Self-Assembled Interwoven Nanohierarchitectures of NaNbO₃ and NaNb₁₋ₓTaₓO₃ (0.05 ≤ x ≤ 0.20): Synthesis, Structural Characterization, Photocatalytic Applications, and Dielectric Properties

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ABSTRACT: Dependence on fossil fuels for energy purposes leads to the global energy crises due to the nonrenewable nature and high CO₂ production for environmental pollution. Therefore, new ways of nanocatalysis for environmental remediation and sustainable energy resources are being explored. Herein, we report a facile surfactant free, low temperature, and environmentally benign hydrothermal route for development of pure and (5, 10, 15, and 20 mol %) Ta-doped horizontally and vertically interwoven NaNbO₃ nanohierarchitecture photocatalysts. To the best of our knowledge, such a type of hierarchical structure of NaNbO₃ has never been reported before, and changes in the microstructure of these nanoarchitectures on Ta-doping has also been examined for the first time. As-synthesized nanostructures were characterized by different techniques including X-ray diffraction analysis, electron microscopic studies, X-ray photoelectron spectroscopic studies, etc. Ta-doping considerably affects the microstructure of the nanohierarchitectures of NaNbO₃, which was analyzed by FESEM analysis. The UV−visible diffused reflectance spectroscopy study shows considerable change in the band gap of as-synthesized nanostructures and was found to be ranging from 2.8 to 3.5 eV in pure and different mole % Ta-doped NaNbO₃. With an increase in dopant concentration, the surface area increases and was equal to 5.8, 6.8, 7.0, 9.2, and 9.7 m²/g for pure and 5, 10, 15, and 20 mol % Ta-doped NaNbO₃, respectively. Photocatalytic activity toward the degradation of methylene blue dye and H₂ evolution reaction shows the highest activity (89% dye removal and 21.4 mmol g⁻¹ catalyst H₂ evolution) for the 10 mol % NaNbO₃ nanostructure which was attributed to a change in the conduction band maximum of the material. At 100 °C and 500 kHz, the dielectric constants of pure and 5, 10, 15, and 20 mol % Ta-doped NaNbO₃ were found to be 111, 510, 491, 488, and 187, respectively. The current study provides the rational insight into the design of nanohierarchitectures and how microstructure affects different properties of the material upon doping.

1. INTRODUCTION

The demand for environmentally benign materials for water remediation, energy generation, and storage applications has increased vastly due to the population explosion in last few decades. Therefore, to meet the challenges due to exponential growing population, different new methods of environment remediation, green energy generation, and storage are being explored. Among different techniques, photocatalytic remediation of wastewater and photocatalytic production of hydrogen from water splitting has gained prime importance due to being environment friendly and the renewable nature of water. An important application of photocatalysis is the removal of hazardous organic pollutants from the water. To carry out the photocatalytic water splitting and degradation of organic pollutants from wastewater, different inorganic nanophotocatalysts like metal oxides (NaNbO₃, NaTaO₃, TiO₂, Cu₂O, Ag, KNbO₃, La₁₋ₓSrₓCoO₃, Pr₂Sn₂O₇, holmium oxide), metal tungstites, and molybdates have been used. The use of diverse inorganic photocatalysts starts from the pioneering work carried out by Fujishima using TiO₂ as a photocatalyst for water splitting. Among different explored photocatalysts, porovskite photocatalysts like NaNbO₃, NaTaO₃, KNbO₃, etc. have gained a lot of interest as an alternative to TiO₂ due to their environment friendly nature and comparable band gap to TiO₂.
With NaNbO$_3$ being a typical perovskite structure having a large pool of important properties like cost-effective, abundant, high crystallinity, environmentally friendly, and high chemical stability. These properties make NaNbO$_3$ a fascinating material having great scientific, research, and technological interest. However, the large band gap associated with NaNbO$_3$ limits the prospect of utilizing it as an efficient photocatalyst. To have an excellent photocatalytic application of NaNbO$_3$, strenuous efforts are being made to improve the light absorption range and to limit the recombination rate of photogenerated charge carriers. In this context, different strategies like development of one-dimensional nanostructures (which show continuous electron transport thus retards the charge recombination), development of heterostructures between different photocatalysts (which reduces the band gap and thus improves the absorption range of photocatalysts) and doping of the “Na” site or “Nb” site with different elements is being developed to improve the activity of NaNbO$_3$. To control the band structure of the target photocatalysts, doping with foreign element is recognized as one of the potential strategies to improve the photocatalytic activity. The ionic charge balanced doping of Na site in NaNbO$_3$ perovskite has been mostly employed in improving the activity of the photocatalyst. Similarly, Jana et al., have used doping of rare earth metal to improve the photocatalytic activity of NaTaO$_3$. However, such a type of doping has little impact on the band structure. In NaNbO$_3$, the conduction band is mainly constituted of the Nb$^{5+}$ orbital and thus to change the electronic properties significantly doping of Nb site is more favorable. Jana et al. have studied the effect of doping of isovalent Nb$^{5+}$ at the Ta$^{5+}$ site on photocatalytic properties of NaTaO$_3$. Also, Toresspardo et al. have studied the effect of substitution of Nb by isovalent Ta on electric and dielectric properties of NaNb$_{1-x}$Ta$_x$O$_3$. To the best of our knowledge, NaNb$_{1-x}$Ta$_x$O$_3$ has not been investigated for its photocatalytic activity. However, the investigation of effect of doping of Nb by isovalent Ta on dielectric properties of NaNb$_{1-x}$Ta$_x$O$_3$ has been done previously, and the method used for synthesis of NaNb$_{1-x}$Ta$_x$O$_3$ include high temperature solid state reactions. Also, to improve the properties the development of nanodimensional materials using different synthesis approaches like the solvothermal, polymeric precursor, hydrothermal, and reverse micellar methods and the use of different structure, morphology, and shape controlling agents have been employed.

