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# Photocatalytic synthesis of N-benzyleneamine from benzylamine on ultrathin BiOCl nanosheets under visible light

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## ABSTRACT

Ultrathin BiOCl nanosheets (NST) with the thickness about 1.5 nm was prepared as a photocatalyst for the oxidation of benzylamine (BA) to N-benzyleneamine under visible light. The photocatalytic activity of NST is over 2.5 times higher than that of its bulk counterpart. More oxygen vacancies (OVs) in NST were revealed by EPR and XPS. UV-DRS result indicates that light adsorption of NST can be extended to visible light due to the presence of OVs. In addition, rich OVs result in Bi atoms in sublayer to be exposed as Lewis acid sites. In situ FTIR spectrum shows that BA is chemosorbed on the Lewis acid sites forming surface -N•••Bi- coordination species, resulting in the activation of BA. The surface coordination species would also result in the red shift of the photo-absorption spectrum. Finally, a synergistic mechanism based on surface coordination activation and photocatalysis was proposed to explain the enhanced photocatalytic activity over NST.

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## 1. Introduction

Catalytic oxidation of amine to imine has always been a research hotspot since imines are indispensable intermediates for fine chemicals and pharmaceuticals [1–3]. Traditionally, imines are produced though the dehydration condensation of amines and carbonyl compounds. However, the carbonyl compounds are extremely reactive and make the condensation difficult to control [4]. In recent years, it has been reported that imines can be direct oxidation from two moles of the primary amines in the presence of a catalyst. Nevertheless, the reaction requires high temperatures, typically >100 °C, as well as the use of precious metals [5]. Therefore, an efficient and economical method is desired for the synthesis of imines from amines under mild conditions.

As a green process, photocatalysis has been applied in many fields, such as water splitting,  $CO_2$  reduction and pollutants degradation [6–9]. Photocatalytic organic synthesis has also attracted wide attention [10–15]. Photocatalytic conversion of benzylamine to the corresponding imine under visible light appears to be an ideal green approach [3,16–18]. It was reported that the conversion of BA would be improved by loading precious metals on a

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https://doi.org/10.1016/j.jcat.2019.10.018 0021-9517/© 2019 Elsevier Inc. All rights reserved. catalyst for photocatalysis oxidation coupling of BA to Nbenzyleneamine [5,19]. In addition, based on the semiconductor valence band theory, a photocatalytic process is generally explained by the action of electron-hole pairs [20]. However, the coordination and activation of reactant molecules on the catalyst surface were less concentrated on [21]. Therefore, to explore the interaction between reactant molecules and the surface of a catalyst is necessary to understand the intrinsic mechanism for photocatalytic organic transformation at a molecular level.

Ultrathin two-dimensional nanosheets has attracted attention due to their larger surface area, more active sites, and faster electron-hole separation capabilities, such as monolayer  $Bi_2MOO_6$ nanosheets [22,23], monolayer  $H_xTi_yO_4$ ·H<sub>2</sub>O nanosheets [24–26] and monolayer HNb<sub>3</sub>O<sub>8</sub> nanosheets [21], which could show excellent photocatalytic activity in organic reactions [27]. BiOCl, as one of the typical layered compounds, has aroused extensive attention in recent years [28–32]. It consists of  $[Bi_2O_2]^{2+}$  layers sandwiched between two halogen ions slabs. The thickness of monolayer BiOCl nanosheets is only about 0.7 nm [33]. More unsaturated sites, such as oxygen defects, could be produced on the surface of NST as reducing its thickness into molecular level. The OVs induced local state could extend the photoresponse to visible light and effectively capture charge carriers, resulting in enhancing photoreactivity [34,35]. Moreover, native OVs possess abundant localized

electrons which can easily activate  $O_2$  to further producing reactive oxygen species [36,37]. In addition, more exposed unsaturation metal sites could act as Lewis acid sites. The unsaturated metal centers can coordinate with organic molecules and activate them [38]. This process is critical to the overall photocatalytic reaction. Therefore, NST could as an ideal catalyst for photocatalytic synthesis of N-benzyleneamine from BA. Finally, this structure provides a reference for researching the role of defects in photocatalytic organic synthesis due to its unique electronic construction.

