Enhanced Photocatalytic Activity of Hierarchical Bi$_2$WO$_6$ Microballs by Modification with Noble Metals

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Abstract: Visible-responsive photocatalysts for environmental purification and fuel generation are, currently, highly sought after. Among the possible candidates, Bi$_2$WO$_6$ (BWO) has been considered due to its efficient light harvesting, stability, and promising activities. Here, hierarchical BWO microballs have been prepared using a hydrothermal method, and additionally modified with deposits of noble metals (gold, silver, copper, palladium and platinum) by the photodeposition method. The structure, morphology, photoabsorption properties, and surface composition of bare and metal-modified BWO samples were investigated by XRD, SEM, DRS and XPS analyses. The photocatalytic activity was evaluated by the oxidative degradation of model dye (methyl orange (MO)) under UV/vis, and hydrogen generation under vis and/or UV irradiation. It was found that hierarchical morphology is detrimental for high photocatalytic activity in both tested systems, resulting in the improved degradation of MO (ca. 65% during 90 min of UV/vis irradiation), and hydrogen evolution (0.1 and 0.4 µmol h$^{-1}$ under vis and UV/vis irradiation, respectively). Moreover, the type of noble metal and its properties influence the overall photocatalytic performance. It was found that, under UV/vis irradiation, only platinum accelerates hydrogen evolution, whereas under vis irradiation the activity follows the order: BWO < BWO/Cu < BWO/Ag < BWO/Pt < BWO/Pd < BWO/Au. It was concluded that zero-valent metal is recommended for high vis response, probably due to plasmonic photocatalysis, efficient light harvesting ability, and co-catalytic role.

Keywords: Bi$_2$WO$_6$; hierarchical microballs; flake balls; noble metals; plasmonic photocatalysis; vis response; hydrogen generation; dye degradation

1. Introduction

Global energy and environmental crises are considered the most urgent problems to be solved. Among various solutions, hydrogen has been proposed as an alternative fuel due to its high specific energy (three times the heating value of petroleum) and environmentally friendly nature, i.e., its combustion results in the formation of only a clean product—water (“maker of water” in Greek) [1]. However, the most significant is the clean production of hydrogen itself, and thus, usage of fossil fuels should be avoided. Accordingly, green processes, such as photocatalysis, have been considered for hydrogen generation [2–5]. For example, semiconductor photocatalysis might solve both energy and environmental problems (including ones related to drinking water), particularly when performed under natural solar radiation [6–8]. The photocatalysts could split water into hydrogen and oxygen, as well as decompose all pollutants (microorganisms and organic and inorganic compounds), and thus heterogeneous photocatalysis has attracted a lot of attention in recent decades [9–12]. Among the various semiconductors, titanium(IV) oxide (TiO$_2$, titania, titanium dioxide) has been the most explored due to its low cost,
high activity, low toxicity, abundance, and pollution-free nature [13–15]. However, titania also has some shortcomings. First, titania is only responsive to the UV part of the solar spectrum due to its large bandgap, and thus, only a minor part of solar energy can be efficiently used (3–4%). Second, the recombination of charge carriers results in a lower than 100% quantum efficiency of photocatalytic reactions. Third, the most active titania photocatalysts are usually in the form of fine particles, which raises some problems with photocatalyst reuse and circulation (high costs of ultrafiltration). In contrast, the application of immobilized photocatalysts is connected with a low specific surface area, and thus a decrease in photocatalytic efficiency [16–18]. Therefore, the synthesis of highly efficient materials for the broad range of solar radiation, and easy recyclability, is a hot topic of present studies. For example, wide-bandgap semiconductors were either surface modified [19–21] or doped [22–24] with various elements, as well as coupled with other semiconductors of narrower bandgaps [25–28]. Moreover, new chemical compounds have been synthesized and proposed as efficient photocatalysts, such as oxynitrides [29], graphitic carbon nitride [30], germanium nitride [31], and graphene derivatives [32]. However, a narrower bandgap allows for fast charge carriers’ recombination. Therefore, these new materials have also been further modified/coupled (e.g., MoS₂-C-g-C₃N₄ [33]) to obtain an efficient transfer of charge carriers (via type II heterojunction or/and Z-scheme [5,34]), and thus, high yields of photocatalytic reactions.

