Enhancement of Photocatalytic activity of γ- Bi_2MoO_6 with Graphite flake under Visible light irradiation

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Abstract: *The influences of the various preparation parameters (including the pH value, reaction temperature, and holding time) on the phase formation and morphology development were investigated in detail. Graphite was observed on the surface of γ- Bi_2MoO_6 after the co-precipitation and calcination treatment. The synthesized γ–Bi_2MoO_6 –Graphite flake composite nanoparticles (NP's) were characterized with X-ray diffraction (XRD) for identify crystalline phases and particle size, Raman spectroscopy is identify active species during the reaction, UV-Visible diffuse reflectance spectroscopy (UV-DRS) revealed for band energy of semiconductors, Field emission scanning electron microscopy(FE-SEM) to determine morphology and shape of supported particles and Energy dispersive X-ray analysis (EDX) for elemental analysis of synthesized nanoparticles. The photocatalytic activity of γ–Bi_2MoO_6 catalyst was evaluated using the degradation of Methylene blue under Visible light irradiation at room temperature. A remarkable enhancement in the visible photo light activity was observed over the Bi_2MoO_6-Graphite composite compared to pure Bi_2MoO_6.*
Keywords: Co-precipitation, Graphite, Photocatalytic degradation, Calcination

I. Introduction

Photocatalytic degradation of organic pollutants by semiconductor photo catalysts is promising for environmental purification and energy conversion[1],[2]. Photocatalytic activity of semiconductor oxide depends on its physical and chemical properties, the recombination of photo excited electrons and holes at crystal lattice defects, crystalinity is one of the main factors for photo catalytic reaction efficiency. Titanium dioxide (TiO_2) has been investigated extensively as a photocatalyst for degradation of contaminants in wastewater due to its low cost, photoactive and stable properties[3],[4], TiO_2 as the photocatalyst is a high band gap (~3.2 ev) semiconductor and responds only to the ultraviolet light (λ< 400 nm), which limits the efficient utilization of solar energy for TiO_2 photocatalysis[5],[6]. Besides, the traditional titanium dioxide nanoparticles are difficult to recover and reuse because they cannot be simply separated by sedimentation from an aqueous suspension[7]. Bismuth molybdate (α–Bi2Mo3O12 ,β–$Bi_2Mo_2O_9$,γ –Bi_2MoO_6) have become one of the promising photo catalysts due to their narrow band gap[8]. Bismuth molybdate have the general chemical formula Bi_2O_3 .n MoO_3 where n=3,2 or 1 corresponding to α, β and γ - phases respectively. The three phases of Bi-Molybdates include alternative MoO_2^{2+} (A) layers, $Bi_2O_2^{2+}$ (B) layers and O_2^{2-} (O) layers[9].Arrangement of the layers in the α–phase= $(BOAOAOAO)_m$ and band gap = 2.88ev , β–phase = $(BOAOAO)_m$ and band gap = 3.10ev , γ– phase = $(BOAO)_m$ and band gap = 2.70ev[10]. Most researchers agree that the β–$Bi_2Mo_2O_9$ phase is more active than the α–Bi2Mo3O12 phase [11],[12]. However, it is known that β–$Bi_2Mo_2O_9$ thermally unstable could be decomposition at temperatures ranging from 400 - 550^0c to α and γ phases[13],[14], it could be obtained above 550^0c. However the activity of γ –Bi_2MoO_6 is disputed. Some researcher claim it to be the most active phase than other two phases[8],[15]. γ –Bi_2MoO_6 is a typical Aurivillius-phase perovskite with a structure consisting of pervoskite layers ($A_{m-1}B_mO_{3m-1}$) between bismuth oxide layers (Bi_2O_2) in bismuth Oxide family[16].Based on photo physical properties and photo catalytic activity of Bismuth molybdate under visible light irradiation, Yoshiki shimodaira et al [17] concluded that the corner sharing structure of the MoO_6 octahedra consistituted to the visible light response and photo catalytic performance because excitation energy and/or photo generated electron and hole pairs begin to migrate easily in Aurivillus structure.

Bi_2MoO_6 possesses pervoskite shape consisting of MoO_6 octahedra where as Bi2Mo3O12 has a certain connection between MoO_4 tetrahedra and MoO_6 octahedra. It results in the photo catalytic activities of Bi_2MoO_6 and $Bi_2Mo_2O_9$ are larger than that of Bi2Mo3O12. γ –Bi_2MoO_6 is interesting due to its unique physical properties of ion conduction[18], photoconductors[18], and gas sensors[19],small band gap compared to other phases[10]. γ –Bi_2MoO_6 have been widely studied because of their industrial applications in the oxidation of propylene, butane and isobutene, and in the ammoxidation of propene: yielding acrolein[20], butadiene[21], methacrolein[22], and acrylonitle[23].