Herein, we prepared ultrathin BiOCI nanosheets with a thickness of about 1.5 nm for photocatalytic oxidation coupling of BA to N-benzyleneamine, which exhibit superior photocatalytic performance compared to its bulk counterpart. The unique ultrathin structure, large specific surface area and strong light absorption were revealed by TEM, AFM, BET and UV-vis DRS. OVs on the surface of nanosheets were investigated by EPR and XPS. In addition, the interactions between BA molecules and surface acidic sites of nanosheets were presented by in situ FTIR. Based on the detailed characterization, a possible mechanism was proposed at a molecule level for the photocatalytic oxidation coupling BA to Nbenzyleneamine over NST.

#### 2. Experimental section

### 2.1. Reagents and chemicals

All reagents with analytical grade were used as received without further purification. NaCl, mannitol, polyvinylpyrrolidone K30 (PVPK30) and bismuth nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O) are purchased from Sinopharm Chemical Reagent Co. (SCRC). Benzylamine (99%) and N-benzyleneamine (99%) are obtained from J&K Scientific Ltd. and Alfa Aesar China Co., Ltd., respectively.

### 2.2. Catalyst preparation

Ultrathin BiOCl nanosheets (denoted as NST) was prepared by using a modified method reported by Xie et al [33]. Firstly, 0.800 g of PVPk30 and 0.002 mol of  $Bi(NO_3)_3$ - $5H_2O$  were successively dissolved in 50 mL of mannitol solution (0.1 M) under vigorous stirring. Then, 10 mL of saturated sodium chloride solution was slowly added into the mixed solution under continuous stirring. Next, the mixture was continually stirred for 10 min and then transferred into a 100 mL Teflon-lined stainless-steel autoclave, which was heated at 160 °C for 5 h. The precipitates were collected by centrifugation and washed with deionized water and ethanol to remove residual ions. Finally, the products were dried at 60 °C for 6 h. In order to compare, bulk BiOCl (denoted as Bulk) was also prepared in the same procedure without PVPK30.

#### 2.3. Materials characterization

The X-ray diffraction (XRD) of prepared samples were characterized on the Bruker D8 Advance X-ray diffractometer with Nifiltered Cu Kirradiation ( $\lambda = 1.5406$  Å) at 40 kV and 40 mA. The field emission scanning electron microscope (SEM) was used to reveal the morphologies of the samples on a FEI Quanta 200F electron microscope. Transmission electron microscopy (TEM) and higherresolution transmission electron microscopy (HRTEM) images were acquired on a JEOL model JEM2010 EX microscope at an accelerating voltage of 200 kV to further investigate the structure and morphology of samples. Atomic force microscopy (AFM) to determine the thickness of nanosheets were recorded on a Nanoscope E multimode. UV–vis diffuse reflectance spectra (UV– vis DRS) were got on an ultraviolet–visible spectrophotometer (Cary 500) with Barium sulfate as reference. Nitrogen adsorption-desorption isotherms were obtained on Micrometric 3020 M. The samples were degassed in vacuum at 160 °C for 8 h and then analyzed at 77 K. X-ray photoelectron spectra (XPS) were carried on a PHI Quantum 2000 XPS system with Al K $\alpha$  as the excitation source and the reference C1s binding energies is 284.8 eV. Electron paramagnetic resonance (EPR) signals were recorded on a Bruker A300 spectrometer at room temperature using a 300 W Xe lamp with a 400 nm cutoff filters as light source (Beijing Trustech, PLS-SXE300c). NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub>– TPD) was carried out on a Micromeritics AutoChem II 2920 instrument. 100 mg of a sample was pretreated at 260 °C for 2 h under helium stream and then cooled to 30 °C. Then, 3% NH<sub>3</sub>/He gas was introduced and maintained for 30 min at flow rate 30 mL/min. Desorption was conducted with increasing temperature up to 270 °C (10 °C/min).

