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One-pot synthesis of three bismuth oxyhalides (BiOCl, BiOBr, BiOI) and their photocatalytic properties in three different exposure conditions

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Abstract: BiOCl, BiOBr, and BiOI have been synthesized by wet chemical route using bismuth nitrate (Bi(NO₃)₃.5H₂O) and potassium halides, KCl, KBr, and KI, using a mixture of de-ionized water and ethanol as the solvent. Synthesized samples were characterized by X-ray diffraction and high-resolution SEM to observe the crystal-line phase and crystallite size. Effective surface areas of the synthesized samples were estimated by Brunauer–Emmett–Teller studies. Photoactive properties of these samples were studied under three types of light exposure conditions viz. UV light from mercury vapour lamp, natural sunlight, and visible radiations from a 100-W incandescent tungsten filament. Degradation of methyl orange (MO) in aqueous media was estimated spectrophotometrically in visible range from the area under the curve with a peak at 464 nm. Kinetic constant for degradation reaction was calculated assuming the pseudo-first-order degradation mechanism. It was revealed that all the three samples show excellent degradation of MO in UV exposure with BiOCl as the most efficient photocatalyst in these radiations. BiOBr shows highest photodegradation performance among the three samples under natural sunlight exposure. Overall performance of the three photocatalyst samples is much better than the popular titanium dioxide photocatalyst.

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PUBLIC INTEREST STATEMENT
Air, water, and soil pollution is one among the serious issues of the twenty-first century as it is directly related to human health. The problem is seen as the side effect of societal development which we cannot stop, but effective corrective measures are desired to control pollution. Heterogeneous photocatalysis utilizing solar energy is the most economic way to tackle this problem. Several semiconductors, in bulk and nano forms, are being explored for the effective photocatalysis under sunlight to degrade the environmental pollutants. Until now, TiO₂ enjoyed the prime place due to cost and toxicity issues. But limited activity of TiO₂ under visible light is a major hindrance. Now, layered bismuth oxyhalides (BiOX; X = Cl, Br or I) are being explored and promising results have been reported. Research interests have shifted to develop modified BiOX to fight environmental pollution efficiently using freely available solar energy.
1. Introduction

During the last few decades, low-dimensional nanostructured materials have attracted special interest due to their novel properties and potential applications in photocatalysis, solar energy harvesting, electronics, and photonic devices (Ai, Ho, Lee, & Zhang, 2009; Byon & Choi, 2006; Cesano et al., 2008; Chang et al., 2010; Cheng, Huang, & Dai, 2014; Cheng, Huang, Qin, Zhang, & Dai, 2012; Cui & Lieber, 2001; Deng, Chen, Peng, & Tang, 2008; Fang, Huang, Yang, Wang, & Cheng, 2011; Henglein & Gutiérrez, 1983; Hoffmann, Martin, Choi, & Bahnemann, 1995; Kudo & Miseki, 2009; Li, Wang, Yao, Dang, & Li, 2011; Miller, Musgrave, Falconer, & Medlin, 2011; Peng, Chan, Meister, Zhang, & Cui, 2009; Pirkanniemi & Sillanpää, 2002; Sene, Zeltner, & Anderson, 2003; Xiong, Cheng, Li, Qin, & Chen, 2011; Ye et al., 2012; Yu, Yu, Fan, Wen, & Hu, 2010; Zhang, Ai, Jia, & Zhang, 2008; Zhang, Shi, et al., 2008; Zhu, Xie, Zheng, Yin, & Tian, 2002). As these novel properties are highly dependent on shape and size, the size and morphological control of nanostructured materials become increasingly important in nanoscience and nanotechnology. Nanostructures are extremely desirable in photocatalytic actions (Wang et al., 2006) because of their enhanced surface-to-volume and substrate–support ratios.

