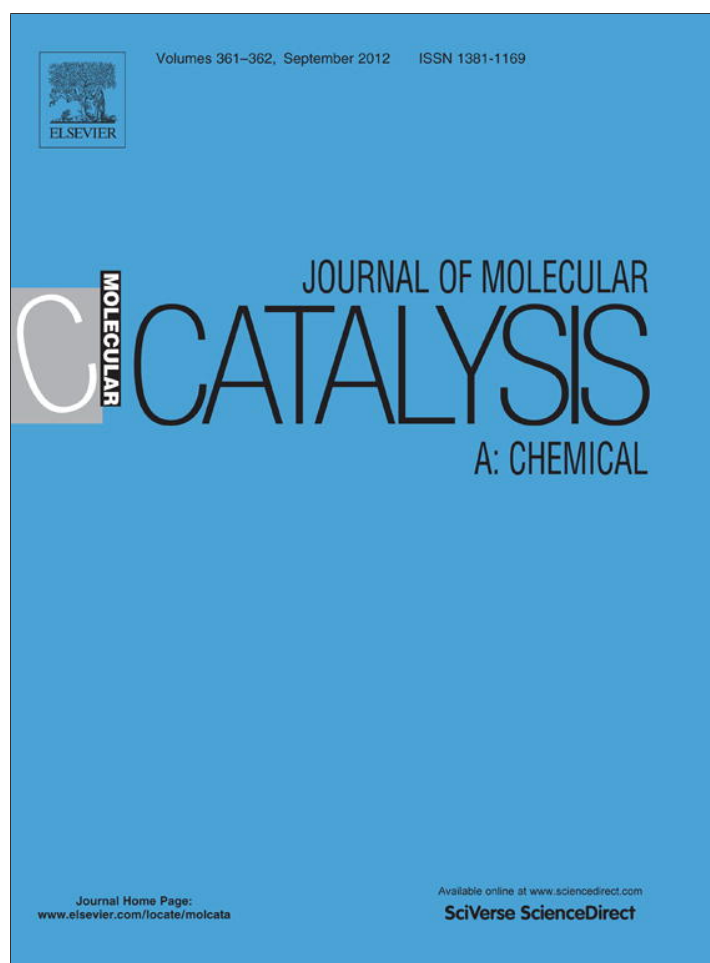




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Photodegradation of CV over nanocrystalline bismuth tungstate prepared by hydrothermal synthesis

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ABSTRACT

A nanocrystalline bismuth tungstate (Bi₂WO₆) with sheets morphology was successfully prepared by hydrothermal method and characterized by the field emission scanning electron microscopy with the energy dispersive X-ray spectrometer (FE-SEM-EDS), the X-ray diffractometer (XRD), and the high resolution X-ray photoelectron spectroscopy (HR-XPS). At alkaline condition, having pH 9, Bi(NO₃)₃·5H₂O and H₂WO₄ as the starting materials, the reaction mixture was kept at 160 °C for 24 h, 48 h and 72 h to produce a high yield of Bi₂WO₆ with flower-like architecture. Moreover, the binding energy shift of Bi element was clearly observed, proposing that Bi^(+3-x) formal oxidation state could most probably be attributed to the substoichiometric forms of Bi at outer site of the particles, and the formation of the low oxidation state resulted in oxygen vacancy in the crystal surface. The photocatalytic activities of the as-synthesized catalysts were evaluated by the photodegradation of crystal violet (CV) dye, while the nineteen intermediates were separated and characterized by the HPLC-PDA-ESI-MS techniques. The results demonstrated that the *N*-de-methylation degradation and the oxidative degradation of the CV dye took place during the degradation process. Based on these products, the probable degradation mechanisms were further proposed and discussed.

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1. Introduction

Over 700,000 tons dyes and pigments are produced annually worldwide, of which about 20% are in industrial effluents from textile dyeing and finishing processes [1]. There are many classes of dyes such as acidic, basic, neutral, azo, disperse, direct, and reactive dyes. Since most of these dyes have a complicated polyaromatic structure and could not be treated successfully by conventional methods, the photocytotoxicity of triphenylmethane dyes based on reactive oxygen species production is tested intensively with regard to their photodynamic therapy [2,3]. Thyroid peroxidase-catalyzed oxidation of the triphenylmethane dyes results in the formation of various *N*-de-alkylated primary and secondary aromatic amines, which have structures similar to aromatic amine carcinogens [4]. The effects on the immune system and reproductive system and its genotoxic and carcinogenic properties have been studied [5]. From an ecological and physiological point of view, the elimination of toxic chemicals from wastewater is currently one of the most crucial subjects in pollution control.

Water is a prime source for all living organisms including human beings. Wastewater containing dyes coming from dyeing and finishing industry is generally high in both color and organic content. Their release as wastewater in the ecosystem is a dramatic source of esthetic pollution, eutrophication, and perturbations in aquatic life. Therefore, decolorization of wastewater from textile effluents has been the target with great attention in the past few years [6,7]. TiO₂, which has higher photocatalytic activity, was intensively used as photocatalysts for environmental remediation due to chemicals. However, with a large band gap (3.2 eV), TiO₂ can only absorb ultraviolet light ($\lambda < 400$ nm). Therefore, we can only use ultraviolet to irradiate it [8]. Poor solar efficiency (maximum 5%) hinders the practicality of TiO₂ [9]. Therefore, exploitation new photocatalyst system has received considerable attention new visible-light-induced photocatalytic activity system. In recent years, Bi₂WO₆, a typical Aurivillius oxide with the WO₆ and (Bi₂O₂)²⁺ layered crystal structure, has been proved to be an excellent visible light photocatalyst. Kudo and Hiji [10] first found the photocatalytic activity of Bi₂WO₆ for O₂ evolution from AgNO₃ solution. Subsequently, various methods, such as sol-gel and hydrothermal, were utilized to synthesize Bi₂WO₆ and the visible photocatalytic activities were evaluated, which were attributed to different morphology and preparation methods [11–15]. As the photocatalytic

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activity closely correlated to the size, structure, and morphology of the photocatalysts [5,16], many researchers have paid their attention to the exploitation of Bi_2WO_6 photocatalysts with special structure and morphology [14,17–21]. Moreover, several papers also reported that the Aurivillius phase $\text{Bi}_2\text{W}_2\text{O}_9$ could be converted into a tungstic acid ($\text{H}_2\text{W}_2\text{O}_7 \cdot n\text{H}_2\text{O}$) by acid treatment [22,23].

The hydrothermal method is the most commonly applied research method as it may yield metal oxides with various morphologies depending on the organic templates. Besides, each parameter of the synthesized conditions contributes considerable influence on the properties of the resulting materials [18,24–26]. It was believed that hierarchically structured Bi_2WO_6 was an ideal system for obtaining new insights into the relations among synthesis, morphology and their photocatalytic functions. Moreover, it was interesting to understand the fundamental photocatalytic degradation mechanisms of CV dye by HPLC/MS. In this current work, a simple and efficient hydrothermal autoclave method to prepare Bi_2WO_6 with nanosheets crystalline structure, and the degradation mechanism toward crystal violet (CV) dye have been reported. The potential applications using hydrothermal autoclave method to synthesize the transition metal oxide-based photocatalysts were further discussed.

2. Experiment

2.1. Materials and preparation of photocatalysts

The purchased H_2WO_4 (Aldrich), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and CV dye (TCI) were obtained and used without any further purification. Reagent-grade ethylene glycol, nitric acid, sodium hydroxide, ammonium acetate and HPLC-grade methanol were obtained from Merck. The de-ionized water used in this study was purified with a Milli-Q water ion-exchange system (Millipore Co.) for a resistivity of $1.8 \times 10^7 \Omega \text{ cm}$.

0.17 mmol of H_2WO_4 and 4 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were first mixed in a 100 mL flask and followed by adding 20 mL ethylene glycol. With continuous stir, 25% NH_3 was added dropwise to adjust the pH value to 9. When a white precipitate was formed, the mixture was transferred into a 30 mL Teflon-lined autoclave, which was heated to 160°C for 24, 48, and 72 h and then naturally cooled to room temperature. The precipitate was then filtered, washed and dried at 60°C for overnight. The precipitates were further characterized by the electron microscopy with the field emission scanning electron microscopy with FE-SEM-EDS, XRD, HR-XPS, and BET measurement.

