Two-Dimensional Bi₂WO₆ Nanosheets as a Robust Catalyst toward Photocyclization

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Supporting Information

ABSTRACT: The present work describes the improved photocatalytic activity of cetyl trimethylammonium bromide (CTAB)-assisted Bi₂WO₆ (CBTH) toward the synthesis of bioactive benzazoles. X-ray diffraction analysis of CBTH suggests that crystal growth has occurred along the (200) plane, whereas field-emission scanning electron microscopy images confirm two-dimensional rose bud morphology and high-resolution transmission electron microscopy analysis suggests the formation of thin nanosheets possessing an orthorhombic structure. Temperature-programmed desorption of ammonia and Py-IR measurements indicate substantial acidity with the generation of Brønsted acid sites on the surface of CBTH. It is observed that the catalytic activity is retained up to five consecutive cycles with marginal decrease in % yield. Such a feature can be ascribed to the photostability of the photocatalyst even after continuous exposure to light, implying that the surface active sites remained unaltered as evident from the X-ray photoelectron spectroscopy analysis of pre- and post-characterization of CBTH. Moreover, decrease in the surface hydroxyl groups after five catalytic cycles also accounts for the generation of enhanced Brønsted sites owing to the presence of Bi−O on the surface of CBTH. It exhibits better catalytic activity as compared to other photocatalysts employed for the synthesis of benzazoles. Thus, CBTH serves as a robust photocatalyst for the facile synthesis of these heterocycles in a sustainable manner.

INTRODUCTION

Photocatalysis is a process that involves effective utilization of light for various applications such as environmental remediation, solar energy absorption, H₂ generation, sequestering of CO₂, biomass conversion, and green synthesis of commodity chemicals. This phenomenon is manifested by a photocatalyst that efficiently absorbs the radiation, thereby generating an electron–hole pair which is responsible for the oxidation or reduction of substrates in an eco-friendly manner. Various semiconductor-based photocatalysts have been explored for this purpose with major emphasis on the utilization of their potentiality under visible light. For example, TiO₂ is one of the most promising photocatalysts that has been employed for photocatalytic processes including organic transformations. Primarily, photocatalysis of organic substrates is a key step in light-driven photochemical transformations using semiconductor-based photocatalysts that efficiently bring about chemical conversions with high selectivity. Benzazoles are one such chemical moiety that have been synthesized via a photochemical route with excellent yields under either UV or visible light.

Classically, azoles are synthesized by the condensation of aryl aminophenol/α-diamine/aminothiophenol with acids or aldehydes in an oxidizing atmosphere. Although these methodologies are effective, serious environmental concerns such as generation of secondary waste, use of hazardous reagents, and tedious workups have restricted their potential applicability at the industrial scale. Catalytic processes have gained prominence owing to their effectiveness, selectivity, and sustainability. Among them, heterogeneous catalysis is found to be a viable alternative that can overcome lacunas of both conventional and homogeneous catalytic routes. One of the offshoots of the heterogeneous catalyst focuses on the absorption of light via the photocatalytic process involving a photocatalyst that efficiently transfers the absorbed energy for organic conversions. For example, various homogeneous photocatalysts have been explored for the synthesis of heterocycles under visible light that has resulted in moderate to excellent yields, although catalyst separation and its successive usage are some of the...
demerits. On the other hand, heterogeneous photocatalysts have recently been considered as the better alternative that can overcome these shortcomings. TiO$_2$, a prominent, UV-active, and environmental benign photocatalyst, yielded substituted benzimidazoles using nitroaniline and aldehyde; however, the reaction proceeds under UV light and the yields are comparatively poor. Doping of noble metals such as Au, Ag, and Pt shifts the band gap in the visible light which is beneficial for the preparation of substituted benzazoles. Nanocomposites, such as Pt/TiO$_2$, Ag/TiO$_2$, and Au/TiO$_2$, exhibit better photocatalytic activity for the synthesis of benzimidazoles and benzothiazoles. The potentiality of metal chalcogenides such as CdSe, CdTe, ZnS, CdS etc. is well-explored as photocatalysts in various reactions such as dye degradation, water splitting, and organic transformations. For example, Das et al. demonstrated that CdS nanospheres can be effectively used for the synthesis of 2-substituted benzothiazoles.

