New type of \([\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3\cdot 1.5\text{H}_2\text{O}\) sheets photocatalyst with high photocatalytic activity on degradation of phenol

Yuxiao Yang\(^{a,1}\), Huoyan Liang\(^{a,1}\), Na Zhu\(^{a,1}\), Yaping Zhao\(^{c,*}\), Changsheng Guo\(^{b,*}\), Lu Liu\(^{a,*}\)

\(^{a}\) College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China \\
\(^{b}\) Department of Environmental Science, East China Normal University, Shanghai 200062, China \\
\(^{c}\) State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

**Highlights**

- Novel \([\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3\cdot 1.5\text{H}_2\text{O}\) sheets photocatalyst was synthesized and characterized.
- The catalyst exhibited better photocatalytic effects superior to that of classic TiO\(_2\) P25.
- Photodegradation mechanism was direct oxidation/reduction product of phenol by HO\(_2\).

**Article info**

Article history:
Received 25 March 2013
Received in revised form 19 June 2013
Accepted 20 June 2013
Available online 14 August 2013

Keywords:
[\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3\cdot 1.5\text{H}_2\text{O}
Phenol
UV illumination
Photocatalysis

**Abstract**

A new type of \([\text{Bi}_6\text{O}_6(\text{OH})_3](\text{NO}_3)_3\cdot 1.5\text{H}_2\text{O}\) sheets photocatalyst was synthesized via a hydrothermal route. The photocatalytic properties were characterized by SEM, TEM, XRD and UV spectroscopy. It exhibited slightly better photocatalytic activity on phenol degradation than that of classic TiO\(_2\) P25 under UV illumination. Hydroquinone, catechol, resorcinol, and benzoquinone were identified as photodegradation intermediates. It has the advantages of high effective photodegradation efficiency and easy separation properties.

**1. Introduction**

Various contaminants such as azo dyes, organochlorine and aromatic hydrocarbons in natural water environments have been detected. At present, some promising technologies such as biological methods (Fukuda et al., 2001; Kang and Kondo, 2002; Xuan et al., 2002; Fent et al., 2003) have been used for eliminating organic pollutants. Highly effective treatment methods are necessary for transforming organic pollutants into CO\(_2\) and water. Owing to mineralization of organic substances, advanced oxidation processes (AOPs) have drawn great attention during the last two decades. AOPs have been studied to alleviate the deterioration of natural environments created by toxic pollutants. In AOPs, the metal oxide TiO\(_2\) is often used as a catalyst. For example, TiO\(_2\) nanoparticles (Kong et al., 2011; Tachikawa et al., 2011), nanotubes (NTs) (Macak et al., 2007), nanobelts (Zhou et al., 2011), nanosheets (Yang et al., 2009) and mesosponge layers (Lee et al., 2010), have been explored for photocatalytic applications. The unique photocatalytic properties of TiO\(_2\) have attracted increasing interest (Fujishima et al., 2008).

Very recently, 3D ordered TiO\(_2\) assemblies of NTs have arisen great attention (Zheng et al., 2009; Liu et al., 2010), and a few materials have been synthesized and applied in mineralization of endocrine disrupting chemicals (Liu et al., 2008; Guo et al., 2010). The advantages of the microspheres are: (1) there are high surface-to-volume ratios with effective prevention of further aggregation of the nanoparticles, so as to retain high catalytic activity and (2) due to the energy difference between the lowest unoccupied and highest occupied molecular orbitals, size-quantized, nanometer-sized semiconductor particles have higher redox potentials as a result of the increase in band-gap energy (Liu et al., 2008). Although 3D microsphere catalysts have been improved, it is still difficult for both nanomaterials and water to be separated after water treatment. Therefore synthesis of new catalysts is necessary to achieve highly effective photodegradation and easier separation.

In the present paper, a facile hydrothermal method was applied to synthesize a new type of photocatalyst, bulk \([\text{Bi}_6\text{O}_6(\text{OH})_3]\)
(NO₃)₂·1.5H₂O sheets, which comprised tooth meshing side faces. The preparation method is simple and mild, and no templates were used during the whole synthetic route. The catalyst was used for the photocatalytic degradation of phenol, a typical organic compound. The degradability and degradation kinetics including the reaction products were identified by HPLC–MS analysis. The degradation intermediates/products were further applied to investigate the reaction pathways.