For example, as a material with a narrower bandgap than that of titania, bismuth-based compounds have attracted much attention [35]. It has been shown that bismuth tungstate (Bi₂WO₆, BWO) with a layered structure of WO₆ and [Bi₂O₂]²⁺ (perovskite-like plates) has exhibited good photocatalytic efficiency under vis irradiation [36–39]. However, the photogenerated charge carriers recombine easily, and thus result in a low photocatalytic efficiency. Accordingly, many methods have been used for BWO modification, such as morphology optimization [37,38,40,41], elemental doping [42,43], surface modification (e.g., with noble metals [44–47]), and the formation of heterojunctions, e.g., Bi₂WO₆/Zn-Al [48], Bi₂Fe₄O₉/Bi₂WO₆ [49], MoS₂/Bi₂WO₆ [50].

It is known that noble metals can effectively improve the photocatalytic performance of photocatalysts, being an electron pool, and thus hinder the recombination of charge carriers. Various semiconductors with deposited noble metals have already been prepared, such as titania [51–54] and other photocatalysts, e.g., Bi₂MoO₆ nanoparticles (Ag) [55], BiOCl nanospheres (Ag) [56], carbon nitride nanorods (Au) [57], g-C₃N₄ (Cu) [58], and BiOBr (Pd) [59]. It should be mentioned that though modification with noble metals (to improve UV-photocatalytic activity) has been known for more than 40 years, novel research has been started recently on plasmonic photocatalysis, in which noble metals play another function, i.e., the activation of wide-bandgap semiconductors towards a vis response due to plasmonic properties [60–62].

Although both pristine and modified BWO samples have been investigated for various photocatalysts reactions, there are no reports showing a direct comparison between BWO photocatalysts modified with different noble metals. In this study, the influence of five metals (Au, Ag, Cu, Pd and Pt) on the properties, and thus overall activity, of BWO (in the form of hierarchical microballs for cheap recycling) is investigated for the first time. The photocatalytic activity has been tested for hydrogen generation and the decomposition of methyl orange (MO; common and toxic dye [63]) since both “green” fuel production and environmental purification (especially the degradation of organic compounds) are the most urgent problems facing humanity.

2. Results and Discussion

2.1. Characterization of Samples

The successful preparation of BWO by a hydrothermal method has been confirmed by XRD analysis, as shown in Figure 1. All pristine samples, prepared at different temperatures, show almost identical diffraction patterns with clear peaks at ca. 28.3, 32.8, 47.2, 55.8, 58.5, 68.7, 76.1 and 78.5 degrees, indicating (131), (002), (202), (133), (262), (004), (333) and (460).
crystal planes of russellite Bi$_2$WO$_6$, respectively. An increase in hydrothermal temperature results in peak sharpening, suggesting that larger crystallites have been formed. Indeed, Scherrer analysis confirms that the crystallites prepared at 140 °C reach 13.6 nm, whereas higher temperatures (180 °C and 160 °C) cause the formation of larger crystallites (14.8 nm and 16.2 nm, respectively).

Figure 1. XRD patterns of BWO samples prepared at different temperatures.

The microscopic observations revealed that a hydrothermal reaction results in the formation of microballs composed of nanosheet subunits, as shown in Figure 2. The best morphology was obtained at the lowest temperature of reaction (140 °C), as the S1 sample exhibits a regular spherical flower-like structure with a relatively uniform size distribution, and the microballs are composed of flat sheets (Figure 2a,b). A worsening of the morphology was noticed after increasing the temperature of the hydrothermal reaction. Accordingly, though microballs in the S2 sample are still mainly spherical (Figure 2c,d), the substructured sheets are irregular and uneven in size. Finally, the worst morphology was achieved for the S3 sample (Figure 2e,f), for which the spherical morphology is no longer obvious, and the structure of built-in flakes is likewise incomplete. Based on the presented data, it has been found that the spherical structure of BWO was destroyed gradually, and substructure sheets were fragmented by increasing the hydrothermal reaction temperature, indicating that temperature is crucial for the morphology of BWO samples. Accordingly, the S1 sample with the best morphology (and highest photocatalytic efficiency, as discussed further) was selected for the modification with noble metals.