Azoles are a key moiety in the core structure of many pharmacophoric molecules that act as a precursor for a variety of drugs exhibiting a wide range of biological activities such as anticancer, bactericidal, fungicidal, analgesic, and antiviral properties. Some of these derivatives possess therapeutic usages against cardiovascular diseases. Among azoles, imidazoles are common scaffolds for different biomolecules such as biotin, a key amino acid histidine, histamine, the pilocarpine alkaloids, and other alkaloids, whereas 5,6-dimethyl-1-(α-D-ribofuranosyl) benzimidazole is an important biological building block of vitamin B$_1$. Esomeprazole and lansoprazole are well-known derivatives of benzimidazoles, which act as proton-pump inhibitors whose mode of action involves pronounced and long-lasting decrease in gastric acid production. Besides the medicinal/biological applications, benzimidazole derivatives such as 2-methylbenzimidazole and 2-mercaptopbenzimidazole have also been used as corrosion inhibitors. Some of the derivatives of benzothiazoles act as enzyme inhibitors and plant growth regulators. Benzimidazoles and benzothiazoles are also used in fluorescent materials such as organic light-emitting diodes.

Considering these aspects, an attempt has been made toward the visible-light-induced facile synthesis of benzimidazoles and benzothiazoles using robust CTAB-assisted Bi$_2$WO$_6$ (CBTH) as a photocatalyst. This mixed metal oxide belonging to Aurivillius oxide family is well-explored for its photocatalytic activity toward water splitting. It also exhibits excellent property toward light-driven remediation of organic pollutants via the oxidative mechanism and selective oxidation of aromatic alcohols. Compared to other photocatalysts, this material is resistant to photocorrosion as well as harsh reaction conditions that enable its effectiveness as a photocatalyst for organic synthesis with better conversion and excellent reusability.

**RESULTS AND DISCUSSION**

**Structural Characterization of the Photocatalyst.** The X-ray diffraction pattern of hydrothermally synthesized Bi$_2$WO$_6$ (BTH) and CBTH is shown in Figure 1. Comparison of these two patterns suggests that there exist dissimilarities for the intensity and broadness of the individual peak. For example, the peak at 32.89° corresponding to (200) is broadened with increased intensity at the expense of decrease in the intensity for the (131) plane observed at 28.27°. It implies that the epitaxial growth of BTH along the latter plane is arrested with concomitant expansion along the former plane owing to the addition of cetyl trimethylammonium bromide (CTAB). A similar feature is also found to be associated with other peaks appearing at 47.09°, 55.93°, 58.60°, 68.77°, 75.92°, and 78.37° corresponding to (202)/(260), (133)/(331), (262), (400), (102), and (204) crystallographic planes, respectively. It resembles a perovskite-like structure indexed to an orthorhombic Bi$_2$WO$_6$ phase with lattice parameters $a = 5.461$ Å, $b = 5.431$ Å, and $c = 16.422$ Å. The morphology and microstructure of BTH and CBTH are investigated by field-emission scanning electron microscopy (FESEM) and TEM analyses. The FESEM image of BTH (Figure 2a) displays nanoplates that are arranged in two dimensions with the thickness of about 200 nm, whereas high-magnification FESEM image (Figure 2b) clearly reveals the formation of thin nanoplates displaying very thin and two-dimensional (2D) microstructures. On the other hand, when Bi$_2$WO$_6$ is coated with CTAB, layers of nanoflakes are formed (Figure 2c) that are arranged in a manner similar to the tip of the rose bud (Figure 2d). This observation is further supported by high-resolution transmission electron microscopy (HRTEM) images of both nanocrystals (Figure 3). The formation of elongated cubical morphology such as a nanochip is seen in the absence of CTAB, whereas its presence has significantly modified the shape of BTH nanocrystals into 2D nanosheets with smaller thickness. Such a feature has already been noted for the CTAB-assisted hydrothermal synthesis of Bi$_2$WO$_6$ where the monolayer formation of Bi$_2$WO$_6$ nanocrystals is achieved by controlling the amount of CTAB added during the hydrothermal synthesis. In our case, the top-down approach seems to be feasible as CTAB has resulted in the formation of 2D nanosheets.