Graphite is a allotrope of carbon. Carbon is having one of the unique characteristic to exit in a number of allotropic forms, which remarkably varying physical and chemical properties due to the diverse nature of

chemical bonds and arrangement of carbon atoms in 3D (diamond), 2D (Graphite), 1D (carbine)[24][25].Graphite is one of most important allotrope of carbon, in spite of being a non-metal, which is an efficient conductor of electricity. It has diverse applications ranging from every day purpose such as lead pencils to big industrials uses like steel making due to its versatile properties [27].Recently reported Xiaoya Yuan et al ,graphite-like carbon nitride (g-C$_3$N$_4$), polymer semiconductor, exhibit excellent photocatalytic activities toward many organic pollutants under visible light irradiation[28]. Now a day the improvement of photocatalytic activity is also an important challenge for its photocatalysis in splitting water into hydrogen and oxygen and degrading organic pollutants in the water of air for solving the energy shortage and the environment pollution. Due to the potential excellent photocatalytic property under visible light, and bismuth molybdate with graphite composite showing excellent photocalytic observed these work due to bismuth molybdate have attracted extensive due to the Aurivillius structure and graphite have large surface area. The Photocalytic activity of   γ- Bi$_2$MoO$_6$ - Graphite flake composite under Visible light irradiation is reported first time in this paper.

II. Materials And Methods

Graphite Flakes (Sigma Aldrich), N-Hexane, Bismuth Nitrate [Bi(NO$_3$)$_3$ .5H$_2$O], Nitric acid [HNO$_3$ 78%], Ammonium molybdate [(NH$_4$)$_6$Mo$_7$ O$_{24}$ .4H$_2$O] and Ammonium hydroxide [NH$_4$OH], Methylene blue. All chemicals received from Merck India except Graphite Flakes and used without further purifier.

CO-PRECIPITATION METHOD

Graphite flake (1g) mixed with n-hexane and then sonicated 5 hours for dispersion of Graphite flake uniformly distribution. Synthesis of γ−Bi$_2$MoO$_6$-Graphite composite to known amount of bismuth nitrate (0.49M Bi(NO$_3$)$_3$ .5H$_2$O) was dissolved in diluted nitric acid (1.5M HNO$_3$)). The solution was then added drop wise into the aqueous solution containing known amount of ammonium molybdate (0.035M (NH$_4$)$_6$Mo$_7$ O$_{24}$ .4H$_2$O) under vigorous stirring and the solution of sonicated Graphite flake is added to the reaction mixture. During the co-precipitation step, pH of the mixed solution was precisely controlled by adjusting the amount of ammonia solution added. The pH values were kept at 3.0 in the preparation of γ−Bi$_2$MoO$_6$-Graphite phase. The reaction of the solution continuously constant stirred vigorously at room temperature for 8h, the precipitate was filtered to obtain a solid product. The solid product was dried and then it was calcined at 475^0 C for 5h to yield the γ−Bi$_2$MoO$_6$-Graphite composite.

CHARACTERIZATION

The crystalline structure of the product was characterized by power X-ray diffraction (XRD, PanAlytical, X-Pert pro, Netherland) with Cu Kα (λ-1.54218 A)radiation. Maximum peak position compared with the standard files to identify the crystalline phase. Raman spectroscopy provides insight into the structure of oxides, their crystallinity, and the coordination of metal oxide sites. Fourier transform infrared (FT-IR) spectra of the sample were recorded on a FT-IR spectrometer using conventional KBr pellets with in a wavenumber range 5000 – 500cm^{-1} and Raman spectra recorded to the raman shift range 200 – 1200cm^{-1}. The size and morphology of the product were obtained with a scanning electron microscope (FESEM-CARL Zeiis Germany, Model Ultra 55 FESEM, Gemini column, 1nm Resolution, detector is INLENSE), EDX (Oxford company, model 20nm X Ma) UV-vis diffuse reflectance spectra of the sample were obtained in the range 300 – 800nm using a UV-vis spectrophotometer (UV2550, Shimadzu, Japan) BaSO4 was used as a reflectance standard.

PHOTO CATALYTIC TEST

MB were chosen as a pollutant to evaluate the photocatalytic activities of the as synthesized samples . A 400 W HgX lamp was used as the light source to provide the simulated solar light. The experiments performed at an ambient temperature. The photocatalysts(0.05 g) were added into 50 mL of Methylene blue (MB, 5ppm) dye solution , and suspension was magnetically stirred for 30 min in the dark to reach an adsorption-desorption equilibrium with the photocatalysts. At given time intervals, a 3 mL solution collected and then analyzed on UV-vis spectrophotometer during the photo-degradation process. The concentration of MB was determined by monitoring the variations in the main absorption centered at 664 nm.