In addition to the development of new ways to generate energy, the demand for efficient energy storage materials is also increasing. More research and technological efforts are being made to develop high energy and power density materials which could further help in integration of miniaturized electronic devices. For this purpose, ceramic dielectric material has shown fascinating application due to their high chemical, mechanical, and thermal stabilities and high permittivity with high working temperature.

In this paper, low-temperature hydrothermal synthesis and structural characterization of pure NaNbO$_3$ and NaNb$_{1-x}$Ta$_x$O$_3$ were carried out. The photocatalytic applications of synthesized hierarchical interwoven nano Nb$_{1-x}$Ta$_x$O$_3$ was screened by carrying out the degradation of organic pollutant and by carrying out H$_2$ evolution from the water splitting reaction. With varying the concentration of Ta doping, the interwoven nano-hierarchical of Nb$_{1-x}$Ta$_x$O$_3$ showed improved photocatalytic activity compared to pure NaNbO$_3$. In addition to photocatalytic application, the effect of doping of isovalent Ta at the Nb site on dielectric properties of NaNbO$_3$ was also investigated. From the investigation, it was observed that doping of Nb by isovalent Ta improves both photocatalytic activity and dielectric properties of NaNbO$_3$ nanoparticles. The changes in both photocatalytic activity and dielectric properties of Ta doped NaNbO$_3$ were correlated with the possible changes in the band structure and microstructure taken place due to doping of Ta.

2. EXPERIMENTAL SECTION

2.1. Materials. All the chemicals used in the synthesis process were of analytical grade. To synthesize pure NaNbO$_3$ and NaNb$_{1-x}$Ta$_x$O$_3$, NaOH (Merck, 97%) was used as a source of Na, Nb$_2$O$_5$ (Alfa Aesar, 99%) was used as a precursor for Nb, and Ta$_2$O$_5$ (Alfa Aesar) was used as the Ta source. To check the photocatalytic removal of organic pollutants, methylene blue dye (MB) (Merck) was used as a model pollutant. Other chemicals used include silver nitrate (Merck, 99.5%), benzoquinone (Merck, 97%), ammonium oxalate (Merck, 30%), and isopropanol (RANKEM, 99%). All the chemicals were used as received without further purification.

2.2. Synthesis of Sodium Niobate Nanohierarchitectures. Sodium niobate nanoparticles with hierarchitected morphology were first time synthesized by using a simple low-temperature hydrothermal route. The hydrothermal route employed for the synthesis of pure NaNbO$_3$ nanoparticles is reported somewhere else. In a typical synthesis process, 0.025 mol of Nb$_2$O$_5$ was added in 10 M NaOH solution. The solution was stirred at room temperature for 4 h. After that, the solution was transferred to a 75 mL Teflon lined autoclave and was heated at 180 °C for 4 h. The solution could cool naturally and was centrifuged and then washed several times, first with distilled water and then with ethanol.

2.3. Synthesis of Ta Doped Sodium Niobate Nano-hierarchitectures. NaNbO$_3$ doped with different concentrations of Ta was synthesized by a similar hydrothermal route except the addition of Ta$_2$O$_5$ as a precursor for Ta. In a typical synthesis process, 0.025 mol of Nb$_2$O$_5$ was added to 10 M solution of NaOH followed by addition of 5, 10, 15, and 20 mol % of Ta$_2$O$_5$ in the reaction mixture. The whole reaction mixture was stirred for 4 h and transferred to a 75 mL Teflon lined autoclave. The reaction mixture was heated at 180 °C for 4 h and then cooled to room temperature. To get the final product, the reaction mixture was centrifuged at 7000 rpm and was washed with distilled water and ethanol several times. The final product was dried in a vacuum oven at 60 °C and was used for further analysis. All the synthesized samples were coded as (NN) for pure NaNbO$_3$ and NN1, NN2, NN3, and NN4 for 5%, 10%, 15% and 20% Ta doped NaNbO$_3$, respectively.

2.4. Characterization. Powder X-ray diffraction analysis (XRD) was carried out by employing a Rigaku diffractometer using Cu Kα radiation having a wavelength equal to 1.5406 Å. All the samples were scanned with a scan rate and step size equal to 5°/min and 0.02°, respectively. X-ray diffraction analysis was carried out with 2θ ranging from 10 to 70°. Fourier transformation infrared spectroscopic (FTIR) analysis was carried out by using pellets of as synthesized samples in the presence of KBr. FTIR analysis was carried out using a PerkinElmer FT-IR spectrophotometer model IR affinity1. Transmission electron microscope (TEM) analysis was carried out by using the samples dispersed in ethanol and mounted on a carbon coated copper grid. The grids for TEM analysis were prepared by carrying out the drop casting of the sample on the
copper grid. TEM analysis was done using a TELOS instrument with an accelerating voltage of 200 kV. For field emission scanning electron microscopy (FESEM), samples were mounted in the form of powder on the grid with gold coating. FESEM analysis was carried out using FEI NOVA NanoSEM 450 having an accelerating voltage of 20 kV. In addition to FESEM, EDAX and elemental mapping of the samples was carried out using FEI NOVA NanoSEM 450. The binding energy and oxidation state analysis of the samples was carried out by using X-ray photoelectron spectroscopy (XPS). XPS analysis was carried out in survey mode by carrying out surface charge neutralization. For XPS analysis operating a flood gun having 30 eV pass energy, a 0.01 eV step size was used. All the peaks in the XPS spectra were calibrated with respect to C 1s having a peak position at 284.8 eV. XPS measurements were carried out using Thermoscientific XPS having Al Kα radiation, with \( hν = 1486.6 \text{ eV} \). The band gap was determined by using diffused reflectance UV–vis spectroscopy (DRS). Reflectance analysis of the samples was carried out using a PerkinElmer Lambda365 UV–vis spectrophotometer with BaSO₄ as a reference sample in the range of 200–800 nm. By employing reflectance data, a band gap was calculated using the Kubelka–Munk equation. Surface area analysis was carried out by using the Brunauer–Emmett–Teller (BET) surface area analysis technique. For surface area analysis, a Nova 2000e (Quantachrome Instruments Limited, USA) was used. All the measurements were carried out in the presence of liquid nitrogen having a bath temperature of 77 K. Before carrying out the analysis, all the samples were degassed under vacuum conditions at 150 °C for 12 h to remove the unwanted adsorbed gases on the samples. The weight of the samples was measured before and after degassing to calculate the actual amount of sample having no adsorbed gases on their surfaces. Photoluminescence (PL) analysis of the synthesized samples was carried out using an F-7000 Hitachi fluorescence spectrophotometer with an excitation wavelength ranging from 400 to 500 nm.