2.2. Instruments

XRD patterns were recorded on a MAC Science, MXP18 X-ray diffractometer with $\text{Cu K}\alpha$ radiation, and operated at 40 kV and 80 mA. FE-SEM-EDS measurements were carried out with a field-emission microscope (JEOL JSM-7401F) at an acceleration voltage of 15 kV and an HR-XPS measurement was carried out with ULVAC-PHI XPS. The $\text{Al K}\alpha$ radiation was generated with a voltage of 15 kV. The BET specific surface areas of the samples were measured with an automatic system (Micromeritics Gemini 237 °C) using nitrogen gas as the adsorbate, at liquid nitrogen temperature. The HPLC-PDA-ESI-MS system consisted of a Waters 1525 binary pump, a 2998 photodiode array detector, and a 717 plus autosampler. Besides, a ZQ2000 micromass detector and an Atlantis™ dC18 column (250 mm $\times$ 4.6 mm i.d., $\text{dp} = 5 \mu\text{m}$) were used for separation and identification. The column effluent was introduced into the ESI source of the mass spectrometer.

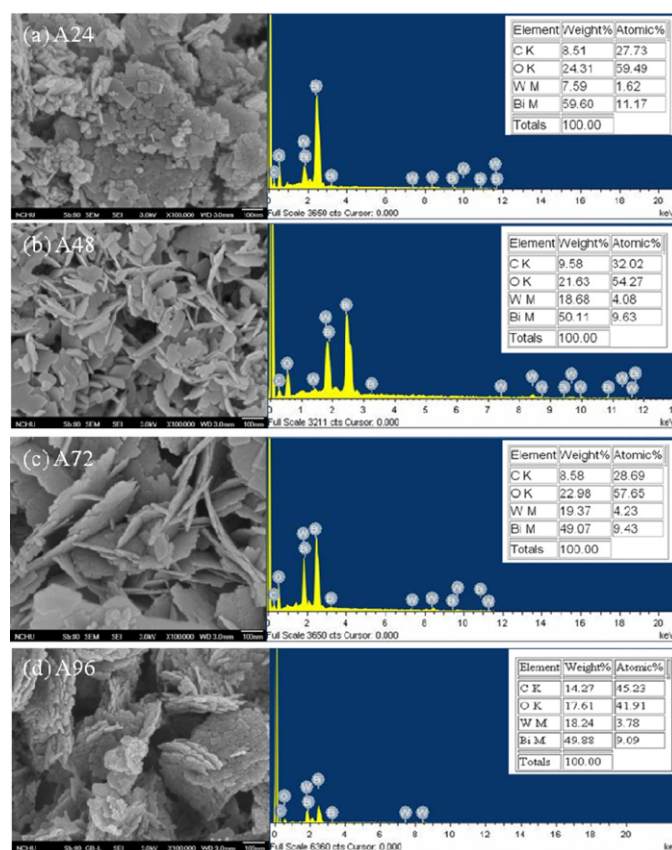


Fig. 1. SEM images and EDS of the nanosheets Bi_2WO_6 structures prepared by the hydrothermal autoclave method at 160°C : for 24 h (a), 48 h (b), 72 h (c), and 96 h (d).

2.3. Photocatalytic activity measurement

Photocatalytic activities of Bi_2WO_6 were studied by the degradation of crystal violet under visible light irradiation of a 20 W lamp. A 20 W commercial tungsten lamp was used as the simulated solar light source. A piece of Pyrex glass was used to cut off the UV light below 400 nm. An average irradiation intensity of 5.2 W/m^2 was maintained throughout the experiments and was measured by internal radiometer. Aqueous dispersions of CV (100 mL, 10 ppm) and the given amount of catalyst powder were placed in a Pyrex flask. The pH value of the dispersions was adjusted by adding either NaOH or HNO_3 solutions. Before irradiation, the dispersions were magnetically stirred in the dark for 30 min to reach an adsorption/desorption equilibrium between the dye and the

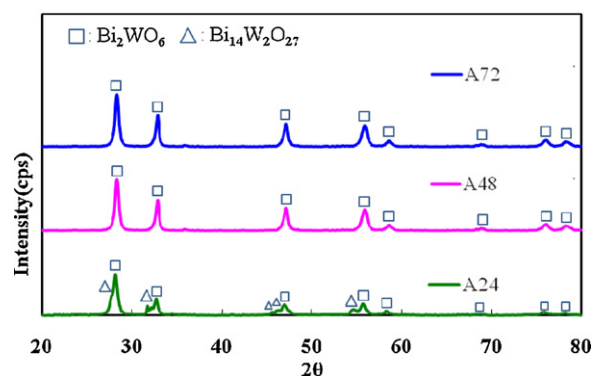


Fig. 2. X-ray diffraction patterns of the samples prepared by hydrothermal autoclave method at 160°C for different time.

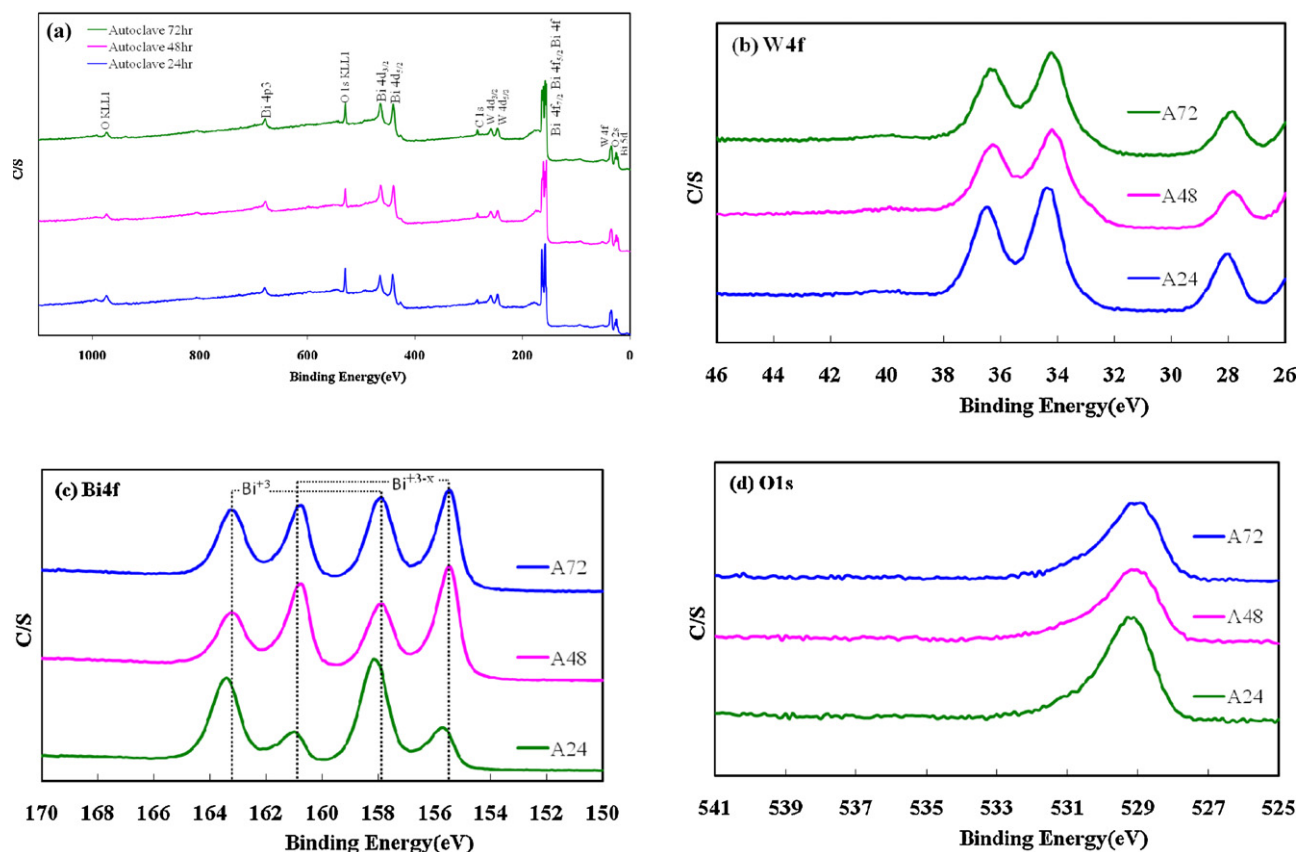


Fig. 3. High resolution XPS spectra of the nanocrystalline Bi_2WO_6 : (a) total survey, (b) W 4f, (c) Bi 4f, and (d) O 1s.