Nowadays, there is a strong demand for effective catalysts for the degradation of organic pollutants to clean the environment for a healthy living. Photocatalytic degradation of these pollutants over semiconductor surfaces, particularly oxide semiconductors, has attracted much attention to clean atmospheric air and water by degrading the organic pollutants present in them by photo-aided processes utilizing solar energy. Among various oxide semiconductors, TiO$_2$ has received much attention as a photocatalyst because of its biological and chemical inertness, strong oxidizing power, biocompatibility, non-toxicity, and long-term stability against photo and chemical corrosion. However, due to its relatively wide band gap (~3.2 eV), it can absorb only ultraviolet part of the spectrum, which is merely about 3–5% in the solar spectrum. Because of this inherent limitation, the abundant solar energy reaching the Earth surface cannot be utilized for the purpose. It should be noted that UV radiation by lamps or ozone production is expensive. Therefore, research is now focusing more on those photocatalysts which can be driven by solar radiation, i.e. light with a wavelength longer than 300 nm, generally between 400 and 700 nm. Attention has been devoted to explore and synthesize new materials that are capable of efficient generation and separation of photo-induced electron–hole pairs by absorption of visible light. But the search for visible light-driven photocatalysts with high efficiency and good stability is still the issue of leading investigation.

Bismuth oxyhalides BiOX (X = Cl, Br, I) are also being considered as visible light-active photocatalysts. Despite the wide energy band gap, these materials are presently being explored and modified for efficient performance under visible natural light for photocatalytic degradation of harmful organic compounds in air and water (Ai et al., 2009; Chang et al., 2010; Cheng et al., 2012, 2014; Deng et al., 2008; Fang et al., 2011; Li et al., 2011; Miller et al., 2011; Peng et al., 2009; Xiong et al., 2011; Ye et al., 2012; Yu et al., 2010; Zhang, Ai, et al., 2008; Zhang, Shi, et al., 2008; Zhu et al., 2002). Photocatalytic behavior of these materials is strongly dependent on the composition and microstructure of the compound. Various methods, viz. hydrolysis (Shi, Wang, Fan, Wang, & Ding, 2011; Wang, Huang, Lin, & Yang, 2008), hydrothermal (Kodama, Horiiuchi, & Watanabe, 1988; Robenau, 1985), solvothermal (Zhong, Ai, et al., 2008), microemulsion (Cheng, Huang, Wang, & Qin, 2013), and ionothermal (Zhang, Wen, Jiang, Li, & Yu, 2012), have been applied in the synthesis of BiOX (X = Cl, Br, I) nanostructured materials. These routes are either complex, requiring tight control over the synthesis parameters and/or use of a surfactant, or result in poor quality end product. Xiao et al. (2012) have synthesized oxygen-rich BiOX from B$_2$O$_3$ by the one-pot method, using strong acid (HNO$_3$), whereas Deng, Wang,
Peng, Wang, and Li (2005) have synthesized low-dimensional structures of bismuth oxyhalides from bismuth nitrate strictly controlling the synthesis parameters by autoclaving and with the help of surfactant, cetyltrimethylammonium bromide.

Hydrothermal synthesis has been extensively used to prepare bismuth oxyhalides due to its versatility and ability to control particle size, shape, and crystallinity by adjusting the hydrothermal treatment parameters. Hydrothermal synthesis generally takes place in alkaline aqueous solutions at high temperature (Deng et al., 2005). The basic environment of the alkaline aqueous solutions leads to varied composition and morphology of bismuth oxyhalides at elevated temperatures during synthesis (Deng et al., 2005). Jiang’s group has also reportedly performed hydrothermal synthesis under acidic conditions with favorable results (Wang & Li, 2003). Photocatalytic activity of the material synthesized by hydrothermal methods is reported to be lower than those synthesized by template- or emulsion-assisted methods. Ongoing research is yet to discover a general suitable synthesis method that produces materials with high photocatalytic performance. In this work a simple wet chemical route to synthesize BiOX (X = Cl, Br, I) with enhanced properties has been reported. Photodegradation ability of the synthesized materials was evaluated by estimating their degradation efficiency of methyl orange (MO) under UV and visible light exposure.