2.5. Photocatalytic Studies. Degradation of methylene blue was carried out in the presence of sunlight to elucidate the photocatalytic activity of as-prepared nanoparticles. To carry out the analysis, a stock solution of MB dye having a concentration equal to \( 1 \times 10^{-5} \text{ M} \) was prepared in aqueous medium. A total of 20 mg of nanoparticles was dispersed in 50 mL of the dye solution and was kept in the dark for 1 h to ensure adsorption–desorption equilibrium between the dye and the nanocatalysts. The dye-catalyst suspension was then exposed to sunlight irradiation to initiate the photocatalytic degradation reaction. After every 10 min, adequate aliquots were taken and centrifuged to remove the suspended catalyst particulates for spectral analysis. Similar experiments were carried out either in the dark or without catalysts to confirm the degradation process is solely photocatalytic driven. The efficiency of the catalyst for photodegradation process was monitored by a change in intensity of the characteristic absorption peak of MB at \( \sim 664 \text{ nm} \) using a PerkinElmer Lambda365 UV–vis spectrophotometer. The percentage removal of the dye was computed by using eq 1.

\[ \text{Percent Removal} \ (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1) \]

where \( C_i \) is the initial concentration of MB dye after adsorption–desorption equilibrium before irradiation and \( C_f \) is the concentration of dye after time interval \( t \) (in minutes). In addition to UV–visible spectra, liquid chromatography–mass spectrometry (LC-MS) of the dye solution was carried out to attest whether the dye has been degraded or not. Mass spectral studies were carried out by using an API2000 Applied Biosystems LC/MS/MS/MS instrument.

2.6. Photocatalytic Water Splitting Measurements. The photocatalytic activities for hydrogen generation were also studied for all synthesized samples in an external irradiation cell with a light source of a 200 W Hg (Xe) lamp (New Port, Mercury–Xenon, 200 W model 66906-200HXF-R15 ozone-free) at an intensity of 190 W without a cutoff filter under full arc irradiation. For the photocatalytic \( \text{H}_2 \) evolution experiments, a 100 mL cylindrical quartz cell with its flat surfaces being exposed to the light source was charged by 20 mg of the photocatalyst and 0.128 moles of \( \text{Na}_2\text{S}_2 \), 0.079 moles of \( \text{Na}_2\text{SO}_3 \) as the sacrificial agents were dispersed uniformly in 50 mL of double distilled water. The cell containing the solution was closed with

Figure 1. (a) XRD patterns of the as-synthesized NN, NN1, NN2, NN3, and NN4 nanostructures and (b) zoomed in XRD pattern showing shifting of peaks with Ta doping.
an airtight rubber septum at the top and kept in an inert atmosphere by purging N₂ gas into the cell for half an hour prior to carrying out the measurements and to remove any impurities of the gases. After degassing, the solution mixture was placed under light on constant stirring and kept at a constant temperature of around (25 °C). The quantification of the amount of evolved H₂ gas was done by using gas chromatography (PerkinElmer, Clarus 590 GC) equipped with a TCD detector using N₂ as the carrier gas. The gaseous components were monitored by per hour sampling, and evolved H₂ was estimated with the reference hydrogen gas by comparing the GC plot.

2.7. Dielectric Measurements. Dielectric properties of the as-prepared samples were measured using 6505 P, Wayne Kerr Electronics, U.K. Dielectric properties of the samples were analyzed as a function of frequency and temperature ranging from 20 Hz to 1 MHz and 50–500 °C respectively. To study the dielectric properties of the synthesized samples, a parallel plate capacitor was developed by using sample disks having a 8 mm diameter and 0.8 mm thickness and coated with a silver conducting surface which acts as an electrode. For the preparation of pellets, poly(vinyl alcohol) (PVA) was used as a binder. All the synthesized samples were mixed with 5% PVA in a mortar and pestle, and pellets were formed by applying pressure equal to 5 tons using a technosearch KBr press model M-5. All the pellets were annealed at 800 °C before dielectric measurements were carried out.

