# **Electronic Supplementary Information**

# Hydrothermal Synthesis of Bismuth Oxybromide-Bismuth Oxyiodide

Composites with highly visible light Photocatalytic performance for the

# degradation of CV and Phenol

Yu-Rou Jiang, Shang-Yi Chou, Jia-Lin Chang, Ho-Pan Lin, Shiuh-Tsuen Huang, Chiing-Chang Chen \*

Department of Science Application and Dissemination, National Taichung University of Education, Taichung 403, Taiwan, ROC

\* Author to whom correspondence should be addressed E-mail: <u>ccchen@mail.ntcu.edu.tw</u> ; <u>ccchen@ms3.ntcu.edu.tw</u> Fax: +886-4-2218-3560 Tel: +886-4-2218-3406

### **2.3 Instruments and Analytical Methods**

XRD patterns were recorded on a MAC Sience, MXP18 X-ray diffractometer, with 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 HRXPS measurement was carried out with ULVAC-PHI XPS. The field-emission transmission electron microscopy (FE-TEM) images, SAED patterns, high-resolution transmission electron microscopy (HRTEM) images and an energy-dispersive X-ray spectrum (EDS) were taken on a JEOL- 2010 transmission electron microscope with an accelerating voltage of 200 kV. The Al K $\alpha$  radiation was generated with a voltage of 15 kV. Crygenic cathodoluminescence (CL) measurements were carried out on JEOL JSM7001F. 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.

# **3.2 Morphological structure and Composition**

BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub> is prepared with Bi (NO<sub>3</sub>)<sub>3</sub>•5H<sub>2</sub>O and the mixture of KBr and KI by the hydrothermal methods at 110 °C for pH 4, 7, 9, and 13. The surface morphology of the photocatalysts is examined by FE-SEM-EDS (Figures S8-S9 of supplementary materials). In **Table 1**, it is found that, with the increase of pH value ranging from 1 to 14, a gradual change in the crystal phase of the reflection peaks takes place, which indicates a formation in the crystal phase from BiOBr/BiOI,  $Bi_3O_4Br/$   $Bi_7O_9I_3$ , Bi<sub>5</sub>O<sub>7</sub>Br/Bi<sub>5</sub>O<sub>7</sub>I, Bi<sub>3</sub>O<sub>4</sub>Br/Bi<sub>5</sub>O<sub>7</sub>I,  $Bi_4O_5Br_2/Bi_7O_9I_3$ and BiOBr/Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>/BiOI composites to  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> at different pH values. In Figure S8, the FE-SEM image shows that the morphology of the bismuth oxybromoiodide samples obtained KBr/KI = 1/2 molar ratio at different pH values turns from irregular sheets to rods composed of irregular super-thin-sheets and rods composed of square-plates and then becomes micro-rectangular-pillar crystals. Figure S9 shows that the morphology of the sample obtained on KBr/KI = 2 molar ratio at different pH values turns from sheets crystals to thin sheets, irregular multi-sheets, and irregular plates and then becomes micro-rectangular-pillar crystals of between pH = 1 to pH = 14. These samples display irregular nano-sheet shapes with a lateral size of several decade micrometers and a thickness between 5 and 60 nm and a rectangular-pillar shape with a lateral size of several to several decade micrometers. From Table 2, the EDS results show that the main elements of these samples are bismuth, bromine, iodine, and oxygen under different pH values. The Br (or I) atomic ratios (%) of the samples are within the range of 19.21-0.06 (or 17.59-5.52), which correspond to Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>/BiOI,

BiOBr/BiOI, Bi<sub>3</sub>O<sub>4</sub>Br/Bi<sub>7</sub>O<sub>9</sub>I<sub>3</sub>, BiOBr/Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>/BiOI, Bi<sub>3</sub>O<sub>4</sub>Br/Bi<sub>5</sub>O<sub>7</sub>I, Bi<sub>5</sub>O<sub>7</sub>Br/Bi<sub>5</sub>O<sub>7</sub>I composites, and bromoiodo-doped Bi<sub>2</sub>O<sub>3</sub>, compared to the stoichiometric ratio (Bi: Br = 1, 2, 2.4, 3, 5, 6 and Bi:I = 1, 2, 2.3, 5), and could be selectively prepared through a facile solution-based hydrothermal method.