2. Materials and methods

2.1. Materials

All chemicals were of analytical grade and used as received without further purification. The [Bi₆O₆(OH)₃(NO₃)₃]·1.5H₂O catalysts were synthesized via a hydrothermal process. In a typical preparation of the [Bi₆O₆(OH)₃(NO₃)₃]·1.5H₂O sample, 0.485 g of Bi(NO₃)₃·5H₂O was dissolved in 20 mL of distilled water, and the resulting solution was stirred for 20 min. Afterward, all was transferred to a 30 mL Teflon-lined autoclave, which was filled with water to 80% of its total volume. The autoclave was then heated at 180 °C for 12 h, and it was allowed to cool to room temperature. The product in the autoclave was collected, washed with deionized water and absolute ethanol, and dried at 80 °C for 2 h. The dried samples were then stored for further use (sample A). To study the influence of reactant concentration on morphologies, 0.2 and 0.4 g Bi(NO₃)₃·5H₂O were respectively added into the system while keeping other conditions unchanged. The obtained products were denoted as sample B and sample C.

2.2. Sample characterization

XRD analysis was carried out using an X-ray diffractometer (Model D/MAX2500, Rigaka) with Cu Kα radiation (λ = 1.54056 Å). The morphology of the as-prepared products was characterized by scanning electron microscopy (SEM, Hitachi-530, SEM/EDX JEOL JSM-6700F) and transmission electron microscopy (TEM, JEOL-2010, operating voltage of 200 kV). The UV–Vis diffuse reflectance spectra (DRS) were measured by Shimadzu UV-3600 UV–Vis spectrophotometer.

2.3. Photocatalytic activity evaluation

The photocatalytic activity of the samples was monitored through the degradation of phenol under UV (300 W Hg lamp) in a cylindrical quartz reactor with water circulation facility. 0.2 g photocatalyst and 200 mL phenol solution with the initial concentration of 10 mg L⁻¹ were added into the reactor and stirred in dark for 30 min to achieve adsorption–desorption equilibrium. The pHs of reaction solutions without adjusting pH were 5.74 and reaction was performed at 20 ± 1 °C. The parallel experiments were done with the RSD less than 5%. Then the light was turned on, and about 3 mL aliquot of the reaction solution was taken at time interval of 15 min during the experiment. The solution was filtrated through 0.45 μm water filter, and the concentration of phenol was evaluated at the wavelength of 270 nm with a UV–Vis spectrophotometer (UV2550, Shimadzu). Total organic carbon (TOC) was measured on a Shimadzu TOC-V CPH analyzer.

The intermediates formed during the photocatalytic process were monitored by HPLC/MS (Agilent 6410 triple quadrupole) equipped with an electrospray ionization source (ESI) in negative ionization mode. MS spectra were acquired using a selective ion monitoring mode with a dwell time of 200 ms and the scan range m/z was detected from 50 to 300. The HPLC separation was performed using an Agilent 1200 series (Palo Alto, CA, USA) equipped with an Agilent Zorbax Eclipse XDB-C18 column (2.1 × 100 mm, 3.5 μm). During the sample analysis, the column was maintained at 30 °C. The intermediates were detected in an isocratic elution program. Methanol/water = 40:60 (v/v) were used as mobile phase, the injection volume was 10 μL, and flow rate was set at 0.2 mL min⁻¹.