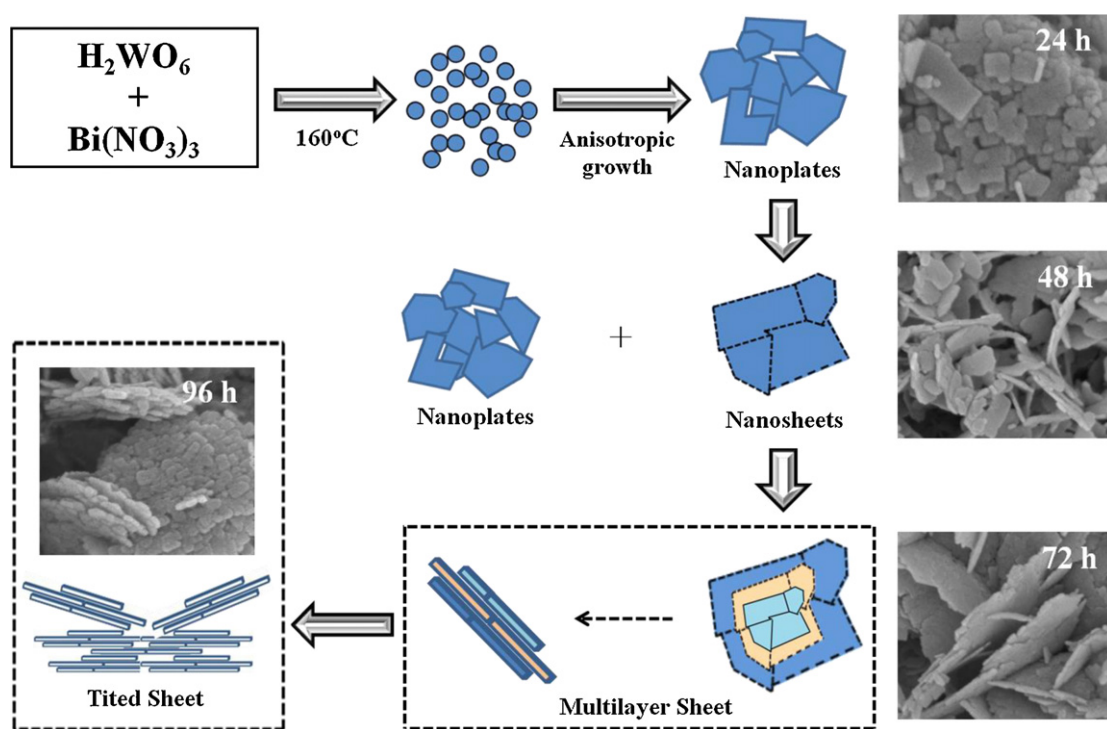


Fig. 4. Schematic illustration of the growth process of the hierarchically structured Bi_2WO_6 .

Table 1

Physical and chemical properties of the Bi_2WO_6 .

Catalyst	Specific surface area (m^2/g)	Pore volume (cm^3/g)	XPS element (at%)				EDS element (at%)			
			W	Bi	O	C	W	Bi	O	C
A24	50.1	11.5	8.89	20.78	52.52	17.8	1.62	11.17	59.49	27.73
A48	35.2	12.3	9.18	25.42	46.43	18.97	4.08	9.63	54.27	32.02
A72	34.9	12.4	9.11	25.6	43.57	21.72	4.23	9.43	57.65	28.69

surface of the catalyst under ambient air-equilibrated conditions. At the given irradiation time intervals, 5 mL aliquot was collected and centrifuged to remove the catalyst. The supernatant was analyzed by HPLC-ESI-MS after readjusting the chromatographic conditions in order to make the mobile phase compatible with the working conditions of the mass spectrometer.

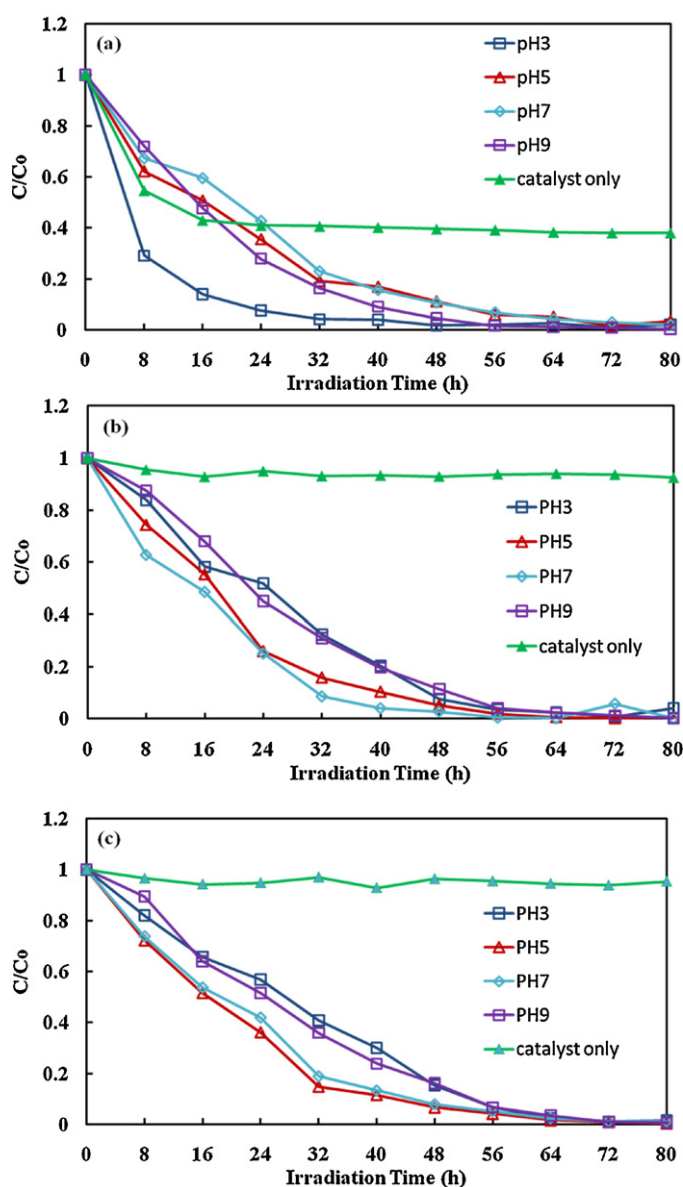


Fig. 5. pH effect on the CV photodegradation rate with the concentrations of Bi_2WO_6 being 0.5 g L^{-1} and CV being 0.05 g L^{-1} for (a) 24 h, (b) 48 h, and (c) 72 h.

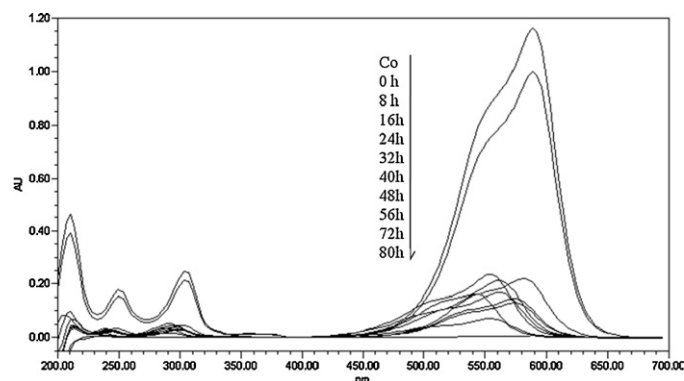


Fig. 6. UV-vis spectra change of CV in aqueous Bi_2WO_6 suspensions being 0.5 g L^{-1} and CV being 0.05 g L^{-1} ; pH 3 (A72).

