Electronic Structure of Visible Light-Driven Photocatalyst \( \delta\)-Bi\(_{11}\)VO\(_{19}\) Nanoparticles Synthesized by Thermal Plasma

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ABSTRACT: Size confinement for tailoring of electronic structures can in principle be explored for enhancement of photocatalytic properties. In the present work, vanadium-doped bismuth oxide nanoparticles, with an average particle size of 36 nm, are synthesized for the first time, using the thermal plasma method, in large scale with high yield to explore for photocatalytic applications. The electronic and crystallographic structures of the sample are studied experimentally and theoretically. Systematic investigations of the electronic structure of the fluorite type cubic phase of Bi\(_{11}\)VO\(_{19}\) nanoparticles are reported for the first time. Enhancement is observed in the photocatalytic activity as compared to other delta phases of bismuth vanadate. The valence band is found to comprise mainly of O 2p states, whereas the conduction band arises from V 3d states giving rise to a band gap value of 2.26 eV. Absence of excess O in \( \delta\)-Bi\(_2\)O\(_3\) results in shrinking of the band gap because of O 2p, Bi 6s and 6p states from the surrounding atoms at doping sites. Bi\(_{11}\)VO\(_{19}\) nanoparticles show an efficient visible light absorption and exhibit excellent photodegradation properties of methylene blue solution under visible light irradiation.

1. INTRODUCTION

Photocatalytic splitting of water into hydrogen and oxygen, and the photocatalytic degradation of organic pollutants are promising applications as far as energy and environmental issues are concerned. After the report of Honda—Fujishima on photoelectrochemical water splitting, considerable progress has been made on the research front in the applications of photocatalysts both in energy and environmental issues. Tremendous interest has been generated for the discovery of efficient photocatalysts and different approaches to improve the performance of semiconductor-based artificial photocatalytic processes. TiO\(_2\) is an extensively studied semiconductor photocatalyst because of its nontoxic nature and chemical stability. However, because of the wide band gap of TiO\(_2\), ultraviolet (UV) light is essential for excitation which restricts its practical applications. The main objective in photocatalytic water splitting is to efficiently utilize visible light to conduct the photoelectrochemical reaction. Among large number of catalysts used for H\(_2\) and O\(_2\) evolution under visible light, semiconductors with appropriate valence band (VB) edge have attracted more attention. In that direction, significant research efforts have been devoted to metal oxide semiconductors, such as BiVO\(_4\), Bi\(_2\)O\(_3\), Bi\(_2\)WO\(_6\), WO\(_3\), and Fe\(_2\)O\(_3\) because of their visible light photocatalytic activities.

Among the various narrow-band-gap (1.8–2.8 eV) semiconductors, bismuth oxide is known to be a suitable candidate because of its unique properties including adequately high oxidation power of valence hole (∼+3.13 V vs NHE), nontoxic nature, and superior band edge potential suitable for H\(_2\) and O\(_2\) evolution on water splitting. Bismuth oxide occurs in six crystal phases; \( \alpha\), \( \beta\), \( \gamma\), \( \delta\), \( \epsilon\), and \( \omega\) phases. Monoclinic \( \alpha\)-Bi\(_2\)O\(_3\) is the most stable phase at room temperature and atmospheric pressure. A phase transition occurs from \( \alpha\)-Bi\(_2\)O\(_3\) to \( \delta\)-Bi\(_2\)O\(_3\) on heating above 1000 K, which restricts its application at room temperature, and this phase is stable up to the melting point. The metastable \( \beta\) and \( \gamma\) phases are observed during the cooling of \( \delta\)-Bi\(_2\)O\(_3\). \( \epsilon\)-Bi\(_2\)O\(_3\) can be obtained by the hydrothermal route, whereas the \( \omega\)-Bi\(_2\)O\(_3\) phase is reported to be formed on the BeO substrate. The chemical instability is known to be the main obstacle for the application of Bi\(_2\)O\(_3\) as a photocatalyst. These barriers are reported to be overcome by metal doping or by making composites. An enhancement in the visible light sensitivity is achieved by engineering the narrow band gap. \( \delta\)-Bi\(_2\)O\(_3\) is a technologically important oxide ion conductor because of its high oxide ion conductivity governed by the high concentration of oxygen vacancies and high anionic mobility. In the defected fluorite structure, the high polarizability of the Bi\(^{3+}\) cation with its lone pair of electrons can act as an enhancing factor for observed ionic conductivity along with the possible weak Bi–O bond, promoting a greater mobility of the oxygen vacancies in the lattice.
Bismuth oxide (Bi₂O₃)-based compounds are of interest for their potential as photocatalysts due to their low band gaps and presence of oxygen vacancies. The Pechini method has been used for the synthesis of these compounds, and it has been shown that their photocatalytic activities are influenced by the band gap. The band gap can be easily modified by introducing a small amount of other elements, which can be done by applying a thermal plasma method. This method is of increasing interest because it allows for the synthesis of nanoparticles of various metals and metal oxides in large scales. The thermal plasma process used here to synthesize the nanoparticles of Bi₂O₃ is convenient and economical, and it provides high yields.

The thermal plasma method is of increasing interest because of its ability to synthesize nanoparticles of variety of metals and metal oxides in large scales. The thermal plasma process used here to synthesize the nanoparticles of Bi₂O₃ is convenient and economical, and it provides high yields. This process gives a clean reaction atmosphere, which is essential for the synthesis of high purity compounds. It also provides high enthalpy which is important for the synthesis of such compounds. In the present study, we have adopted the approach of synthesizing high-temperature δ phase of Bi₁₁VO₁₉ nanoparticles using the thermal plasma method.