# 3.5 Specific surface areas and pore structure

Figure S10 (a) of supplementary materials shows the nitrogen adsorption-desorption isotherm curves of BiO<sub>p</sub>Br<sub>a</sub>/BiO<sub>m</sub>I<sub>n</sub> samples in different pH values. The isotherm of all samples are close to Type IV (Brunauer-Deming-Deming-Teller, BDDT, classification) with a hysteresis loop at highly relative pressure between 0.6 and 1.0 [App. Catal. B: Environ. 136-137 (2013) 112-121]. From Figure S10 (b), the shape of the hysteresis loop is close to Type H3, suggesting the existence of slit-like pores generally formed by the aggregation of plate-like particles, which is consistent with the self-assembled nanoplate-like morphology of samples [Catal. Commun., 2011, 13, 63]. This result is consistent with FE-SEM that the self-assembled nanosheets or nanoplates result in the formation of 3D hierarchical architecture. Figure S11 shows the corresponding pore-size distribution (PSD) of BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub> samples. As can be seen, PSD curves are tri-modal with small mesopore (2-4 nm), medium mesopore (10-50 nm), and large macropore (50-290 nm) for the BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub> samples. As the nanosheets do not contain pores (Figures S8-S9), the smaller mesopores in the range of 2-4 nm may reflect the porosity within nanosheets. The larger mesopores in the range of 10.0–50 nm may be ascribed to the pores formed between stacked nanosheets. The macropores in the range of 50-290 nm may be ascribed to the pores formed between nanosheets. Such self-organized porous architecture might be extremely useful in photocatalysis because they provide efficient transport pathways for reactant and product molecules [J. Hazard. Mater. 219-220 (2012) 26-34]. The pore parameters of BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub> samples are summarized in Table S2 of supplementary materials.

In **Table S2**, BET of BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub> is about 0.9-38 m<sup>2</sup>/g, which is lower than that of P25-TiO<sub>2</sub> with BET 45 m<sup>2</sup>/g due to the increased particle size. The pore volume and size of composite samples distribute to 0.006-0.3 cm<sup>3</sup>/g and 221-549 Å, compared to pure BiOBr (0.04 cm<sup>3</sup>/g and 402 Å) and BiOI (0.02 cm<sup>3</sup>/g and 424 Å). A greater specific surface area and pore volume of photocatalyst can supply more surface active sites and make reactants transport easier, leading to an enhancement of the photocatalytic performance [Adv. Funct. Mater. 17 (2007) 1984-1990]. BB1I2-4-110-12 and BB2I1-4-110-12 have the larger BET and the pore volume. Thus, the large BET and pore volume of BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub> composites may play a role in enhancing the photocatalytic activity. This nanosheet structure can provide efficient transport paths for reactants and more active sites for the photocatalytic reaction. The structure is also favorable to efficient photo-energy harvesting and introducing the separation of electron-hole pairs, thus promoting the photocatalytic activity.

## **3.6 Photocatalytic activity**

The aqueous solution of CV and phenol was fairly stable under visible light radiation in the absence of BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub>. However, CV and phenol can be degraded efficiently in aqueous BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub> dispersions by visible light irradiation. The changes of the UV-vis spectra during the photodegradation process of CV and phenol in the aqueous BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub> dispersions under visible light irradiation are illustrated in **Figure S12** of supplementary materials. It is wholly degraded after visible light irradiation for 16 h, ca. 99.5% of CV and after UV irradiation for 36 h, ca. 99.9% of phenol. During visible light irradiation, the characteristic absorption band of the CV dye around 588.3 nm decreases rapidly with slight hypsochromic shifts (555.3 nm), but no new absorption band appears even in ultraviolet range ( $\lambda > 200$  nm), indicating that there might be the formation of a series of *N*-de-methylated intermediates and cleavage of the whole conjugated chromophore structure of the CV dye. Further irradiation causes the decrease of absorption band at 555.3 nm, but no further wavelength shift is observed, inferring that the band at 555.3 nm is that of the full *N*-de-methylated product of the CV dye.

The photocatalytic performance of the BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub> catalysts is evaluated by degrading CV and with 0.5 g/L of catalyst under visible light irradiation. The degradation efficiency as a function of reaction time is illustrated in Figure S13 of supplementary materials. The removal efficiency is enhanced significantly in the presence of BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub> catalysts. After 48h irradiation, BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub> shows superior photocatalytic performance, with CV removal efficiency up to 99%. To further understand the reaction kinetics of CV degradation, the apparent pseudo-first-order model [Chem. Mater., 2008, 20, 2937] expressed by the  $\ln(C_0/C) =$  $k_{app}$ t equation is applied in this experiments, where  $k_{app}$  is the apparent pseudo-first-order rate constant  $(h^{-1})$ , C is CV concentration in the aqueous solution at time t (mg/L), and  $C_0$  is initial CV concentration (mg/L). Via the first-order linear fit from the data of Figure S13 shown in Table 3, kapp of BB1I2-4-210-12 is obtained at the maximal degradation rate of  $5.285 \times 10^{-1}$  h<sup>-1</sup>, greatly higher than the others composites. The result shows that the Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>/BiOI composite is a much more effective photocatalyst than the others. Therefore, the Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>/BiOI composite shows the best photocatalytic activity. However, this result displays that BB112-4-110-12 with the highest BET does not represent the highest photocatalytic activity among the samples, which suggests that the major changes in the

