Development of Cuboidal KNbO₃@α-Fe₂O₃ Hybrid Nanostructures for Improved Photocatalytic and Photoelectrocatalytic Applications

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ABSTRACT: Monophasic and hybrid nanostructures of KNbO₃ and α-Fe₂O₃ have been prepared using a hydrothermal process for photoelectrocatalytic and photocatalytic applications. Powder X-ray diffraction studies showed the formation of KNbO₃, α-Fe₂O₃, and KNbO₃/α-Fe₂O₃ with average grain sizes of 18.3, 11.5, and 26.1 nm and Brunauer−Emmett−Teller (BET) specific surface areas of 4, 100, and 20 m²/gm, respectively. Under simulated solar irradiation, the as-prepared heterostructure shows enhanced photoelectrocatalytic oxygen evolution reaction (OER) activity compared to pristine KNbO₃ and α-Fe₂O₃. Significant photocatalytic activity of as-synthesized KNbO₃/α-Fe₂O₃ heterostructure photocatalyst was obtained for removal of methylene blue organic dye under visible light, and the percentage activity was found to be 11, 49, and 89% for KNbO₃, α-Fe₂O₃, and KNbO₃/α-Fe₂O₃ photocatalysts, respectively. The dielectric constant was found to be 250.2, 65.2, and 251.5 for KNbO₃, α-Fe₂O₃, and KNbO₃/α-Fe₂O₃ heterostructure, respectively, at 50 °C and 500 kHz frequency.

1. INTRODUCTION

The utilization of fossil fuels as an energy source has created a great burden on the environment due to their nonrenewable nature and emission of CO₂.¹ Hence, it is of utmost importance to develop new technologies that could give better environmentally friendly ways to generate renewable energy. Among the different sources of energy, solar energy is considered as one of the cleanest and environmentally friendly renewable sources of energy that could be used as an alternative to fossil fuels. Different processes like photocatalysis, photoelectrocatalysis, and electrocatalysis are being developed to utilize solar energy in an efficient way for energy generation and environmental remediation.²⁻⁴ For fuel production, photoelectrocatalytic (PEC) water splitting is recognized as one of the promising artificial photosynthetic approaches. For PEC water splitting, the light absorption flux of photoanode is suppressed for large-band-gap materials like ZnO, TiO₂, etc.⁵⁻⁷ The photoelectrocatalytic (PEC) water splitting ability of semiconductor photocatalysts is affected by their band structure and effective separation of charge carriers.³ It has been observed that there are only few materials that fulfill the basic criteria for being considered as an efficient photoelectrocatalyst. Therefore, it is imperative to develop either new single-material systems or a combination of materials that could act as an efficient catalyst by satisfying the basic requirements. Most of the researchers are now focusing on the development of heterostructures to enhance the PEC efficiency by improving visible light harvesting and interfacial charge separation.

Another important application of semiconductor photocatalysts is wastewater treatment.⁸⁻¹³ For wastewater treatment, different techniques, such as biological, physical, and chemical, are being employed to remove different toxic substances like dyes, medicinal wastes, pesticides, etc. from water. The most promising technological approaches for removing these toxic materials from water include adsorption and photocatalysis.¹⁴ Currently, photocatalytic (PC) treatment of wastewater has attracted global interest and different photocatalysts are being developed to have a wide-range
absorption spectrum. To date, different photocatalysts have been developed. However, most of the developed photocatalysts have a narrow-range solar absorption spectrum and are active under UV irradiation. Therefore, efforts are being made to develop new photocatalyst materials having a wide-range solar absorption spectrum and showing catalytic activity under visible light irradiation.