Photocatalytic activity depends on the physical properties such as crystal structure, surface area, particle size, and surface hydroxyls of Bi₁₁VO₁₉. Along with the physical properties, it also depends on the operating conditions (e.g., initial concentration of chemicals and their pH values, amount of catalyst, and light intensity). In the bismuth-based oxides, slightly distorted crystal structures can also enhance the lone pair impact of Bi 6s states. This provides a handle to tune optical properties to achieve excellent photocatalytic activity.

To the best of our knowledge, Bi₁₄VO₃₉ has been successfully synthesized for the first time using the thermal plasma method and the present work reports a detailed study. The nanoparticles in the size range of 30–35 nm are investigated for structural studies, surface morphology, and optical properties by X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), and UV–vis absorption spectroscopy. The X-ray photoelectron spectroscopy (XPS), VB spectroscopy (VBS), and X-ray absorption spectroscopy (XAS) measurements are performed to study electronic properties such as the chemical state, density of states, and lone pair-induced lattice distortions. The methylene blue (MB) dye degradation experiment is carried out under visible light irradiation to study the efficient photocatalytic activity of Bi₁₄VO₃₉ nanoparticles. Electronic structure calculations are performed, and theoretical results are compared with experiments to shed light on crystallographic and electronic structural information.

2. RESULTS AND DISCUSSION

2.1. Theoretical Calculations. The δ-Bi₂O₃ is known to be stable above 1000 K adopting the fluorite structure. Each unit cell of δ-Bi₂O₃ has two vacant oxygen sites which provide stable transport sites for oxygen atoms causing its known high conductivity. There has been huge debate over type and combination of O vacancies; however, till date no clear theory is widely accepted. Three types of simple vacancies are popularly proposed to be stable, namely two O vacancies in ⟨111⟩ direction, one O vacancy in ⟨100⟩, and ⟨110⟩ directions.13,27–32 Other complex combinations of divacancy are also reported.27 However, all the simple vacancy structures are known to be dynamically unstable, and the breaking of symmetry by local distortion around Bi is reported to be essential for describing the electronic and crystallographic structure of δ-Bi₂O₃.32 In the present work, a configuration of O vacancies in the ⟨111⟩ direction is adopted because it is reported to be isoostructural with As₂O₃ and Sb₂O₃.42 The cohesive energy and structural parameters of such δ-Bi₂O₃ and α-Bi₂O₃₂₃ are shown in Table 1, which are found to be in agreement with the previously reported results.14 On account of higher electron negativity of Bi than V, substitutional doping is expected for V at Bi site. The vanadium doping at 8.3, 12.5, and 25% of Bi is
carried out by forming requisite supercells namely δ-Bi₁₂O₁₈, δ-Bi₈O₁₂, and δ-Bi₄O₆ and replacing one Bi by V, respectively. Respective local minimum energy state geometries can be found in Supporting Information (S2). It is to be noted that on potential landscape these are expected to be the shallow local minima states because of the large number of available O vacant sites and known ionic mobility of O ions in pristine and transition metal-doped δ-Bi₂O₃. Figure 1a shows the local minimum energy state geometry of the δ-Bi₁₁VO₁₈ structure. In this unit cell, the vanadium site is surrounded by four oxygen atoms which form a VO₄ tetrahedron and the bismuth sites are surrounded by 3 and 4 oxygen atoms, forming BiO₃/₄ complexes per unit cell. The respective cohesive energies and structural information are incorporated in Table 1. The stability (compared by $E_C$/atom and $E_{sub}$) and the respective bond lengths are found to decrease with increase in V concentration. This is expected as bonding of V with O is stronger than bonding of Bi with O, and it causes significant distortion at substitutionally doped V site resulting in the decrease of the average bond length.

To the best of our knowledge, despite extensive work carried out for various phases of transition metal-doped bismuth oxide, only a single report has suggested the existence of the δ-Bi₁₁VO₁₉ phase. However, geometrical and electronic structures and their effect on photocatalytic and optical properties are not clear. Hence, in the present work, we exclusively focus on the structural and electronic properties of δ-Bi₁₁VO₁₉ and their effect on photocatalytic and optical properties of the material.