Figure 2. BWO samples obtained at different temperatures: (a,b) S1 (140 °C), (c,d) S2 (160 °C) and (e,f) S3 (180 °C).
The XPS was used for the surface characterization of both pristine and modified samples. All samples are composed of Bi$_2$WO$_6$ (Figure 3). Although slight shifts in the binding energy were observed with an increase in the temperature of the hydrothermal reaction, it seems to be irrelevant for the chemical composition, as previously reported [64]. Taking the S1 sample as an example, the XPS spectra of Bi 4f and W 4f show the binding energies of 159.0 eV (Bi 4f$_{7/2}$), 164.31 eV (Bi 4f$_{5/2}$), 37.33 eV (W 4f$_{7/2}$) and 35.2 eV (W 4f$_{5/2}$), indicating that bismuth and tungsten exist in tri- [65] and six-valent [66] oxidation states, respectively. In the case of the oxygen (O 1s) spectrum, two peaks at 530.05 eV and 531.53 eV could be seen, relating to W-O and Bi-O, respectively. Thus, the chemical formula of Bi$_2$WO$_6$ was confirmed [67].

![Figure 3](image-url)

**Figure 3.** XPS results for: (a) Bi 4f, (b) O 1s and (c) W 4f.

In the case of modified S1 samples, XPS data have confirmed that noble metals were efficiently loaded onto the BWO surface, as shown in Figure 4 and Table 1. It has been found that silver exists in two oxidation forms, i.e., Ag$^+$ and Ag(0), with binding energies of 367.51 eV and 368.3 eV, respectively, with the oxidized form being predominant (ca. 90%). In contrast, three forms of gold, i.e., Au($\delta^+$), Au(0) and Au($\delta^-$), were observed with binding energies of 932.16 eV, 83.6 eV and 83.94 eV, respectively. Here, the zero-valent form of gold is the most predominant, reaching 92%. In the case of copper, only its oxidized forms could be detected, i.e., Cu$^+$ (932.16 eV [68]; 58%) and Cu$^{2+}$ (932.28 eV [68]; 42%), confirming the instability of zero-valent copper under ambient conditions [69–71]. As expected, palladium and platinum exist mainly in the zero-valent form, reaching 80% and 79%, respectively, making up the minority of the oxidized forms of metals (probably PdO [72] and Pt($\delta^+$) [68]). Similar data have been commonly found for semiconductors modified with noble metals, where less noble metals (silver and copper) exist, predominantly in the oxidized forms, whereas precious metals (gold, platinum and palladium) are present as zero-valent deposits [69–71,73–75]. It must be underlined that, during photodeposition (anaerobic environment), though metal cations are reduced efficiently, forming zero-valent NPs (as confirmed by the color change, e.g., violet for Cu/S1 due to the plasmonic properties), the
direct contact of the sample with air (after photodeposition) results in the partial oxidation (surface) of less noble metals.

Figure 4. XPS results for S1 sample modified with noble metals: (a) Ag 3d\textsubscript{5/2}, (b) Au 4f\textsubscript{7/2}, (c) Cu 2p\textsubscript{3/2}, (d) Pd 3d\textsubscript{5} and (e) Pt 4f\textsubscript{7/2}.

Table 1. Surface composition of pristine and modified S1 samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>S1</th>
<th>Pt/S1</th>
<th>Au/S1</th>
<th>Ag/S1</th>
<th>Cu/S1</th>
<th>Pd/S1</th>
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<tr>
<td>content (at%)</td>
<td>Bi</td>
<td>17.3</td>
<td>20.5</td>
<td>20.3</td>
<td>18.2</td>
<td>18.2</td>
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<tr>
<td></td>
<td>C</td>
<td>31.6</td>
<td>26.8</td>
<td>21.1</td>
<td>28.0</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>43.8</td>
<td>43.6</td>
<td>51.1</td>
<td>46.2</td>
<td>49.1</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>7.3</td>
<td>8.7</td>
<td>7.4</td>
<td>7.1</td>
<td>7.0</td>
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<tr>
<td></td>
<td>Pt</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
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<td></td>
<td>Ag</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>0.5</td>
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<tr>
<td></td>
<td>Cu</td>
<td>-</td>
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<td>0.4</td>
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<td></td>
<td>Pd</td>
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The photoabsorption properties of bare and modified BWO materials are presented in Figure 5. It has been confirmed that BWO can absorb visible light up to ca. 450 nm, which corresponds to bandgap of ca. 2.75 eV (evidently narrower than that in titania). Moreover, as expected (considering the same crystalline form and similar crystallite sizes), all bare samples (S1–S3) show almost identical photoabsorption properties (Figure 5a). Furthermore, a significant increase in vis absorption was observed after BWO modification with noble metals. The characteristic plasmonic peaks (localized surface plasmon resonance; LSPR) were observed for Au/S1 and Ag/S1 at ca. 545 nm and ca. 490 nm, respectively, suggesting the formation of fine gold NPs (10–20 nm) and larger silver deposits (ca. 80 nm [76]). It should be mentioned that the LSPR wavelength is influenced by both the properties (size/shape/surroundings) and the type of the metal, and thus smaller and spherical NPs possess LSPR at shorter wavelengths [77]. For example, spherical NPs of 10–20 nm show LSPR at ca. 200 nm [78], 395–405 nm [79], 420–430 nm [80], 530–540 nm [81] and 560–570 nm [82] when composed of palladium, platinum, silver, gold, and copper, respectively. The formation of a Ag\textsubscript{2}O/Bi\textsubscript{2}WO\textsubscript{6} heterojunction should also be considered as a similar photoabsorption feature has been observed (the peak at ca. 500 nm) for other semiconductors (e.g., titania) modified with silver(I) oxide (even though a very different photoabsorption feature of sole Ag\textsubscript{2}O is obtained due to its dark brown color) [26]. In the case of samples containing palladium and platinum, it is difficult to observe a clear LSPR peak (expected at UV range), and thus the efficient light absorption in the whole vis region
could be caused by either the presence of large particles or scattering of the light on the metal deposits. In contrast, though a clear peak at near IR was observed for Cu/S1 sample, its origin is due to CuO rather than zero-valent copper (the lowest light absorption at main LSPR wavelength of 560 nm for spherical Cu NPs), thus it has been confirmed (similar to XPS data) that copper exists mainly in the oxidized form [83–86].