photocatalytic activity result from the  $BiO_pBr_q/BiO_mI_n$  composite rather than BET. From **Table 3**, BB1I2-4-110-12 and BB2I1-4-110-12 have also the larger BET and the pore volume. Thus, the large BET and pore volume of  $BiO_pBr_q/BiO_mI_n$  composites may also play a role in enhancing the photocatalytic activity. In the absence of catalysts, CV could not be degraded under visible light irradiation. The superior photocatalytic ability of  $BiO_pBr_q/BiO_mI_n$  may be ascribed to its efficient utilization of visible light and the high separation efficiency of the electron-hole pairs with its composites.

The durability of the  $Bi_4O_5Br_2/BiOI$  (BB1I2-4-210-12) composite is evaluated through the recycle of the used catalyst. For each cycle, the catalyst is collected by centrifugation. There is no apparent loss of photocatalytic activity in removing crystal violet in the fifth cycle, and even in the tenth run, the declination in photocatalytic activities is less than 3% (see **Figure 6 (a)**). The used  $Bi_4O_5Br_2/BiOI$  is also examined by XRD, and there is no detectable difference between the as-prepared and used samples (**Figure 6 (b)**). Therefore, it can be deduced that the  $Bi_4O_5Br_2/BiOI$ composite has good photostability.

## 3.7 Cathodoluminescence spectrum

As being known, the photocatalysts are excited to generate electron-hole pairs directly after the illumination in the photocatalytic process. Moreover, the photocatalytic efficiency mainly depends on the recombination rate or lifetime of the photogenerated electron-hole pairs. The faster recombination occurs, the less time is for the chemical reactions. Therefore, the cathodoluminescence (CL) spectrum is utilized for investigating the recombination rate of the photogenerated electron-hole pairs [J. Hazard. Mater. 150 (2008) 62-67]. To investigate the separation capacity of photogenerated carriers in heterostructures, the CL spectra of BiOBr, BiOI, and BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub> are measured and the results are given in Figure 7. Strong emission peaks around 2.01 and 1.85 eV appear for BiOBr (BC3-1-110-12) and BiOI (BB3-1-110-12), which may be derived from the direct electron-hole recombination of band transition. However, the characteristic emission peak around 2.01 eV nearly disappears for the BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub> heterostructure, indicating that the recombination of photogenerated charge carriers is inhibited greatly. The efficient charge separation could increase the lifetime of charge carriers and enhance the efficiency of interfacial charge transfer to adsorbed substrates, and then improve the photocatalytic activity.

In **Figure 7**, the lowest relative CL intensity of BB1I2-7-110-12 and BB2I1-110-4-12 composite suggests that it has the lowest recombination rate of electron–hole pairs, which results in the higher photocatalytic activities of BC1I2-7-110-12 and BC2I1-110-4-12, as shown in **Figure S13** and **Table 3**.

5

Therefore, it is believed that the CV degradation is initiated not only by a photocatalytic process but also by a photosensitization process.

## **3.8 Separation and Identification**

With visible irradiation, temporal variations occurring in the solution of CV dye during the degradation process is examined by HPLC coupled with a photodiode array detector and ESI mass spectrometry. Given the CV irradiation up to 24 h at pH 4, the chromatograms are illustrated in **Figure S14** of supplementary materials and recorded at 580, 350, and 300 nm, and nineteen intermediates are identified, with the retention time under 50 min. The CV dye and its related intermediates are denoted as species **A-J**, **a-f**, and  $\alpha$ - $\gamma$ . Except for the initial CV dye (peak A), the peaks initially increase before subsequently decreasing, indicating the formation and transformation of the intermediates.

In Figure S15 of supplementary materials, the maximum absorption of the spectral bands shifts from 588.5 nm (spectrum A) to 541.5 nm (spectrum J), from 377.0 nm (spectrum a) to 339.0 nm (spectrum f), and from 309.1 nm (spectrum  $\alpha$ ) to 278.3 nm (spectrum  $\gamma$ ). The maximum adsorption in the visible and ultraviolet spectral region of each intermediate is depicted in Table S3. They are identified as A-J a-f, and  $\alpha$ - $\gamma$ , respectively corresponding to the peaks A-J, a-f, and  $\alpha$ - $\gamma$  in Figure S14. These shifts of the absorption band are 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 **Figure S14 (a)** and illustrated in **Figure S15 (a)** for UV-vis absorption spectroscopy. The wavelength position of the major adsorption band of the intermediates of *N*-de-methylated CV dye moves toward the blue region,  $\lambda_{max}$ , **A** (CV), 588.5 nm; **B**, 580.9 nm; **C**, 574.5 nm; **D**, 580.9 nm; **E**, 566.7 nm; **F**, 569.9 nm; **G**, 563.5nm; **H**, 566.1 nm; **I**, 555.0 nm; **J**, 541.5 nm. The *N*-de-methylation of the CV dye causes the wavelength shifts, depicted in **Table S3** of supplementary materials, due to an attack by one of the active oxygen species on the *N*,*N*-dimethyl or *N*-methyl group. It is previously reported [Catal. Commun., 2011, **12**, 972] that the CV dye is *N*-de-methylated in a stepwise manner (i.e., methyl groups are removed one by one as confirmed by the gradual peak wavelength shifts toward the blue region) and this is confirmed as the **Table S3** shown.