In the present experimental work, excess O is found in V-doped systems, hence knowing lower electronegativity of V than Bi, δ-Bi₁₁VO₁₉ is expected to form by the addition of one O atom near the V site in the δ-Bi₁₁VO₁₈ system. The initial structure of the δ-Bi₁₁VO₁₉ unit cell has been chosen to be consisting of three Bi₂O₃ units along c-axis with single Bi replaced by V. It has two oxygen vacancies along the ⟨111⟩ direction per Bi₂O₃ unit in the supercell (except BiVO₃ unit). Ab-initio molecular dynamics (MD) simulation run is performed as described in Section 4.1, and several local lowest energy structures are picked and ionically relaxed to obtain local minimum energy state δ-Bi₁₁VO₁₉ geometry as shown in Figure 1b. The geometry of the relaxed structure is found to be considerably distorted for O sites. Five O atoms are found to have an average bond length of 1.81 Å with V, whereas one O atom has a bond length of 2.25 Å. The skeleton of Bi atoms with respect to the initial structure (cubic) is found to be slightly distorted after MD simulation, with distortion in unit cell angles up to 0.02%, which however breaks the symmetry. No negative vibrational frequencies (refer Supporting Information S3) are observed for the proposed δ-Bi₁₁VO₁₉ structure, suggesting that it is energetically stable. $E_C$/atom and $E_{sub}$ of the system are found to be larger than δ-Bi₁₁VO₁₈.
suggesting its higher stability. Indeed, $E_{\text{ib}}$ is found to be highest for $\delta$-Bi$_{11}$VO$_{19}$ among all the structures studied in the present work. This suggests higher affinity of the V-doped system for excess O atoms at the V site. Inclusion of more than one O atom per unit cell is structurally not feasible without distorting structure from $\delta$-phase bismuth oxide; hence, higher numbers of oxygen atoms are not included. To understand the effect of V–V interaction and its distance dependence, $2 \times 2$ supercells of $\delta$-Bi$_{11}$VO$_{18}$ and $\delta$-Bi$_{11}$VO$_{19}$ are formed by selecting appropriate V-doping sites having a distance more than 7 Å as shown in Figure 1b for $\delta$-Bi$_{44}$V$_4$O$_{72}$ and 1d for $\delta$-Bi$_{44}$V$_2$O$_{76}$. As expected, the $E_c$/atom and $E_{ib}$ for such supercells are found to be higher compared to respective unit cells. This can be understood from the fact that V doping induces local structural deformation as compared to the pristine system. However, the trend of higher band gap than in the excess O system is found to remain intact with increase in the nearest neighbor V–V distance. MD simulation on the $\delta$-Bi$_{44}$V$_4$O$_{76}$ system is performed and local ground state geometry is obtained by ionic relaxation. The major structural change in the local optimized structure in comparison to the initial structure is that the original structure has four tetrahedrally bonded VO$_4$ complexes, whereas the local ground state structure has two VO$_4$ complexes and two deformed trigonal bipyramidal VO$_5$ complexes, with the resultant structure 3 eV lower in energy. After the MD simulation, the average bond length of VO$_4$ complex is 1.73 Å, whereas the average bond length increases in the VO$_5$ complex to 1.85 Å.

The effect on the electronic structure after vanadium doping in $\delta$-Bi$_2$O$_3$ is studied to understand the mechanism of the observed enhanced photocatalytic performance of Bi$_{11}$VO$_{19}$. The site-projected partial density of states (l-DOS) [with the Fermi energy ($E_f$) adjusted to zero] is plotted in Figure 2 for (a) $\delta$-Bi$_{11}$VO$_{19}$ and (b) $\delta$-Bi$_{11}$VO$_{18}$ and for respective supercells in (c,d). The l-DOS plot for other systems can be found in Supporting Information S4). The band gap is found to vary from 1.8 to 2 eV with vanadium doping. As shown in Figure 2, dominant contributions from O 2p, Bi 6s, and V 3d states are mostly located between $-6$ and $0$, $-12$ and $-8$, and 1 and 2 eV, respectively with significant hybridization of these states. In case of $\delta$-Bi$_{11}$VO$_{19}$, the VB is found to be mostly contributed by p states of O with significant but comparatively small contribution from Bi 6s and 6p states. Larger contribution of Bi 6s states is found to be between $-10$ and $-8$ eV below $E_f$, which are composed of highly polarized lone pair electrons, consistent with earlier reports for bismuth oxide systems. In the energy range $-6$ eV to $E_f$, major contributions from Bi 6p and O 2p states, along with small contribution of V 3d states, are observed. The CB minimum is mostly contributed by degenerate d states of V at around 2 eV. The contribution of Bi 6p and O 2p states are found to be small at the CB edge and it is found to increase rapidly at higher energies. The l-DOS landscape of the $\delta$-Bi$_{44}$V$_4$O$_{76}$ structure is found to be similar to the Bi$_{11}$VO$_{19}$ structure except that degeneracy of V 3d states is lifted which reduces the effective band gap to 1.65 eV. For $\delta$-Bi$_{11}$VO$_{19}$, the entire l-DOS landscape is found to shift to lower energy as shown in Figure 2c,d. Significant but small numbers of oxygen states are found in the forbidden region; $E_f$ shifts toward the CB, resulting in reduction in the band gap significantly. Similar results are found for higher concentrations of V doping (refer Supporting Information S4). To investigate these states in the forbidden region, l-DOS of first neighboring Bi and O atoms to V is plotted as shown in Figure 3a, whereas the l-DOS for the rest of the Bi atoms of the unit cell is plotted in Figure 3b. It is clear from these plots that the decrease in the band gap is due to distorted first and second nearest neighbors at the doped site. Hence, it is concluded that on V doping in bismuth oxide, the decrease in the band gap is due to local distortion at the V-doped site, while the band gap is found to increase with additional O atom around the V site because of interaction with these local first nearest neighbor Bi atoms. The calculated band gap of Bi$_{11}$VO$_{19}$ value $\sim$1.65 eV is in agreement with the experimental results.

The distortion of VO$_4$ tetrahedron is known to cause centers of positive and negative charges to separate, resulting in an internal electric field. This effect is essential for the separation of electron–hole pairs, which enhances the photocatalytic property. The electron transitions are either from the top of VB to CB or from the top of VB to the impurity states (V 3d) and from the impurity state to CB, which reduces the effective band gap. The narrowed band gaps help the transmission of photogenerated electrons from V 3d states to Bi 6p states, which shows a red shift of the light absorption region, enhancement of photocatalytic activity, and improvement of the quantum yield of the Bi$_{11}$VO$_{19}$.

2.2. Experimental Results. In the photocatalysis study, the crystal structure is one of the most important factor to enhance the photocatalytic activity. According to our theoretical results, we doped vanadium at the bismuth site. To confirm the theoretical predictions, we characterize the sample mainly by XRD, VBS, and XAS. Our calculated crystallographic parameters are in good agreement with the theoretical results. A slight difference occurs because the experiments are carried out at room temperature while the theoretical calculations are at 0 K.

Figure 4 shows the XRD pattern of the Bi$_{11}$VO$_{19}$ nanoparticles obtained at room temperature along with the Rietveld refinement method using FULLPROF software.