2. Experimental

2.1. Preparation of photocatalysts

In this work, five samples of each oxyhalide viz. BiOCl, BiOBr, and BiOI have been synthesized using five different solvent compositions prepared by mixing de-ionized water (s ≤ 10−6 Ω cm−1) and ethanol. These solvent compositions contained water:ethanol in ratios 10:90, 25:75, 50:50, 75:25, and 90:10. To synthesize the first sample of BiOCl, 100 ml of bismuth nitrate solution was prepared by dissolving 4.85gm of Bi(NO3)3·5H2O in the first solvent i.e. water:ethanol:10:90 and 50 ml of KCl solution was prepared by dissolving 0.75 g of KCl in the first solvent. Bi(NO3)3·5H2O solution is taken in a conical flask with a Teflon-coated bit placed on the magnetic stirrer and KCl solution in a burette was set to drop this solution into the conical flask. KCl solution was allowed to flow into the Bi(NO3)3·5H2O solution in the conical flask at 2.5 ml/min with continuous stirring. After complete addition of 50 ml KCl solution, 5 ml of 25% NH3 solution was added to maintain the pH of the mixture as 2.0 and stirring was further continued for 10 h to ensure completion of the reaction, i.e. for the precipitation of bismuth oxychloride. Resulting precipitates were collected by filtration on Whatman No. 1 filter paper and washed several times with de-ionized water for complete removal of undesired water-soluble products. Solid compound so obtained is subsequently dried at 80°C for 6 h in an electric oven under normal atmospheric conditions. The above procedure was repeated to synthesize four other samples of BiOCl using solvent compositions: water:ethanol as 25:75, 50:50, 75:25, and 90:10. Five samples each of BiOBr and BiOI were synthesized in the similar manner using aforesaid all five solvent compositions and KBr and KI as halogen salt solutions, respectively. KBr solutions were prepared by dissolving 1.19 g of KBr in a 50-ml solution and KI solution was prepared by dissolving 1.66 g of KI in a 50-ml solution.

2.2. Structural and basic characterization

Structural analysis of the synthesized material was carried out by power X-ray diffraction (XRD) recorded for 2θ values between 10° and 80° at a scan rate of 2 degrees per minute with Bruker D8 Advance X-ray diffractometer which uses Cu-Kα radiation (λ = 1.5418 Å) to probe the sample. The average crystallite size, in different samples, was estimated from the strongest XRD peak using Scherrer relation. Ultraviolet–visible light (UV–vis) absorption spectra of the solutions were recorded at room temperature on SHIMADZU UV-1601: UV–visible spectrometer. Selected area scanning electron microscopy studies are carried out on EVO-50 scanning electron microscope, equipped with an energy-dispersive X-ray spectroscopy (EDAX). Porosity and surface area investigations were performed to record BET/BJH curves for surface area and pore size analysis. Samples were degassed at 150°C for 5 h in N2 gas flow before investigating surface area at liquid nitrogen temperature (77 K).
2.3. Photocatalytic activity measurements

Photocatalytic activity of the synthesized samples was evaluated by studying degradation kinetics of MO in aqueous solution (0.02 mM) under UV light from Hg vapour lamp, visible light from a 100-W tungsten filament lamp, and natural sunlight. Fifty milligrams of the synthesized sample (BiOCl, BiOI, or BiOBr) was suspended in 200 ml of aqueous MO solution and exposed to respective radiations with constant stirring. Source of light was kept at sufficient distance away from the solution to avoid increase in temperature of the test solution by IR radiations from the source of light. About 2 ml of MO solution was taken out after different time durations of light exposure to estimate the remaining amount of MO in the solution. Amount of MO was estimated spectrophotometrically by recording the absorption spectra of the extracted solution in UV–visible range (200–800 nm) and the area under the peak at wavelength $\lambda = 464$ nm was monitored and related to the concentration of MO in the solution. Kinetic constant for the dye degradation reaction was calculated by assuming the pseudo-first-order mechanism for the degradation reaction as per relation $C = C_0 \exp (-kt)$, where $C_0$ and $C$ are the concentrations of MO in the solution before exposure and after exposure, respectively, for time duration “t” and “k” is the degradation reaction rate constant.