The second family is marked in the chromatogram of **Figure S14 (b)** and illustrated in **Figure S15 (b)** for UV-vis absorption spectroscopy. The destruction of CV yields **a**,  $\alpha$ , and their *N*-de-methylated products *N*-hydroxymethylated intermediates. The wavelength position of the major adsorption band of the *N*-de-methylation of **a** and the *N*-hydroxymethylated intermediates of the

*N*-de-methylated **a** species, produced by the cleavage of the CV chromophore ring structure, moves toward the blue region,  $\lambda_{max}$ , **a**, 377.0 nm; **b**, 366.8 nm; **c**, 361.9 nm; **d**, 360.0 nm; **e**, 357.5 nm; **f**, 339.0 nm. The proposed intermediate (**a**) is compared with a standard material of

4-(N,N-dimethylamino)-4'-(N',N'-dimethylamino)benzophenone. The retention time and the absorption spectra are identical.

The third family is marked in the chromatogram of **Figure S14 (c)** and illustrated in **Figure S15 (c)** for UV-vis absorption spectroscopy. The wavelength position of the major adsorption band of the *N*-de-methylation of  $\alpha$ , produced by the cleavage of the CV chromophore ring structure, moves toward the blue region,  $\lambda_{max}$ ,  $\alpha$ , 309.1 nm;  $\beta$ , 290.1nm;  $\gamma$ , 278.3 nm. The proposed intermediate ( $\gamma$ ) is compared with the standard material of 4-aminobenzophenone. The retention time and the absorption spectra are identical.

The intermediates are further identified using the HPLC-ESI mass spectrometric method, and the relevant mass spectra are illustrated in **Figures S16** and **Table S3** of supplementary materials. The molecular ion peaks appear in the acid forms of the intermediates. The results of mass spectral analysis confirm the components **A** (CV), m/z = 372.23, **B**, m/z = 358.18; **C**, m/z = 344.18; **D**, m/z = 344.18; **E**, m/z = 330.12; **F**, m/z = 330.12; **G**, m/z = 316.12; **H**, m/z = 316.12; **I**, m/z = 302.12; **J**, m/z = 288.07; **a**, m/z = 269.28; **b**, m/z = 255.23; **c**, m/z = 241.17; **d**, m/z = 241.18; **e**, m/z = 227.11; **f**, m/z = 219.01; **a**, m/z = 136.92, in liquid chromatogram.

## 3.9 Mechanism of photocatalytic degradation CV

Generally speaking, three possible reaction mechanisms are suspected to be involved in the dye photodegradation by a semiconductor, namely (i) photolysis process, (ii) dye photosensitization process, and (iii) photocatalytic process [App. Catal. B: Environ., 2013, **136-137**, 112]. For the photolysis process, a photoinduced electron on the induced dye directly reacts with O<sub>2</sub> to produce a singlet oxygen atom that can work as an oxidant for the pure dye photolysis [App. Catal. B: Environ., 2013, **136-137**, 112]. In this experiment, CV degradation by the photolysis process upon visible light in the blank experiment is not observable. This means that CV is a kind of structure-stable dye, thus, the CV decomposition by the photolysis mechanism is negligible.

For a dye photosensitization process, the energy of irradiation light can stimulate the dye to form photoinduced electrons which transfer to the conduction band of the catalyst that absorbs the dye, and subsequently react with  $O_2$  to generate  $O_2^{\bullet}$  oxidant [App. Catal. B: Environ., 2013, **136-137**, 112; 2012, **117-118**, 148]. As previous studies shown, the properties of the dye, such as the structural stability of the dye, the adsorbability of the dye on catalyst surface, and the absorbance of the dye, are responsible for a dye photosensitization mechanism. In this study, slight changes in the CV concentration over different samples can be detected in 30 min of dark adsorption experiment before the photocatalytic reactions. The slight CV adsorptions on the catalyst benefits the transfer of charge carriers between the dye and the catalyst surfaces in the dye photosensitization process. Presuming that the photosensitization processes take place with  $BiO_pBr_q/BiO_mI_n$ , that is to say, the photosensitization mechanism in the CV decomposition is not also neglectable.