Figure 3. Site-projected l-DOS plots of $\delta$-Bi$_{11}$VO$_{19}$ for (a) Bi and O atoms near V atom and (b) average of the rest of the Bi atoms in the cell. Respective Fermi energy is adjusted to 0 eV.

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(pseudo-Voigt function) of diffracted peaks of Bi$_{11}$VO$_{19}$. It indicates the crystalline phase with fluorite type cubic symmetry having space group $Fmar{3}m$. There are no indications of secondary or impurity peaks observed in the XRD pattern. The lattice parameters of Bi$_{11}$VO$_{19}$ determined at room temperature are $a = b = c = 5.56$ Å with unit cell volume = 171.88 Å$^3$ (PDF2 no. 45-0363), which is consistent with our theoretical ($a = b = 5.55$, $c = 5.39$ Å with total volume = 166.03 Å$^3$) results and an earlier report. The estimated average particle size is in the range of 30−35 nm, determined using Scherrer’s formula.

The microstructures were characterized by TEM images as shown in Figure 5. The TEM micrographs demonstrate that the morphology of Bi$_{11}$VO$_{19}$ is spherical in nature. The spherical nanoparticle size having a diameter of ∼36 nm is analogous with the average particle size calculated using XRD. The selected area electron diffraction (SAED) pattern with rings confirms the polycrystalline nature of Bi$_{11}$VO$_{19}$ nanoparticles. The observed $d$ spacing value of 0.326 nm is in good agreement with the lattice spacing 0.320 nm for the family of planes (5 1 1) of fluorite type cubic Bi$_{11}$VO$_{19}$. The inset of Figure 5c shows inverse FFT of the selected area of the Bi$_{11}$VO$_{19}$ nanoparticle which reveals sharp and clear lattice fringes, confirming the crystalline nature of the synthesized particles.

Energy dispersive X-ray spectroscopy (EDX) spectra confirm the elemental composition with the average Bi/V ratio to be 10.92, which is close to the stoichiometric value of the chemical formula of Bi$_{11}$VO$_{19}$. The scanning electron microscopy and EDX data are incorporated in Supporting Information (S5). The elemental mapping shows the homogeneous distribution of Bi, V, and O in the Bi$_{11}$VO$_{19}$ compound (S5).

The Brunauer−Emmett−Teller (BET) measurement performed to determine the specific surface area. The measured BET has the average pore size, specific surface area, and pore volume of Bi$_{11}$VO$_{19}$ is about 6.44 Å, 10.05 m$^2$ g$^{-1}$, and 0.039 Å, respectively. The $N_2$ adsorption−desorption isotherm of Bi$_{11}$VO$_{19}$ nanoparticles perform at 77 K reveals hysteresis loop with adsorption desorption branches at high relative pressure. The IUPAC classification of adsorption isotherm shows the physisorption isotherm categorized as type IV, which represents mesoporous nature and the clear advantage of degrading organic pollutants in water (S7).

Diffuse reflectance spectroscopy (DRS) shows a sharp absorption edge in the visible region. The band gap of Bi$_{11}$VO$_{19}$ nanoparticles is estimated from the absorption edge by the Wood Tauc plot and is found to be 2.26 eV, which is
significantly narrower than the reported Bi\textsuperscript{3+} compounds such as \(\alpha\)-Bi\textsubscript{2}O\textsubscript{3} (2.8 eV),\textsuperscript{37} \(\beta\)-Bi\textsubscript{2}O\textsubscript{3} (3.4 eV),\textsuperscript{38} t-BiVO\textsubscript{4} (2.9 eV),\textsuperscript{2} and \(\beta\)-Bi\textsubscript{2}Mo\textsubscript{2}O\textsubscript{9} (3.06 eV).\textsuperscript{39}

The photochemical property of semiconductor materials was studied using photoluminescence (PL) spectra. The PL emission originated from the recombination of the excited electron and holes of the semiconductor. A sharp blue green emission band centered at 484 and 583 nm can be observed which is directly related to the charge transfer with the VO\textsubscript{4}\textsuperscript{2-} and VO\textsubscript{5}\textsuperscript{2-} group, respectively (DRS and photoluminescence spectra included in Supporting Information S8 and S9, respectively).

The bonding states in the coordination polyhedral of nanoparticles are probed by Raman spectroscopy to analyze local crystal structures. Figure 6 represents a deconvoluted Raman spectrum of Bi\textsubscript{11}VO\textsubscript{19} nanoparticles excited by a green (532 nm) laser source. The major deconvoluted Raman vibrational spectrum has five bands at 307, 368, 703, 824, and 890 cm\textsuperscript{-1}. The distinct V–O stretching frequencies are known to be in the range of 650–950 cm\textsuperscript{-1}. The stretching mode at 824 cm\textsuperscript{-1} and the weak band at 703 cm\textsuperscript{-1} are assigned to the symmetric Ag\(\nu_3\) (V–O) and asymmetric Ag\(\nu_2\) (V–O) stretching modes, respectively. According to the literature, the deconvoluted peak observed at tail of high frequency, 890 cm\textsuperscript{-1}, can be assigned to vibration mode of V–O bonds of distorted VO\textsubscript{4} trigonal bipyramids.\textsuperscript{40} The bands at 307 and 368 cm\textsuperscript{-1} are assigned to asymmetric and symmetric bending vibrations of the VO\textsubscript{4} tetrahedron, respectively. The V–O bond length by the Raman stretching frequencies is determined by Brown and Wu, Franklin and Wachs empirical equations (\(\nu = 21349 \times \exp(-1.917R)\), where \(\nu\) is the Raman shift in cm\textsuperscript{-1} and \(R\) is the V–O bond length in Å).\textsuperscript{41,42} The calculated V–O bond length of symmetric V–O stretching mode at 824 cm\textsuperscript{-1} is 1.70 Å and for 890 cm\textsuperscript{-1} the bond length is 1.66 Å. The calculated average bond length for VO\textsubscript{4} is larger than VO\textsubscript{5} complex; hence, the strong peak is assigned to VO\textsubscript{4} stretching whereas the weak peak is assigned to VO\textsubscript{4} in close agreement with reported VO\textsubscript{4} stretching but is in contradiction with the results of Attos et al.\textsuperscript{40} According to our theoretical calculation, the bond length from the strong peak corresponds to the VO\textsubscript{4} stretching mode, whereas the weak peak at higher wave number gives the VO\textsubscript{5} contribution, which is in close agreement with reported VO\textsubscript{4} stretching mode.\textsuperscript{24} It is to be noted that the area under the peak at 890 cm\textsuperscript{-1} (assigned to V–O bonds VO\textsubscript{4}) is very small in comparison to the area under the peak at 824 cm\textsuperscript{-1} (assigned to V–O bonds of distorted VO\textsubscript{4}). This fact may be a result of VO\textsubscript{4} residing near the surface of nanoparticles and O-excess trigonal bipyramids VO\textsubscript{5} in the core of nanoparticles.\textsuperscript{33}