III.   Results And Discussion

All relevant XRD peaks were identified and indexed based on the available JCPDS(Joint Committee for Powder Diffraction Studies) data. Across the catalysts there is no detection of any peak attributable to impurities. The XRD results shown in Fig.1.The expanded diffraction peaks revealed that the crystalline phase was nanosized.The crystalline size was calculated from the XRD line boarding using Scherrer relationship, d=0.9λ/(βcosθ), where d was the diameter in A^o, β was the half maximum line width and λ was the wavelength

of x-rays. The crystalline size of the Pure $\gamma-Bi_2MoO_6$, Graphite Flake, $\gamma-Bi_2MoO_6$- Graphite flake composite is 47.58nm,42.6nm,47.33nm respectively. The diffraction (XRD) pattern shows the synthesis of $\gamma-Bi_2MoO_6$ by co-precipitation process presence and absent of Graphite flake. The diffraction (XRD) peaks agree with JCPDS card no 41-1487 for Graphite flake and 21-0120 for $\gamma-Bi_2MoO_6$. Distinctive differences in the peak intensities of the (002) and (131) planes are observed.
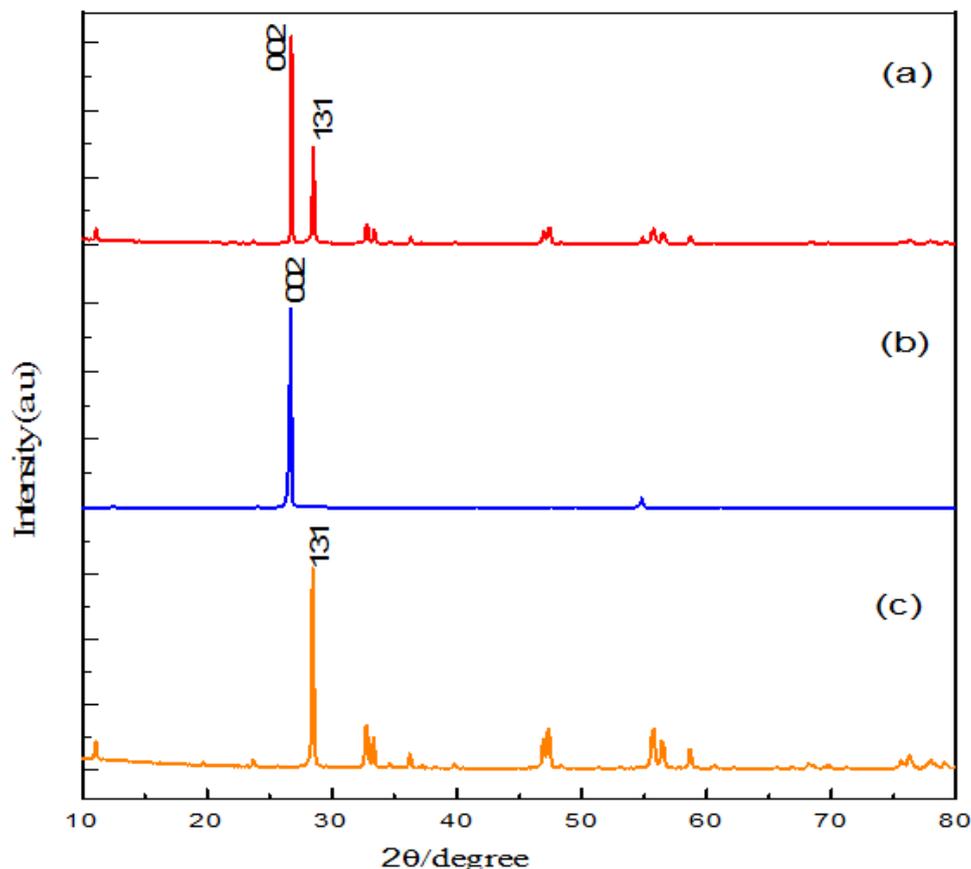
Fig 1. XRD patterns of the samples (a) $\gamma-Bi_2MoO_6$- Graphite flake composite (b) Graphite flake (c) $\gamma-Bi_2MoO_6$