#### 2.4. In-situ FTIR measurement

The in-situ FTIR spectra of BA and pyridine adsorbed on BiOCl samples were carried out on a NICOLET IS50 Fourier transform infrared (FT-IR) spectrometer. A total of 64 scans at a resolution of 4  $\rm cm^{-1}$  were performed to obtain each spectrum. Firstly, a powder sample (16 mg BiOCl + 8 mg KBr) was pressed into a selfsupporting IR disk. The disk was then put into the sample holder which could be moved vertically along the cell's tube. Before measurements, the disk was treated under dynamic vacuum  $(4 \times 10^{-2} \text{ hPa})$  at 200 °C for 3 h to remove surface contaminants. After the disk cooling to room temperature, 20 µL of BA or pyridine was spiked into the cell with a syringe via a septum. After adsorption equilibrium was reached for 30 min later, FTIR spectrum of a sample was collected. The physisorbed BA or pyridine were removed by a further evacuation at 150 °C for 3 min under  $4 \times 10^{-2}$  hPa, and then, another FTIR spectrum was taken for revealing the information of organic substrates chemisorbed on a sample.

#### 2.5. Electrochemistry measurement

The working electrode was prepared on fluorine-doped tin oxide (FTO) glass. Firstly, FTO glasses were successively cleaned by sonicating in chloroform, acetone and ethanol for 30 min. Then, an FTO slide was coated with 10 µL of slurry. The slurry was obtained by sonicating the mixture of 5 mg of a sample and 0.5 mL of DMF for 1 h. After the slide was dried at 60 °C for 1 h, the uncoated part of the electrode was isolated with an epoxy resin and the exposed area of the electrode was 0.25 cm<sup>2</sup>. The electrochemical measurements were performed in a conventional three electrode cell, using a Pt plate and a saturated Ag/AgCl electrode as counter electrode and reference electrode, respectively. The working electrode was immersed in a 0.2 M of Na<sub>2</sub>SO<sub>4</sub> aqueous solution without any additive for 30 s before measurement. The Mott-Schottky plots were obtained at three different frequencies (0.5 k, 1 k and 1.5 kHz) on a Zahner electrochemical workstation. Then, we make a line tangent to its straight line, which is indicated by the black symbol. Three tangent lines intersect on the X-axis to obtain the flat-band potential value [39-41].

#### 2.6. Photocatalytic activity test

The photocatalytic oxidation coupling of benzylamine (BA) was carried out as follows. A mixture of BA (0.2 mmol) and 8 mg of a sample was added with the solvent of acetonitrile (1 mL) in a 10 mL of Pyrex glass reaction tube. Then, the mixture was stirred for 30 min at  $O_2$  atmosphere to evenly mix the sample in the solution. Next, the suspension was irradiated by a 300 W Xe arc lamp with a 400 nm-Cut filter. After irradiated for 10 h, the mixture

was centrifuged to completely remove the catalyst particles. The supernatant solution was determined with a Shimadzu Gas Chromatograph (GC-2014C). Gas chromatography-mass spectrometry (GC-MS) was carried out to confirm the identity of the products on an Agilent gas chromatograph 7890B-mass spectrometry 5977B. The conversion of BA and the selectivity of Nbenzyleneamine were defined as follows:

 $Conversion(\%) = [(C_0 - C_{BA})/C_0] \times 100$ 

 $\textit{Selectivity}(\%) = [C_{\textit{N-benzyleneamine}} \times 2/(C_0 - C_{\textit{BA}})] \times 100$ 

 $Yield(\%) = (2 \times C_{N-benzyleneamine}/C_0) \times 100$ 

Where  $C_0$  is the initial concentration of BA.

#### 3. Results and discussion

The crystal phases of samples were confirmed by XRD analysis. As shown in Fig. 1, the single-phase diffraction patterns of prepared samples are matched well with the published data (JCPDS No. 6-0249) [42]. No characteristic peak of any other phase is observed. This indicates that the BiOCI samples with pure phase were successfully prepared. Furthermore, the half width of the peaks for NST are significantly broadened than those for Bulk, revealing the existence of different morphology in NST.