![Figure 6. Deconvoluted Raman spectra of Bi\textsubscript{11}VO\textsubscript{19} nanoparticles.](image-url)

![Figure 7. High-resolution X-ray photoemission spectra of the Bi\textsubscript{11}VO\textsubscript{19} nanoparticles: (a) survey scan, (b) Bi 4f, (c) V 2p, and (d) O 1s core level.](image-url)
The XPS spectrum of Bi$_{11}$VO$_{19}$ reveals better understanding of the chemical states of the present compound on the photocatalyst surface as shown in Figure 7. The full survey confirms the presence of Bi, V, and O elements in the sample. The XPS spectra exhibit the characteristic spin–orbit splitting of Bi states into 4f$_{7/2}$ and 4f$_{5/2}$ and V into 2p$_{3/2}$ and 2p$_{1/2}$. The peak signals of Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$ states are observed at the values of binding energies 158.6 and 163.9 eV, ascribed to the Bi$^{3+}$ state, which is consistent with the reported data. The binding energy separation of states corresponding to Bi 4f peaks is at 5.32 eV, which is also consistent with reported spin–orbit splitting measured in Bi$_2$O$_3$ and Bi$_{11}$VO$_{19}$ nanoparticles by the Pechini method. Figure 7c shows the states of V 2p included regions 2p$_{3/2}$ and 2p$_{1/2}$ at binding energies 515.7 and 523.1 eV, respectively, with spin–orbit splitting of 7.4 eV signifying the 5+ state of V. The binding energy values are well-matched with the reported values for vanadates (V$^{5+}$) in LiNiVO$_3$ and BiVO$_4$ compounds, signifying that the V$^{5+}$ ions are dominant in the present Bi$_{11}$VO$_{19}$ compound. The peak for oxygen 1s state occurs at the binding energy of 529.3 eV, confirming the oxygen to be in the O$^{2-}$ state which is related to Bi–O or V–O chemical bonding in Bi$_{11}$VO$_{19}$.

Figure 8 demonstrates the normalized VB photoemission spectra of Bi$_{11}$VO$_{19}$ nanoparticles recorded for the incident photon energy of 40 eV. It clearly shows contribution due to V 2p derived states in the VB photoemission spectra, which is consistent with our theoretical calculations. As shown in Figure 8, the VB spectrum is deconvoluted with six peaks by using the XPSPEAK 41 software. The spectrum of Bi$_{11}$VO$_{19}$ nanoparticles contains six features, marked as A, B, C, D, E, and F at 1.16, 3.22, 4.77, 6.31, 8.29, and 10.27 eV, respectively. The O 2p dominated VB is observed between 0 and 5 eV with respect to the highest occupied state, with additional peaks above 8 eV due to Bi 6s states. Features A and B are related to the unhybridized O 2p mixed with Bi 6s states and the O 2p derived states. Features C and D show the hybridized O sp$^2$ to V 3d states near the binding energy at 4.77 and 6.31 eV, respectively. The Bi 6s contribution is largely confined to the bands appearing between 8 and 10 eV (features E and F). The binding energies of all features are well-consistent with calculated DOS and previously reported data. It is to be noted here that although the composition remains almost the same, the present study indicates that the phase is extremely temperature-sensitive due to inherent mobility of oxygen ions and available O vacancy sites. This also presents the possibilities of use of the present compound in high-temperature ionic conductivity devices.

Soft X-ray absorption study gives the fundamental electronic structure of the unoccupied states within the CB at the V L-edge and O K-edges of Bi$_{11}$VO$_{19}$. In the XAS study, by considering the orbital selection rules (Δ = 0), the V L-edges offer probes of 2p to 3d and the O K-edge 1s to 2p excitations. In this bismuth vanadate system, the CB mainly consist of hybridized antibonding V 3d states with antibonding O sp$^2$ states. The strong characteristic of the Bi 6p state is detected in the upper region of CB. In case of bismuth vanadate, the V L and O K-edges are observed to be partially overlapping. The combined experimental V L$_{II}$ absorption edge and O K-edge spectrum of Bi$_{11}$VO$_{19}$ fitted with Voigt functions is shown in Figure 9a,b. The deconvoluted Voigt functions of core-hole deconvoluted with instrument broadening for the V L-edge reveals four peaks A, B, C, and D at 515.9, 517.1, 518.0, and 518.9 eV, respectively, which have originated from the ligand field splitting of V 3d states. The first two peaks A and B show the triplet states originating from atomic multiplet effects, which shows transition from occupied 2p$_{3/2}$ states to unoccupied 3d states of V$^{5+}$. The XAS spectra give evidence of a distorted tetrahedral environment of V$^{5+}$ in the fluorite type cubic Bi$_{11}$VO$_{19}$.53

Figure 8. VB spectra for Bi$_{11}$VO$_{19}$ nanoparticles with the incident photon energy of 40 eV. The inset shows the enlarged view near 0 eV.