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction (XRD) Studies. The phase composition, phase purity, crystal structure, and crystallinity of pure NaNbO₃ and NaNb₁₋ₓTaₓO₃ having different compositions of Ta (5–20 mol %) was determined by XRD analysis as shown in Figure 1a. From the XRD patterns, it was observed that pure monophasic NaNbO₃ having an orthorhombic crystal structure was synthesized using the hydrothermal route. All the reflection peaks observed in the XRD were matched with the JCPDS card no. 89-5173. The resultant Ta doped NaNbO₃ samples have quite identical isostructural orthorhombic crystal structures. Peaks at 2θ values of 22.89°, 32.77°, 46.85°, 52.61°, 58.06°, and 68.19° correspond to (100), (110), (200), (210), (211), and (220) crystal planes, respectively. With an increase in concentration of Ta in NaNbO₃, the peaks are little shifted toward higher 2θ values as shown in Figure 1b, and this apparent shifting in peaks was attributed to the small ionic radii of Ta (0.64 nm) as compared to Nb (0.72 nm) thus causing the lattice contraction in Ta-doped NaNbO₃ samples.39 The XRD results obtained were employed to determine the crystallite size of the as-synthesized nanoparticles. To determine the crystallite size, Scherrer’s equation was used, and the calculated crystallite sizes were equal to 23.1, 27.9, 24.9, 24.6, and 20.3 nm for NN, NN₁, NN₂, NN₃, and NN₄ samples, respectively. Using XRD results, the crystal parameters and crystal structure of as-synthesized nanoparticles were deduced by using Quantum espresso software. Using the XRD results along with the crystallography open database (COD) file for NaNbO₃, the crystal structure of the as synthesized NaNbO₃ was deduced. The obtained crystal structures are shown in Figure 2a,b for pure NaNbO₃ and Ta-doped NaNbO₃ nanostructures, respectively.

3.2. Fourier Transformation Infrared Spectroscopic (FTIR) Studies. FTIR studies were carried out to determine the formation of M–O bond using KBr as a carrier for as synthesized samples. Figure 2c represents the IR spectra (500–4000 cm⁻¹) of as synthesized samples. From the obtained results, the peak present between 500 and 650 cm⁻¹ confirms the formation of a metal oxide (M–O) bond. In all the synthesized samples, the IR peak is present at 625 cm⁻¹ and thus confirms the successful formation of Ta–O or Nb–O bonds, and no other prominent peaks were observed in any of the synthesized samples.
3.3. Transmission Electron Microscopic (TEM) Studies. Figure 3 represents the TEM micrographs of the as-prepared samples. From TEM analysis, it was observed that typical single layered pure NaNbO₃ nanoflakes were synthesized successfully as evident in Figure 3a. With the addition of Ta as a dopant, the formation of the layered structure is restricted as observed in Figure 3b–e. From TEM analysis, it was observed that above 10 mol % Ta doping, the small flake shaped particles start to appear.
as shown in Figure 3d,e. From the TEM micrographs of the as-synthesized samples, the average particle size distribution was calculated and the obtained histogram is represented in the inset of Figure 3a–e. The average particle sizes for the samples NN, NN1, NN2, NN3, and NN4 were found to be 100, 90, 60, 70, and 40 nm, respectively. To the best of our knowledge, no such flake-like layered nanoparticles of pure NaNbO3 and Ta-doped NaNbO3 have been reported previously.

3.4. Field Emission Scanning Electron Microscopic (FESEM) Studies. The FESEM technique was used to investigate the microstructure and micromorphology of as-prepared pure NaNbO3 and Ta-doped NaNbO3 samples. FESEM micrographs of all the samples are shown in Figure 4. It is observed that as-prepared pure NaNbO3 shows large building blocks with hierarchical arrangement of intercrossed horizontal and vertical nanoflakes (Figure 4a). Similarly, in 5% Ta doped NaNbO3, the interwoven nanoflakes are present but the hierarchy is slightly disturbed. With a further increase in concentration of Ta to 10 mol %, intercrossed nanoflakes decrease and little particle formation starts to appear. A further increase in the concentration to 15 and 20 mol %, the needle shaped particles with flowerlike structures are formed. The magnified FESEM micrographs of as-synthesized nanostructures are shown in Figure S1a–e. The detailed observation of the single building blocks showed that these blocks are composed of several small flakes. These small flakes are interconnected horizontally and vertically, thus forming a hierarchical structure. It was also observed that the surface of small flakes was not smooth, which was attributed to Ostwald ripening/coarsening. Figure S1f–j further demonstrate that the nanoflakes were composed of small nanoparticles.

To determine the elemental composition of the as-synthesized pure and Ta-doped NaNbO3 nanoflakes, EDAX analysis was carried out. From the EDAX study, it was observed that peaks in the spectra correspond to Na, Nb, and O with no impure peak present in the NaNbO3 sample as shown in Figure S2a. EDAX of the NaNbO3 samples doped with Ta show the presence of Ta in the spectra (Figure S2b–e). Also, from the EDAX of the samples, it was observed that with increasing the concentration of Ta, the atomic weight percent of Nb decreases which is due to the fact that Ta is doped at Nb sites of the samples. The atomic weight percentage of different constituent

![Figure 4. FESEM micrographs of (a) NN, (b) NN1, (c) NN2, (d) NN3, and (e) NN4 nanostructures.](https://pubs.acs.org/doi/10.1021/acsomega.1c07250)
elements of the as synthesized nanostructures is given in Table S1. In addition to EDAX analysis, elemental mapping of the as-prepared samples was carried out. Figure 5a−e shows the elemental mapping of pristine NaNbO₃ (NN) and Ta-doped NaNbO₃ (NN1−NN4) samples. From element mapping of all the samples, it was seen that Na, Nb, and O are distributed uniformly in pristine NaNbO₃ sample, whereas, in the samples doped with Ta, coexistence of Ta along with other elements was observed. It was also observed that the density of Ta distribution in all Ta-doped samples increases with an increase in concentration of Ta.

