# Two-step ionic liquid supported synthesis of $BiOBr/Bi_2WO_6$ thin film with superior visible light photocatalytic performance


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## INTRODUCTION

Recently, bismuth-based heterojunction has attracted a lot of attention in exploring the applications of heterogeneous photocatalysis due to their superior abilities such as visible light photoresponse, higher photoquantum yields, and negligible toxicity. The methods used so far led to receiving the photocatalysts mainly in a powder form, meanwhile, the advantages of the electrochemical method are related to a low processing temperature, low investment and operational costs and a possibility to form highly stable and recycle materials. In this regard, we demonstrated a novel two-step ionic liquid (IL) assisted procedure for a controllable synthesis of $BiOBr/Bi_2WO_6$ heterojunction on metallic foil. The preparation route involved anodic oxidation of W foil and subsequently transformation of the as-anodized oxide $WO_3 \cdot 2H_2O$ into $BiOBr/Bi_2WO_6$ heterojunction in the presence of N-butylpyridinium bromide [BPy][Br]. The IL served as a $Br^-$ source leading to the formation of bismuth oxybromide.


## RESULTS AND DISCUSSION

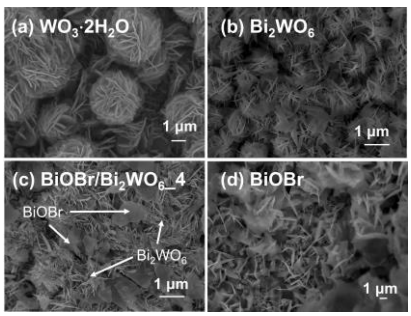



**Figure. 1** SEM images of **(a)** $WO_3 \cdot 2H_2O$, **(b)** $Bi_2WO_6$, **(c)** $BiOBr/Bi_2WO_6$_4, and **(d)** BiOBr.

**Table 1.** Sample code, molar ratio of IL or KBr to Bi precursor, average crystallite size, and diffraction peak intensity.

| Sample code | Molar ratio of IL to Bi precursor | Molar ratio of KBr to Bi precursor | Average crystallite size (nm) | | Diffraction peak intensity (a. u.) | |
|---|---|---|---|---|---|---|
| | | | $Bi_2WO_6$ (112) | BiOBr (102) | $Bi_2WO_6$ (112) | BiOBr (102) |
| $Bi_2WO_6$ | - | | 9.4 | - | 6485 | - |
| **$BiOBr/Bi_2WO_6$_20** | 1:20 | | 8.9 | 8.5 | 3785 | 294 |
| **$BiOBr/Bi_2WO_6$_10** | 1:10 | | 32.4 | 16.3 | 1076 | 433 |
| **$BiOBr/Bi_2WO_6$_4** | 1:4 | - | 21.2 | 19.8 | 397 | 481 |
| **$BiOBr/Bi_2WO_6$_1** | 1:1 | | 19.8 | 28.9 | 44 | 2453 |
| **BiOBr** | 1:1 | | - | 27.9 | - | 2472 |
| **$BiOBr_KBr/Bi_2WO_6$_1** | - | 1:1 | 9.8 | 6.6 | 2302 | 473 |

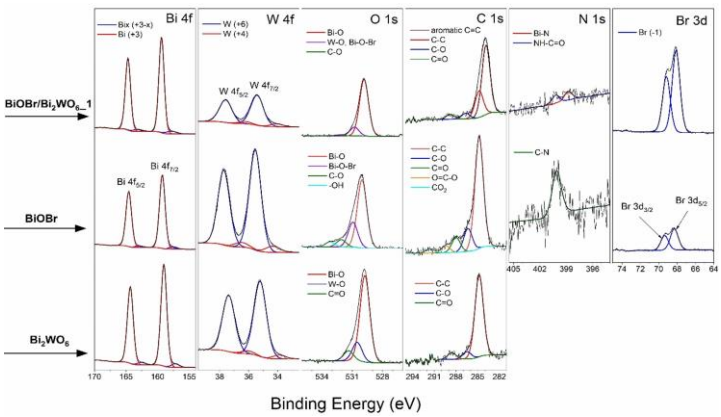
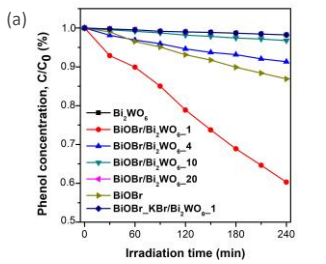



**Figure 3.** High resolution Bi4f, W4f, O1s, C1s, N1s, and Br3d XPS spectra recorded on $BiOBr/Bi_2WO_6$_1, BiOBr and $Bi_2WO_6$ photocatalysts.