Figure 5. DRS spectra of: (a) bare BWO samples and (b) bare and modified S1 samples.

2.2. Photocatalytic Activity

The photocatalytic activities of obtained photocatalysts were evaluated in two reaction systems: (1) the decomposition of MO (aerobic environment) and (2) generation of hydrogen (anaerobic environment) under vis and/or UV irradiation.

First, the photocatalytic activity of bare BWO samples was examined in comparison to two reference samples, pure commercial WO₃ (purchased by Aladdin (Vienna, VA, USA)) and Bi₂WO₆ (homemade), and the obtained data for MO degradation are presented in Figure 6. It is obvious that both reference samples are barely active, which is reasonable considering that oxides with narrower bandgap than that in titania suffer from charge carriers’ recombination due to negligible activity for the one-electron reduction of oxygen. Conduction band (CB) position must be more negative than −0.284/−0.046 V vs. NHE (O₂ + e⁻ = O₂⁻ (aq.)/O₂ + H⁺ + e⁻ = HO₂ (aq.)) for the consumption of photogenerated electrons and degradation of organic matter by photogenerated holes [87,88]. In contrast, hierarchical microballs exhibit superior photocatalytic activity, which correlates with their morphology; i.e., the most active sample (S1) has the best morphology. It should be emphasized that all samples possess nearly identical properties, such as the crystallite size, crystallinity, composition and photoabsorption properties, except for morphology, and thus the difference in the activity should be caused by the morphology. Accordingly, it could be concluded that “flake balls” are responsible for the oxidative decomposition of organic compounds with the possibility of a multi-electron transfer mode, as suggested by Hori et al. [89].

Figure 6. Photocatalytic activity of MO discoloration under UV/vis irradiation for synthesized (S1, S2, S3) and reference (commercial WO₃ and homemade BWO) samples.
Similarly, S1 sample shows to be the most active for hydrogen evolution, as shown in Figure 7a. However, the reaction rates for S1 and S2 photocatalysts are very similar, reaching 0.38 µmol/h and 0.33 µmol/h, respectively. In contrast, a twice-as-slow rate has been obtained for S3 sample with partly destroyed sheets’ structure. Therefore, it is obvious that the morphology is detrimental to achieving a high photocatalytic activity. However, it seems that a perfect sheet structure is more important for hydrogen generation, whereas microball morphology is detrimental for the decomposition of organic compounds.

![Figure 7. Photocatalytic hydrogen generation on: (a) BWO microballs (S1, S2 and S3) under UV/vis irradiation, and (b) bare and modified S1 samples under UV/vis (black) and vis (red) irradiation.]