Raman Spectroscopy provides insight into the structure of oxides, their crystallinity, the coordination of metal oxide sites, and even the spatial distribution of phases through a sample when the technique is used in microprobe mode. The Raman Spectra of $\gamma-Bi_2MoO_6$ sample, obtained by co-precipitation method are show in Fig.2, which correspond well to the result of Raman spectroscopy. The typical vibrational bands for the $\gamma-Bi_2MoO_6$ sample was observed $849cm^{-1}$ (s), $795cm^{-1}$ (vs), $715cm^{-1}$ (w), $401cm^{-1}$ (vw), $352 cm^{-1}$ (w), $325 cm^{-1}$ (vw), $282 cm^{-1}$ (vs). The vibrational bands $849cm^{-1}$, $795cm^{-1}$ (vs) peaks can be ascribed to the stretching modes of Mo-O bonds and vibrational band $715cm^{-1}$ (w) peak can be ascribed to the stretching modes of Bi-O/Bi-O-Mo stretching observed. The Raman spectrum of $\gamma-Bi_2MoO_6$ phase shows a very strong band at $795cm^{-1}$, which is A_{1g} mode and represents the symmetric stretch of the MoO_6 octahedron. The band with strong intensity at $849cm^{-1}$ also have A_{1g} character and are due to orthorhombic distortion of the octahedron. The modes between $280 cm^{-1}$ and $360 cm^{-1}$ have E_g character, plausibly due to the rocking mode of the octahedron [20-22]. The vibrational bands for the $\gamma-Bi_2MoO_6$- Graphite flake composite was observed $286cm^{-1}$(w),$339cm^{-1}$(w),$721cm^{-1}$(vw),$888cm^{-1}$(vw),$804cm^{-1}$(vs)
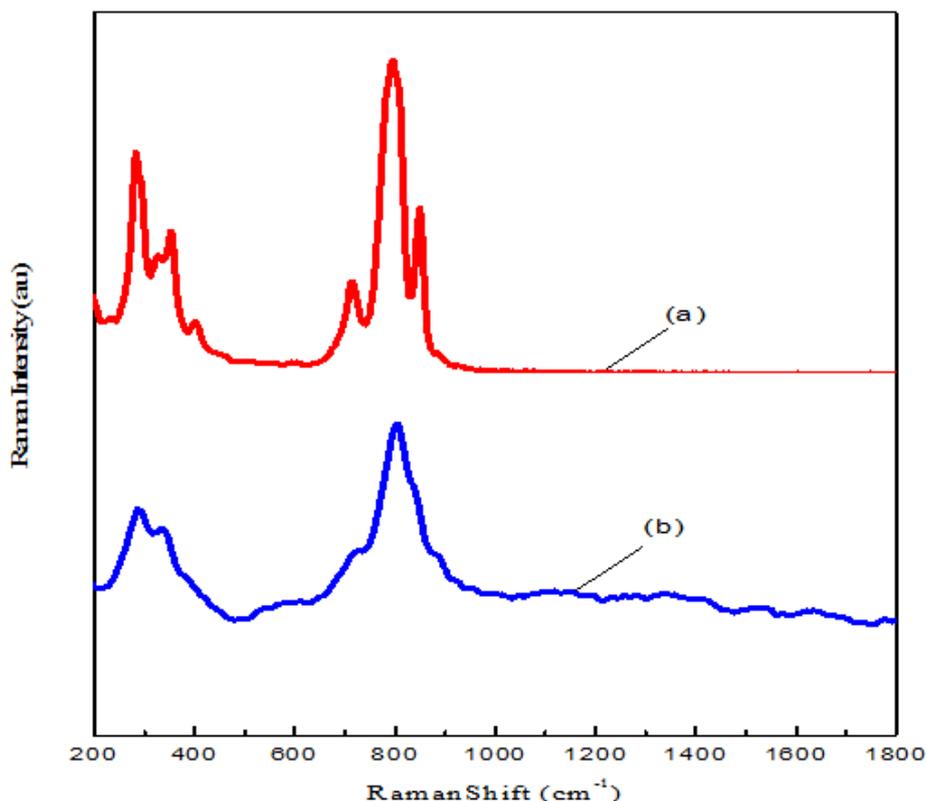
Fig.2. Raman spectrum of (a) γ− Bi2MoO6 sample (b) γ− Bi$_2$MoO$_6$- Graphite flake composite

