

Synthesis and characterization of multifunctional mineral beyerite ($\text{CaBi}_2\text{O}_2(\text{CO}_3)_2$)

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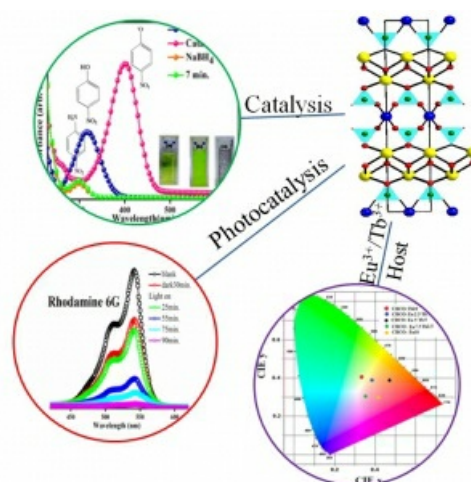
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Heterogeneous catalysis and photocatalysis have emerged as the most sought after research topics towards minimizing the environmental impacts from unwanted and harmful chemical products. Specially semiconductor photocatalysis developed initially on TiO_2 , soon resulted in a rapid surge of several other materials. The materials containing Bi^{3+} cation offer an attractive choice by providing nontoxic, photostable semiconductors with reduced band gap because of the overlap of its 6s band with the 2p band of the anionic oxygen. Apart from BiVO_4 , other bismuth containing compounds such as Bi_2MoO_6 , Bi_2WO_6 , Bi_2CuO_4 , $\text{Bi}_2\text{O}_2\text{CO}_3$ and BiOX ($X = \text{Cl}, \text{Br}, \text{I}$) have been investigated extensively. Most of these materials have also been made into different heterostructures in order to improve the photocatalytic efficiency specially under visible light irradiation. In this regard ($\text{Bi}_2\text{O}_2\text{CO}_3$), bismuth subcarbonate, naturally occurring as mineral Bismutite, has been found to be an important compound. $\text{Bi}_2\text{O}_2\text{CO}_3$ belongs to the family of sillen phases and is an intergrowth of $[\text{Bi}_2\text{O}_2]^{2+}$ layers and $(\text{CO}_3)^{2-}$ layers formed in such a way that the plane of the $(\text{CO}_3)^{2-}$ group is orthogonal to the plane of Bi-O layers. Bismuth subcarbonate has long been the material of investigation for medical purpose because of its antibacterial activity. More importantly, because of its band gap of 3.38 eV, it has been investigated as a potential photocatalyst under UV light irradiation. Subsequently, several research groups have attempted to enhance the photocatalytic efficiency through different synthetic methods to achieve nanotubes, plates, sponge, nanosheets, nanoscale crystallites, and crystallites with flower like morphologies [1]. We found that the other bismuth carbonate containing calcium, known as mineral Beyerite, $\text{CaBi}_2\text{O}_2(\text{CO}_3)_2$ has been relatively less explored except for a brief study of luminescence [2]. Beyerite has the $[\text{Bi}_2\text{O}_2]^{2+}$ layers along with the additional Ca^{2+} ions and the layer sequence is $(\text{Bi}_2\text{O}_2)^{2+} - \text{CO}_3^{2-} - \text{Ca}^{2+} - \text{CO}_3^{2-} - (\text{Bi}_2\text{O}_2)^{2+}$ [3]. Herein, we present bismuth calcium oxy carbonate; $\text{CaBi}_2\text{O}_2(\text{CO}_3)_2$ synthesized via single step solvothermal route having different morphologies. The as synthesized beyerite is phase pure and the Rietveld refinements of the PXRD measurements confirmed the structure (S.G. Immm, $a = 3.76283(5) \text{ \AA}$; $b = 3.75493(8) \text{ \AA}$; $c = 21.6611(5) \text{ \AA}$). Pristine Beyerite with a band gap of 3.97 eV and its heterostructures with BiOI were tested as a photocatalyst. In addition, the material is found to be an excellent catalyst for reduction reactions such as p- nitrophenol and 2, 4 di-nitrophenol. Finally, Beyerite has also been utilized as a host lattice for the incorporation of optically active metal ions (Tb^{3+} , Eu^{3+} and $\text{Tb}^{3+}/\text{Eu}^{3+}$) possessing emission in a wide range of wavelength. The characterization of this unique mineral obtained from techniques including Powder X-ray diffraction (PXRD), Fourier Transformed infrared (FT-IR), Raman, Thermogravimetric analysis (TGA), Ultra-violet Diffuse reflectance Spectroscopy (UV-DRS) and Field Emission-Scanning electron microscopy (FE-SEM), Photoluminescence (PL) measurements will be presented. Significant results showing the mineral's ability to perform as a catalyst, photocatalyst and as a luminescent host will be included.

[1] Ni, Z. et al. (2016) Phys. Chem. Chem. Phys. 18, 7768-7779.

[2] Blasse, G. & Dirksen, G. J. (1988) Mat. Res. Bull. 23, 1591-1596.

[3] Malik, V. et al. (2016) RSC adv. 6, 38252-38262.



Keywords: [Beyerite](#), [Catalysis](#), [Hydrothermal synthesis](#)