3. Results and discussion

3.1. Characterization of the synthesized photocatalysts

Bi_2WO_6 was prepared with $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and H_2WO_4 by the hydrothermal method at 160°C for 24 h, 48 h and 72 h. The surface morphology of the photocatalysts was examined by FE-SEM-EDS (Fig. 1). These samples displayed a nanoplates, nanosheets and sheet-like flower shape with a lateral size of several hundred nanometers and a thickness between 5 and 10 nm. Sample A24 exhibited a plate-like rectangular shape with a lateral size of several hundred nanometers as the reported results by several research groups. However, the morphology of sample A48 showed the aggregate of sheets with irregular shape and size. Moreover, a sheet-like

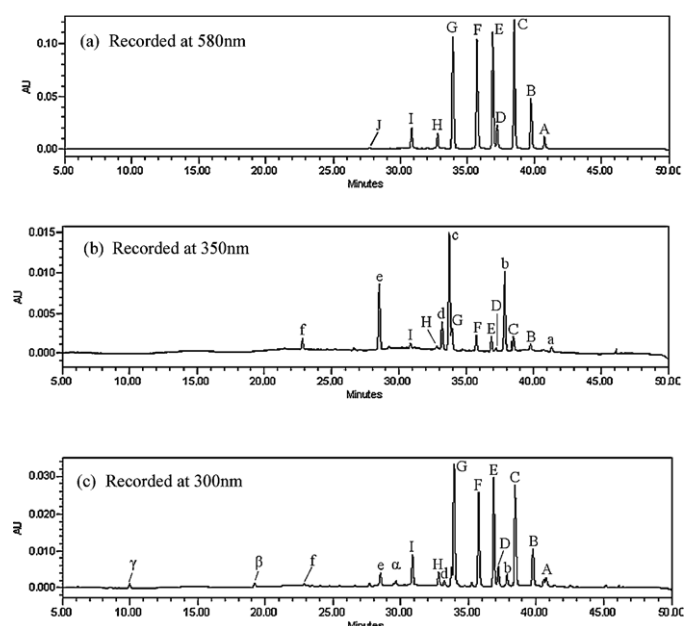


Fig. 7. HPLC chromatogram of the degraded intermediates at different irradiation intervals, recorded at (a) 580 nm, (b) 350 nm, and (c) 300 nm.

Table 2

Intermediates of the photocatalytic degradation of CV identified by HPLC-ESI-MS. Conditions: Bi_2WO_6 , 10 mg L^{-1} CV, irradiation 24-h.

HPLC peaks	Intermediates	Abbreviation	ESI-MS spectrum ions (m/z)	Absorption maximum (nm)
A	<i>N,N,N',N',N'',N''</i> -Hexaethylpararosaniline	CV	372.19	585.5
B	<i>N,N</i> -Dimethyl- <i>N',N'</i> -dimethyl- <i>N''</i> -methyl pararosaniline	DDMPR	358.21	581.2
C	<i>N,N</i> -Dimethyl- <i>N'</i> -methyl- <i>N''</i> -methylpararosaniline	DMMPR	344.15	573.9
D	<i>N,N</i> -Dimethyl- <i>N',N'</i> -dimethyl pararosaniline	DDPR	344.19	577.5
E	<i>N</i> -methyl- <i>N'</i> -methyl- <i>N''</i> -methyl pararosaniline	MMMPR	330.14	566.5
F	<i>N,N</i> -dimethyl- <i>N'</i> -methylpararosaniline	DMPR	330.14	570.2
G	<i>N</i> -Methyl- <i>N'</i> -methylpararosaniline	MMPR	316.12	562.9
H	<i>N,N</i> -Dimethylpararosaniline	DPR	316.12	565.9
I	<i>N</i> -Methylpararosaniline	MPR	302.07	555.5
J	Pararosaniline	PR	288.09	544.5
a	4-(<i>N,N</i> -Dimethylamino)-4'-(<i>N',N'</i> -dimethylamino)benzophenone	DDBP	269.11	373.5
b	4-(<i>N,N</i> -Dimethylamino)-4'-(<i>N'</i> -methylamino)benzophenone	DMBP	255.08	366.3
c	4-(<i>N</i> -Methylamino)-4'-(<i>N'</i> -methylamino)benzophenone	MMBP	241.06	362.7
d	4-(<i>N,N</i> -Dimethylamino)-4'-aminobenzophenone	DBP	241.10	362.9
e	4-(<i>N</i> -Methylamino)-4'-aminobenzophenone	MBP	227.05	357.0
f	4,4'-Bis-aminobenzophenone	BP	213.20	339.0
α	4-(<i>N,N</i> -Dimethylamino)phenol	DAP	137.93	288.9
β	4-(<i>N</i> -Methylamino)phenol	MAP	N/A	285.3
γ	4-Aminophenol	AP	N/A	278.2

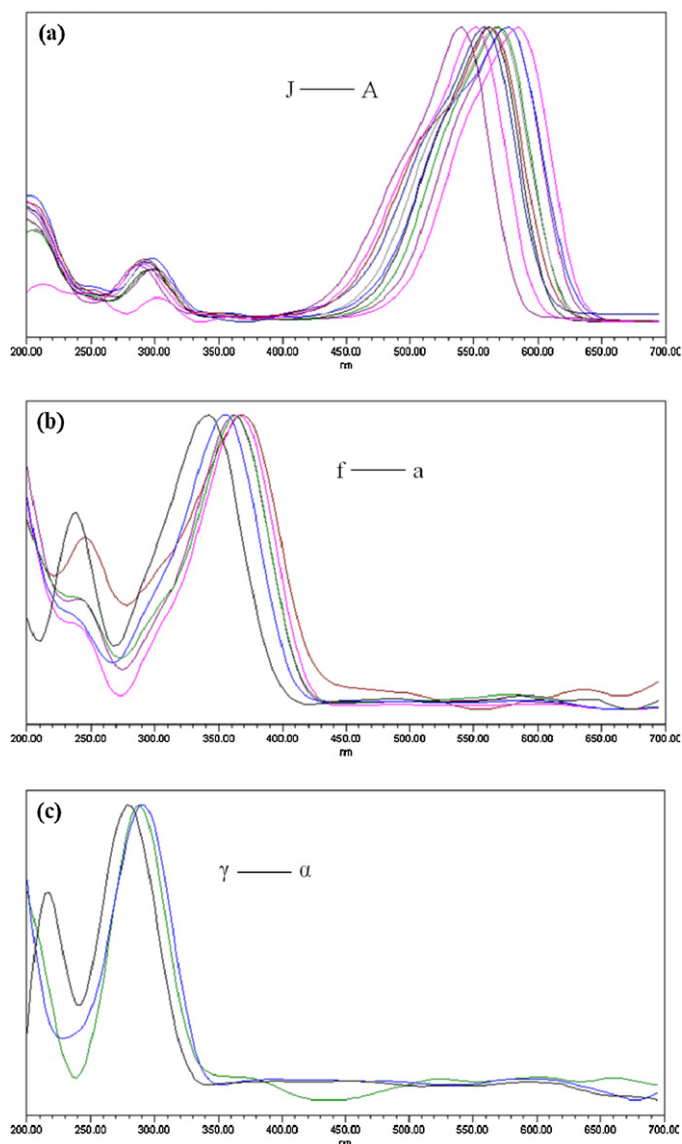


Fig. 8. Absorption spectra of the intermediates formed during the photodegradation process of the CV dye corresponding to the peaks in the HPLC chromatograph.

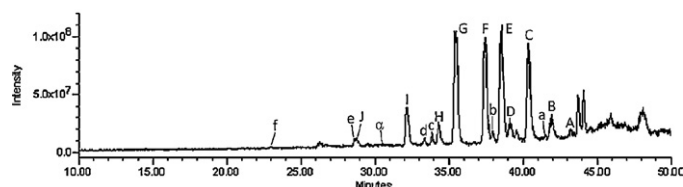


Fig. 9. Total ion chromatogram of the photodegraded intermediates with A72 dispersions at pH 9 under 16 h irradiation.