3.5. X-ray Photoelectron Spectroscopy (XPS) Study. Oxidation state and the surface chemical composition of the synthesized photocatalyst samples were elucidated by employing the XPS technique. The binding energies of all the samples were calibrated with respect to C 1s having a binding energy centered at 285.8 eV. Figure 6a represents the survey spectra of pure NaNbO₃ and Ta doped (with different mole %) NaNbO₃ nanoparticles. From the survey scan of pure NaNbO₃, the peaks corresponding to Nb, Na, and O were present. While as in addition to the peaks corresponding to Na, Nb, and O, a peak corresponding to Ta was also present in the samples doped with 10, 15, and 20 mol % Ta. From the XPS analysis, it was observed that no peak corresponding to Ta in the sample with 5 mol % of Ta doping was observed. This was due to a low concentration of Ta present on the surface of the sample. High-resolution XPS of all the samples was carried out as shown in Figure 6. Figure 6b represents the high-resolution XPS spectra of Na 1s, which corresponds to Na 1s. The peak present at 1071 eV shows that Na is present in +1 oxidation in all the synthesized samples. Figure 6c represents the high-resolution XPS spectra of O 1s, which is centered at a binding energy equal to 529 eV confirming the −2 oxidation state of O. The peak corresponding to O 1s originates due to −Nb−O in pure NaNbO₃ or due to −Ta−O present in Ta-doped NaNbO₃ samples. Figure 6d shows the high-resolution XPS spectra of Nb element present in the synthesized photocatalysts. The peak corresponding to Nb 3d was deconvoluted into two peaks centered at 206.3 and 209.5 eV, which corresponds to Nb 3d₅/₂ and Nb 3d₃/₂, respectively. The difference between the two deconvoluted peaks corresponding to Nb was found to be 3 eV, which evidenced that Nb is present in the +5 oxidation state in all the synthesized samples.

3.6. Diffused UV−Visible Reflectance Spectroscopy (DRS) Study. UV−vis DRS spectra of the synthesized samples are shown in Figure S3. The obtained reflectance data was used to calculate the band gap of the materials using the Kubelka−Munk equation. Reflectance was converted to absorbance of the samples using eq 2.

$$ F(R) = a/s = (1 - R)^2 / 2R $$

In eq 2, F(R∞) represents the Kubelka−Munk function and is equal to the diffused reflectance of the infinite thick sample, the terms F, α, s, and R represent the Kubelka−Munk function, absorption coefficient, scattering factor, and reflectance of the material, respectively. Figure S3b represents the plot of band gap energy versus (F(R∞)hν)¹/². From the DRS study, it was observed that pure NaNbO₃ shows a band gap equal to 2.89 eV.
whereas the photocatalysts doped with 5, 10, 15, and 20 mol % Ta have band gaps equal to 2.92, 3.0, 3.18, and 3.2 eV, respectively. The band gap calculated in this report for pure NaNbO3 is in accordance to the previously reported results. From the calculated bandgap, it is observed that the band gap of Ta-doped NaNbO3 photocatalysts is more than pure NaNbO3. The increase in the band gap is due to substitution of Ta5+ at Nb5+ sites in the pristine NaNbO3 photocatalyst. In most of the metal oxides, the O 2p and d orbital of the transition metal constitute the valence and conduction bands, respectively. Thus, the top of the valence band of each prepared sample comprises the O 2p orbital. By substitution of Ta at Nb sites, the conduction potential of Ta-doped NaNbO3 becomes more negative, thus resulting in an increase in the band gap of the as-synthesized Ta-doped nanostructures. This more negative conduction potential is considered as beneficial for driving and separation of photogenerated charge carriers, which could be highly useful for improved photocatalytic activity of the synthesized nanoparticles. However, the large bandgap of a material decreases the absorption range of a photocatalytic material which could reduce the activity of a material as a photocatalyst.

3.7. Brunauer–Emmett–Teller (BET) Surface Area Analysis. Surface area of the sample plays vital role in the catalytic activity of the materials. BET surface area analysis was used to determine the surface area of the synthesized samples. Figure 7a shows the BET N2 adsorption–desorption isotherm of as prepared photocatalysts. From the BET surface area measurements, it was observed that all the samples show type IV adsorption isotherms with a H3 hysteresis loop which

![Figure 6](image-url)
conirms the as prepared nanoparticles are having a well-defined mesoporous structure.\textsuperscript{46} This type of isotherm indicates that multilayer adsorption is taking place followed by condensation. The isotherm possesses a hysteresis loop which is formed because of condensation process taking place on mesoporous solids.\textsuperscript{47} Using desorption points, the pore size distribution of as-prepared samples was evaluated from the Barrett–Joyner–Halenda (BJH) plot as shown in Figure 7b. From the BJH plot, it was observed that all the samples show monomodal pore distribution centered between 15 and 20 Å. The average pore size of all the samples was deduced from adsorption desorption points of the isotherm by using Dubinin–Astakhov (DA) analysis. Figure 7c represents the DA plot of synthesized NaNbO\textsubscript{3} and Ta doped NaNbO\textsubscript{3} nanoparticles. The specific surface area, DA average pore size, and BJH pore radius of the samples calculated from BET analysis is given in Table 1. From the BET studies, it was observed that using the hydrothermal route, nanoparticles with enhanced surface area were obtained compared to the samples prepared by the conventional solid state route.\textsuperscript{44} Also, it was observed that with an increase in the amount of Ta, the surface area increases which was attributed to formation of small particles as observed in TEM and FESEM analysis.