As being known, various primary reactive species, such as hydroxyl radical HO<sup>•</sup>, photogenerated hole  $h^+$ , superoxide radical  $O_2^{-\bullet}$  and singlet oxygen  ${}^1O_2$ , can be formed during the photocatalytic degradation process in the UV-vis/semiconductor system [Scr. Mater., 2007, 56, 669]. Shenawi-Khalil and his coworkers showed that the Rhodamine-B photodegradation by  $yBiO(Br_xI_{1-x})-(1-y)$  bismuth oxide hydrate under visible light was dominated by  $O_2^{-}$  and  $h^+$  oxidation being the main active species [Appl. Catal. B: Environ., 2012, 117-118, 148]. Cao et al. investigated that the hydroxyl radicals and direct holes were the primary reactive species in the Methyl Orange degradation by BiOI/BiOBr spheres under visible light irradiation [Catal. Commun., 2011, **13**, 63-68]. Chen *et al.* proposed the pathway for generating active oxygen radicals ('OH) on the surface of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>/BiOI for the degradation of Rhodamine-B, Methylene Blue, and Crystal Violet [Ind. Eng. Chem. Res., 2012, 51, 6760-6768]. Xiao's group revealed that highly efficient visible light driven bisphenol-A removal with BiOBr/BiOI could be attributed to effective separation and transfer of photoinduced charge carriers in BiOBr/BiOI with narrower band gap and more negative conduction band position, which favored the photogenerated holes [J. Hazard. Mater., 2012, 233-234, 122-130]. Sanaa et al. reported 'OH and h<sup>+</sup> being two main actives in the whole degradation process [J. Phys. Chem. C. 116 (2012) 11004-11012]. Wang et al. reported that 'OH radicals were generated by multistep reduction O<sub>2</sub><sup>-•</sup> [Appl. Catal. B: Environ. 136-137 (2013) 112-121]. The generation of  $O_2^{-}$  could not only inhibit the recombination of photoinduced charge carriers, but also benefit the dechlorination of chlorinated phenol derivative. The hydroxyl radical HO<sup>•</sup> might only be generated via an  $e^{-} \rightarrow O_2^{-} \rightarrow H_2O_2 \rightarrow OH$  route. Meanwhile, OH radicals were generated by multistep reduction  $O_2^{-}$  in system. In a valence band of Bi<sup>3+</sup>, holes formed by photoexcitation were regarded as Bi<sup>5+</sup> [J. Phys. Chem. B. 109 (2005) 22432-22439]. The standard redox potential of  $Bi^{V}/Bi^{III}$  was more negative than it of OH<sup>•</sup>/OH<sup>-</sup> [Environ. Sci. Technol. 36 (2002) 2019-2025]. Therefore, photogenerated holes on the surface of Bismuth Oxyhalides were not expected to react with  $OH^{-}/H_{2}O$  to form 'OH, suggesting that the decomposition of bisphenol-A [J. Hazard. Mater., 2012, 233-234, 122-130] and Rhodamine [Phys. Chem., 1996, 100, 8436-8442] could be attributed to a direct reaction with the photogenerated holes or with superoxide radical (generated by the excited electron) or both species. Zhu et al. reported that photocatalytic experiments in the presence of N<sub>2</sub> and the radical scavenger suggested 'OH and  $O_2^{-}$ ' were two main actives in the whole degradation process [Appl. Catal. B: Environ., 2011, **102**, 316-322]. According to previous studies [Environ. Sci. Technol. 46 (2012) 7318-7326], the dominant active oxygen species generated in direct oxidation and photocatalytic reactions were <sup>1</sup>O<sub>2</sub> and 'OH radicals, respectively. Besides, in this visible light-induced semiconductor system, hydroxylated compounds are also identified for the photocatalytic degradation of CV and Ethyl Violet [J. Chrom. A. 1189 (2008) 355-365].

In order to evaluate the effect of the active species during the photocatalytic reaction, a series of quenchers are introduced to scavenge the relevant active species.  $OH, O_2^{-}, O_2$ , and  $h^+$  are investigated by adding 1.0 mM benzoquinone (BQ, a quencher of O<sub>2</sub><sup>•</sup>) [Environ. Sci. Technol., 2009, **43**, 8361-8366], 1.0 mM isopropanol (IPA, a quencher of 'OH) [Environ. Sci. Technol., 2010, 44, 1392-1398], 1.0 mM ammonium oxalate (AO, a quencher of h<sup>+</sup>) [Catal. Commun., 2011, **12**, 972-975], and 1.0 mM Sodium azide (SA, a quencher of <sup>1</sup>O<sub>2</sub>) [Chemosphere, 2009, 76, 1185-1191], respectively. The method is similar to the former photocatalytic activity test. As shown in Figure 8, the photocatalytic degradation of CV was not affected by the addition of SA, whereas BQ, IPA, and AO quenching decreased the degradation efficiency compared with that for no quenching, indicating that  ${}^{1}O_{2}$  can be negligible, whereas  $O_2^{-}$  is a critical active species in the CV degradation process. In addition, IPA and AO quenching also decreased the degradation efficiency, suggesting that 'OH and  $h^+$  were also involved in the process of CV degradation after eliminating the role of 'OH. Therefore, the quenching effects of various scavengers showed that the reactive  $O_2^{\bullet}$  played a major role and 'OH and h<sup>+</sup> played a minor role in CV degradation. But, 'OH is an extremely strong, non-selective oxidant, which leads to the partial or complete mineralization of several organic chemicals.