SEM belongs to the group of electron microscopy, which is a fairly straightforward technique to determine the size and shape of supported particles, which can also reveal information on the composition and internal structure of the particles. The morphology observed with Field -emission scanning electron microscopy (FE-SEM) gives clearly showing (Fig.4 (a-c)) octahedral structure of γ−Bi$_2$MoO$_6$ and Graphite flake on the surface of γ−Bi$_2$MoO$_6$ (Fig.4 (c-e)). The EDS analysis(Fig.5) to the confirmation of Bi$_2$MoO$_6$ and Graphite compound.
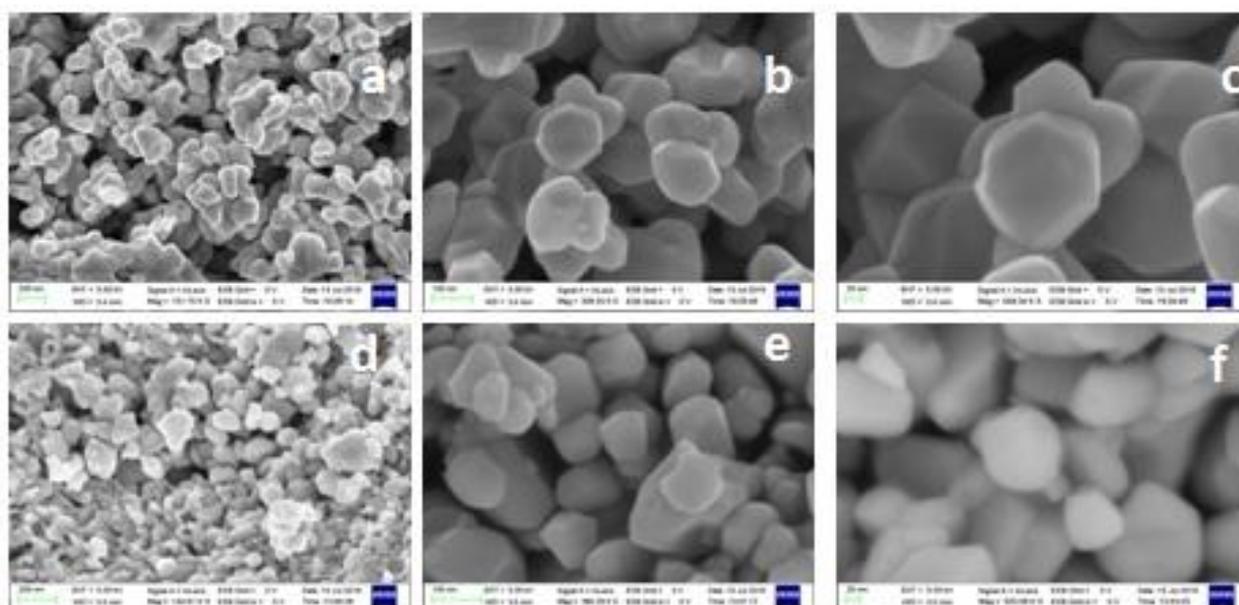
Fig.4. SEM images of γ− Bi$_2$MoO$_6$ (a-c) with 200nm,100nm,20mn scale respectively with octahedral structure and γ− Bi$_2$MoO$_6$- Graphite flake composite (d-f) with 200nm,100nm,20nm scale respectively with Graphite surface on the Bismuth molybdate.
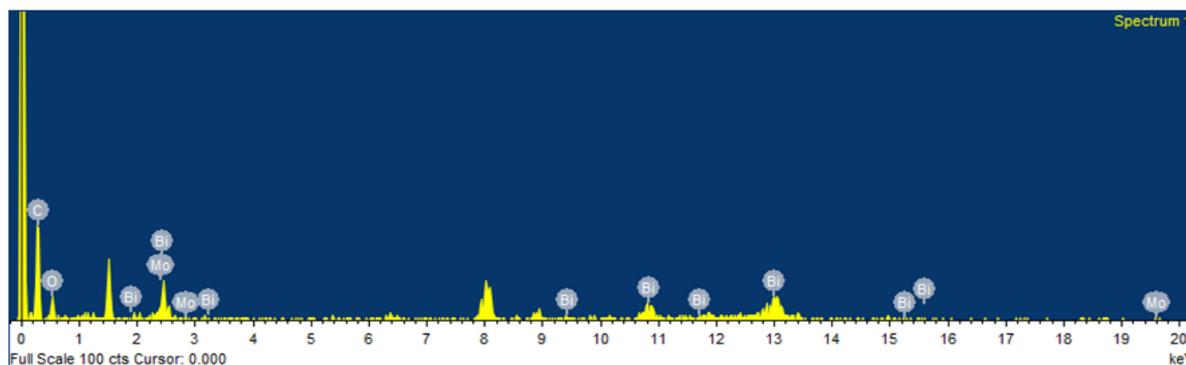
Fig.5. Elemental analysis of Energy-Dispersive X-ray spectroscopy (a) γ− Bi_2MoO_6 (b) γ− Bi_2MoO_6- Graphite flake composite