### 3.8. Photocatalytic Studies

#### 3.8.1. Photocatalytic Dye Degradation Studies

To check the photocatalytic activity of as-prepared nanoparticles, methylene blue (MB) was used as a model pollutant. A $1 \times 10^{-5}$ M stock solution of MB was prepared followed by addition of 20 mg of as-prepared photocatalysts. The dye solution along with the photocatalyst nanoparticles were kept under dark condition for 1 h to attain adsorption desorption equilibrium. From the adsorption study, it was observed that the negligible amount of dye has been adsorbed on the catalyst surface. Also, the dye solution without photocatalyst was exposed to sunlight to check the photolysis of MB dye. After adsorption–desorption equilibrium, the dye solution was exposed to solar radiations. After every 10 min, 3 mL of dye solution was extracted to check the change in the absorption maxima of the MB dye in the presence of solar radiation and photocatalyst. The process of photocatalysis was carried out for 80 min. Figure S4a–e represents the UV–visible absorption spectra of MB dye in the presence of as-synthesized photocatalysts and light. From Figure S4a–e, it was observed that with an increase in exposure time, the intensity of absorption maxima of MB dye decreases continuously, confirming the degradation of MB dye with time in the presence of sunlight and as-synthesized photocatalysts. From UV–vis spectra it was also observed that with an increase in Ta doping up to 10 mol %, the photocatalytic activity of NaNbO\textsubscript{3} increases, and with a further increase in concentration of dopant the photocatalytic activity decreases. Using UV–visible absorption spectra, percentage removal of MB dye was calculated as represented in Figure 8a. From the obtained results, a maximum decrease in the concentration of MB dye was observed in 10 mol % Ta doped NaNbO\textsubscript{3} photocatalyst. From Figure 8a, maximum degradation of 89% was observed in 10 mol % Ta doped

| Sample | BET surface area (m\textsuperscript{2}/g) | DA average pore size (Å) | BJH pore size distribution (Å) |
|--------|----------------------------------------|-------------------------|-------------------------------|
| NN     | 5.8                                    | 11.6                    | 18.7                          |
| NN-1   | 6.8                                    | 13.3                    | 18.8                          |
| NN-2   | 7                                      | 11.3                    | 18.7                          |
| NN-3   | 9.2                                    | 11.1                    | 18.8                          |
| NN-4   | 9.7                                    | 11.7                    | 18.8                          |
NaNbO₃. The percentage removal of MB dye using different photocatalysts is tabulated in Table 2. To determine the kinetics of the photocatalytic degradation reaction of MB dye using as-synthesized nanoparticles, different models were used. From the kinetic study, it was observed that all the synthesized photocatalysts obey the Langmuir–Hinshelwood mechanism as shown in Figure 8b. The kinetics of the photocatalysts was determined by using eq 3.

\[ \ln \frac{C}{C_0} = kRt = Rt \]  

where \( C \) and \( C_0 \) represents concentration after time \( t \) and initial concentration at \( t = 0 \), respectively, and \( R \) is the rate constant of the photocatalytic reaction. From the kinetic study, it was observed that degradation process carried out by as-synthesized photocatalysts follow pseudo first order kinetics, which was confirmed by the straight line obtained from the semi-logarithmic plot of concentration versus irradiation time. The rate constant of the degradation process was determined by using linear fitting of the curves. Table 2 shows the rate constant and \( R^2 \) values of the photocatalytic degradation process of the MB dye in the presence of pure and Ta-doped NaNbO₃ photocatalysts.

In addition to UV–visible spectral studies, the degradation of MB dye was confirmed by using LC-MS. The samples with least intensity (obtained after 80 min) in the UV–vis spectra were used to carry out the LC-MS analysis. LC-MS spectra of MB dye after carrying out photocatalytic degradation using as-synthesized photocatalysts are shown in Figure S5a–e. The possible chemical formulas and structure of degradation fragments obtained from LC-MS spectra were deduced using the Chemdraw structural tool and are shown in Figure S6a–e.

The role of different active species (OH•, O₂•−, e−, H⁺) generated during the photocatalytic process was elucidated by carrying out the quenching process using different scavengers as discussed in the Supporting Information of the manuscript.

![Figure 8](image_url) (a) Percentage removal efficiency and (b) kinetic plots of the photocatalytic degradation reaction using the as-synthesized pure and Ta-doped NaNbO₃ photocatalysts.

![Figure 9](image_url) (a) Photocatalytic hydrogen evolution of pure and Ta-doped NaNbO₃ photocatalysts with irradiation time using Na₂S and Na₂SO₃ as sacrificial agents, and (b) PL spectra of pure and Ta-doped NaNbO₃ nanoparticles.

### Table 2. Percentage Removal of MB Dye and Rate Constant of Photocatalytic Reactions Carried out by the Synthesized Nanocatalysts

| sample | percentage removal | rate constant | \( R^2 \) |
|--------|--------------------|---------------|----------|
| NN     | 44.90              | 0.12          | 0.97     |
| NN1    | 44.90              | 0.13          | 0.99     |
| NN2    | 89                 | 0.36          | 0.98     |
| NN3    | 74.84              | 0.21          | 0.97     |
| NN4    | 60.96              | 0.16          | 0.96     |
Figure S7 represents the effect of different scavengers on photocatalytic activity of as-synthesized photocatalysts. Using the results obtained from the quenching experiments, the following possible mechanism for photocatalytic activity was deduced.