3. Results and discussion

Typical absorption curves of MO solutions exposed to light energy from three different sources for different durations are shown in Figure 1. Areas under the absorption peak at 464 nm (in the visible range) were related to the amount of MO present in the solution. We have recorded absorption spectra of our samples under three different exposure environments (UV, 100-W lamp, and natural sunlight). Assuming “$C_n$” as the initial concentration (before exposure) of MO dissolved in the solution, $\log (C_n/C_i)$ was calculated where $C_n = C_{i1}, C_{i2}, C_{i3}, \ldots$ etc. are the concentrations of MO remaining after 1, 2, 3, ... hours of light exposure. Slope of the plot between [−log ($C_n/C_i$)] vs. exposure time (hours), fitted to a straight line, is defined as the kinetic constant for the degradation reaction. Numerical value of the kinetic constant is indicative of the photocatalytic degradation power of the sample. MO degradation studies are carried out on five samples of each compound synthesized by taking five different mixtures of water and ethanol as the solvent, as described in the experimental section above. Highest photodegradation rates of the MO was observed for the sample synthesized with solvent containing water to ethanol ratio as 50:50, in the particular series of BiOX compound (Figure S1 of the supporting information). Further investigations were concentrated on these samples only, i.e. BiOCI, BiOBr, and BiOI samples were synthesized using equi-volume mixture of ethanol and water as the solvent.

Figures 2–4 show a plot for the kinetic constant of BiOCl, BiOBr, and BiOI samples under three different exposures i.e. UV, natural sunlight, and visible light from a 100-W incandescent electric lamp. Figure 5 is a comparison of the three samples under one particular type of exposure. It is clear from these plots that all the samples show highest photoactivity under UV exposure followed by the sunlight and light from 100-W electric lamp. Among different samples under UV exposure, highest photoactivity is exhibited by BiOCl followed by BiOBr and BiOI (BiOCl > BiOBr > BiOI), whereas in sunlight and 100-W electric lamp exposure, BiOBr exhibits higher activity than BiOCl or BiOI. Lowest photoactivity is observed in BiOCI in sunlight and 100-W electric lamp radiations. But all the samples exhibit significant photoactivity in sunlight or under a 100-W electric lamp, which is contrary to TiO$_2$ photocatalyst, which shows reasonable photoactivity only under UV exposure.