Recently, ferroelectric/piezoelectric materials have been used to easily segregate charge carriers (generated during photoinduced reactions) in the space charge layer and transfer these charges in opposite directions due to spontaneous polarization for enhanced photoelectrocatalytic (PEC) and photocatalytic (PC) applications. Keeping in view of the unique properties of ferroelectric/piezoelectric materials, extensive work has been done to develop efficient ferroelectric nanophotocatalysts such as NaNbO$_3$, BaTiO$_3$, NaTaO$_3$, KNbO$_3$, YFeO$_3$, CuCrO$_2$, and LaFeO$_3$. However, most of the ferroelectric materials usually are high-band-gap materials, which show absorption in the UV region only, thus hindering their use as efficient photocatalysts. Therefore, heterostructures of these ferroelectric materials are developed to make them efficient photocatalysts. For example, it has been demonstrated that H$_2$ generation is strongly influenced by polarization conditions of thin films of TiO$_2$ poled on the crystals of LiNbO$_3$ and BaTiO$_3$. It might be associated with ferroelectric polarization, which results in the mobility of charge carriers in semiconductor thin films. Hence, heterostructured photocatalysts and/or photoelectrocatalysts such as Pb$_5$Zr$_3$Ti$_{6}$ (PZT)/TiO$_2$, BiFeO$_3$/TiO$_2$, and PbTiO$_3$/TiO$_2$ have been developed, which provides a feasible band structure for water splitting. In addition, enhanced surface area also plays a significant role in the improved activity of these systems.

Potassium niobate (KNbO$_3$) has shown considerable photocatalytic application and has attracted considerable interest due to its chemical stability, inertness, low toxicity, and more importantly, its perovskite structure having NbO$_6$ octahedra, which is highly beneficial for easy migration of charge carriers during photocatalytic reaction. However, due to its large band gap, KNbO$_3$ shows absorption in the UV region of the solar spectrum, which limits its application in photocatalysis and motivates the development of composite and heterostructures. Another important and promising application of KNbO$_3$ is in electronic devices due to its energy production (piezoelectric) and energy storage (dielectric) properties as well as electromechanical coupling in piezoelectrics. To improve the electrical characteristics and low-density issues of KNbO$_3$, various strategies such as sintering methods, sintering aids, additives, etc. have been developed. Similarly, incorporation of small amounts of additives like LaFeO$_3$, BiFeO$_3$, MnO$_2$, and ZnO results in improved density and electrical properties of KNbO$_3$.

Keeping in view, we have developed a KNbO$_3$/α-Fe$_2$O$_3$ heterostructure catalyst composed of KNbO$_3$ nanocubes and α-Fe$_2$O$_3$ nanoparticles for enhanced photocatalytic and electrical properties. The design of the KNbO$_3$/α-Fe$_2$O$_3$ photocatalyst is based on the fact that spontaneous polarization of KNbO$_3$ can act as a driving force to separate the photogenerated electron–hole pairs effectively. On the other hand, due to its great abundance, chemical stability, low toxicity, low cost, and suitable band gap energy for water splitting, hematite (α-Fe$_2$O$_3$) was widely used for photoelectrocatalytic water splitting and environmental treatment processes. However, due to slow kinetics of reactions, faster and severe recombination rate of charge carriers, and mismatch between water splitting potential and its band structure, the PEC efficiency of α-Fe$_2$O$_3$ remains very low. To improve the efficiency of α-Fe$_2$O$_3$, a combination of α-Fe$_2$O$_3$ with ferroelectric and p-type semiconductors to develop an n–p-type heterostructure is considered as an efficient strategy. Several methods such as reverse microemulsion, solvothermal method, solvent evaporation, polymeric citrate precursor route, hydrothermal method, etc. are used to develop nanodimensional photocatalysts; however, in our study, the hydrothermal/solvothermal route was preferred to develop the seed nanomaterial. Recently, ruthenium oxide nanoparticles have been developed by a simple wet chemical route for efficient multifunctional catalytic and sensing properties. In this study, we have used KNbO$_3$ as a ferroelectric component of the heterojunction photoanode, which has shown promising photocatalytic activity. The PEC activity of the heterojunction photoanode was studied, and it was observed that heterostructured photoelectrocatalyst showed enhanced PEC activity compared to the single counterparts of the heterojunction. In addition to PEC measurements, the effect of development of heterostructure on the photocatalytic and dielectric properties of the pristine components was also studied.

### 2. RESULTS AND DISCUSSION

#### 2.1. X-ray Diffraction (XRD) Studies

X-ray diffraction study was carried out to determine the phase composition, phase purity, and crystal structure of as-prepared samples. Figure 1 shows the diffraction pattern of as-prepared KNbO$_3$, α-Fe$_2$O$_3$, and KNbO$_3$/α-Fe$_2$O$_3$.