Chen *et al.* reported [J. Hazard. Mater., 2011, **185**, 227-235] that  $Pt-TiO_2$  accumulated less negative species on catalyst surfaces, which deteriorated reaction rates, than pure TiO<sub>2</sub> did in an acidic environment. The 'OH radical is produced subsequently, as also shown in eqs.18-23.

$O_2^{-\bullet} + H^+ + e^- \rightarrow HOO^{\bullet}$	(18)
$HOO^{\bullet} + H_2O \rightarrow {}^{\bullet}OH + H_2O_2$	(19)
$O_2^{-\bullet} + 2H^+ \longrightarrow H_2O_2$	(20)
$H_2O_2 + e^- \rightarrow OH + OH^-$	(21)
$h^+ + OH^- \rightarrow OH$	(22)
$h^+ + H_2O \rightarrow OH + H^+$	(23)

These cycles continuously occur when the system is exposed to the visible light irradiation. Finally, after several cycles of photo-oxidation, the degradation of CV by the formed oxidant species can be expressed by eqs. 24-26.

$CV + h^+ \rightarrow CV^{+\bullet} \rightarrow degraded compounds$	(24)
$\text{CV} + \text{OH}^{\bullet} / \text{O}_2^{\bullet} \rightarrow \text{degraded compounds}$	(25)
$CV^{+\bullet} + OH^{\bullet}/O_2^{-\bullet} \rightarrow degraded compounds$	(26)

It has been reported that dye exhibits a mechanisms of dye sensitized degradation [23]. This photocatalytic degradation is also attributed to the photodegradation of CV through the photocatalytic pathway of CV photosensitized  $BiO_pBr_q/BiO_mI_n$ . CV absorbing a visible photon is promoted to an excited electronic state CV\*, from which an electron can be transferred into the conduction band of  $BiO_pBr_q/BiO_mI_n$ :

$$CV + hv \rightarrow CV^{*}$$

$$CV^{*} + BiO_{p}Br_{q}/BiO_{m}I_{n} \rightarrow CV^{**} + BiO_{p}Br_{q}/BiO_{m}I_{n} (e^{-})$$

$$O_{2} + e^{-} \rightarrow O_{2}^{-*}$$

$$(29)$$

Once the electron reaches the  $BiO_pBr_q/BiO_mI_n$  conduction band, it subsequently induces the generation of active oxygen species (eq.29 and eqs.18-21), which result in the degradation of CV. Clearly, apart from the photodegradation of CV through the pathway of  $BiO_pBr_q/BiO_mI_n$ -mediated and photosensitized processes, there is another kind of photocatalytic pathway to account for the enhanced photocatalytic activity. Both the photocatalytic process and the photosensitized process would work concurrently, shown in **Figure 9**.

In earlier reports [Catal. Today, 2011, 174, 148-159, J. Hazard. Mater., 2011, 185, 227-235], the *N*-de-alkylation processes were preceded by the formation of a nitrogen-centered radical while the oxidative degradation (destruction of dye chromophore structures) was preceded by the generation of a carbon-centered radical in the photocatalytic degradation of Triphenylmethane dye. On the basis of above experimental results, the dye degradation mechanism is tentatively proposed, depicted in Figure S17 of supplementary materials. The excited dye injects an electron into the conduction band of  $BiO_pBr_q/BiO_mI_n$ , where it is scavenged by  $O_2$  to form  $O_2^{-\bullet}$ . De-methylation of CV dye occurs mostly through the attack by the active species, which is a perfect nucleophilic reagent, on the N-methyl portion of CV. Furthermore, O<sub>2</sub><sup>-•</sup> subsequently reacts with H<sub>2</sub>O to generate <sup>•</sup>OH radicals and the other active radical. The probability for the formation of 'OH should be much lower than that for  $O_2^{-}$ . OH is an extremely strong, non-selective oxidant, which leads to the partial or complete mineralization of several organic chemicals. All the above active radicals drive the photodegradation or mineralization of the dye molecule. Under visible light irradiation, all the intermediates identified in these two studied topics have the same result. There is no doubt that the major oxidant is the 'OH radical, not  $O_2^{-\bullet}$ .