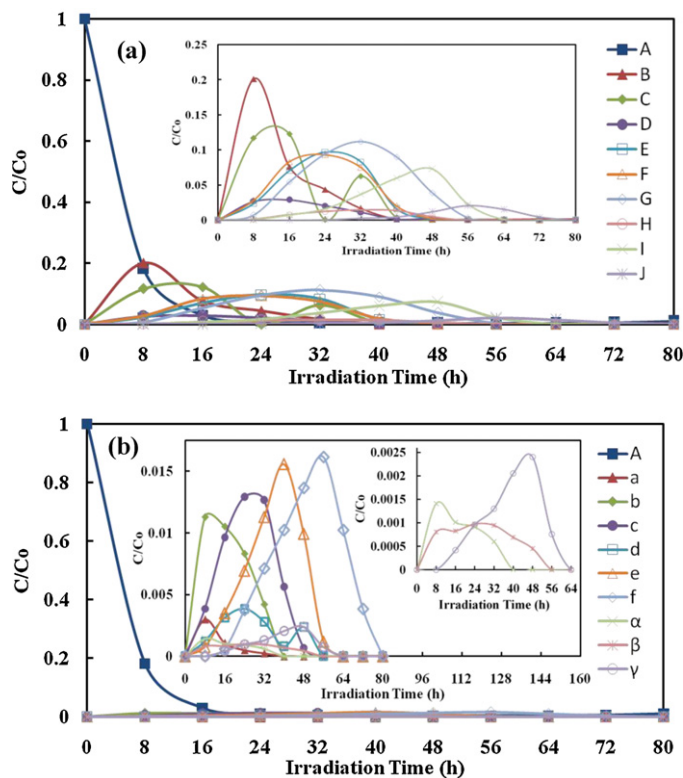


Fig. 10. Variations in the relative distribution of the intermediates obtained from the photodegradation of CV as a function of irradiation time.

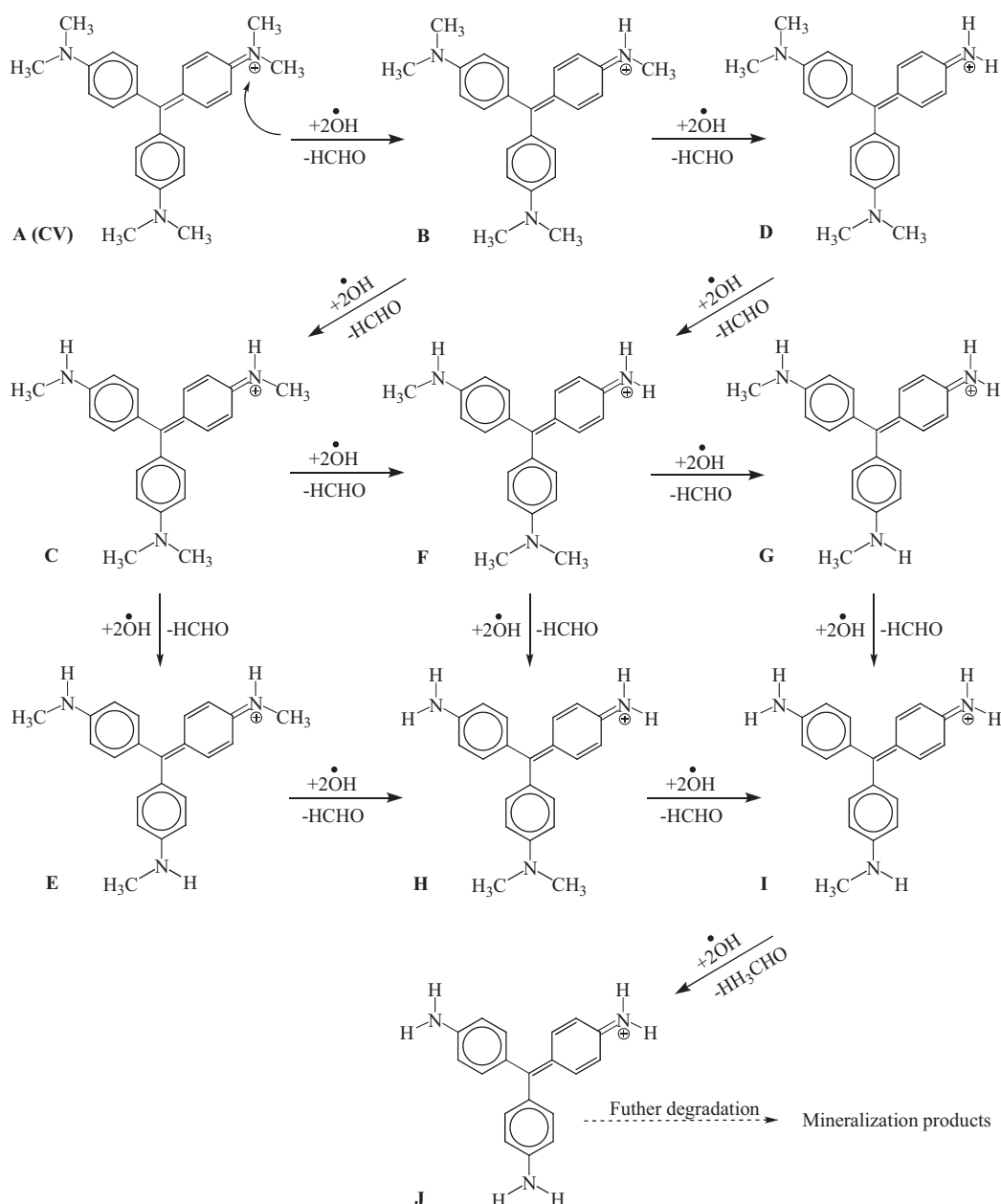


Fig. 11. Proposed N-de-methylation pathway of the CV dye.

flower shape with a lateral size of several hundred nanometers, and a thickness of 5–10 nm of sample A72 were isolated. Each sheet-like flower was an assembly of a number of sheets. The magnification images (Fig. 1c and d) demonstrated clearly a boat the nano-sheets composed of well-developed platelets of FE-SEM-EDS, and the multilayer sheet composed of small-sized platelets. The hierarchical structure of the sheet aggregates (A72) resembled the Bi_2WO_6 hierarchical particles reported recently by few other research groups [19,25].

The chemical composition and BET surface areas of the prepared samples A24, A48 and A72 are as listed in Table 1. The EDS, HR-XPS and BET results showed that the main elements of the three products were tungsten, bismuth, oxygen, and carbon. The W/Bi atomic ratio of A24 was well corresponded with the atomic ratio (W:Bi = 1:2). The Bi/W atomic ratio of the samples, A48 and A72, was within the range of 2.23–2.81, which corresponded to 23–81% excess of Bi compared to the stoichiometric ratio (W:Bi = 1:2). From

Table 1, the excessive oxygen and the carbon in the examined catalysts were possibly due to the organic contaminant. The BET surface areas of samples were estimated to be ca. 50.1, 35.2 and 34.9 m^2/g for A24, A48, A72, respectively. These results showed the specific area that decreasing along with Bi_2WO_6 nanocrystals with relatively small crystal size and large surface area could be synthesized by the progress of hydrothermal reaction time. However, the pore volume for the three photocatalysts was kept quite similar.

The crystallinity and phase purity of the products were also confirmed by XRD. As the reaction time progressed, the A24, A48 and A72 peaks of the XRD patterns of Russellite Bi_2WO_6 (JCPDS 79-2381), corresponded to the indices of (1 3 1), (0 0 2), (2 0 2), (1 3 3), (2 6 2), (0 0 4), (3 9 1), and (2 0 4) planes. To similar features of good quality nanocrystal were found in all samples, use the hydrothermal autoclave method. As shown in Fig. 2, the diffraction peaks of A24 with two crystallites were detected by XRD. Clearly, the A24 samples consisted of $\text{Bi}_{14}\text{W}_{20}\text{O}_{27}$ (JCPDS 79-2381) and Bi_2WO_6 .