\[
\text{(NN, NN1–NN4)} + \text{hv} \rightarrow \text{(NN, NN1–NN4)}(e^-_{\text{CB}} - h^+_{\text{VB}})
\]

\[
\text{(NN, NN1–NN4)}(e^-_{\text{CB}}) + \text{O}_2 \rightarrow \text{(NN, NN1–NN4)}\text{O}^*^-
\]

\[
2\text{O}^*^- + \text{H}_2\text{O} \rightarrow \text{HO}_2^* + \text{OH}^-
\]

\[
\text{HO}_2^* + \text{H}_2\text{O} \rightarrow \text{HO}^* + \text{H}_2\text{O}_2
\]

\[
\text{H}_2\text{O}_2 \rightarrow 2\text{OH}^*
\]

\[
2\text{OH}^* + \text{MB} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

where NN corresponds to pure NaNbO₃ and NN1–NN4 correspond to 5–20 mol % Ta-doped NaNbO₃, respectively. The electrons in the conduction band after photoexcitation are represented by \(e^-_{\text{CB}}\), and the holes in the valence band are designated by \(h^+_{\text{VB}}\).

3.8.2. Photocatalytic Water Splitting Studies. The photocatalytic activity for hydrogen generation using water splitting phenomenon was evaluated for all the samples. The evolution of hydrogen was measured as a function of time for pure NaNbO₃ and NN1–NN4 compositions. Herein, we have reported the H₂ evolution for pure sample and NN2 sample with the highest activity and for NN4 to show with a further increase in Ta concentration photocatalytic activity decreases. Figure 9a shows the rates of H₂ generation of pure NaNbO₃, 10 mol % Ta-doped NaNbO₃ (NN2), and 20 mol % Ta-doped NaNbO₃ (NN4) samples under full arc irradiation. During the investigation, it
was observed that the amount of H₂ generated was equal to 1.7, 21.4, and 5.5 mmol g⁻¹ in the presence of pure NaNbO₃, NN₂, and NN₄ respectively, in 8 h. From the obtained results the highest H₂ production rate was observed in the NN₂ sample. With the increasing concentration of Ta, the photocatalytic H₂ evolution activity increases until 10 mol % as sample NN₂ shows the highest activity. Thus, the improvement in photocatalytic activity could be attributed to the increase in surface area and change in the reduction potential of the conduction band. With addition of Ta at the Nb sites, the position of the conduction band is altered and is shifted to a more negative reduction potential, which favors the easy separation of photogenerated charge carriers, while as with a further increase in Ta concentration, photocatalytic activity decreases, which is attributed to an increase in band gap due to which photo-absorption activity of a material is reduced.

To further investigate the reason responsible for enhanced photocatalytic activity of as synthesized Ta-doped NaNbO₃ nanostructures, photoluminescence (PL) investigation was carried out. Figure 9b represents the PL spectra of the synthesized pure NaNbO₃ and different mole % Ta-doped NaNbO₃ samples. From the PL spectra, the excitation peak for all the samples was observed at 472 nm. It was also observed that with an increase in Ta doping, the intensity of the peak present at 472 nm decreases, thus confirming the delay in the recombination of photogenerated charge carriers due to the entrapment of excitons. ⁴⁸

3.9. Dielectric Studies. Variation of dielectric properties including dielectric constant (ε) and dielectric loss (D) of all the synthesized samples was evaluated with frequency ranging from 20 Hz to 1 MHz at 100 °C. Also, the variation of (ε) and (D) of pristine NaNbO₃ and Ta-doped NaNbO₃ nanoparticles with a

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Figure 11. Variation of dielectric constant and dielectric loss with temperature of (a) NN, (b) NN₁, (c) NN₂, (d) NN₃, and (e) NN₄ samples at 500 kHz.
temperature range (50–500 °C) was measured at 500 kHz. Figure 10a–e shows the variation of (ε) and (D) of pure NaNbO3 and 5, 10, 15, and 20 mol % Ta doped NaNbO3 nanoparticles with frequency at 100 °C. From Figure 10, it was observed that with an increase in frequency, the dielectric constant of as-prepared nanoparticles decreases rapidly at lower frequencies and remains stable and constant at higher frequencies. At lower frequencies, all these nanoparticles show high dielectric dispersion. Similar behavior is demonstrated by dielectric loss, which shows high value at lower frequency and decreases with an increase in frequency. The whole dielectric behavior can be explained based on Maxwell–Wagner interfacial polarization theory of dielectrics. At lower frequencies, different structures including space charge, dipoles, and ions contribute to the overall polarization of the materials. At lower frequencies, these structures have enough time to undergo the relaxation process and follow the external applied electric field. With an increase in frequency, the space charge polarization does not get enough time to follow the applied electric field and therefore is relaxed out at higher frequencies. According to Koop’s theory, another important reason for the decrease in the dielectric constant with frequency is contribution from grain boundaries and grains which are relaxed out at higher frequencies. The energy dissipation or dielectric loss of all the synthesized samples decreases with increase in frequency because of the contribution of dipoles toward polarization. The variation of the dielectric loss curve follows similar behavior as that of the dielectric constant. The high value to dielectric loss at lower frequency is due to high resistive grain boundaries which are more prominent than grains.

In addition, the variation of (ε) and (D) in pure NaNbO3 and Ta-doped NaNbO3 with temperature is shown in Figure 11a–e. The detailed measurements of dielectric properties were carried out in the temperature range of 50–500 °C at a selected frequency of 500 kHz with a temperature interval of 50 °C. From Figure 11, it was observed that at 500 kHz all the samples show an increase in the dielectric constant with an increase in temperature. In the pure NaNbO3 sample, the dielectric constant increases in the temperature range 50–400 °C and shows a maximum value at 400 °C. With a further increase in temperature, the dielectric constant decreases. The temperature having a maximum value of the dielectric constant corresponds to a Curie temperature of the sample. From dielectric dependence on temperature, at 500 kHz dielectric constant, maxima were observed in all the samples with different compositions. From the results, it was observed that with an increase in the dopant concentration, the dielectric constant maximum is shifted toward lower temperature. Also, with an increase in the doping concentration, the dielectric constant increases up to 5 mol % doping of Ta in NaNbO3, and with a further increase in dopant concentration, the dielectric constant starts decreasing.