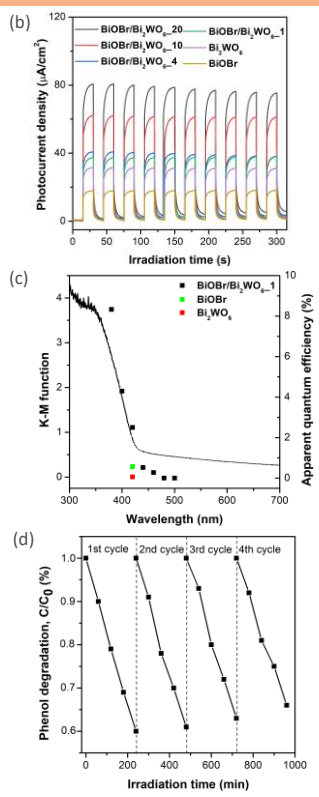




**Figure 4. (a)** Photocatalytic decomposition of phenol, **(b)** photocurrent response registered at 1.0 V in 0.5 M $Na_2SO_4$, **(c)** AS for phenol oxidation over $BiOBr/Bi_2WO_6$_ 1, BiOBr and $Bi_2WO_6$ (AQE – squares) vs. absorption spectrum of $BiOBr/Bi_2WO_6$_1 (K-M function – line), and **(d)** photostability of the most photoactive sample ($BiOBr/Bi_2WO_6$_1) in four consecutive cycles under visible irradiation (optical filter > 420 nm).

## CONCLUSION

- The formation of BiOBr plates occurred on the flower-like $Bi_2WO_6$ surface, creating a morphology similar to the core ($Bi_2WO_6$)-shell (BiOBr) structure;
- The replacement of the IL with the inorganic salt, KBr, made it difficult to form a heterojunction by using this method;
- The highest phenol degradation efficiency was achieved when the highest amount of IL was used (AQE was almost 8 and 71.5 times higher compared to BiOBr and $Bi_2WO_6$, respectively);
- Phenol decomposition occurred mainly via superoxide radicals ($\bullet O_2^-$), while the participation of other species, electrons (e-), holes (h+), or hydroxyl radicals ($\bullet$OH) was negligible;
- The enhancement photoactivity originated from *(i)* incorporation of the nitrogen atoms into BiOBr structure originated from partially decomposed IL, *(ii)* interaction of bromide ions, and *(iii)* the close interface contact between BiOBr and $Bi_2WO_6$ with matchable energy band gap positions and improved electron-hole separation;
- This research provides a new insight into the design and fabrication of a highly stable, advanced heterojunction structure prepared in IL-assisted systems with enhanced photocatalytic and photoelectrochemical properties under visible irradiation.

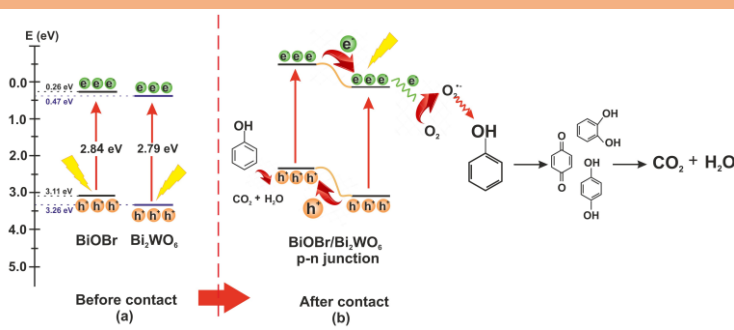



**Figure 5. (a)** Schematic diagram of the energy positions of BiOBr and $Bi_2WO_6$ before contact, and **(b)** possible photocatalytic mechanism of phenol degradation after p-n heterojunction formation under visible-light irradiation.

## ACKNOWLEDGMENTS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