To evaluate the stability of the synthesized compounds, three samples from each compound viz. BiOCI, BiOBr, and BiOI were dispersed in distilled water separately in nine beakers (three beakers of each compound). These beakers were divided into three groups A, B, and C, containing three beakers, one from each compound. Group A was exposed to UV radiations from a Hg lamp, Group B was exposed to radiations from a 100-W electric lamp, and Group C was exposed to natural sunlight. Exposure was continued for 10 days with five hour a day (10:00 am to 3:00 pm for sunlight exposure). The compounds were collected from all the nine beakers by filtration and their photoactivities were evaluated again by their degradation efficiency of MO, as described above. Five to nine percent change in photoactivities of BiOCl and BiOBr was observed after the three types of exposure. BiOI
sample exposed to natural sunlight showed ~7% decrease in photodegradation ability, whereas about 12 and 21% decrease in photoactivity was observed in the BiOI samples exposed to a 100-W electric lamp and UV radiations, respectively. These studies showed that BiOI had a tendency to degrade particularly under UV light exposure.
Figure 6 shows XRD patterns of BiOCl, BiOI, and BiOBr synthesized by taking the solvent ratio as 50:50. These samples resulted in well-defined XRD patterns in all the three samples. XRD peaks from BiOCl sample appear at 2θ values: 12.1, 24.246, 26.0, 32.598, 33.6, 36.7, 41.0, 46.7, 49.8, 54.781, 55.2, 58.7, 60.548, 68.2, 75.1, and 77.6 which are assigned hkl values as 001, 002, 101, 110, 102, 003, 112, 200, 113, 104, 212, 220, 213, 214, and 006, respectively, according to JCPDS card No. 85-0861. XRD
peaks from BiOI sample appear at 19.3, 29.5, 31.44, 36.80, 39.2, 45.2, 49.931, 51.2, 55, 60.5, 65.2, 69.9, and 76.5, 2θ values with corresponding hkl values as 002, 012, 110, 013, 004, 020, 005, 114, 122, 115, 016, 025, and 017, respectively, as per JCPDS card No. 73-2062. BiOBr sample shows XRD peaks at 2θ values 10.82, 21.7, 25, 31.5, 32.82, 39.1, 44.5, 46.195, 46.815, 50.5, 56.016, 57, 61.7, 66.1, and 69.4 with hkl values as 001, 002, 101, 102, 003, 112, 004, 200, 113, 104, 114, 212, 105, and 204, respectively, according to JCPDS card No. 78-0348. Average value of crystallite size, calculated from Scherrer’s formula, was 24, 32, and 30 nm for BiOCl, BiOI, and BiOBr, respectively. No unidentified or second phase peaks were observed in the XRD pattern (Figure 6) of all the three compounds, this confirms that they are well crystallized and having single phase.
Selected area SEM micrograph of the three samples viz. BiOCl, BiOI, and BiOBr are presented in Figure 7. SEM pictures show layered structure in all the three samples. In BiOCl and BiOI samples, the layers are comprised of needle- and flake-like nanostructures. BiOBr crystallizes in the form of well-defined plates with round corners and variable dimensions. There are distinct differences in platelet/particle shape and size from the three bismuth oxyhalides. The lateral dimensions (length or breadth) of the flakes or plates are between 1 and 2 μ and thickness around 10 nm confirming very thin layers of the material which results in large effective surface area per gram of the material. Brunauer–Emmett–Teller (BET) studies have been carried out to calculate the effective surface area in the three samples confirm effective surface areas of 13.639 m²/g in BiOCl, 3.44 m²/g in BiOBr, and 6.307 m²/g in BiOI. These values are presented...
in Table 1. Overall, all the samples exhibit large surface areas, but variations within the samples are also evident. BiOCl showed highest surface area and BiOBr has shown minimum surface area. These observations are also supported by the SEM pictures (Figure 7). The large variation in the particle/crystallite size has been reported by various groups (Cheng et al., 2014; Deng et al., 2008; Deng et al., 2005; Geng, Hou, Lv, Zhu, & Chen, 2005; Jiang et al., 2010; Lei, Wang, Song, Fan, & Zhang, 2009; Li, Liu, Jiang, & Yu, 2011; Peng et al., 2009; Wu et al., 2010, 2011).