Figure 9. X-ray absorption spectrum measured in total electron yield (TEY) mode at (a) V L$_{III}$ and (b) O K edges.
The O K-edge absorption spectrum of Bi$_{11}$VO$_{19}$ nanoparticles involve transition from occupied 1s core levels to empty O 2p states as shown in Figure 9b. The results of O K-edge of XAS show perfectly deconvoluted five peaks located at binding energies of 529.8 (peak A), 531.1 (peak B), 532.6 (peak C), 533.6 (peak D), and 534.8 eV (peak E) values, which are mainly contributed by unoccupied metal states hybridized with oxygen valence states. The characteristic peaks at 529.8, 531.1, and 532.6 eV reveal the O 2p−V 3d hybridization, and it is in agreement with the tetrahedral crystal field splitting of V $t_{2g}$ and $e_g$ states. The O K-edge data are consistent with density functional theory (DFT) predictions of Bi 6p orbital contributions to upper CB. Peaks D and E (533.6 and 534.8 eV, respectively) are assigned to the contribution from Bi 6p states.

The relative positions and qualitative variation of all experimentally observed states are in excellent agreement with the present theoretical results, confirming the presence of V-doped Bi$_2$O$_3$ in Bi$_{11}$VO$_{19}$ in the $\delta$-phase. The vanadium doping on the Bi site in $\delta$-Bi$_2$O$_3$ affects the energy states and distribution of electrons in orbitals of VB and CB. This leads to the decrease in the electron and hole effective masses. The doping of V creates some impurity states both as acceptor and donor electrons, which decrease the band gap. This results in red shift in photon absorption which can enhance the utilization rate of photon energy. The impurity levels act as not only acceptor but also the donor of electrons. In the band energy, the impurity level formed by V can help electrons in VB to absorb photons with small energy and to jump into the impurity levels near CB. The narrow band gap increases the utilization rate of photon energy in the visible region, which enhances the degradation rate of MB of vanadium doped $\delta$-Bi$_2$O$_3$.

The photocatalysis of Bi$_{11}$VO$_{19}$ nanoparticles is observed by degradation of MB under visible light irradiation. The change in the MB absorption ($\lambda = 672$ nm) under visible light irradiation is shown in Figure 10. The absorption peak of MB solution exhibits a rapid decrease in the absorption in the visible region and a blue shift of absorption maximum. The UV−vis spectra show a decrease in intensity with increasing irradiation time, (higher than $\delta$-Bi$_2$O$_3$) which indicates decolorization of MB. No additional peaks are found in the UV−vis spectra during the degradation process, which signifies that no reaction intermediates are formed. Under the visible light irradiation, the absorption maximum of MB solution shifts gradually from 672 to 625 nm with color of dispersion changing from blue to colorless. The spectral change associated with hypsochromic effects of MB caused by N-demethylation under the visible light and oxidative degradation occurs concomitantly.

Under the visible light irradiation, the Bi$_{11}$VO$_{19}$ nanoparticle shows the excellent photodegradation rate for MB within 105 min. In the photocatalytic mechanism, when visible light is incident on the nanoparticles, photoinduced electrons ($e^-$) are ejected from VB to CB, and it generates the holes ($h^+$) in the VB (Figure 11). Here, these holes react with adsorbed water on the surface of Bi$_{11}$VO$_{19}$ nanoparticles to form highly reactive hydroxyl radial (OH$^*$), whereas O$_2$ forms superoxide anion radicals (O$_2$•$^-$) which act as an oxidizing agent or an additional source of OH. These radical can degrade MB dye effectively into nontoxic organic compounds. The photocatalytic reaction mechanism of Bi$_{11}$VO$_{19}$ is given below

$$\text{Bi}_{11}\text{VO}_{19} + \text{hv} \rightarrow \text{Bi}_{11}\text{VO}_{19} (e^-_{\text{VB}} + h^+)$$