Since the photocatalytic activity data for pristine samples have indicated that S1 is the most active, this sample was selected for the modification with noble metals, and the obtained results are presented in Figure 7b. Interestingly, only modification with platinum resulted in a significant generation of hydrogen under UV/vis irradiation. It must be emphasized that this differs greatly from the titania case, for which modification with any noble metal increases the photocatalytic activity for hydrogen evolution [70,81,90–94]. It has been proposed that molecular hydrogen is directly formed on the deposits of noble metals [95,96]. It should be mentioned that the low activity of BWO for hydrogen evolution has already been suggested (even after modification with platinum) [97], likely resulting from insufficient redox properties (too positive a conduction band). However, there are also some reports showing the photocatalytic activity of BWO for hydrogen generation [98]. Here, hierarchical microballs modified with platinum have exhibited a noticeable generation of hydrogen. Accordingly, it is proposed that platinum might work as an electron pool and a catalyst (dark) for the formation of molecular hydrogen.

Interestingly, the activity under sole vis irradiation is quite different, where gold-modified sample shows the highest activity. Additionally, samples with platinum and palladium are much more active than pristine BWO sample. Therefore, it might be concluded that zero-valent metals are responsible for efficient hydrogen evolution. Two reasons could be considered, i.e., (i) plasmonic photocatalysis or (ii) catalytic “dark” reaction on the metallic deposits. Considering the catalytic “dark” properties of metals (volcano plot), the activity should be in the following order: platinum > palladium > gold ≥ copper > silver [99]. Here, Au/S1 is the most active, with a broad plasmonic peak (500–650 nm), and thus it is expected that the efficient light absorption by plasmonic metal might be the main reason for enhanced activity under vis irradiation. There are two mechanisms of plasmonic photocatalysis, i.e., an energy transfer, and an electron transfer [60,100–102]. It seems that both could be involved as even a slight overlapping of photoabsorption bands (LSPR and semiconductor) could result in the energy transfer. Moreover, the double function of noble metals must also be considered: (i) plasmonic sensitizer, and (ii) catalytic center for hydrogen generation. Obviously, zero-valent metals are crucial for both activities. The slight increase in activity by silver modification might also result from the presence of zero-valent silver (ca. 10%). Of course, the formation of heterojunctions between two oxides, e.g., Ag₂O/BWO, Cu₂O/BWO and CuO/BWO, could also be inspected. However,
the inactivity of the copper-modified sample suggests that these types of heterojunctions are not working for hydrogen evolution (again, in contrast to the case of titania [26,27,103,104]). Therefore, it could be concluded that zero-valent noble metals are necessary for the efficient enhancement of photocatalytic efficiency of BWO under vis light.

3. Materials and Methods

3.1. Preparation of BWO

Na$_2$WO$_4$·2H$_2$O, Bi(NO$_3$)$_3$·5H$_2$O, and cetyltrimethylammonium bromide (CTAB) were purchased from Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China) (AR, 99%), and used without further treatment. BWO was synthesized by hydrothermal reaction. In brief, 2 mmol of Na$_2$WO$_4$·2H$_2$O and 4 mmol of Bi(NO$_3$)$_3$·5H$_2$O were placed in a 100 mL beaker, to which 60 mL deionized water was added, and then the content was stirred magnetically for half an hour. Afterwards, 0.05 g of CTAB was added, the content was stirred for 15 min, and the white suspension (the pH value of 1.44) was poured to a 100 mL Teflon tube. The tube was placed inside the oven for a 24 h hydrothermal reaction, performed at three different temperatures. The final product was collected, washed with deionized water, centrifuged, and freeze dried. The obtained yellowish powders were marked as S1, S2 and S3 for BWO samples prepared at 140 °C, 160 °C and 180 °C, respectively.

3.2. Modification of BWO with Noble Metals

H$_2$PtCl$_6$·6H$_2$O, HAuCl$_4$·3H$_2$O, AgNO$_3$, CuSO$_4$·5H$_2$O, and K$_2$PdCl$_6$ were purchased from Aladdin company (Vienna, VA, USA) (AR, 99%). For the modification, S1 sample (prepared at 140 °C) and aqueous solution (40 g/L) of respective salts, i.e., H$_2$PtCl$_6$·6H$_2$O (Aladdin (Vienna, VA, USA)), HAuCl$_4$·3H$_2$O (Aladdin (Vienna, VA, USA)), AgNO$_3$ (Aladdin (Vienna, VA, USA)), CuSO$_4$·5H$_2$O (Aladdin (Vienna, VA, USA)) and K$_2$PdCl$_6$ (Aladdin (Vienna, VA, USA)), were used, and the obtained samples were named accordingly, i.e., Pt/S1, Au/S1, Ag/S1, Cu/S1 and Pd/S1. In brief, 500 mg of S1 sample was added to a glass tube containing 25 mL of water/methanol (1:1) solution, and then the aqueous solution of noble metal (2 wt% of noble metal in respect to BWO) was added gradually by a micropipette under continuous stirring. Afterwards, the glass tube was covered with a latex stopper, and argon gas was purged through a thin plastic tube placed at the bottom of the tube for 15 min to remove oxygen (working as an electron scavenger). Then, the tube was sealed and wrapped with tape. The tube was irradiated with a xenon lamp (300 W, 100 mW cm$^{-2}$, 10 cm distance from the lamp) and the content was continuously stirred during 1 h irradiation. Finally, the obtained powder was collected after finishing operations, i.e., centrifugation, washing (2 times with ethanol and 2 times with deionized water), freeze drying and grinding.