Table 1. BET analysis of the three samples; BiOCl, BiOI, and BiOBr

| Material | Slope   | Surface area (m²/gm) | Intercept  | Correlation coefficient | C constant |
|----------|---------|----------------------|------------|-------------------------|------------|
| BiOCl    | 188.517 | 13.639               | 6.682x10^1 | 0.967108                | 3.821      |
| BiOI     | 518.362 | 6.307                | 3.380x10^1 | 0.986445                | 16.338     |
| BiOBr    | 2231.105| 3.440                | 1.872x10^1 | 0.997312                | 12.916     |
EDAX curves for composition estimation for the three samples are shown in Figure 8 and results of EDAX investigations are summarized in Table 2. These studies reveal that all the samples are oxygen rich, whereas bismuth to halide composition is almost stoichometric (i.e. equal), except iodine which is smaller than bismuth in the respective sample. These studies revealed that all the three samples contained significant amount of carbon. To investigate the source of carbon in the samples, few samples with only distilled water as the solvent have been synthesized. EDAX analysis negated
The presence of carbon in this sample (Figure S2). This shows that the presence of carbon in these samples is from ethanol in the solvent and annealing temperature of 80°C is not sufficient for the removal of carbon from the sample.

The BiOX single crystalline material has a layered 2D structure, with symmetry of space groups P4/mmm/ and/or I4/mmm. They grow usually in the form of platelets with the c-axis normal to the platelets. Investigations have shown that they are isotropic along normal to the layers (Zhou, Ke, Li, & Lu, 2003). Each Bi atom is eight coordinated by four O atoms and four X (halogen) atoms in the form of an asymmetric decahedron (Ganesha, Arivuoli, & Ramasamy, 1993). Each atom (Bi, O, and X) occupies a special position with multiplicity 2. The faces of the decahedron are two rectangles (O–O–O–O, X–X–X–X, which are parallel to the (1 1 0) plane and eight isosceles triangles (four X–O–X and four O–X–O). The decahedra are linked to each other by a common O–X edge along the a and b axes. Regarding the coordination of O and X, each O atom is linked to four Bi atoms forming a tetragonal pyramid with the O atom at its apex; also each X atom forms tetragonal pyramid with the neighboring Bi atoms with X atom at its apex. These decahedra form layers along (0 0 1), which are connected by common O–X edges and neighboring layers of the decahedra, are connected by common O–O or X–X edges. The X atom is bonded with four Bi atoms in a planar square to form a pyramid and with its nonbonding (lone pair) electrons pointing to the other side of the square. The [BiOX] layers are stacked together by the nonbonding interactions (van der Waals) through the X atoms along c-axis. Therefore, the structure is not closely packed in this direction. When one photon excites an electron from X np states (n = 3, 4, 5 for Cl, Br, and I, respectively) to Bi 6p states in BiOX, the layered structure can provide the space large enough to polarize the related atoms and orbitals (Keramidas, Voutsas, & Rentzeperis, 1993). These internal electric fields in layered materials are considered to favor charge separation, which can subsequently induce redox reactions on the semiconductor surface and contribute to enhance the photocatalytic activity of these materials (Zhang, Liu, Huang, Zheng, & Wang, 2006; Zhao et al., 2013). The permanent static electric fields between [Bi2O2] and [X2] layers can work as accelerators for the separation of electron–hole pairs upon photoexcitation to increase photocatalytic efficiency of the material (Wang et al., 2013). This induced dipole can separate the hole–electron pair efficiently, enhancing photocatalytic activities. Further, the BiOX has an indirect transition band gap, so that the excited electron has to travel certain k-space distance to be emitted to the valence band (VB). This k-space varies with X (X = Cl, Br or I), and therefore different BiOX exhibit varying activities in the three lights.

In order for a photocatalysis process to occur, two principle criteria must be met: (1) absorption of solar irradiation and (2) effective separation of electron–hole pairs with little energy loss before they lose their input energy through recombination.

As a general rule, the photocatalytic activity of a semiconductor is closely related to the mobility of photo-generated charge carriers and the positions of the conduction band (CB) and VB in the photocatalyst (Jiang, Zhao, Xiao, & Zhang, 2012). In metal oxide photocatalysts, the VB is commonly composed of O 2p. However, the VB of materials containing Bi mostly consists of O 2p and Bi 6s hybrid orbitals and the CB consists of Bi 6p. It is reported that a broad VB increases the mobility of the photo-generated carriers (An et al., 2007). Bismuth-based photocatalysts exhibit this phenomenon because the Bi 6s orbital is largely dispersed, which is more beneficial to increase in the mobility of the photo-generated carriers (Jiang et al., 2012). There are reports that the Bi–O sites in Bi3+-doped TiO2 acted as electron traps in the photocatalytic reaction (He & Gu, 2006). Therefore, materials containing Bi are potentially highly active photocatalysts.