Diffuse-reflectance spectroscopy (DRS) is an important method for charactering the electronic state, optical state and calculates the band gap of semiconductor materials. The DRS spectra of as prepared γ−Bi_2MoO_6, γ−Bi_2MoO_6 - Graphite flake composite and pure graphite flake are show in Fig.6. The samples of γ−Bi_2MoO_6, γ−Bi_2MoO_6 - Graphite flake composite exhibited an intense absorption in the visible-light range, which suggests the property of being photoactive under visible –light irradiation and Pure graphite flake exhibited zero band gap, which suggest to graphite flake was non semiconductor. The adsorption edges of γ−Bi_2MoO_6 and γ−Bi_2MoO_6 - Graphite flake composite are located around 482 and 613 respectively. Their band gaps are estimated to be 2.57 eV and 2.02 eV, which suggests enhancement the photocatalytical activity of γ−Bi_2MoO_6 with graphite flake compared to pure γ−Bi_2MoO_6. The bang gap was mainly influenced by the coordination of oxygen ions to a molybdenum ion. The synthesis materials γ−Bi_2MoO_6 and γ−Bi_2MoO_6 - Graphite flake composite in this study exhibited a narrower band gap compared with that reported by Kudo and co-workers.
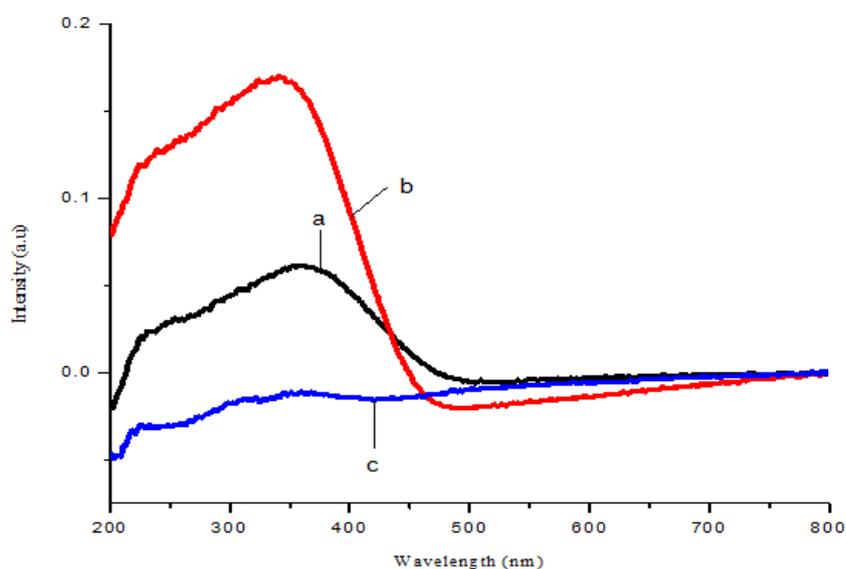
**Fig.6** UV-DRS spectra of (a) γ− Bi_2MoO_6 (b) γ− Bi_2MoO_6- Graphite flake composite (c) Graphite flake