3.3. Sample Characterization

The crystalline properties of samples were examined by X-ray diffraction (XRD; PANalytical Empyrean X-ray diffractometer). The morphology was observed with scanning electron microscopy (SEM, SU8010, Hitachi Limited Company, Tokyo, Japan) The surface properties (chemical composition and state of elements) were evaluated by X-ray photoelectron spectroscopy (XPS, PHI5000, ULVAC-PHI, Inc, Kanagawa, Japan) with C 1s (284.8 eV) as a reference for binding energy. The photoabsorption features were estimated by UV/vis diffuse reflectance spectroscopy (DRS, UV3600, Shimadzu Corporation, Kyoto, Japan).

3.4. Photocatalytic Activity

The photocatalytic performance was evaluated for two model reactions: oxidation (photodegradation of methyl orange) and reduction (generation of hydrogen). For the oxidative decomposition of methyl orange, a 300 W xenon lamp (100 mW cm$^{-2}$) was settled in 15 cm distance from the glass reactor. First, 150 mg of photocatalyst and 150 mL of MO (20 mg/L) were placed into the glass reactor, stirred for half an hour in a dark box to reach the equilibrium of adsorption/desorption, and then irradiated. Every 15 min the portion of
suspension (ca. 6 mL) was withdrawn from the reactor, centrifuged for 5 min (5000 rpm), and then the absorbance of the supernatant was analyzed by a UV/vis spectrophotometer (UV-1800PC).

For hydrogen generation, a closed glass reaction system—an automatic on-line trace gas analysis system (Labsolar-6A, Beijing Perfectlight Technology Co., Ltd., Beijing, China) was used. First, the photocatalyst (50 mg) was added to 100 mL aqueous solution with triethanolamine (TEOA, 10 vol%, a sacrificial electron donor). The reactor was evacuated with a vacuum pump and irradiated with a xenon lamp (300 W, 100 mW cm$^{-2}$). For vis activity measurements, a cut-off filter ($\lambda > 420$ nm) was installed on the front of the lamp. The amount of generated hydrogen was determined by on-line gas chromatography system (GC7900II).

4. Conclusions

BWO hierarchical microballs can be easily prepared by a simple hydrothermal method and then modified with nanoparticles of different noble metals. It has been found that a uniform morphology of microballs, composed of similar sheets, is necessary for the efficient degradation of methyl orange under UV/vis, which results in 65% decomposition over 90 min of illumination. In contrast, the flat sheet surface seems detrimental to hydrogen generation, as two different samples (S1 and S2) have caused similar effects, generating ca. 0.4 µmol h$^{-1}$ of hydrogen under UV/vis irradiation. The type of noble metal and its properties are crucial for the photocatalytic performance. Under UV/vis irradiation, only platinum enhances the evolution of hydrogen (2.77 µmol h$^{-1}$), probably due to the best catalytic (dark) property. In contrast, under vis irradiation, gold enhances the activity of BWO the most, reaching ca. 0.25 µmol h$^{-1}$ of hydrogen generation. Based on the XPS analysis, it has been found that zero-valent metals are the most highly recommended for activity enhancement under vis light, probably due to plasmonic photocatalysis, efficient light harvesting, and the catalytic effect.

Although the obtained data indicated that BWO hierarchical balls are prospective for both hydrogen generation and decomposition of organic compounds, further experiments are necessary to confirm the complete degradation (mineralization) of pollutants, e.g., with the use of a total organic carbon (TOC) analyzer. Moreover, the application of another test compound (colorless) for activity testing to avoid the possibility of photocatalyst sensitization [54,105–107] is under study for the detailed discussion on the reaction mechanisms.

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