The increase in dielectric constant as compared to pure NaNbO3 up to 5 mol % Ta doping is attributed to the change in the microstructure of the samples. It had been observed that dielectric properties of the material are influenced by grain size, porosity, applied temperature, and substituent/dopant concentration. As investigated by SEM analysis, the concentration of Ta as dopant in NaNbO3 plays an important role in controlling the microstructure. As reported earlier, it is observed that grain size distribution plays an important role in the dielectric properties of the material. The variation of the dielectric constant in Ga doped K1−xNaₓNbO3 and BaTiO3 with grain size was reported, and from these results it was explained how domain twining, microstructure, and internal stress at the grain boundaries play an important role in the dielectric constant of the material. In this report, we speculate similar behavior responsible for the variation of the dielectric constant with temperature. As observed from dielectric analysis, the sample having 5 mol % Ta doping concentration has the highest value of the dielectric constant and it decreases with a further increase of Ta doping. This behavior is attributed to electronic or ionic defect migration taking place on addition of a dopant in the host material.

All the synthesized samples with different concentration ranges have comparable dielectric loss all over the measuring temperature range as shown in Figure 11. The increase in dielectric loss with temperature of as-prepared samples is attributed to the change in mobility of ionic defects with an increase in temperature. Table 3 represents the value of the dielectric constant and dielectric loss at 100 °C and 500 kHz frequency of as-prepared samples.

| sample | dielectric constant | dielectric loss |
|--------|---------------------|----------------|
| NN     | 111                 | 0.031          |
| NN1    | 510                 | 0.06           |
| NN2    | 491                 | 0.044          |
| NN3    | 488                 | 0.047          |
| NN4    | 188                 | 0.05           |

3.10. AC Conductivity Studies. To understand the conduction mechanism and evaluate the parameters controlling the process of conduction for pure and Ta-doped NaNbO3 nanoparticles, AC conductivity measurements were carried in the frequency range 20 Hz to 1 MHz at 50 °C as shown in Figure S8. From conductivity measurements, it was observed that with an increase in frequency, the conductivities of all the samples increase. The presence of hopping channels is responsible for hopping conduction; therefore, with an increase in frequency, the hopping channels are facilitated and becomes more active, which promotes more charge carrier hopping. The Jonscher power law (eq 4) was used to understand the underlying mechanism for the conduction behavior of as-prepared nanoparticles.

\[ \sigma = A\omega^n \]  

(4)

where A is a constant, ω represents angular frequency, and exponent n represents the frequency dependent slope. The value of n determines the mechanism responsible for the conduction behavior of the samples. For η < 1 and η > 1 conduction follows the Maxwell–Wagner type mechanism and barrier hopping conduction mechanism, respectively. From fitting of the conductivity plots of different samples, it was observed that all the samples have η < 1 and follow the conduction hopping barrier mechanism, which involves short-range translational hopping along with the small and large polaron hopping mechanisms. From AC conductivity measurements, it was also observed that conductivity first decreases with an increase in Ta %, and with a further increase in Ta above 5 mol %, conductivity increases.
4. CONCLUSION

Successful synthesis of pristine NaNbO$_3$ and Ta-doped NaNbO$_3$ nanohierarchal building blocks was carried out by a simple hydrothermal route. XRD and electron microscopic investigations confirm the formation of highly crystalline, monophasic, typical single layered nanoflakes of pristine NaNbO$_3$, and with an increase in percentage doping of Ta, thin layered nanosheet formation was restricted. The addition of Ta in NaNbO$_3$ owned a strong influence on its band structure, which obviously improves the photocatalytic activity and dielectric properties of NaNbO$_3$. The highest photocatalytic water splitting activity (21 μmol/g) and 89% removal of MB organic dye was observed in 10 mol % Ta-doped NaNbO$_3$ as compared to pure NaNbO$_3$. Similarly, in 5 mol % Ta-doped NaNbO$_3$, an enhanced dielectric constant of 510 was observed. Improved photocatalytic activity and a dielectric constant of Ta-doped NaNbO$_3$ was attributed to the improvement in the separation of photogenerated charge carriers, absorption ability, and structural changes due to Ta doping.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c07250.

- Figure S1, detailed view of hierarchitectures of NN, NN1, NN2, NN3, and NN4 samples and magnified micrographs of NN, NN1, NN2, NN3, and NN4 nanohierarchitectures; Figure S2, EDAX spectral analysis of as prepared samples; Table S1, atomic percentage and stoichiometry of as-synthesized samples obtained by using EDAX analysis; Figure S3 and S4, UV-visible DRS spectra, Kubelka–Munk plot of synthesized samples, and UV–visible spectra of dye solution in the presence of light and synthesized photocatalysts; Figure S5, LC-MS spectra of MB dye after photocatalysis; Figure S6, degradation fragments from MB dye after the photocatalytic degradation process; section S1, mechanism of the photocatalytic dye degradation process deduced by using different scavengers; Figure S7, variation of photocatalytic activity in the presence of different scavengers; and Figure S8, variation of conduction with frequency for as-synthesized samples at 100 °C (PDF).

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Notes

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