FTIR was carried out to verify the purity of the prepared samples. It can be seen from the Fig. S2 that the spectra of NST and Bulk are similar. The peaks at  $3455 \text{ cm}^{-1}$  and  $1637 \text{ cm}^{-1}$  can be assigned to the stretching vibration and the bending vibration of O-H for the adsorbed H<sub>2</sub>O, respectively. The stretching vibrations for C-H at about 2900 cm<sup>-1</sup> and N-H at about 3300 cm<sup>-1</sup> are not observed, indicating the absence of residual PVP in the prepared samples. Therefore, this result shows the prepared samples with high purity.

The morphological features of the prepared samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It is apparent that the bulk sample (Fig. 2a and b) is typical squarelike plates. NST (Fig. 2c and d) exhibits thinner and typical nanosheet morphology. Moreover, the transparent feature image of TEM (Fig. 3a) also indicates NST is ultrathin. The HRTEM image (Fig. 3b) shows that the spacing between the lattice stripes is 0.275 nm, that indicates the angle of 90° matches well with the (1 1 0) atomic planes of BiOCl. As shown in Fig. 3c, the corresponding selected-area electron diffraction (SAED) pattern displays a regular point distribution, indicating the nanosheets exist in the form of the single-crystalline. The angle





between adjacent points is 45°, which is corresponding to the theoretical value of the angle between the (1 1 0) and (2 0 0) planes of BiOCl. This means a group of diffraction points is indexed to the [0 0 1] region axis, which is in good agreement with the XRD result. Moreover, in order to further characterize the thickness of NST, we performed the AFM measurement. The AFM image (Fig. 3d–f) suggests the thickness of NST is about 1.5 nm. Considering that the c parameter of BiOCl is 7.37 Å [33], it means NST with a 1.5 nm thickness consists of nearly 2 [Cl—Bi—O—Bi—Cl] units.

The changes of morphological for a sample may have an important influence on its surface area. Therefore,  $N_2$  adsorptiondesorption was carried out to determine the surface area of prepared samples. As shown in Fig. S3, the surface areas for NST and Bulk are 9.3 m<sup>2</sup>/g and 4.3 m<sup>2</sup>/g, respectively. The surface area of NST is 2 times higher than that of Bulk because NST has overcome the spatial inhibition of adjacent layers. The more active sites would be exposed on the surface of the sample NST with the large surface area and ultrathin character. Therefore, more reagent molecules could be adsorbed on the active sites to enhance the photocatalytic activity.

X-ray photoelectron spectroscopy (XPS) was conducted to determine the chemical composition of the prepared samples and the chemical state of each element. Fig. S4 displays the survey of the prepared samples, which shows that Bi, O and Cl elements are presented in both of samples. The peak at about 400 eV for N is not observed, which further reveal the prepared samples with high purity. As shown in Fig. 4, O1s spectra of NST and Bulk can be de-convoluted into three peaks, which represent the lattice oxygen (O1), coordination of oxygen in OH (O2) and adsorbed oxygen species (O3), respectively [43]. The binding energy of each peak is shown in Table 1. Simultaneously, the estimated atom percentages (at. %) of adsorbed oxygen species for NST is 17.5%. It is higher than that for Bulk (6.7%), suggesting that NST has more oxygen vacancies. The estimated atom percentages (at. %) of oxygen in OH (38.2%) for NST is also higher than that for Bulk (18.8%), which can be attributed to the large surface area of NST. Therefore, the estimated atom percentages (at. %) of lattice oxygen for NST (44.3%) is lower than that for Bulk (74.5%) due to the more Bi-O bonds for Bulk. It can be clearly seen that the binding energy of oxygen species in NST shows lower values compared with Bulk. These shifts demonstrate that more electrons are transferred from Bi to O atoms in NST, implying the electrons in Bi-O bonds are redistributed due to more OVs in NST [22,44]. Meanwhile, Bi 4f spectra of NST and Bulk (Fig. 4(2)) have further confirmed these results. Both of them can be de-convoluted into two peaks, Bi  $4f_{7/2}$  and Bi  $4f_{5/2}$ , that indexed to Bi<sup>3+</sup>. Bi 4f peaks of NST shift to higher binding energy compared with Bulk, which may result from the adjacent oxygen vacancies with high attracting electron effect.