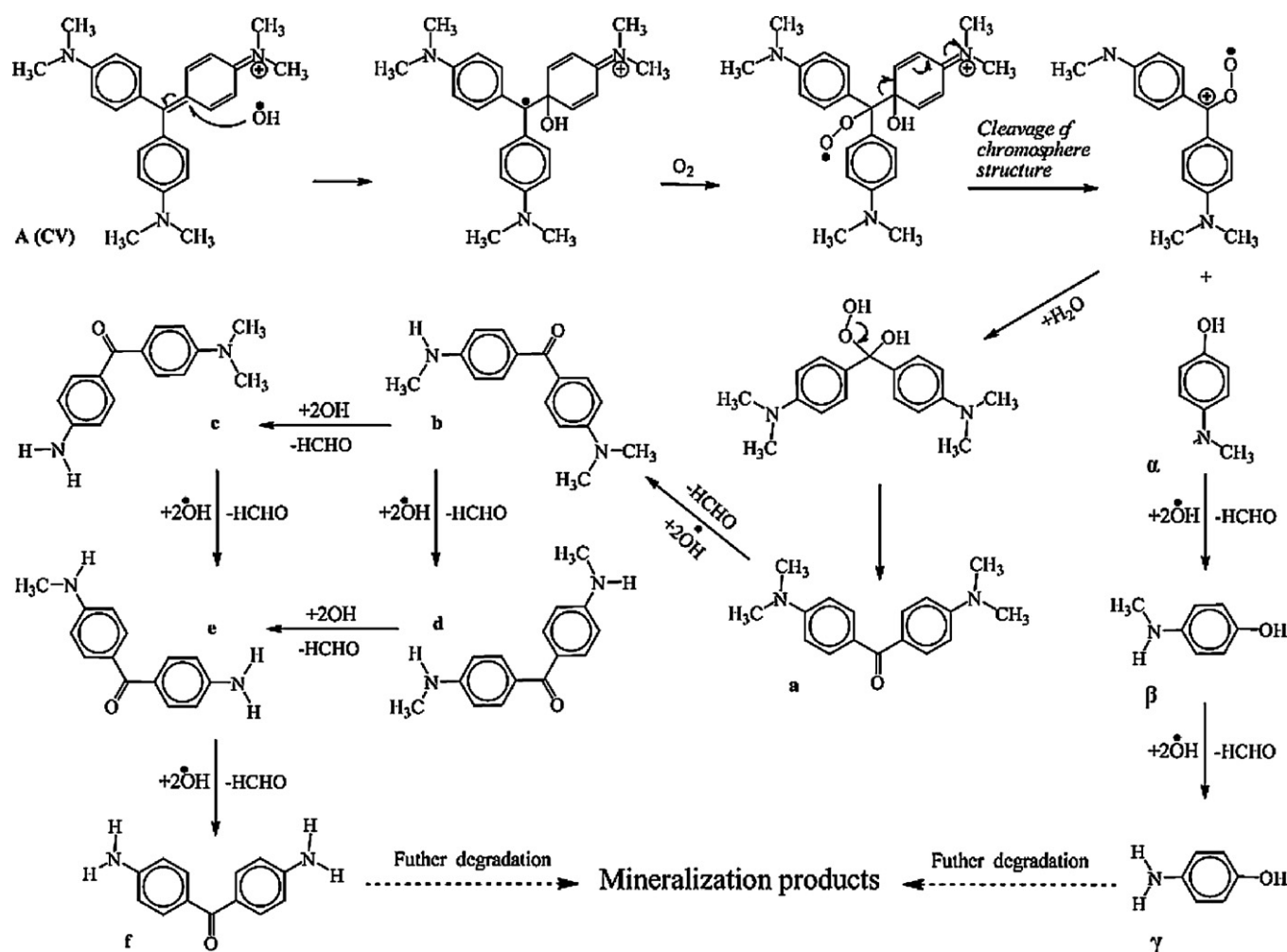


Fig. 12. Proposed pathway of the destruction of the conjugated structure of the CV dye.

Fig. 3a shows the total survey spectra of the Bi 4f, W 4f, O 1s XPS of the three Bi_2WO_6 samples A24, A48 and A72. The characteristic binding energy value of 157.9 eV for Bi 4f_{7/2} (Fig. 3b) revealed a trivalent oxidation state for bismuth. An additional spin–orbit doublet with binding energy of 155.5 eV for Bi 4f_{7/2} was also observed in all samples, suggesting that some parts of bismuth existed in the (+3–x) valence state. This indicated that the trivalent bismuth was partly reduced to the lower valence state by the hydrothermal autoclave method. The ethylene glycol, which was reported as both a solvent and a reductant under microwave irradiation, might serve as both a solvent and a reductant under the hydrothermal autoclave method [20,27]. A similar chemical shift of about 2.4–2.6 eV for Bi 4f_{7/2} was also observed by Jovalekic et al. [28]. They concluded that Bi^(+3–x) formal oxidation state could most probably be attributed to the substoichiometric forms of Bi within the Bi_2O_3 layer, and the formation of the low oxidation state resulted in oxygen vacancy in the crystal lattice. However, we thought that Bi^(+3–x) formal oxidation state could most probably be attributed to the substoichiometric forms of Bi at outer site of the particles, and the formation of the low oxidation state resulted in oxygen vacancy in the crystal surface.

Fig. 4 shows a plausible process of the sheet-like flower formation. It started from fine amorphous particles and then became the aggregation of platelets. Finally, the sheet-like flowers were produced through crystal plane-selective growth. Such anisotropic crystal growth was generally achieved by a selective adsorption of additives on specific sites suppressing isotropic

crystal growth. In the basic condition, an excessive amount of the tungsten precursor and ethylene glycol, which was needed for the sheet-like flower formation, might induce the anisotropic growth of poorly crystallized Bi_2WO_6 from nucleus. However, in the case of low concentrations of the starting materials, a mixture of less crystallized nanoparticles and aggregated platelets was obtained in this study. In addition, it was understood that a diffusion-limited growth condition, such as high supersaturation, was also needed for the formation of polycrystalline aggregates with a multi-branching form [20,29]. After 48 h reaction, further crystal growth would result in the formation of sheet with relatively lateral size of a few hundred nanometer through the Ostwald ripening process, in which smaller particles disappeared due to their high solubility and crystallized to larger particles again (Gibbs–Thomson effect). Minimization of the surface free energy resulted in the formation of sheet-like flower. The particle size of a few hundred nanometer was almost constant after 72 h of reaction, and further reaction resulted in increase in crystallite size as well as improvement in crystallinity of the platelets in sheets, which appeared at 96 h of reaction. In this step, polyhedron single-crystal sheets would be developed due to the low super-saturation, in which kinetically limited crystal growth was favored [29]. The mechanism of sheet-like flower formation was proposed through two stages, namely anisotropic crystal growth and Ostwald ripening process, depending on the concentration of dissolved precursor changes during crystallization.