3. Results and discussion

3.1. Properties of the catalyst

XRD was used to characterize the phase structure of the obtained products. It can be seen from Fig. 1a that the XRD pattern is in conformity with tetragonal [Bi₆O₆(OH)₃(NO₃)₃]·1.5H₂O (a = b = 3.818 Å, c = 17.149 Å, JCPDS: 53-1038). No characteristic peak was observed for other impurities such as Bi₂O₃, Bi(NO₃)₃, or Bi, which indicates that pure crystalline [Bi₆O₆(OH)₃(NO₃)₃]·1.5H₂O was formed via the hydrothermal process. In Fig. 1a, it
can also be seen that (008), and (0012) facets show stronger diffraction peaks, and the relative diffraction intensities of either (008)/(102) or (0012)/(102) are unusually higher than the corresponding conventional values (JCPDS: 53-1038). Fig. 1b shows UV–Vis optical absorption properties of the prepared catalysts. Transmission measurements were performed on colloidal dispersions in ethanol that were translucent brown in color (inset, Fig. 1b). The solutions exhibit continuous absorption across the UV–Vis spectrum with increasing absorption near the UV region. For the sample behaving like a bulk semiconductor, the absorption coefficient $a$ can be described by the relationship $a \propto \frac{1}{\text{photon energy}} h v$. This relationship is valid close to the band gap edge where the single parabolic band approximation holds. An estimate of the band gap ($E_g$) of the sample can also be obtained from the intercept of this plot. The sample exhibits a clear region of linearity in $(a h v)^{0.5}$ vs $h v$, and an estimated $E_g \approx 3.1$ eV (400 nm), indicating that the catalyst can absorb UV radiation.

Low magnification SEM observations show that the as-obtained [Bi$_6$O$_6$(OH)$_3$]$_3$(NO$_3$)$_3$·1.5H$_2$O samples are composed of many sheet-like architectures ranging from 3.9 to 10.4 μm in diameter (Fig. 2a). High magnification SEM images reveal that [Bi$_6$O$_6$(OH)$_3$]$_3$(NO$_3$)$_3$·1.5H$_2$O sheets are built on the tooth meshing side face with thickness from 0.6 to 3.5 μm (Fig. 2b and c). Fig. 2d shows a typical TEM image of [Bi$_6$O$_6$(OH)$_3$]$_3$(NO$_3$)$_3$·1.5H$_2$O sheet-based superstructures. The high-resolution TEM image from the edge portion of the superstructure shows the monocrystalline structure (Fig. 2e). The distances of adjacent lattice fringes, measured as 1.4 Å, are the interplanar distances of [Bi$_6$O$_6$(OH)$_3$]$_3$(NO$_3$)$_3$·1.5H$_2$O (008) facets, in agreement with the literature value of the (008) d-space (JCPDS Card No. 53-1038).

3.2. Photodegradation of phenol

The photocatalytic activity of [Bi$_6$O$_6$(OH)$_3$]$_3$(NO$_3$)$_3$·1.5H$_2$O sheets, and of P25 TiO$_2$ on the degradation of phenol was investigated. The results are presented in Fig. 3a. The absorption peaks of the phenol molecule, especially the sharp peak at 268 nm, the characteristic
peaks decreased gradually with the exposure time. Also, the effects of catalyst loading on the photodegradation rate of phenol can be examined, so the characteristic absorption of phenol at 268 nm was chosen as the monitored parameter for the photocatalytic degradation process. No detectable degradation of phenol was observed without \( [\text{Bi}_6\text{O}_6\text{(OH)}_3\text{)(NO}_3\text{)}_3\text{.1.5H}_2\text{O} \) in the dark condition. For the \( [\text{Bi}_6\text{O}_6\text{(OH)}_3\text{)(NO}_3\text{)}_3\text{.1.5H}_2\text{O} \) samples, adsorption was below 4% over the initial 1 h pre-equilibration period carried out in the dark, indicating that adsorption did not contribute to the observed phenol removal. The initial concentration was taken to be 10 mg L\(^{-1}\) of phenol in all cases. The catalyst dose corresponding to a suspension concentration of 0.5 mg L\(^{-1}\) was selected as the optimal amount of photocatalyst for the following experiments. The removal efficiency of phenol dramatically increased in the presence of \( [\text{Bi}_6\text{O}_6\text{(OH)}_3\text{)(NO}_3\text{)}_3\text{.1.5H}_2\text{O} \) sheets suspension: 99.7% removal of phenol was achieved after 60 min. Fig. 3b shows the observed decrease of TOC. TOC decreased comparably in the reaction with \( [\text{Bi}_6\text{O}_6\text{(OH)}_3\text{)(NO}_3\text{)}_3\text{.1.5H}_2\text{O} \) sheets as the catalyst (95% in 5 h) rather than in the reactor using P25 TiO\(_2\) nanoparticles as the catalyst (90% in 5 h).