During the initial period of CV dye photodegradation by  $BiO_pBr_q/BiO_mI_n$ , competitive reactions between *N*-de-methylation and oxidative degradation occur based on the intermediates identified. The detailed mechanisms are illustrated in the **Figures S18-S19** of supplementary materials. The first pathway involves in a hydroxyl radical attack on the *N*,*N*-methylamino group of CV, resulting in a reactive cationic radical, the subsequent de-methylation and oxidation of which eventually yield the first group intermediates. The results indicate that the *N*-de-methylation degradation of CV dye takes place in a stepwise manner to yield mono-, di-, tri-, tetra-, penta-, hexa- *N*-de-methylated CV species during the process. The second pathway involves in a hydroxyl radical attack on the central carbon atom of CV, yielding a reactive cationic radical, with a bond between the central carbon atom and the *N*,*N*-dimethylamino phenyl ring that is cleaved to give one set of intermediates **a** and **a**. In addition, these intermediates can further be attacked by

hydroxyl radicals, giving a reactive cationic radical which is de-methylated, resulting in **f** and  $\gamma$ . The latter intermediates are further oxidized to form mineralization products.



**Figure S1.** XRD patterns of as-prepared  $BiO_pBr_q/BiO_mI_n$  samples under different emperature. (Molar ratio KBr/KI =1/2, hydrothermal conditions: temp = 160°C, pH = 1-13, time = 12 h)



**Figure S2.** XRD patterns of as-prepared  $BiO_pBr_q/BiO_mI_n$  samples under different temperature. (Molar ratio KBr/KI =1/2, hydrothermal conditions: temp = 210°C, pH = 1-13, time = 12 h)



**Figure S3.** XRD patterns of as-prepared  $BiO_pBr_q/BiO_mI_n$  samples under different temperature. (Molar ratio KBr/KI =1/2, hydrothermal conditions: temp = 260°C, pH = 1-13, time = 12 h)



**Figure S4.** XRD patterns of as-prepared  $BiO_pBr_q/BiO_mI_n$  samples under different temperature. (Molar ratio KBr/KI = 2/1, hydrothermal conditions: temp = 110°C, pH = 1-13, time = 12 h)



**Figure S5.** XRD patterns of as-prepared  $BiO_pBr_q/BiO_mI_n$  samples under different pH values. (Molar ratio KBr/KI =2/1, hydrothermal conditions: temp = 160°C, pH = 1-13, time = 12 h)



**Figure S6.** XRD patterns of as-prepared  $BiO_pBr_q/BiO_mI_n$  samples under different temperature. (Molar ratio KBr/KI =2/1, hydrothermal conditions: temp = 210°C, pH = 1-13, time = 12 h)



**Figure S7.** XRD patterns of as-prepared  $BiO_pBr_q/BiO_mI_n$  samples under different temperature. (Molar ratio KBr/KI =2/1, hydrothermal conditions: temp = 260°C, pH = 1-13, time = 12 h)



**Figure S8**. SEM images of  $BiO_pBr_q/BiO_mI_n$  prepared by the hydrothermal autoclave method at different pH values. (Molar ratio KBr/KI = 1/2, hydrothermal conditions: temp = 110°C, pH = 1-13, time = 12 h)



**Figure S9.** SEM images of  $BiO_pBr_q/BiO_mI_n$  prepared by the hydrothermal autoclave method at different pH values. (Molar ratio KBr/KI = 2/1, hydrothermal conditions: temp = 110°C, pH = 1-13, time = 12 h)



**Figure S10.** N<sub>2</sub> adsorption-desorption isotherm distribution curves for (a) as-prepared  $BiO_pBr_q/BiO_mI_n$  samples under different pH values and (b) enlarged view of BB112-4-110-12...



**Figure S11.** The pore distribution curves of as-prepared BiO<sub>p</sub>Br<sub>q</sub>/BiO<sub>m</sub>I<sub>n</sub> under different pH values. (BC1B2)



**Figure S12**. Temporal UV-vis adsorption spectral changes during the photocatalytic degradation of (a) CV and (b) phenol over aqueous BB1I2-4-110-12 under visible light irradiation.





 $BiO_pBr_q/BiO_mI_n$  photocatalysts. Molar ratio KBr/KI (a) 1/2, (b) 2/1.



**Figure S14.** HPLC chromatogram of the degraded intermediates at different irradiation intervals, recorded at (a)580nm (b)350nm (c)300nm



Figure S15. Absorption spectra of the intermediates formed during the photodegradation process of the CV dye corresponding to the peaks in the HPLC chromatograph.





**Figure S16.**ESI mass spectra of intermediates formed during the photodegradation of the CV dye a fter they were separated by HPLC method.



Figure S17. Proposed photodegradation mechanism of the CV dye.