PHOTOCATALYTIC EFFECT

Visible light adsorption of γ−Bi_2MoO_6 revealed by the plane-wave-based DFT method to be due to a transition from the valence band consisting of the O 2p orbitals to the conduction band derived from the primary Mo 4d orbitals in MoO6 octahedra and the secondary Bi 6p orbitals [29]. To demonstrate that the γ−Bi_2MoO_6 semiconductors were preferred for efficient charge separation, the photocurrents generated on the sample different phases measured. Generally , the value of the photocurrent indirectly reflects the semiconductor's ability to generate and transfer a photogenerated charge carrior under irradiation, which correletes with the photocatalytic acivity[30],Fig .7 shown that the γ−Bi_2MoO_6 with Graphite composite spectra are more efficient in photocurrent generation compared to pure γ−Bi_2MoO_6 phase. Therefore, the γ−Bi_2MoO_6 –Graphite flake composite enhanced the charge carrier transfer and reduced the electron hole recombination.
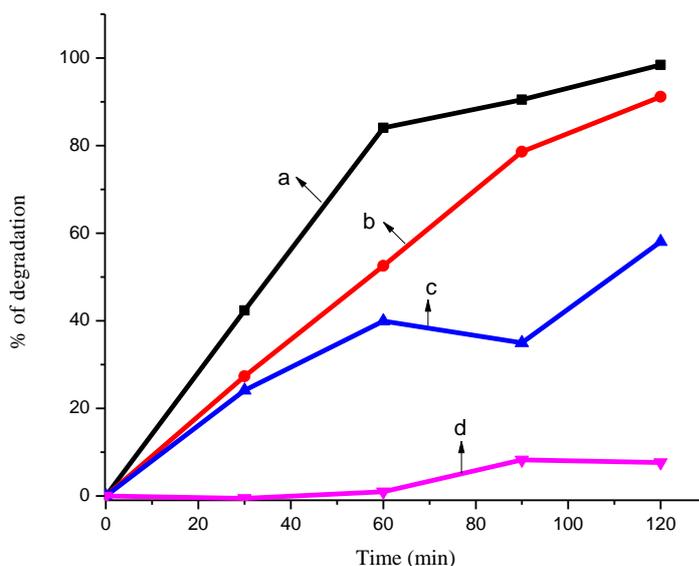
Fig.7. Plot of photo degradation of MB as a function of the % of degradation verses time of the prepared samples (a) γ–Bi₂MoO₆-Graphite flake composite (b) pure γ–Bi₂MoO₆ phase (c) pure graphite flake (d) MB dye without catalyst
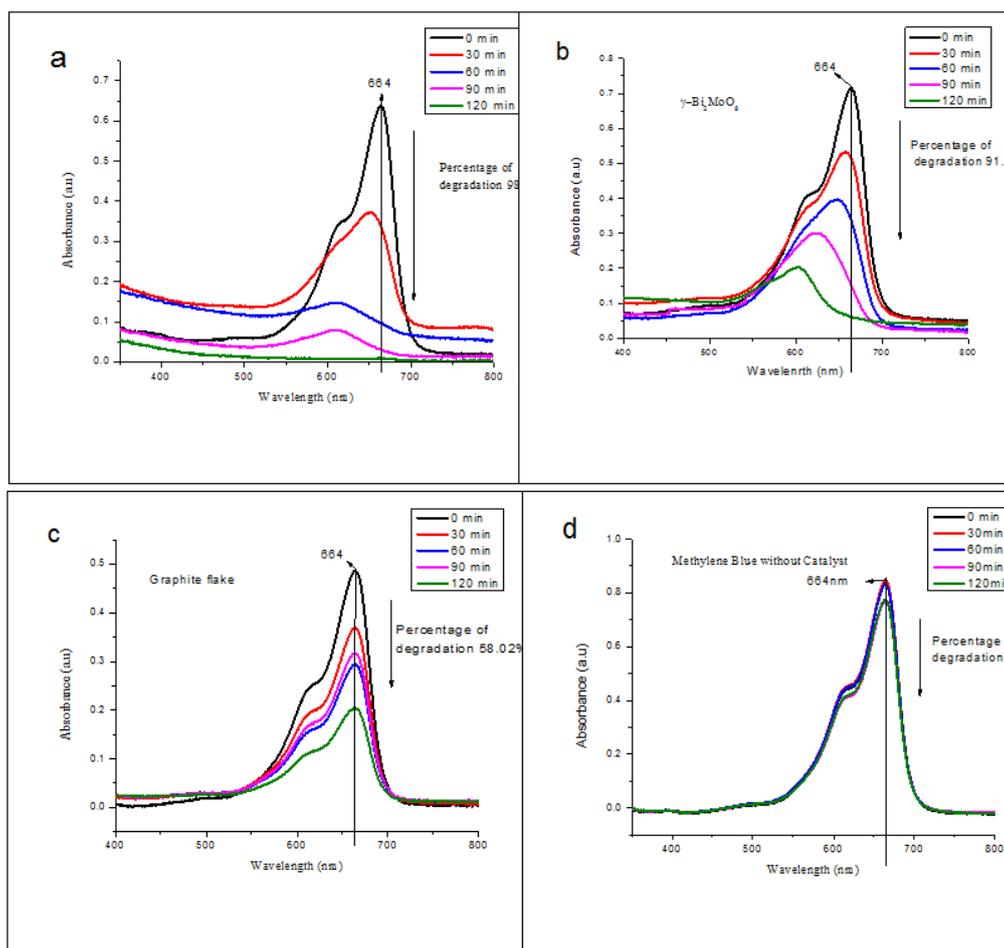
Fig.8. UV-visible spectra of (a)γ–Bi₂MoO₆-Graphite flake composite (b) pure γ–Bi₂MoO₆ phase (c) pure graphite flake (d) MB dye without catalyst

It is assumed the interaction between γ−Bi$_2$MoO$_6$ and Graphite flake are more favorable for enhancing the photocatalytic activity of γ−Bi$_2$MoO$_6$ –Graphite flake composite.Fig.8 clearly indicates the percentage of degradation of dye with respective catalyst, Directly Graphite flake 58.02 % of dye degradable within 120 minutes of time and directly dye without any catalyst only visible light 7.62% of dye degradable, pure γ−Bi$_2$MoO$_6$ catalyst 91.17%, γ−Bi$_2$MoO$_6$ –Graphite flake composite 98.43% of dye degradable within 120 minutes of time. Fig 5.showing the time irradiation of catalyst and clearly indicates γ−Bi$_2$MoO$_6$ –Graphite flake composite is more catalytic activity and fastly degradable of dye compared to pure γ−Bi$_2$MoO$_6$.

IV.   Conclusion

The synthesis of γ−Bi$_2$MoO$_6$ and γ−Bi$_2$MoO$_6$ –Graphite flake composite was successfully synthesized by the Co-precipitation method by controlled specific pH condition and followed by calcination treatment. Formation of γ−Bi$_2$MoO$_6$ and γ−Bi$_2$MoO$_6$ –Graphite flake composite catalysts was well confirmed by XRD and EDS analysis.the photocatalytic activity of γ−Bi$_2$MoO$_6$ with Graphite composite spectra are more efficient in photocurrent generation compared to pure γ−Bi$_2$MoO$_6$ phase. Therefore, the γ−Bi$_2$MoO$_6$ –Graphite flake composite enhanced the charge carrier transfer and reduced the electron hole recombination. It is assumed the interaction between γ−Bi$_2$MoO$_6$ and Graphite flake are more favorable for enhancing the photocatalytic activity of γ−Bi$_2$MoO$_6$ –Graphite flake composite