$$e^-_{\text{CB}} + O_2 \rightarrow O_2^{•^-}$$

$$h^+ + H_2O \rightarrow (\text{OH} + H^+)$$

$$O_2^{•^-} + H_2O \rightarrow H_2O_2 + OH^-$$

$$H_2O_2 \rightarrow 2OH$$

MB + OH → oxidation products

The MB degradation rate ($C_t/C_0$) as a function of irradiation time for Bi$_{11}$VO$_{19}$ and $\delta$-Bi$_2$O$_3$ calculated from Figure 10 is shown in Figure 12a,b, where $C_0$ and $C_t$ are the initial MB concentration and visible light irradiation concentration at time ($t$), respectively. In the dark condition, MB is found to be stable and the degradation rate was very less. For comparison, the photocatalytic performance of $\delta$-Bi$_2$O$_3$ was also investigated under the same experimental conditions. The detail experimental results of $\delta$-Bi$_2$O$_3$ can be found in Supporting Information (S10−S12). In comparison with the pristine sample, the $\delta$-Bi$_{11}$VO$_{19}$ nanoparticles have a higher degradation rate on account of smaller particle sizes as well as reduced band gap. The degradation efficiency reaches up to 80% in 105 min, whereas the degradation efficiency of $\delta$-Bi$_2$O$_3$ is up to 35%. Photocatalytic activity is known to increase with decrease in the particle size and increase in the surface area. The high surface area is a key factor for the photocatalytic degradation of organic compounds for adsorption of the compound. The kinetic constant ($k$) is calculated by using the pseudo-first order reaction rate equation of ln($C_0/C_t$) = $kt$, where $k$ is the kinetic constant of pseudo-first order reaction rate equation. When the initial concentration of MB dye is low, the pseudo-first order reaction rate equation can be used for quantitative understanding of the reaction rates of the MB degradation. ln($C_0/C_t$) versus $t$ plot shown in Figure 12b depicts a linear fit. The kinetic constant $k$, determined from this pseudo first order equation, has a value of 0.07628 min$^{-1}$, which is 23% higher than the $\delta$-Bi$_2$O$_3$ (0.00319 min$^{-1}$). Some bismuth photocatalyst are reported to have the pseudo-first order kinetic constant to be lower, such as BiVO$_4$ film (0.0138 min$^{-1}$), nano-BiVO$_4$ (0.629 $\times$ 10$^{-3}$ min$^{-1}$) 35 Bi$_{2}$VO$_{13}$ (0.0263 min$^{-1}$), 37 and Bi$_{11}$VO$_{19}$ by the Pechini method (0.00242 min$^{-1}$). 14 In comparison, our results show a more efficient photocatalytic activity. The Bi$_{11}$VO$_{19}$ nanoparticles synthesized using the thermal plasma technique having a large

Figure 10. Absorption spectra of Bi$_{11}$VO$_{19}$ nanoparticles in MB solution under visible light irradiation.
Effective surface area and tuned electronic structure along with positive threshold energy of VB top are responsible for enhanced photocatalytic activity.

3. CONCLUSIONS

In conclusion, we report for the first time the successful synthesis of Bi$_{11}$VO$_{19}$ nanoparticles using the high-temperature thermal plasma method having particle sizes $\sim$35 nm with high effective surface areas. The theoretical local ground state geometries proposed from our calculations for V-doped $\delta$-Bi$_2$O$_3$ and experimentally Rietveld fitted graph confirm the structure of nanoparticles to be cubic fluorite type of $\delta$-Bi$_{11}$VO$_{19}$ phase. The electronic structure of Bi$_{11}$VO$_{19}$ has been examined first time using both theoretical calculations and experimental results. The VB is found mainly to be composed of hybridized O 2p states with Bi 6s states, with small contribution of Bi 6p states. The states in the energy range $-10$ to $-8$ are mainly contributed by Bi 6s states. The CB minimum mainly consists of V 3d and small contribution of O 2p and Bi 6p states. Engineering V 3d states of CB by substitutional doping V at Bi sites leads to band gap values in the visible region. The presence of extra O near the V site is found to be essential for the observed band gap. The band gap of Bi$_{11}$VO$_{18}$ is found to shrink because of the presence of stereochemically active Bi$^{3+}$ 6s$^2$ lone electron pair, rich oxygen ion vacancies, presence of V=O complexes, and strong polarization fields. The experimental results are supported by theoretical calculations and enhance the understanding of the electronic as well as crystallographic structure. Owing to engineered band gap and high effective surface area on account of the present synthesis method, the Bi$_{11}$VO$_{19}$ nanoparticles show very high photocatalytic activity for photodecomposition of MB dye under UV-vis light irradiation. The calculated kinetic constant of the pseudo-first order reaction rate has a value of 0.0763 min$^{-1}$, which is highest among reported $\delta$-Bi$_2$O$_3$. This work provides a large-scale high-yield simple way to prepare highly active visible light-driven photocatalysts for the treatment of organic pollutants of wastewater.

4. EXPERIMENTAL SECTION

4.1. Computational Methodology. DFT$^{58-60}$-based spin-polarized electronic structure calculations are performed at 0 K using the accurate plane augmented wave method$^{61}$ as implemented in Vienna Ab-initio Simulation Package.$^{52-65}$ The exchange–correlation energy functional within generalized gradient approximation is employed as given by Perdew et al.$^{66,67}$ A cut off of 400 eV is used for the plane wave basis set. The ionic positions are relaxed to minimize the total energy of system using the conjugate gradient algorithm till the electronic energy and ionic forces converge to within $10^{-4}$ eV and 0.02 (eV/Å), respectively. Gauss broadening up to 0.001 eV is used to treat partial occupancies by the Gaussian smearing scheme.
Ab-initio MD calculation at single \( k \) point is performed within the canonical ensemble approach at a constant temperature using the Nosé–Hoover thermostat method. The system is kept at 773 K temperature for 4 ps in steps of 1 fs to find the various local ground state geometries.

The stability of the system is characterized by comparing respective cohesive energy \( (E_{\text{coh}}) \) and substitutional energy \( (E_{\text{sub}}) \) calculated through eqs 1 and 2, where \( e_i \) is the total energy per atom of species \( i \) and \( n_i \) is the number of atoms of species \( i \) in the bismuth vanadate system. \( E_r \) and \( E_f \) are the total energies of the pristine and V-doped bismuth vanadate systems, respectively. Higher positive values for \( E_{\text{coh}} \) and \( E_{\text{sub}} \) indicate more stable structures.

\[
E_{\text{coh}} = \sum_{i=1}^{3} n_i \times e_i - E_f^V
\]

\[
E_{\text{sub}} = E_r - E_f^V - e_{\text{Bi}} - E_{\text{Bi}}^V
\]

4.2. Synthesis. The nanoparticles of Bi\(_{11}\)VO\(_{19}\) are synthesized by using a direct current transferred arc thermal plasma reactor (DCTATPR) via the homogeneous gas phase condensation process. The plasma reactor consists of a plasma torch comprising of a water-cooled thoriated tungsten tip and a primary anode made up of copper to initiate the plasma in the torch. After ignition of plasma plume, it is transferred to a secondary anode using dc voltage. The pellet is made by mixing Bi\(_2\)O\(_3\) and V\(_2\)O\(_5\) oxide powders (99.9% purity of Sigma-Aldrich powders) with the atomic weight ratio of 1:1 (2 at. wt % vanadium doped in Bi\(_2\)O\(_3\)) along with graphite powder so as to make it conducting, and it is then put over the water-cooled graphite secondary anode. These powders pelletized with 100 kg/cm\(^2\) of pressure using hydraulic press.