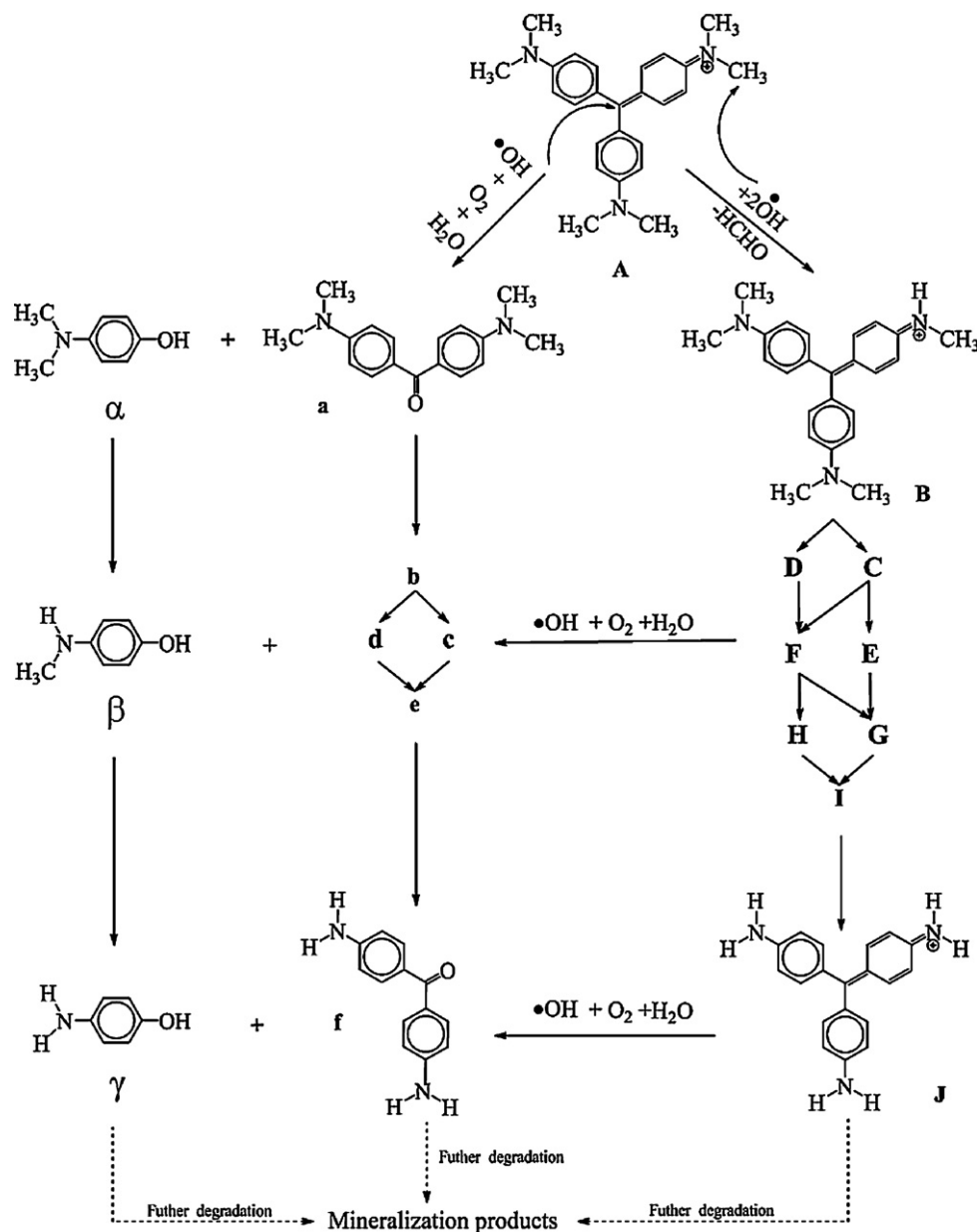


Fig. 13. Proposed photodegradation mechanism of the CV dye.

3.2. Photocatalytic activity evaluation

In photocatalytic processes, the amount of photocatalyst is an important factor in the degradation rate of organic compounds. Catalyst optimization depends on the nature of the powder [30]. Hence, the effect of photocatalysts on the photodegradation rates of the CV dye was investigated by employing different hydrothermal time varying from 24 to 72 h at different values of pH. The solution was analyzed by a spectrophotometer and the adsorption peak at 580 nm was monitored. The photocatalytic efficiency was calculated according to the following equation:

$$\text{efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100$$

where C_0 and C represented the initial concentration of CV prior to irradiation and the concentration of CV after irradiation for a given time, respectively. The photodegradation rate of the CV was found to decrease with the increase of reaction time (Fig. 5). The

adsorption resulted in a decrease of about 59.8%, 7.2%, and 3.8% in the CV concentration after 24 h, and a decrease in the photocatalytic efficiencies of 92.1% (pH 3), 75.0% (pH 7), and 65.4% (pH 5) in the CV concentration being decolorized after 24 h for A24, A48, A72, respectively. After more than 64 h, the initial rate of CV degradation was not further affected by a progressive time increase. The maximal initial degradation rate for CV appeared at 48 h hydrothermal time (A48). It was clear that A24 could absorb the largest amount of CV due to its highest BET surface area of 50.1481 m²/g. All Bi₂WO₆ superstructures and the flower-like sheet had much smaller BET surface areas and could not adsorb CV molecules more efficiently than the A24 sample did. In addition, with the transformation of Bi₂WO₆ from a 2D plate-like structure to a 3D flower-like superstructure, the BET surface area of the samples decreased, resulting in an decrease of adsorption percentages of CV molecules.

The adsorption of the substrate onto the Bi₂WO₆ surface directly affected the occurrence of electron transfer between the excited dye and Bi₂WO₆ and further influenced the degradation rate. The

formation of active $\cdot\text{OH}$ species was favored at high pH value, not only due to the improvement of the holes transferring to the adsorbed hydroxyls at high pH, but also for the electrostatic attractive effect between the negatively charged Bi_2WO_6 and the cationic dyes in the solution. The results indicated that the Bi_2WO_6 surface was negatively charged and the CV adsorbed onto the Bi_2WO_6 surface through the positive ammonium groups. The proposed adsorption mechanisms were in good agreement with earlier reports [31].

Fig. 5a shows the lower pH values of the higher photocatalytic activities of the A24 and slightly the dependence of photocatalytic activity of the Bi_2WO_6 samples upon pH values (5–9) of the suspensions. Active $\cdot\text{OH}$ radicals formed at low concentration and hence the photodegradation process of CV remained slow. However, an observation of the pH 3 curve in Fig. 5a showed that the photodegradation rate of CV was actually fast. The results of photodegradation rate was different from that found in the cationic dyes in the triphenylmethane/ TiO_2 system [32]. Moreover, a higher degradation rate at acid pH was seen for the found degradation of azo dyes in TiO_2 -mediated experiments, due to the efficient electron-transfer process that occurred with surface complex bond formation [33]. Hydroxyl radicals could be formed by the reaction between hydroxide ions and positive holes. The positive holes were considered as major oxidation species at low pH while hydroxyl radicals were the predominant species at neutral or high pH levels [34]. An additional explanation for the pH effects was related to the changes in the specification of the dye. That is, protonation or deprotonation of the dye could change its adsorption characteristics and redox activity [35]. In addition, BET surface areas (Table 1) increased with the decrease of crystalline grains, which also benefited the enhancement of the photocatalytic activity of A24. In the presence of Bi_2WO_6 particles, the absorbance decreased very largely (Fig. 5a, catalyst only), reflecting the extent of the adsorption of CV on the Bi_2WO_6 surface in the dark. Thus, when Bi_2WO_6 was added to the solutions, reactions analogous to the efficient electron-transfer process could take place by strong surface complex bond formation and produce $\cdot\text{OH}$ radicals by the reaction between hydroxide ions and positive holes. Such reactions also attacked CV, but principally at the aromatic chromophore, leading to the degradation of the CV structure rather than the *N*-de-methylation. Fig. 5b and c shows slightly the dependence of photocatalytic activity of A48 and A72 samples upon pH values (3–9) of the suspensions. Although the CV dye could to some extent adsorb onto the Bi_2WO_6 surface in alkaline media, the dye molecules would change into a colorless carbinol base [36], when the pH value was too high (pH = 10).

3.3. UV–visible spectra

The changes of the UV–visible spectra during the photodegradation process of the CV dye in the aqueous Bi_2WO_6 dispersions are illustrated in Fig. 6. After UV irradiation for 72 h, up to 99.8% of the CV dye was degraded. The characteristic adsorption band of the dye around 585.5 nm decreased rapidly with slight hypsochromic shifts (544.5 nm) during UV irradiation, but no new adsorption bands appeared even in ultraviolet range ($\lambda > 200$ nm), indicating that there might be a formation of series of *N*-de-methylated intermediates, and cleavage of the whole conjugated chromophore structure of the CV dye.

3.4. Separation and identification of the intermediates

With UV irradiation, temporal variations occurring in the solution of CV dye during the degradation process were examined by HPLC coupled with a photodiode array detector and ESI mass spectrometry. Given irradiation of CV up to 24 h at pH 3, the chromatograms are illustrated in Fig. 7, recorded at 580, 350, and

300 nm and nineteen intermediates were identified, with the retention time under 50 min. The CV dye and its related intermediates was denoted as species A–J, a–f, and α – γ . Except for the initial CV dye (peak A), the peaks initially increased before subsequently decreasing, indicating the formation and transformation of the intermediates.