Subsequently, the existence of OVs in BiOCI samples was further confirmed by the characterization of electron paramagnetic resonance (EPR). The EPR signal (Fig. 5) at g = 2.003 is observed over NST, attributed to OVs [45–47]. Under the same conditions, the signal at g = 2.003 is difficult to observe for Bulk. This result further reveals much more OVs could be produced on the surface of the nanosheets as reducing its thickness into molecular level. Moreover, the large surface area of the nanosheets is also the reason for the high exposure of oxygen vacancies. Thence, more Bi atoms would be exposed as Lewis acid sites due to the existence of more OVs. Finally, the Lewis acid sites in NST may be attributed to its ultrathin structure and the larger specific surface area.

More importantly, it is widely known that surface defects can strongly affect the optical properties of semiconductors. Thence, the existence of OVs in BiOCl samples may further change their photocatalytic activities by strongly effect on the band structure [43,48]. UV/vis absorption spectra (DRS) (Fig. 6b) reveal that the band gap of NST and Bulk is about 2.9 eV and 3.3 eV, respectively.

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Fig. 2. SEM images of the prepared samples, Bulk (a and b), NST (c and d).



Fig. 3. TEM (a), HRTEM (b), SAED (c) and AFM images (d-f) for BiOCI nanosheet.

That is to say, the presence of surface OVs extends the absorption range of NST by generating defect levels [22]. The Mott–Schottky plots display the flat-band potential of NST (Fig. 6c) and Bulk (Fig. S5) are ca. -1.1 V and -0.8 V vs. Ag/AgCl at pH 6.8, respectively, corresponding to ca. -0.9 V and -0.6 V vs. NHE, respectively. Compared with  $O_2/O_2^-$  potential (-0.28 V vs. NHE), the positions of the conduction band (CB) over two samples are more negative. This result means that the photogenerated electrons

can reduce oxygen molecules to superoxide radicals, which are the important reactive intermediates in oxidation reactions. Therefore, according to the optical absorption spectra, the valence band (VB) maximum of both NST and Bulk would occur at about 2.0 V and 2.7 V.

The prepared samples were used in the oxidation of BA to Nbenzyleneamine at 25  $^{\circ}$ C with oxygen atmosphere under visible light irradiation. The conversion of BA over NST is increased with

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Fig. 4. XPS spectra for NST (a) and Bulk (b), O 1s (1) and Bi 4f (2).

Table 1Atom percentages of O 1 s peaks determined by the XPS analysis.

Sample	Oxygen species	Position (eV)	at. %
NST	01	529.5	44.3
	02	531.0	38.2
	03	532.2	17.5
Bulk	01	530.0	74.5
	02	531.5	18.8
	03	532.7	6.7
	02 03	531.5 532.7	18.8 6.7



Fig. 5. EPR spectra of the prepared samples under visible light, Bulk (A) and NST (B).

the extension of illumination time. After irradiation for 10 h, the conversion of BA has reached 87.6% and the selectivity of N-benzyleneamine reached 96.9% (Table 2, entry 1). N-benzyleneamine as the main product is further identified by GC-MS (Fig. S6). However, the conversion of BA over Bulk is only 36.9% in the identical conditions (Table 2, entry 2). Furthermore, N-benzyleneamine is not detected without a catalysis and in the dark condition (Table 2, entry 5). Very low conversion of BA is obtained in N<sub>2</sub> atmosphere (Table 2, entry 4). In addition, no product is detected at 80 °C in the present of a catalyst under the dark (Table 2, entry 6). These results indicate that the oxidative coupling BA is carried out under visible light with O<sub>2</sub> atmosphere. Then, recycling experiments for the photocatalytic process were conducted to confirm the stability of NST. After three successive recycles, NST keeps high activities (Fig. S7). What's more, no obvious change is observed in the XRD patterns for fresh and used NST (Fig. S8), indicating that the prepared NST possesses high stability. Our results undoubtedly demonstrate that NST shows superior photocatalytic performance compared with Bulk.