The system is evacuated to base pressure of 10\(^{-2}\) Torr and purged with oxygen to attain operating pressure. The plasma plume is then made to strike onto the pellet. The reactor was then purged with argon gas for removing or minimizing the impurities which are present in the reactor. The reactor is filled with argon up to a desired operating pressure. In the present synthesis, argon with nitrogen is used as plasma-forming gas, whereas ambient gases are argon and oxygen. The pellet is placed onto a graphite holder, which is placed over the water cooled graphite electrode. The experimental operating parameters, schematic, and other details can be found in Supporting Information (S1).

4.3. Characterization. The structure and phase purity of Bi\(_{11}\)VO\(_{19}\) nanoparticles are studied using a X-ray diffractometer (Bruker AXS D8 ADVANCE diffractometer) equipped with Cu \( K_\alpha \) radiations (\( \lambda = 1.54 \) Å). The UV–vis spectrum recorded in DRS spectrum mode is obtained using a JASCO V-670 spectrophotometer. The HRTEM images and SAED patterns are recorded using a HRTEM system (Tecnai G2 20 S-TWIN). The BET surface area of Bi\(_{11}\)VO\(_{19}\) was investigated by using nitrogen adsorption–desorption measurements at 77 K. These nanoparticles are further characterized with a Raman spectrometer (Renishaw InVia micro-Raman spectrometer) using a 532 nm He–Ne laser. The chemical, elemental, and local structural information is obtained using a XPS technique with a monochromatized aluminum source (\( K_\alpha \) line, 1486.6 eV, 14 mA, 9.5 kV) (PHI ESCA-5600). The chamber is maintained at a pressure of 10\(^{-9}\) Torr during the measurements. The VBS measurements are performed using angle integrated photoelectron spectroscopy (AIPES) beamline on an INDUS-1 synchrotron radiation source at the Raja Ramana Centre for Advanced Technology (RRCAT), Indore, India. VBS data are collected using incident photon energy at 40 eV and are calibrated with metallic gold foil. The XAS measurements of V L-edge and O K-edge of Bi\(_{11}\)VO\(_{19}\) nanoparticles are carried out in the TEsY mode at the soft XAS beamline of the INDUS-2 synchrotron radiation source at RRCAT, Indore and are normalized by the incident photon flux taken from the photocurrent from Au.

4.4. Photocatalytic Degradation. The photocatalytic activity of Bi\(_{11}\)VO\(_{19}\) nanoparticles is determined by the decolorization of MB dye under the visible light irradiation. The characteristic absorption peak of MB solution at 665 nm is used to monitor the dye degradation reaction. The photocatalytic experiment is performed under visible light (900 mW/cm\(^2\)). The photocatalyst (0.2 gm) is added into 100 mL of MB (10\(^{-5}\) M) solution, and the experiment performed at ambient temperature. Before exposing the sample to visible light irradiation, the mixture solution is stirred for 30 min in the dark to reach the adsorption–desorption equilibrium for MB. The suspension (2 mL) is collected after each 15 min time interval to study the effect of irradiation. The concentrations of MB are examined by taking the absorption spectrum of the collected sample using the UV–vis spectrophotometer.

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00564.

Schematic and operating parameters of the direct current transferred arc thermal plasma reactor; local minimum energy and l-DOS of local ground state geometries of \( \delta \)-Bi\(_2\)O\(_3\) and vanadium-doped \( \delta \)-Bi\(_2\)O\(_3\) systems: (a) \( \alpha \)-Bi\(_2\)O\(_3\); (b) \( \delta \)-Bi\(_2\)O\(_3\); (c) \( \delta \)-Bi\(_3\)VO\(_{13}\); (d) \( \delta \)-Bi\(_{11}\)VO\(_{19}\); (e) \( \delta \)-Bi\(_{11}\)VO\(_{19}\); (f) \( \delta \)-Bi\(_{11}\)VO\(_{19}\); (g) \( \delta \)-Bi\(_{11}\)VO\(_{19}\); and (h) \( \delta \)-Bi\(_{14}\)VO\(_{42}\) along with respective cohesive energies; vibrational spectra and UV–visible spectra of \( \delta \)-Bi\(_2\)O\(_3\); and XRD, UV, Raman, absorption spectra of \( \delta \)-Bi\(_2\)O\(_3\) nanoparticles in MB solution under visible light.

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S.S.K. designed experiments and characterized sample. P.V.G. and A.K. performed the theoretical calculation using DFT. S.S.K. and S.A.R. synthesized the sample. S.S.K. and P.V.G. analyzed the data and produced the results. S.S.K. designed experiments and characterized sample. P.V.G. analyzed the data and produced the results. S.S.K. and S.A.R. synthesized the sample. S.S.K. and P.V.G. analyzed the data and produced the results. S.S.K. designed experiments and characterized sample. P.V.G. analyzed the data and produced the results.

**Notes**
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