The temperature-programmed desorption of ammonia (NH$_3$-TPD) analysis provides the total acidity in terms of NH$_3$ desorbed on the surface of the photocatalyst (Figure 4). It is observed that the total acidity of BTH has increased from 0.06529 to 0.10462 mmol/g with CTAB coating. Such a two-fold enhancement can be ascribed to the formation of thin layers of BTH that are well-separated from each other in a dispersed manner. Furthermore, these nanosheets with proper edges may account for improved acidity. Also, broad peaks at higher temperature signified the generation of Bronsted acidic sites on the surface of CBTH. These observations are further substantiated with Py-IR absorption analysis of both catalysts (Figure 5). The Py-IR spectra of BTH exhibit multiple peaks in the region of 1450–1650 cm$^{-1}$ with prominent bands at 1640

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**Figure 1.** X-ray diffraction pattern of (a) BTH and (b) CBTH.
and 1596 cm\(^{-1}\) owing to Bronsted acidity, whereas Lewis acidic sites are observed at 1539 and 1487 cm\(^{-1}\). Upon interaction with CTAB, the number of peaks have decreased; however, the nature and positions of peaks corresponding to Bronsted sites remained almost the same, whereas there exists a slight change in the nature and position of the peaks corresponding to Lewis sites. It implies that functionalization of surface hydroxyls present on BTH has occurred as a consequence of interaction with CTAB without altering the Bronsted sites. This observation is further corroborated with IR spectra (Figure S1) where it is observed that CBTH exhibits distinct peaks in the region of 1500–3000 cm\(^{-1}\) owing to the coating of CTAB on the surface of Bi\(_2\)WO\(_6\).

The Raman spectra of BTH exhibit a characteristic broad peak (Figure 6) at 791 cm\(^{-1}\) with a small hump at 821 cm\(^{-1}\) attributed to symmetric and asymmetric stretching vibrations between planar W and O atoms.\(^{33}\) Interestingly, the former peak is retained in CBTH with decreased width, whereas the
latter band splits into two resolved peaks. A similar feature is also observed for the peak at 716 cm\(^{-1}\) that exhibits a splitted pattern due to the distortion in W–O interaction owing to size reduction.\(^{34}\) A band at 635 cm\(^{-1}\) due to the stretching mode of \([\text{Bi}_2\text{O}_2]^{2+}\) disappeared upon interaction with CTAB, which clearly suggests that the nanosheets are situated within the framework of WO\(_6\) octahedrons.\(^{35}\) Similarly, vibrations in the region of 100–450 cm\(^{-1}\) for BTH are mainly attributed to stretching or bending modes of WO\(_6\) octahedron and BiO\(_6\) polyhedron, and Bi–O peaks split into more prominent bands as a consequence of addition of CTAB.\(^{36}\) Furthermore, it is observed that CTAB induces decrease in the thickness as well as disordered morphology for Bi\(_2\)WO\(_6\) sheets. Thus, it may be argued that CTAB is indeed responsible for structural modifications that has resulted in the formation of defects within WO\(_6\) octahedron with decrease in the thickness and shapes of nanoplates.

**Catalyst Screening.** The photocatalytic efficiency of BTH and CBTH photocatalysts is explored toward the photochemical synthesis of substituted benzothiazoles and benzimidazoles under visible light. For this purpose, optimized reaction conditions are evaluated for the synthesis of benzazoles using \(o\)-aminothiophenol and benzaldehyde (Table S1). It is interesting to note that CBTH exhibits an enhanced photocatalytic activity as compared to BTH. For example, there is a significant improvement in the yield with lesser exposure time for CBTH, implying that surface modification has resulted in better reaction rates. It is reported that CTAB coating reduces the band gap of BTH by about 0.2 eV generating holes on the active surface and electrons that are situated in the middle layer of the photocatalyst. This induces effective charge separation and both these moieties are responsible for better catalytic activity. Thus, CBTH is selected for further studies toward the synthesis of benzazoles. Studies on the variation in the amount of CBTH, viz., 3, 5, 10, 15, and 20 mg, suggest that an increase in the yield of the product with concomitant increase in the catalyst amount with maximum yield (94%) is obtained at 15 mg of the photocatalyst. The solvent study carried out using an optimum amount (15 mg) of the catalyst indicates that acetonitrile is the most suitable solvent for this particular reaction as it is observed that acetonitrile can stabilize photogenerated radicals during exposure to light (Figure S2). Thus, 15 mg of the photocatalyst with a 35 W tungsten lamp and acetonitrile solvent are found to be optimum conditions for the photochemical conversion of \(o\)-aminothiophenol and benzaldehyde to corresponding benzothiazoles, and similar conditions are adopted for the synthesis of benzimidazoles.