In order to explore the best reaction time, the experiments for the conversion of BA with relation to time have been done. As is shown in Fig. S9, the conversion of BA and the selectivity of Nbenzyleneamine were obtained by changing reaction time from 4 h to 12 h. It is obviously that the conversion of BA gradually increased as the reaction time prolongation. The conversion of BA is up to 87.6% when irradiation for 10 h. Simultaneously, the selectivity of N-benzyleneamine is keeping at 96.9%. However, when the reaction time reached 12 h, the selectivity of N-benzyleneamine began to decrease with the conversion of BA increased. This result



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#### Table 2

Photocatalytic performances for the oxidation of BA over NST/Bulk under visible light irradiation<sup>a</sup>.



Entry	Catalyst	hv	Atm.	Conv. (%)	Sel. (%)	Yield (%)	TON <sup>c</sup>	$TOF^{d}(h^{-1})$
1	NST	+	02	87.6	96.9	84.9	2.8	0.28
2	Bulk	+	02	36.9	99.0	36.5	1.2	0.12
3	NST	+	Air	62.0	94.3	58.5	2.0	0.2
4	NST	+	N <sub>2</sub>	2.6	98.0	2.5	0.08	0.008
5	NST	-	02	Null	Null	Null	Null	Null
6	NST	_b	02	Null	Null	Null	Null	Null
7	-	+	O <sub>2</sub>	Null	Null	Null	Null	Null

<sup>a</sup> Reaction condition: benzylamine (0.2 mmol), catalyst (8 mg, 0.03 mmol), acetonitrile (1 mL), O<sub>2</sub> (1 atm), irradiation time (10 h).

<sup>b</sup> T = 80 . NST ultrathin BiOCl nanosheets, Bulk: Bulk BiOCl.

<sup>c</sup> Moles of N-benzyleneamine produced per mole of a catalyst.

<sup>d</sup> Moles of N-benzyleneamine produced per mole of a catalyst per hour [49,50].

may be due to the excessive oxidation of BA. Therefore, the best reaction time is 10 h for the oxidative coupling benzylamine to N-benzyleneamine.

The structure and surface properties of a catalyst have important influences on reaction system. The mainly exposed surface of the prepared BiOCl samples is  $(0\ 0\ 1)$  surface. The O terminated  $(0\ 0\ 1)$  surface is more thermodynamically stable [35]. Therefore, O atoms are the outermost exposed atoms and Bi atoms are the sublayer atoms for  $(0\ 0\ 1)$  surface. If OVs are generated, Bi atoms in secondary layer will be exposed as Lewis acid sites [51]. Therefore, in situ FTIR was used to characterize the Lewis acid sites on NST and Bulk. It can be known from the in situ FTIR spectra (Fig. 7a) of pyridine on NST that there are two strong peaks at 1433 and 1485 cm<sup>-1</sup>, which can be considered as pyridine adsorbed on the Lewis acid sites [52]. These peaks also remained even after heating under vacuum condition. It is suggested that the Lewis acid sites are derived from the unsaturated surface Bi atoms. The intensity of the corresponding peaks on Bulk is reduced compared to NST. Therefore, it is concluded from the above results that there are more Lewis acid sites on NST than Bulk, which may be attributed to the larger specific surface area and ultrathin structure for the nanosheets. The acidic sites on the surface of NST play a crucial role in photocatalytic organic conversion. In the progress of photocatalytic oxidation coupling of BA, the Lewis acid sites can serve as



**Fig. 7.** In situ FTIR spectra of NST (a and c) and Bulk (b and d) before and after adsorbed pyridine (a and b) and BA (c and d). Conditions (1) After degassing at 200 for 3 h. (2) Adsorption for 30 min at room temperature (physisorption + chemisorption). (3) Further evacuation of excess probe molecules at 150 for 3 min under  $4 \times 10^{-2}$  hPa (chemisorption). (4) FTIR spectra of BA.

the active sites of the reaction. Therefore, the higher photocatalytic activity for NST may assign to the more acidic sites on the surface of nanosheets.