| Table 2. Elemental composition in different samples by EDAX analysis |
|---------------------------------|----------------|-----------|
| BiOCl atomic ratio of different elements | BiOIC atomic ratio of different elements | BiOBr atomic ratio of different elements |
| Bi | Cl | O | C | Bi | I | O | C | Bi | Br | O | C |
| 19.16 | 17.36 | 27.64 | 35.84 | 26.40 | 18.90 | 30.36 | 24.34 | 25.17 | 24.38 | 26.11 | 24.34 |
4. Conclusions
Solvent used in the synthesis of three bismuth oxyhalides viz. BiOCl, BiOBr, and BiOI plays an important role to tune the photocatalytic activity of the compound. It is possible to induce visible light photoactivity in the three materials by suitable choice of the solvent. This property is very important for the decontamination of air and water from organic pollutants by utilizing solar energy. Highest photoactivity exhibited by a particular bismuth oxyhalide depends upon the nature of radiations used to excite the compound. BiOCl shows highest photoactivity under UV exposure, at the same time, BiOBr shows highest activity under visible light exposure. Induction of visible light activity in BiOCl, a wide energy band gap material (Eg > 3.4 eV), is attributed to the layered morphology with nanostructures. These nanostructures are helpful in effective separation of the photo-generated charge carriers to minimize recombination losses. All the materials are stable and can replace titanium oxide where visible light photoactivity is desired and biocompatibility issues are not important.

Supplementary material
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References
Ai, Z. H., Ho, W., Lee, S., & Zhang, L. Z. (2009). Efficient photocatalytic removal of NO in indoor air with hierarchical bismuth oxybromide nanoplate microspheres under visible light. Environmental Science & Technology, 43, 4143–4150.

http://dx.doi.org/10.1021/es9004366

An, H., Du, Y., Wang, T., Wang, C., Hoo, W., & Zhang, J. (2007). Formal recycling of e-waste leads to increased exposure to toxic metals: An occupational exposure study from Sweden. Rare Metals, 27, 243–251.

Byon, H. R., & Choi, H. C. (2006). Network single-walled carbon nanotube–field effect transistors (SWNT-FETs) with increased Schottky contact area for highly sensitive biosensor applications. Journal of the American Chemical Society, 128, 2188–2189.

http://dx.doi.org/10.1021/ja056897n

Cesano, F., Bertarione, S., Damin, A., Agostini, G., Ussiglio, S., Vitillo, J. G., ... Zacchini, M. A. (2008). Oriented TiO2 nanostructured pillar arrays: Synthesis and characterization. Advanced Materials, 20, 3342–3348.

http://dx.doi.org/10.1002/adma.200700360

Chang, X. F., Huang, J., Cheng, C., Sui, Q., Sha, W., Li, G. B., ... Yu, G. (2010). BiOX (X=Cl, Br, I) photocatalysts prepared using NaBiO3 as the Bi source: Characterization and catalytic performance. Catalysis Communications, 11, 460–464.

http://dx.doi.org/10.1016/j.catcom.2009.11.023

Cheng, H., Huang, B., & Dai, Y. (2014). Engineering BiOX (X = Cl, Br, I) nanostructures for highly efficient photocatalytic applications. Nanoscale, 6, 2009–2026.