Adopting these optimized conditions, the scope of the present investigation is evaluated toward the photochemical synthesis of 2-substituted benzothiazoles (Table 1) and 2-substituted benzimidazoles (Table 2) under identical experimental conditions. It is observed that the formation of benzothiazoles takes place at considerably lesser exposure time (30–90 min) as compared to their benzimidazole analogues (3–5.5 h). Also, the yields are significantly higher (89–96%) for thiazoles, whereas comparatively lower yields (81–96%) are obtained for imidazoles. These variations can be attributed to the easier homolytic cleavage of the S–H bond as compared to that of the N–H bond, which leads to the facile generation of radicals on the sulfur center. Within the individual series, there seems to be the influence of electron-donating and electron-withdrawing substituents on the exposure time and yield. For example, nitro and fluoro substituents favor better yields at faster reaction rates, whereas hydroxyl and methoxy derivatives induce comparatively lower yields at longer exposure time for both the series. This occurs because of the...
increased electrophilic character of the carbonyl group of the aldehyde, resulting in its stronger adsorption on the catalyst surface and thereby lowering the activation energy.

**Reusability Studies.** It is observed that the photocatalytic activity of a catalyst may be hampered after its continuous exposure to light owing to photocorrosion that results in the lowering of yield of the product during successive cycles. To assess this hypothesis, longevity studies of the CBTH catalyst are evaluated toward the synthesis of 2-phenyl benzimidazoles for five successive cycles (Figure 7). After each cycle, the catalyst is centrifuged, washed with acetone or ethanol to remove traces of any adsorbed organic molecule, and subsequently used for the next cycle. Interestingly, % yield of the 2-phenyl benzimidazoles remains almost constant after five cycles, suggesting that the catalyst remains active even after it is continuously exposed to visible light. This also infers to the robustness and photostability of the photocatalyst under severe reaction conditions involving active reactants as well as its surface that remained almost unchanged during chemical transformation. To substantiate these assumptions, X-ray photoelectron spectroscopy (XPS) analysis is carried out for fresh and used CBTH catalyst after five cycles (Figure 8). Inspection of this figure reveals that there exist two regions corresponding to Bi$^{3+}$ and W$^{6+}$ constituents of CBTH. The peaks at 159.12 and 164.41 eV are assigned to 4f$^{7/2}$ and 4f$^{5/2}$ spin states, respectively, originating from the Bi$^{3+}$ ion (Figure 8a), whereas the spin states at the W$^{6+}$ region (Figure 8b) displayed the peaks at 35.36 and 37.50 eV for the fresh CBTH catalyst. On the other hand, these peaks are shifted to higher binding energy by $\sim$0.45 eV for the used catalyst that may be ascribed to the formation of oxygen vacancies. Such a minor shift in the binding energy for Bi$^{3+}$ and W$^{6+}$ ions may arise due to continuous exposure to light, generating small defects on the surface of CBTH. This observation is further corroborated with O 1s spectra of the fresh and used CBTH photocatalyst (Figure S3). Three-peak patterns for this region are observed at 530.11, 531.97, and 533.39 eV which are assigned to W$^\cdot$O, surface hydroxyl, and Bi$^\cdot$O moieties, respectively. Interestingly, these peaks are shifted to higher energy by about 0.4 eV for the used catalyst, a feature noted for Bi$^{3+}$ and W$^{6+}$ ions. Also, the peak intensity of surface hydroxyl is found to be decreased with concomitant increase in the intensity for the Bi$^\cdot$O peak for the used catalyst, although the intensity of the W$^\cdot$O peak remains almost constant. These changes may be ascribed to the increase in the contribution from Bi$^\cdot$O toward the formation of oxygen vacancies on the surface of the CBTH catalyst. Further, it also substantiates the structural arrangement of Bi$_2$WO$_6$ where the surface vacancies are generated because of [Bi$_2$O$_2$]$^{2+}$ sheets present on the surface while WO$_6$ octahedron functions as the source of electron. This aspect is indeed responsible for the improved photocatalytic activity of CBTH.