NH<sub>3</sub>-TPD was conducted to further characterize the properties of the surface for prepared samples [53,54]. As shown in Fig. S10, the TPD signal peak of NH<sub>3</sub> at about 100 °C may be attributed to the interaction between NH<sub>3</sub> and the weak acid sites on NST. The desorption peak occurring at about 254 °C was due to the presence of moderate acid sites. In contrast, the TPD result for the bulk sample shows only one weak desorption peaks at about 263 °C. The concentration of acid sites could be estimated by the total area under the curve for all the desorption peaks. It is clear that the total acidity of NST is much larger than that of Bulk. Since Bi atoms could as Lewis acid sites in NST. This result is consistent with the results of in-situ FTIR. Moreover, moderate acid sites in NST facilitate the adsorption of the reactants and the desorption of the product to increase the photocatalytic activity.

The interactions between the samples and BA molecules have been revealed by in-situ FTIR of BA absorption. As shown in Fig. 7c, BA molecules are chemosorbed and physisorbed on the surface of NST. The peak at 1647 cm<sup>-1</sup> can be assigned to the bending vibration of N-H bond. There two obvious peaks are observed at 1490 and 1453 cm<sup>-1</sup>, which can be assigned to the stretching vibration of C=C in a aromatic ring [21]. In addition, there is a peak appearing at 1319 cm<sup>-1</sup>, which represents the stretching vibration of C=N bond in BA, the surface  $-N \cdots$ Bi- coordination species would be formed. After heating at 150 °C under vacuum condition for 3 min, the peaks at the corresponding positions still remained. It is further indicated the BA molecules are chemosorbed on the surface of NST. However, compared to the strong chemisorption of BA on NST, the adsorption signal intensity of BA on Bulk is much weaker. This result illustrates that NST have more reactive sites.

The interaction between the unsaturated active sites on the surface of samples and BA molecules was further characterized by UV-DRS. As is shown in Fig. 8, Bulk can only absorb UV light. NST has light absorption in the visible range due to in the present of OVs [43]. When BA molecules were absorbed, the absorption spectra for both Bulk and NST have a red shift and extend their absorption ranges. Considering that BA molecules could be adsorbed on Lewis acid sites, we propose that the surface complexes are formed in the samples and BA. The formed complexes may further extend the light response and be excited under visible light irradiation by surface charge transfer from "ligand to metal" [21]. Moreover, there are more unsaturated acid sites on the surface of NST, so that more BA molecules are adsorbed on the surface of NST, which is one of the reasons why the absorption band edge of NST redshifted more than that of Bulk. These are consistent with the in-suit FTIR results.

Furthermore, EPR measurements were carried out to confirm the important role of O<sub>2</sub> molecules in photocatalysis. As shown in Fig. 9, neither Bulk nor NST shows the ESR signal at air atmosphere in the dark condition. Under visible light irradiation, superoxide radical species trapped by 5,5-dimethyl-1-pyrroline N-oxide (DMPO) are observed. The signal intensity of NST significantly stronger than that of Bulk. This result not only confirms the generation of  $.0_2^{-}$  [55,56], but shows that NST can produce more  $.0_2^{-}$  than Bulk. This is due to the large number of Lewis acid sites on the surface of NST. The Lewis acid sites can serve as active sites for trapping and activating oxygen molecules by forming the -Bi-O-O...Bi- complexes. Therefore, NST with rich Lewis acid sites can be introduced as an efficient photocatalyst to activate O<sub>2</sub>. In order to further illustrate the role of  $O_2^-$  in the reaction, we added pbenzoquinone (an effective superoxide radical quencher [57]) to the reaction system, the conversion of BA over NST decreased significantly (Fig. S11). Therefore, superoxide radicals play an important role in this photocatalytic reaction. In addition, when methanol (an effective hole scavenger [58]) is added to the reaction system (Fig. S11), the photocatalytic activity of NST is remarkably suppressed. This result indicates that holes are also important for the reaction.