Cheng, H., Huang, B., Wang, Z., Qin, X. (2011). One-pot miniemulsion-mediated route to BiOBr hollow microspheres with highly efficient photocatalytic activity. Chemistry - A European Journal, 17, 8039–8043.

http://dx.doi.org/10.1002/chem.201102297

Cheng, H. F., Huang, B. B., Qin, X. Y., Zhang, X. Y., & Dai, Y. (2012). A controlled anion exchange strategy to synthesize Bi2S3 nanocrystals/BiOCl hybrid architectures with efficient visible light photocatalytic activity. Chemical Communications, 48, 97–99.

http://dx.doi.org/10.1039/c1cc15487g

Cui, Y., & Lieber, C. M. (2001). Functional nanoscale electronic devices assembled using silicon nanowire building blocks. Science, 291, 851–853.

http://dx.doi.org/10.1126/science.291.5505.851

Deng, H., Wang, J., Peng, Q., Wang, X., & Li, Y. (2009). Controlled hydrothermal synthesis of bismuth oxyhalide nanobelts and nanotubes. Chemistry - A European Journal, 15, 6519–6524.

http://dx.doi.org/10.1002/chem.200900428

Deng, Z. T., Chen, D., Peng, B., & Tang, F. Q. (2008). From bulk metal Bi to two-dimensional well-crystallized BiOX (X = Cl, Br) micro- and nanostructures: Synthesis and
its enhancement of BiOCl nanosheets' photocatalytic activity. Journal of Materials Chemistry, 22, 8354–8360. 
http://dx.doi.org/10.1039/c2jm16829d

Yu, C., Yu, J. C., Fan, C. F., Wen, H. R., & Hu, S. J. (2010). Synthesis and characterization of Pt/BiOCl nanoplate catalyst with enhanced activity under visible light irradiation. Materials Science and Engineering: B, 166, 213–219. 
http://dx.doi.org/10.1016/j.mseb.2009.11.029

Zhang, D., Wen, M., Jiang, B., Li, G., & Yu, J. (2012). Ionothermal synthesis of hierarchical BiOBr microspheres for water treatment. Journal of Hazardous Materials, 211–212, 104–111. http://dx.doi.org/10.1016/j.jhazmat.2011.10.064

Zhang, J., Shi, F. J., Lin, J., Chen, D. F., Gao, J. M., Huang, Z. X., ..., Tang, C. C. (2008). Self-assembled 3-D architectures of BiOBr as a visible light-driven photocatalyst. Chemistry of Materials, 20, 2937–2941. 
http://dx.doi.org/10.1021/cm7031898

Zhang, K. L., Liu, C. M., Huang, F. Q., Zheng, C., & Wang, W. D. (2006). Study of the electronic structure and photocatalytic activity of the BiOCl photocatalyst. Applied Catalysis B: Environmental, 68, 125–129. 
http://dx.doi.org/10.1016/j.apcatb.2006.08.002

Zhang, X., Ai, Z., Jia, F., & Zhang, L. (2008). Generalized one-pot synthesis, characterization, and photocatalytic activity of hierarchical BIOX (X = Cl, Br, I) nanoplate microspheres. Journal of Physical Chemistry C, 112, 747–753. 
http://dx.doi.org/10.1021/jp077471t

Zhao, K., Zhang, L., Wang, J., Li, Q., He, W., & Yin, J. J. (2013). Surface structure-dependent molecular oxygen activation of BiOCl single-crystalline nanosheets. Journal of the American Chemical Society, 135, 15750–15753. 
http://dx.doi.org/10.1021/ja4092903

Zhou, S. X., Ke, Y. X., Li, J. M., & Lu, S. M. (2003). The first mesostructured bismuth oxychloride synthesized under hydrothermal condition. Materials Letters, 57, 2053–2055. 
http://dx.doi.org/10.1016/S0167-577X(02)01138-2

Zhu, L. L., Xie, Y., Zheng, X. W., Yin, X., & Tian, X. B. (2002). Growth of compound Bi III-VI A-VII A crystals with special morphologies under mild conditions. Inorganic Chemistry, 41, 4560. http://dx.doi.org/10.1021/ic025527m

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