The discrepancy shown in Fig. 3 seems to suggest that phenol degradation was a little more complete with \( [\text{Bi}_6\text{O}_6\text{(OH)}_3\text{)(NO}_3\text{)}_3\text{.1.5H}_2\text{O} \) sheets as the catalyst. Meanwhile, the possibility of reusing the catalyst was explored in this work. Experimental results demonstrated that the recycled catalysts could still achieve successful removal for phenol. As we all know, P25 is difficult to be separated from the degradation system, which greatly hinders its reuse. In contrast, \( [\text{Bi}_6\text{O}_6\text{(OH)}_3\text{)(NO}_3\text{)}_3\text{.1.5H}_2\text{O} \) owing to its large particle size, can settle naturally from the suspension within 1 min without centrifugation or filtration, which is beneficial for reuse. Influence of \( \text{Bi(NO}_3\text{)}_3\text{.5H}_2\text{O} \) amounts on the photocatalytic activity was also investigated.

### 3.3. Influence factors of the photodegradation

Several factors may influence the photocatalytic activity of the catalyst, such as the bulk or on the surface, with faster kinetics than surface redox reactions, results in lower quantum efficiency and it is a major limitation to photocatalytic activity (Fu and Zhang, 2008). The influence of initial phenol concentration (\( C_0 \)) on the photocatalytic rate was investigated and the results are shown in Fig. 4. With changing \( C_0 \) from 5 to 20 mg L\(^{-1}\), the plots of \( \ln(C_0/C) \) vs irradiation time (\( t \)) exhibited a nearly straight line. The determined reaction rate constants (\( k \)) were 0.063, 0.055 and 0.019 min\(^{-1}\), respectively. It can be seen that the initial concentration of phenol has a significant effect on the degradation rate. The rate constant of photodegradation of phenol is faster when the initial concentration is lower.

The phenol concentration was 5 mg L\(^{-1}\) in the photo-oxidation system and the degradation behaviour of the phenol was examined by the addition of 2-propanol, a well known scavenger of \( \cdot\text{OH} \) radicals (Li et al., 2004) to monitor the active radicals produced during the photodegradation process seen in Fig. 5a. 67% of the phenol was degraded, so the photocatalytic activity was slightly suppressed by the addition of the hydroxyl radical scavenger...
ger isopropanol, while it was significantly retarded by KI, which is a well known scavenger of hole and superficial hydroxyl radical on the catalyst (Palominos et al., 2008). Only 21% of phenol was degraded with the presence of KI. So we can deduce that the holes rather than the hydroxyl radicals are the main active species to oxidize the pollutants for \([\text{Bi}_6\text{O}_6(\text{OH})_3(\text{NO}_3)_3]_{1.5}\text{H}_2\text{O}\) as photocatalysts.

### 3.4. Photodegradation mechanism

To understand the effect of oxygen, the photocatalytic reactivity in presence/absence of dissolved oxygen should be studied. Phenol photolysis could be carried out with continuous N_2-sparging and thus in a stricter anaerobic condition because phenol is non-volatile. The result is shown in Fig. 5B. Under the anaerobic suspension, the photodegraded rate of phenol was largely inhibited; only 34% phenol was degraded. The presence of oxygen is important, and its effect is to primarily act as an efficient e\(^{-}\)/h\(^{+}\) trap, leading to the generation of O\(_2\) and preventing the recombination of e\(^{-}\) and h\(^{+}\). So the O\(_2\) radicals are the other active species involved into \([\text{Bi}_6\text{O}_6(\text{OH})_3(\text{NO}_3)_3]_{1.5}\text{H}_2\text{O}\) photocatalysis. The reaction possibly includes the following process:

\[
\frac{1}{2}\text{Bi}_6\text{O}_6(\text{OH})_3\left(\text{NO}_3\right)_3_{1.5}\text{H}_2\text{O} + h\nu \rightarrow h^{+} + e^{-} \quad (1)
\]

\[
e^{-} + \text{O}_2 \rightarrow \text{O}_2^{-} \quad (2)
\]

h\(^{+}\) or hydroxyl radicals + Phenol → degradation products \(3\)