References

[1].   (1) Kudo, A.; Omori, K.; Kato, H. J. Am. Chem. Soc., 121, 1999, 1145−1155.
[2].   Xiaojuan Bai, Li Wang, and Yongfa Zh ACS Catal., 2,2012, 2769−2778.
[3].   A.T. Bell, Science., 299,2003, 1688.
[4].   G.Tian, Y.Chen, W.Zhou, K. Pan, C. Tian, X.R. Huang and H.Fu, CrystEngComm.,13,2011, 2994-3000.
[5].   Y.Park, S.H. Lee, S.O.Kang and W. choi, Chem. Commun., 46,2010, 2477-2479.
[6].   D.Kannaiyan, E.Kim, N.Won, K.W. Kim, Y.H. jang, M.A. Cha, D.Y . Ryu, S.Kim and D.H. Kim, J.Mater.Chem.,20, 2010,677-682.
[7].   W.Li, Y. bai, C.Liu, Z.Yang,X.Lu,N.K. vander Laak and k.Y. Chan Environ.Sci.Technol., 43,2009, 5423-5428.
[8].   Shiyi Cao, Chuansheng Chen, Tiangui liu, Yuenhong Tsang, Xuming Zhang, Weiwei Yu, Weiwei Chen. Chemical Engineering Journal., 257, 2014,309–316.
[9].   Ph.A. Batist, J. Catal., 12,1968, 45.
[10].   A.V.Prasada Rao, A.M. Umabala and P.Suresh, J. Applicable Chemistry., 4(4): 2015,1145-1172.
[11].   J.R.Monnier,G.W.Keulks, Preprints Am.Chem.Soc.Div.Petr.Chem., 24,1979,19.
[12].   P.A. Batist, B.C.Lippens, G.C.A.Schuit,J.Catal., 5, 1966, 55.
[13].   Ph.A.Batist, J.F.H. Bouwens, G.C.A. schuit, J. catal., 25,1972, 1.
[14].   Ji chul Jung, Heesoo Kim, Ahn Seop Choi, young-Min Chung, tae jin Kim, Seong Jun Lee, Seung-Hoon Oh, In Kyu Song. Journal of Molecular Catalysis A: Chemical., 259, 2006,166-170.
[15].   Willy J.m.van well,Minh Thang Le, Niels Christian Schiodt, Serge House, Per Stoltze. Journal of Molecular Catalysis A:Chemical., 256, 2006,1-8.
[16].   R.E. Newnman, R.W. Wolfe, J.F. Dorrian, Material research Bulletin 6, 1971, 1029-1039.
[17].   Y.Shimodaira, H.Kobayashi, A.Kudo, J.Phys.Chem.B., 110, 2006,17790-17797.
[18].   L.T.sim,C.K.Lee, A.R. West, Journal of Materials Chemistry., 12, 2002, 17-19.
[19].   T.Sekiya, A.Tsuzuki,Y.Torii, Elaboration, Materials Research Bulletin., 21,1986, 601-608.
[20].   N. Hykaway,W.M. Sears, R.F. Frindt, S.R. Morrison., Sensors and Actuators.,15, 1988, 105-118.
[21].   Y.Obana, K. Yashiki, M.Ito, H.Nishiguchi, T.Ishihara, Y.Takita, J.Jpn.Petrol.Inst.,46, 2003, 53.
[22].   W.J.M. van Well, M.T. Le, N.C. schiodt, S.Hoste,P.Stoltze, J.Mol. catal. A., 256, 2006, 1.
[23].   J.C.Jung, H. Kim, Y.M Chung, T.J.Kim, S.J.Lee, S.H. Oh, Y.S. Kim, I.K. Song, J.Mol. Catal.A., 264, 2007, 237.
[24].   L.M Thang, L.H. bac, I.V. Driessche, S.Hoste, W.J.M van Well catal. Today., 131, 2008, 566.
[25].   L.A Karstova,A.A.Makarov, Russ.J.Appl.Chem.75, 2002, 1725-1731.
[26].   Vadali V. S. S. Srikanth, P. Sampath Kumar, and Vijay Bhooshan Kumar., International Journal of Electrochemistry 2012, Article ID 218393, 7.
[27].   H.C.Shin.W.I.Cho,H.Jang., Electrochim.Acta 52, 2006, 1472-1476.
[28].   Xiaoya Yuan , Chao Zhou , Qiuye Jing , Qi Tang , Yuanhua Mu and An-ke Du, Nanomaterials 6,2016, 173.
[29].   Shimodaira,Y.,Kato,H.,Kobayashi,H.,Kudo,A.J.Phys.Chem.,110, 2006, 17790-17797.
[30].   Kim,H.G.,Borse,P.H.Choj,W.Y.,Lee,J.S.Angew.Chem.,Int.Ed.,44,2005,4585-45.