In Fig. 8, the absorption maximum of the spectral bands shifted from 585.5 nm (spectrum A) to 544.5 nm (spectrum J), from 373.5 nm (spectrum a) to 339.0 nm (spectrum f), and from 288.9 nm (spectrum α) to 278.2 nm (spectrum γ). The maximum adsorption in the visible and ultraviolet spectral region of each intermediates are depicted in Table 2. They were identified as A–J, a–f, and α – γ , respectively corresponding to the peaks A–J, a–f, and α – γ in Fig. 7. These shifts of the absorption band were presumed to result from the formation of a series of *N*-de-methylated intermediates. From these results, several families of intermediates could be distinguished.

The first family is marked in the chromatogram of Fig. 7a and illustrated in Fig. 8a. The wavelength position of the major adsorption band of intermediates of *N*-de-methylated CV dye moved toward the blue region, λ_{max} , A (CV), 585.5 nm; B, 581.2 nm; C, 573.9 nm; D, 577.5 nm; E, 566.5 nm; F, 570.2 nm; G, 562.9 nm; H, 565.9 nm; I, 555.5 nm; J, 544.5 nm. The *N*-de-methylation of the CV dye caused the wavelength shifts, depicted in Table 2, due to an attack by one of the active oxygen species on the *N,N*-dimethyl or *N*-methyl group. It was previously reported that the CV dye was *N*-de-methylated in a stepwise manner (i.e., methyl groups were removed one by one as confirmed by the gradual peak wavelength shifts toward the blue region) and this was confirmed as Table 2 shows.

The second family is marked in the chromatogram of Fig. 7b and illustrated in Fig. 8b. The destruction of CV yielded a, α , and their *N*-de-methylated products *N*-hydroxymethylated intermediates. The wavelength position of the major adsorption band of the *N*-de-methylation of the a and the *N*-hydroxymethylated intermediates of the *N*-de-methylated a species, produced by cleavage of the CV chromophore ring structure, moved toward the blue region, λ_{max} , a, 373.5 nm; b, 366.3 nm; c, 362.7 nm; d, 362.9 nm; e, 357.0 nm; f, 339.0 nm. The proposed intermediate (a) was compared with a standard material of 4-(*N,N*-dimethylamino)-4'-(*N,N'*-dimethylamino)benzophenone. The retention time and the absorption spectra were identical.

The third family is marked in the chromatogram of Fig. 7c and illustrated in Fig. 8c. The wavelength position of the major adsorption band of the *N*-de-methylation of the α , produced by cleavage of the CV chromophore ring structure, moved toward the blue region, λ_{max} , α , 288.9 nm; β , 285.3 nm; γ , 278.2 nm. The proposed intermediate (γ) was compared with the standard material of 4-aminobenzophenone. The retention time and the absorption spectra were identical.

The intermediates were further identified using the HPLC-ESI mass spectrometric method, and the relevant mass spectra are illustrated in Fig. 9 and supporting information and Table 2. The molecular ion peaks appeared in the acid forms of the intermediates. The results of mass spectral analysis confirmed that the component A (CV), $m/z = 372.19$; B, $m/z = 358.21$; C, $m/z = 344.15$; D, $m/z = 344.19$; E, $m/z = 330.14$; F, $m/z = 330.14$; G, $m/z = 316.12$; H, $m/z = 316.12$; I, $m/z = 302.07$; J, $m/z = 288.09$; a, $m/z = 269.11$; b, $m/z = 255.08$; c, $m/z = 241.06$; d, $m/z = 241.10$; e, $m/z = 227.05$; f, $m/z = 213.20$; α , $m/z = 137.93$, in liquid chromatogram.

3.5. Photodegradation mechanisms of CV

In Fig. 10, the relative distribution of the obtained intermediates was demonstrated and the relative intensities were recorded at the maximum adsorption wavelength for each intermediate,

although a quantitative determination of all the photogenerated intermediates was not achieved owing to the lack of appropriate molar extinction coefficients for them and a lack of reference standards. The distributions of all of the *N*-de-methylated intermediates were related to the initial concentration of CV. Nonetheless, it was clearly observed the changes in the distribution of each intermediate during the photodegradation of CV. The successive appearance of the maximum of each intermediate indicated that the *N*-de-methylation of CV, α and β , was a stepwise photochemical process.

Most of the $\cdot\text{OH}$ radicals were generated directly either from the reaction between the holes and surface-adsorbed H_2O or OH^- [31,36–38]. The *N*-de-methylation of the CV dye occurred mostly through attack by the $\cdot\text{OH}$ species on the *N,N*-dimethyl group of CV. The degradation intermediates were clearly observed to reach their maximum concentrations (Fig. 10a). The results discussed above can be seen more clearly in Fig. 11. The degradation of the CV dye occurred mostly through the attack by the $\cdot\text{OH}$ species on the central carbon portion of CV and produced α and β . The degradation intermediates were clearly observed to reach their maximum concentrations (Fig. 10b). The results discussed above can be seen more clearly in Fig. 12.

In earlier reports [39,40], most *N*-de-alkylation processes were preceded by the formation of a nitrogen-centered radical, while the destruction of dye chromophore structures was preceded by the generation of a carbon-centered radical. Consistently, the degradation of CV must occur via two different photodegradation pathways due to the formation of different radicals. It was no doubt that the $\cdot\text{OH}$ attack on the dye yielded a cationic radical, which could then undergo hydrolysis and/or follow various deprotonation pathways, which in turn were determined by different adsorption modes of CV on the Bi_2WO_6 particles surface.

Based on the above experimental results, the photodegradation pathway was tentatively proposed (Fig. 13). The dye molecule in the CV- Bi_2WO_6 system was adsorbed through the positively charged diethylamine function. The attraction by one $\cdot\text{OH}$ radical of a hydrogen atom from the dimethylamine methyl group, and the attack by another $\cdot\text{OH}$ radical on the diethylamine ultimately resulted in *N*-de-methylation. The mono-de-methylated dye derivative, B, could also be adsorbed on the Bi_2WO_6 particle surface and was implicated in other similar events ($\cdot\text{OH}$ radicals attraction and attack, hydrolysis or deprotonation) to yield the bi-de-methylated dye derivatives, C and D. The *N*-de-methylation process as described above continued until the formation of the completely de-methylated dye, J.

In Fig. 13, the dye molecule in the CV- Bi_2WO_6 system was adsorbed through a conjugated structure cleavage of the CV chromophore structure. The attack by $\cdot\text{OH}$ radical on the conjugated structure yielded a carbon-centered radical, which was subsequently attacked by molecular oxygen to lead ultimately to α and β . The same process occurred in the *N*-de-methylated dye to produce the *N*-de-ethylated α and β . The α could also be adsorbed on the Bi_2WO_6 particle surface and implicated in other similar events ($\cdot\text{OH}$ radical attraction and attack, hydrolysis or deprotonation, and/or oxygen attack) to yield a mono-*N*-de-methylated derivative, b. Moreover, the same process occurred in β to produce β . The *N*-de-methylation process, as described above, continued until the formation of the completely *N*-de-methylated α , f, and *N*-de-methylated β , g. All the above *N*-de-methylation processes produced a series of *N*-de-hydroxymethylated intermediates by the hydroxylation of the *N*-methyl group. All the intermediates were subsequently mineralized to result in NO_3^- and CO_3^{2-} [36,41].

4. Conclusions

Bi_2WO_6 with sheet-like flower crystallite, prepared by the hydrothermal autoclave method in alkali solution, was a potential candidate for the photocatalytic degradation of CV dye. With the clear observation of the binding energy shift of Bi element, the $\text{Bi}^{(+3-x)}$ formal oxidation state was suggested to attribute to the sub-stoichiometric forms of Bi within the Bi_2O_3 layer, but the Bi_2WO_6 structure remained undisturbed. The production of a low oxidation state could result in the existence of an oxygen vacancy. With the Bi_2WO_6 as the catalyst, both *N*-de-methylation and conjugated structure of CV dye took place during the degradation process. The reaction mechanisms for UV/ Bi_2WO_6 proposed in this study should offer some insight for the future development of technology applications to the decoloration of dyes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molcata.2012.04.015>.

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