Figure S18. Proposed *N*-de-methylation mechanism of CV dye



Figure S19. Proposed mechanism of cleavage of chromosphere structure of CV dye.

		BB1I2		
ъЦ		Temj	p(°C)	
pm	110	160	210	260
1	BB1I2-1-110-12	BB1I2-1-160-12	BB1I2-1-210-12	BB1I2-1-260-12
4	BB1I2-4-110-12	BB112-4-160-12	BB112-4-210-12	BB1I2-4-260-12
7	BB1I2-7-110-12	BB112-7-160-12	BB112-7-210-12	BB112-7-260-12
10	BB112-10-110-12	BB1I2-10-160-12	BB1I2-10-210-12	BB1I2-10-260-12
13	BB1I2-13-110-12	BB1I2-13-160-12	BB1I2-13-210-12	BB1I2-13-260-12
		BB2I1		
nII		Ten	np(°C)	
рп	110	160	210	260
1	BB2I1-1-110-12	BB2I1-1-160-12	BB2I1-1-210-12	BB2I1-1-260-12
4	BB2I1-4-110-12	BB2I1-4-160-12	BB2I1-4-210-12	BB2I1-4-260-12
7	BB2I1-7-110-12	BB2I1-7-160-12	BB2I1-7-210-12	BB2I1-7-260-12
10	BB2I1-10-110-12	BB2I1-10-160-12	BB2I1-10-210-12	BB2I1-10-260-12
13	BB2I1-13-110-12	BB2I1-13-160-12	BB2I1-13-210-12	BB2I1-13-260-12

 $\label{eq:s1.Codes} \mbox{ Table S1. Codes of } BiO_pBr_q/BiO_mI_n \mbox{ prepared under different KBr/KI molar ratio, pH values, and reaction temperatures at 12 h.}$ 

Catalyst code	BET $(m^2/g)$	Pore size (Å)	Pore volume $(cm^3/g)$
BB1I2-1-110-12	4	456	0.05
BB1I2-4-110-12	38	221	0.3
BB1I2-7-110-12	6	484	0.06
BB1I2-10-110-12	4	477	0.03
BB1I2-13-110-12	0.9	549	0.006
BB2I1-1-110-12	8	315	0.07
BB2I1-4-110-12	27	251	0.2
BB2I1-7-110-12	13	301	0.1
BB2I1-10-110-12	4	463	0.5
BB2I1-13-110-12	2	490	0.01
BB3-1-110-12	5	402	0.04
BI3-1-110-12	2	424	0.02

 $\label{eq:second} \begin{array}{c} \mbox{Table S2. Specific BET surface areas and pore parameters of the as-prepared} \\ BiO_pBr_q/BiO_mI_n \mbox{ samples} \end{array}$ 

HPLC	Do mother lotion intermediated	ESI/MS molecular ions	Adsorption maximum
peaks	De-memylation intermediates	(m/z)	(uu)
V	N, N, N', N'', N'''-hexamethyl-pararosaniline	372.23	588.5
B	<i>N</i> , <i>N</i> -dimethyl- <i>N</i> ', <i>N</i> '-dimethyl- <i>N</i> "-methyl-pararosaniline	358.18	580.9
C	N, $N$ -dimethyl- $N$ -methyl- $N$ "-methyl-pararosaniline	344.18	574.5
D	N, N-dimethyl-N', N'-dimethyl-pararosaniline	344.18	580.9
E	<i>N</i> -methyl- <i>N</i> '-methyl- <i>N</i> "-methyl-pararosaniline	330.12	566.7
ľ	N, $N$ -dimethyl- $N$ -methyl-pararosaniline	330.12	569.9
Ð	<i>N</i> -methyl- <i>N</i> '-methyl-pararosaniline	316.12	563.5
Η	N, $N$ -dimethyl-pararosaniline	316.12	566.1
Ι	<i>N</i> -methyl-pararosaniline	302.12	555.0
ſ	pararosaniline	288.07	541.5
а	4-(N,N-dimethy lamino)-4'-(N',N'-dimethy lamino) benzophenone	269.28	377.0
þ	4-(N, N-dimethylamino)-4'-(N-methylamino) benzophenone	255.23	366.8
c	4-(N-methylamino)-4'-(N'-methylamino)benzophenone	241.17	3619
þ	4-(N, N-dimethylamino)-4'-aminobenzophenone	241.18	360.0
e	4-(N-methylamino)-4'-aminobenzophenone	227.11	357.5
f	4,4'-bis-aminobenzophenone	219.01	339.0
α	4-( <i>N</i> , <i>N</i> -dimethylamino)phenol	136.92	309.1
β	4-(N-methylamino)phenol	ı	290.1
γ	4-aminophenol	1	278.3

Table S3. Summary of the CV photocatalytic degradation intermediates identified by the HPLC-PDA-ESI/MS.

33