Previous work on photocatalysis oxidative coupling BA reported that ammonia gas was generated during the reaction [56]. Therefore, ammonium ions may exist in the reaction system. In order to verify the conclusion, we used Nessler reagent to measure the solution before and after the irradiation [59]. As shown in Fig. S12, the reacted solution turns to yellow by adding Nessler reagent. However, the color for the only N-benzyleneamine solution or initiative solution before irradiation does not change. This infers the presence of ammonium ions in the reaction, that is, ammonia gas is produced during the photocatalytic process. Furthermore, benzaldehyde was detected in the solution after the reaction by gas chromatography.

Based on the above analysis, a feasible reaction mechanism is proposed to explain the photocatalytic oxidation of BA to Nbenzyleneamine under visible light irradiation. Firstly, BA molecules are adsorbed and activated on Lewis acid sites on the surface of NST via the surface species -N···Bi-. The remaining Lewis acid



Fig. 8. UV/Vis DRS spectra of Bulk (1), Bulk absorbed BA (2), NST (3) and NST adsorbed BA (4).



**Fig. 9.** EPR spectra of the prepared samples with the presence of DMPO in the solvent of acetonitrile, Bulk in dark (1), NST in dark (2), Bulk under visible light (c), NST under visible light (d).

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**Scheme 1.** Schematic illustration proposed feasible reaction mechanism for selective oxidation of BA to N-benzyleneamine over the samples.

sites allow more O<sub>2</sub> molecules to be adsorbed and activated by forming the  $-Bi \cdots 0 - 0 \cdots Bi$  complexes. As shown in Scheme 1, two reaction pathways may exist in NST system. In pathway A, under visible light irradiation. direct surface charge transfer takes place from coordinated BA molecules to NST (ligand-to-metal) (Scheme 1A1). Simultaneously, excited electrons reduce oxygen molecules to  $O_2^-$ . What's more, since NST would generate photogenerated electrons and holes under visible light (pathway B). The adsorbed  $O_2$  molecules are also reduced to  $O_2^-$  by photogenerated electrons. At the same time, holes can abstract electrons from adsorbed BA molecules to yield BA cations (Scheme 1B1). Subsequently, the activated BA on NST would be deprotonated under the assistance of  $O_2^-$  (Scheme 1C), forming active intermediate species (Ph-CH=NH). Ph-CH=NH would produce benzaldehyde with water and release ammonia (Scheme 1D). The generated benzaldehyde further condenses with the free BA to produce N-benzyleneamine (Scheme 1E). Finally, releasing of Nbenzyleneamine from the surface of NST. The regeneration of Lewis acid sites on the surface of BiOCl sample would be reused to absorb BA and O<sub>2</sub> molecules achieving the reaction cycles. However, Bulk is only responsive to UV, its photocatalytic process is just performed as pathway A. Therefore, more Lewis acid sites and two pathways coexist in NST system, which contributes to the remarkable photocatalytic performance for the oxidative coupling of BA.

#### 4. Conclusion

In summary, ultrathin BiOCl nanosheets (NST) with the thickness about 1.5 nm has been successfully prepared as an efficient photocatalyst for the oxidative coupling of BA to Nbenzyleneamine. The larger surface area and ultrathin structure for NST result in rich OVs in it. The OV-induced localized states in NST could extend light adsorption to visible light and efficiently capture charge carriers to the enhanced photocatalytic activity. In addition, more Bi atoms in sublayer to be exposed as the Lewis acid sites can selectively adsorb and activate BA molecules and O2 molecules via the surface --N····Bi- and --Bi····O-O····Bi- coordination, respectively. The formed surface coordination species would further extend the visible light response. Simultaneously, the activated O<sub>2</sub> and BA molecules would be more easily converted into active species in the next photocatalytic process. Finally, a synergistic effect of surface coordination activation mediated photocatalysis was proposed to reveal why NST exhibits a significantly improved photocatalytic performance for the oxidation of BA. We believe that the present study of ultrathin BiOCl nanosheets with abundant Lewis acid sites will stimulate intensive exploration in

the design of efficient photocatalysts for green and universal photocatalysis applications.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.10.018.

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