| Sr.-No. | Reactant          | Product | Time (min) | Yield (%)$^b$ |
|---------|-----------------|---------|------------|---------------|
| 1       | Benzaldehyde    | ![image](image1.png) | 60         | 93            |
| 2       | 4-(OH)-Benzaldehyde | ![image](image2.png) | 75         | 91            |
| 3       | 4-(OMe)-Benzaldehyde | ![image](image3.png) | 90         | 89            |
| 4       | 4-(NO)-Benzaldehyde | ![image](image4.png) | 30         | 95            |
| 5       | 4- (Cl)-Benzaldehyde | ![image](image5.png) | 45         | 94            |
| 6       | 3 - (Br)-Benzaldehyde | ![image](image6.png) | 60         | 91            |
| 7       | 4- (F)-Benzaldehyde | ![image](image7.png) | 45         | 95            |
| 8       | 2- (Py)-Benzaldehyde | ![image](image8.png) | 30         | 96            |

$^a$Reaction conditions: 1 mmol aldehyde, 1 mmol $\alpha$-aminothiophenol, acetonitrile (15 mL), amount of catalyst—15 mg, and tungsten lamp—35 W.

$^b$Isolated yields.

Table 1. Synthesis of 2-Alkyl Benzothiazoles Using a CTAB-Coated Bi$_2$WO$_6$ Photocatalyst
because of its nanosheet morphology as compared to flake-like morphology for BTH.

To further corroborate these findings, NH$_3$-TPD and Py-IR (Figure 5c) spectral measurements are carried out for the recovered catalyst. It is interesting to note that there is absence of lower temperature peaks (Figure 4c) corresponding to weak acidic sites, implying that CTAB coating may have disappeared with an appearance of a broad peak at higher temperature owing to the generation of strong Brønsted sites as evident from the enhancement in the total acidity by almost 2.5 times (0.2803 mmol/g) after its successive usage. Moreover, such an increase in the total acidity is found to be beneficial as it accelerates the Schiﬀ base formation, a key step in the synthesis of benzazoles that has resulted in retaining the photocatalytic activity of CBTH even after five successive cycles. Signiﬁcantly, Py-IR measurements also conﬁrm the presence of broad unresolved peaks at a higher wave number for CBTH as a result of lowering in the Lewis acidic sites. It can also be inferred that the increased surface hydroxyl groups are responsible for the enhanced Brønsted acidity as evident from the enhanced intensity for the O 1s peak evaluated from the XPS analysis of the used catalyst (Figure S3).

**Plausible Mechanism.** Bi$_2$WO$_6$ being a metal oxide plays a dual role of a Lewis acid as well as a photocatalyst during the course of photocyclization. The first step involves the formation of Schiﬀ’s base which is followed by photocyclization of the imine intermediate, yielding the desired product in a sequential manner (Figure 9a). The Lewis acidity of CBTH is responsible for the formation of Schiﬀ’s base, whereas the photoconducting

| Sr. No. | Reactant                  | Product | Time (h) | Yield (%)$^b$ |
|---------|---------------------------|---------|----------|---------------|
| 1       | Benzaldehyde              |         | 3.5      | 89            |
| 2       | 4-(OH)-Benzaldehyde       |         | 4.5      | 84            |
| 3       | 4-(Cl)-Benzaldehyde       |         | 3.5      | 95            |
| 4       | 2,4-(Cl)-Benzaldehyde     |         | 3        | 92            |
| 5       | 4-(F)-Benzaldehyde        |         | 3        | 95            |
| 6       | 3-(Br)-Benzaldehyde       |         | 4        | 88            |
| 7       | 2,5-(OMe)-Benzaldehyde    |         | 5.5      | 81            |
| 8       | 2-(Py)-Benzaldehyde       |         | 3.5      | 96            |

$^a$Reaction conditions: 1 mmol aldehyde, 1 mmol o-phenylenediamine, acetonitrile 15 mL, amount of catalyst—15 mg, and tungsten lamp 35 W.