The photocatalytic oxidation of phenol involves complicated processes. It has been demonstrated that the photocatalytic process with \([\text{Bi}_6\text{O}_6(\text{OH})_3(\text{NO}_3)_3]_{1.5}\text{H}_2\text{O}\) is energetically favorable for the decomposition of phenolic compounds, and two types of oxidizing species—positive holes and hydroxyl radicals are involved in the transformation of aromatic compounds in oxygenated aqueous \([\text{Bi}_6\text{O}_6(\text{OH})_3(\text{NO}_3)_3]_{1.5}\text{H}_2\text{O}\) suspensions. The HPLC–ESI–MS mass spectrometry chromatogram (Fig. 6) indicated the organic intermediates of phenol upon photocatalytic oxidation by \([\text{Bi}_6\text{O}_6(\text{OH})_3(\text{NO}_3)_3]_{1.5}\text{H}_2\text{O}\). These intermediates were further identified based on the detected specific molecular ions and mass fragment peaks, together with the HPLC–MS library data. Four main product ions at \(m/z\) 109 (A), \(m/z\) 217 (B), \(m/z\) 154 (C) and \(m/z\) 138 (D), were observed in the average mass spectra as shown in Fig. 6. The product ions are identified as the deprotonated molecules of intermediates of phenol degradation. Herein, four main aromatic intermediates/products were formed in the initial stage. They underwent further photocatalytic oxidation and formed aliphatic acids by ring cleavage. Finally, they were completely degraded to...
CO₂ and H₂O. Thus, due to the fast oxidation of the intermediates, it is easy to conclude that the life spans of the intermediates formed at different stages of the reaction were short. Other intermediates were not identified because of their low concentration in the reaction mixture.

Recently, several groups have studied the organic byproducts generated during the degradation of phenol by traditional TiO₂ photocatalyst. According to previous reports, the main intermediates generated during the degradation of phenol by the Fenton reagents, photocatalysis and many other advanced oxidation processes are hydroquinone, catechol, resorcinol and benzoquinone (Nagaveni et al., 2004; Zazo et al., 2006; Liu et al., 2008; Silva and Faria, 2009), which are mainly the oxidation product by HO· an nonselective active species with strong oxidation ability for organic degradation. Moreover, hydroquinone can be produced without the presence of HO· (Iliev et al., 2002). Phenol can be oxidized to benzoquinone or para-benzoquinone under natural conditions by O₂, then reduced to hydroquinone or catechol by O₂, the role of O₂ was confirmed by the N₂ purging experiment. P-benzoquinone is a kind of more common compound compared with o-benzoquinone. During the degradation of phenol, p-benzoquinone rather than o-benzoquinone is synthesized according to previous literature. In this work, the product A (m/z 109) and product B (m/z 217) elute at the early time, which means higher polarity than other intermediates, so we deduce that catechol rather than hydroquinone is formed in the photocatalytic process. The intermediate catechol (A) was the direct oxidation/reduction product of phenol by HO·/O₂. Two catechol molecules link together to form B under the action of holes, and a similar product was mentioned in a former study (liu et al., 2008). Afterwards, the connection of two benzene rings was unlocked and CO₂ was added to the benzene ring to form C.

Afterwards, ring cleavage reaction takes place to form fatty acids. So we believe that the holes and O₂ are two main active species, only small part of HO· exist, the result is consistent with the radical scavenger experiments or experiments of reactivity. Reactive pathways of phenol photodegradation are proposed in Fig. 7. In fact the reaction pathway is not sequential, the intermediates maybe formed in a crossed way.

4. Conclusions

Novel [Bi₆O₆(OH)₃(NO₃)₃]·1.5H₂O sheets photocatalyst was synthesized and characterized, which was suitable to mineralize organic pollutants in water. This catalyst exhibited comparable photocatalytic effects on phenol degradation with that of classic TiO₂ P25, excepting easily separation property. Photodegradation intermediates were identified and photodegradation mechanism was elucidated as the direct oxidation product of phenol by HO· and holes.

Acknowledgment

This work was supported by 2011 Science Foundation of Tianjin (No. 11JCYZC24800), China–US Center for Environmental Remediation and Sustainable Development, and the National Science Foundation of China (No. 21271108).

References