$^b$Isolated yields.

**Figure 7.** Reusability studies of the CBTH photocatalyst toward the synthesis of 2-phenyl benzimidazoles.
nature of the catalyst generates a radical on the heteroatom that initiates the cyclization process. Adsorption of the aldehyde on the catalyst surface increases the electrophilicity of the carbonyl group, followed by the nucleophilic attack of the amino group on the electron-deficient carbonyl center. The photogenerated radical then cleaves the double bond homolytically, giving a diazole ring that further aromatizes in the presence of molecular oxygen, yielding 2-alkyl benzazoles. It is reported that molecular oxygen is necessary for both generation of OH radical and inhibition of the electron–hole recombination process occurring on the surface of Bi2WO6.31 In our case, this feature is also observed when the reaction is carried out under inert atmosphere by continuously bubbling N2 during the benzazole synthesis, implying that cyclization and subsequent aromatization do not occur in the absence of molecular oxygen. Generation of more Brønsted sites at the expense of decrease in the Lewis sites does not hamper the photocatalytic activity of CBTH even after five successive cycles as the first step of Schiiff’s base formation is manifested by the presence of strong Brønsted acidic sites, resulting in almost similar yields of benzazoles (Figure 9b).

Comparative Account. To highlight the potentiality of CBTH, a comparative account of semiconducting nano-composites is tabulated that are employed toward the synthesis of benzimidazoles and benzothiazoles (Table 3). Inspection of this table suggests that the majority of the catalysts exhibit excellent catalytic activity toward the benzazole synthesis; however, in some cases, harsh conditions are required to achieve better conversion. For example, TiO2-based catalyst involves either a UV lamp (entries 4–8) or heating at elevated temperatures (entries 2, 4, 5, and 10) with a comparatively large amount of the catalyst. Reusability is another parameter that has been considered where lower yields are obtained after certain cycles, implying that the number of active sites on the catalyst surface is reduced because of synthetic conditions used for benzazoles as observed for Fe3O4@SiO2/collagen catalyst (entry 1).39 Interestingly, this is the first report of the Bi2WO6 photocatalyst that has been used for light-induced organic synthesis involving a low light energy source. Also, CBTH exhibits an excellent recycling capability up to five cycles with constant yield. These facets certainly can be ascribed to the excellent photocatalytic activity of CBTH owing to the formation of monolayer-like morphology that accounts for better absorption of light and brings about conversion in an efficient manner.

**CONCLUSIONS**

In the present work, we have demonstrated that the morphology of Bi2WO6 indeed influences its beneficial photocatalytic activity. For example, thin nanosheets of CBTH possess better efficiency toward the photochemical synthesis of benzazoles when compared to thick nanoplates of the uncoated Bi2WO6. Such an improved activity can be attributed to increased acidity because of the formation of distinct Lewis and Brønsted sites as well as structural modifications that have occurred on the surface of CBTH. Moreover, generation of oxygen vacancies within [Bi2O2]2+ sheets has significantly contributed toward improved photocatalytic activity through increased Brønsted acidity as a consequence of enhanced oxygen content through the formation of Bi–O linkage. The acidic sites of CBTH favor the formation of Schiiff’s base while photocyclization via the radical process is manifested by the WO6 octahedron of the perovskite-like structure of Bi2WO6. Thus, it can be argued that the CBTH catalyst efficiently harvests visible light because of the nanosheets of the photocatalyst which is responsible for better yields of benzazoles in a sustainable manner. Compared to other photocatalysts, CBTH exhibits superior catalytic activity toward the synthesis of benzazoles under eco-friendly conditions with excellent yields.
EXPERIMENTAL SECTION

Chemicals. All analytical reagent-grade chemicals were used as received without any further purification or treatment. Bismuth nitrate (Bi(NO$_3$)$_3$·5H$_2$O) and sodium tungstate (Na$_2$WO$_4$·2H$_2$O; Loba Chemie, UK), nitric acid (Qualigens), aldehydes, CTAB, o-aminothiophenol, and o-phenylenediamine (Sigma-Aldrich) were used. Precoated aluminum thin-layer chromatography (TLC) plates (silica gel 60 F254) and silica gel for column chromatography (mesh 60–120) were purchased from Merck, India.

Synthesis of BTH. Bi$_2$WO$_6$ nanoparticles were synthesized by a hydrothermal method. In a typical synthesis, 0.60 g of Na$_2$WO$_4$·2H$_2$O was dissolved in 5 mL of deionized water and stirred for 15 min. In another flask, 1.94 g of Bi(NO$_3$)$_3$·5H$_2$O was dissolved in 5 mL of (4 M) nitric acid, and it was then added dropwise to the above solution under vigorous stirring so as to obtain a white precipitate. This white precipitate was stirred for 1 h, and then the pH of the solution was adjusted to

Figure 9. (a) Lewis acid initiated reaction pathway for the synthesis of 2-alkyl benzimidazoles with fresh catalyst and (b) Brønsted acid initiated reaction pathway for the synthesis of 2-alkyl benzimidazoles with reused catalyst.

Table 3. Comparative Account of Various Heterogeneous Catalysts Used for the Synthesis of Benzazoles

| entry | catalyst | methodology | yield (%)$^a$ | reusability | references |
|-------|----------|-------------|---------------|-------------|------------|
| 1     | Fe$_3$O$_4$@SiO$_2$/collagen | rt           | 97–50         | I–IV, 95–73 | 39         |
| 2     | Cu(II)-TD@nSiO$_2$ | 50 °C, air   | 98–87         | I–VIII, 97–95 | 40         |
| 3     | CoO(II)/Co(OH)$_2$ | rt           | 98–82         | I–IV, 96–86 | 41         |
| 4     | TiO$_2$/H$_2$O$_2$ | ambient light, 50 °C | 96–90   |             | 42         |
| 5     | Au–TiO$_2$ | 100 °C      | 86–28         |             | 13         |
| 6     | TiO$_2$–P25 | UV light, λ = 365 nm | 83–52 |             | 9          |
| 7     | Pt–TiO$_2$ | UV, λ = 365 nm | 96–40         |             | 11         |
| 8     | Ag–TiO$_2$/clay | UV-A light | 62$^b$        |             | 12         |
| 10    | mpg-C$_3$N$_4$ | λ > 420 nm, 100 °C | 99$^b$ |             | 43         |
| 11    | CdS nanospheres | 300 W, xenon lamp | 98–60 | I–IV, 96–86 | 15         |
| 12    | CBTH | 35 W, tungsten lamp | 96–81 | I–V, 93–88 | present work |

$^a$Isolated yield. $^b$GC yield.
7 using 1:1 NH₃. The precipitate was then transferred to a Teflon-lined stainless steel autoclave, and it was then heated in an oven at 180 °C for 14 h. The oven is cooled naturally and allowed to attain room temperature. Pale yellow-colored residue thus obtained was filtered, washed with deionized water, and then dried at 80 °C for 6 h.

Synthesis of CBTH. In a typical preparation, 0.60 g of Na₂WO₄·2H₂O and 0.02 g of CTAB were added in 50 mL of deionized water, and 1.94 g of Bi(NO₃)₃·5H₂O was added in 5 mL of (4 M) HNO₃ separately. These solutions were mixed, stirred for 1 h, and then the pH was adjusted to 7 with 1:1 NH₄OH. The whole mixture was transferred to a Teflon-lined stainless steel autoclave, and it was then heated in an oven at 180 °C for 14 h. Finally, the off-yellow product was filtered, washed with ethanol to remove excess of surfactant, and then dried at 80 °C for 6 h.

Characterization. The X-ray powder diffraction data was collected on Shimadzu Lab-X 6100 series using Cu Kα radiation (λ = 0.15418 nm). The powdered samples were placed on a silicon zero-background sample holder, and the X-ray diffraction patterns were recorded. The catalysts were subjected to FESEM analysis using an FEI Nova NanoSEM 450 instrument. The powdered catalyst was placed on a carbon tape, coated with Pt, and then used for the analysis. HRTEM images were taken by placing a drop of the nanoparticles dispersed in methanol onto a carbon-coated copper grid. NH₄-TPD was performed on a Micromeritics Chemisorb 2720 instrument. The catalyst (0.05 g) was taken in a U-shaped quartz tube. Earlier, the catalyst was pretreated in He (25 cm³/min) at 200 °C for 2 h, and the mixture of NH₃ in He (30%) was passed (25 cm³/min) at 50 °C for 1 h. TPD measurements were carried out in the temperature range of 50–700 °C with a heating rate of 10 °C/min. The concentration of NH₃ was monitored with a thermal conductivity detector. Py-IR spectra were recorded on a Shimadzu FTIR 8000 attached with DRIFT assembly. The sample was placed in the DRIFT cell and heated to 400 °C under the flow of inert gas (N₂) for 1 h. It was cooled to 100 °C, and pyridine was adsorbed on the sample. Physisorbed pyridine was removed by flushing the cell with N₂ for 60 min at 100 °C, and the spectra were recorded after maintaining the temperature for 60 min. Raman spectra were obtained on a Horiba JY LabRAM HR 800 micro-Raman spectrometer operating at 17 mW and an excitation wavelength of 632.8 nm. The XPS analysis was carried out on a PHI 5000 Versa probe II instrument (Physical electronics, ULVAC PHI) system equipped with Al Kα (λ = 1486.6 eV) and deconvoluted using XPSPEAK 4.1 software. NMR spectra were recorded in CDCl₃ and DMSO-d₆ solvents using a 500 MHz spectrometer (AVANCE 500, Bruker, Bremen, Germany). The ¹H and ¹³C spectra were recorded at radiofrequencies of 500 and 400 MHz and 125 and 100 MHz, respectively.

General Procedure for the Photochemical Synthesis of 2-Alkyl Benzimidazoles. To a solution of aldehyde (1 mmol) in acetonitrile (5 mL), 15 mg of the photocatalyst was added and stirred for 15 min. After addition of o-aminothiophenol (1 mmol; dissolved in 10 mL of acetonitrile), the reaction mixture was transferred to a 50 mL double-walled quartz photocell (Figure S4). The reaction mixture was then exposed to visible light using a 35 W tungsten lamp, and the temperature of the reaction was maintained by water circulation. The progress of the reaction was monitored by TLC. On completion of the reaction, the catalyst was separated by centrifugation and the filtrate was concentrated under vacuum. The product was purified by a filtration column on silica gel (60–120 mesh) using hexane/ethyl acetate (85:15) to yield pure compounds. The products were characterized using ¹H and ¹³C NMR spectroscopy (Figures S5–S20).

General Procedure for the Photochemical Synthesis of 2-Alkyl Benzothiazoles. A procedure similar to that for the photochemical synthesis of 2-alkyl benzothiazoles was adopted for the synthesis of 2-alkyl benzimidazoles using o-phenylenediamine (1 mmol; dissolved in 10 mL of acetonitrile) instead of o-aminothiophenol. The product was purified by a filtration column on silica gel (60–120 mesh) using hexane/ethyl acetate (90:10) to yield pure products. These pure products were further characterized using ¹H and ¹³C NMR spectroscopy (Figures S21–S36).

Longevity Studies. Recycling experiments were carried out with the CBTH-catalyzed photochemical synthesis of 2-phenyl benzimidazoles. After the completion of the reaction, the filtrate was separated from the catalyst by simple decantation, and the catalyst was washed successively with acetonitrile, ethanol, and acetone so as to remove adsorbed moieties. It was then used for the subsequent cycle by adding an appropriate amount of reactants and illuminated with a tungsten lamp for the same amount of time. This procedure was repeated for five cycles, and the recovered catalyst was subjected for further analysis.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01086.

XPS analysis of oxygen region, catalyst optimization, FT-IR spectra of catalysts, ¹H and ¹³C NMR spectral data of the synthesized compounds, table of preliminary experiments, and table of content graphic (PDF)

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Notes

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ABBREVIATIONS
CTAB, cetlytrimethylammonium bromide; NPs, nanoparticles; CBTH, CTAB-coated Bi3W6O16; BTH, Bi3W6O16; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy; HRTEM, high-resolution transmission electron microscopy; CDCl3, deuterated chloroform; DMSO-d6, deuterated dimethyl sulfoxide

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