**Figure 1.** XRD patterns of as-prepared KNbO$_3$, α-Fe$_2$O$_3$, and KNbO$_3$/α-Fe$_2$O$_3$.

α-Fe$_2$O$_3$ nanoparticles, and KNbO$_3$/α-Fe$_2$O$_3$ nanoheterostructure. The diffraction pattern of the synthesized pure KNbO$_3$ was readily matched with the orthorhombic phase of KNbO$_3$ documented in JCPDS card no. 71-2171, having space group Bmnn2(38) and lattice constants $a$, $b$, and $c$ equal to 5.697, 3.971, and 5.721 Å, respectively. It was also observed that no diffraction peak from any other phase or impurity was detected. As revealed from the X-ray diffraction pattern of α-Fe$_2$O$_3$, the peaks were indexed with standard JCPDS card no. 86-0550 mainly consisting of hexagonal crystal phase, with lattice constants $a = 5.035$ and $c = 13.74$ Å and space group
In the XRD diffraction pattern of KNbO$_3$/($\alpha$-Fe$_2$O$_3$) heterostructure, the diffraction peaks corresponding to $\alpha$-Fe$_2$O$_3$ were not observed, indicating low loading concentration of precursor for $\alpha$-Fe$_2$O$_3$. The results obtained were similar to the results that have been previously reported, which shows that at a low concentration of $\alpha$-Fe$_2$O$_3$ precursor, no peak corresponding to $\alpha$-Fe$_2$O$_3$ in the heterostructure sample$^{51}$ could be seen. However, to analyze whether $\alpha$-Fe$_2$O$_3$ is formed in the heterostructure, a high concentration (0.01 M) of precursor for $\alpha$-Fe$_2$O$_3$ was prepared. Diffraction peaks corresponding to $\alpha$-Fe$_2$O$_3$ were obtained in the XRD pattern, which confirms the presence of $\alpha$-Fe$_2$O$_3$ in the heterostructure, as shown in Figure S1. From the XRD analysis, the average grain sizes of the synthesized nanoparticles were calculated using the Scherrer equation, which were found to be 18.3, 11.5, and 26.1 nm for KNbO$_3$, $\alpha$-Fe$_2$O$_3$ nanoparticles, and KNbO$_3$/ $\alpha$-Fe$_2$O$_3$ heterostructure, respectively. As revealed from the XRD pattern of KNbO$_3$, the possibility of doping/substitution of Fe in KNbO$_3$ during the formation of heterostructure was ruled out because substitution of Fe (lower ionic radius, 0.58 Å) at the Nb (higher ionic radius, 0.64 Å) position would lead to a decrease in lattice parameters and the peaks in the XRD pattern would be shifted to higher 2$\theta$ values, which was not evidenced in Figure 1.

2.2. Electron Microscopy Studies. Transmission electron microscopy (TEM) analysis of as-prepared samples was carried out for size and morphological studies, as shown in Figure 2. The formation of cube-shaped KNbO$_3$ nanoparticles is seen in Figure 2a,b shows well-dispersed polygonal nanoparticles of $\alpha$-Fe$_2$O$_3$. In contrast to Figure 2a, secondary surface of $\alpha$-Fe$_2$O$_3$ has been developed over the smooth surface of KNbO$_3$, as shown in Figure 2c. From the TEM analysis, it has been demonstrated that during the synthesis process, intimate heterojunction was formed between KNbO$_3$ and $\alpha$-Fe$_2$O$_3$ nanoparticles. Based on the TEM results, as evident from the inset of Figure 2c, it was observed that interface morphology has been developed, which can have a significant influence on the PEC and photocatalytic activity of the heterostructure.

To evaluate the surface morphology and chemical composition of as-prepared nanoparticles, field emission scanning electron microscope (FESEM) and energy dispersive X-ray spectroscopy (EDX) studies were carried out. Figure 3 shows the FESEM micrographs of the synthesized KNbO$_3$, $\alpha$-Fe$_2$O$_3$, and KNbO$_3$/ $\alpha$-Fe$_2$O$_3$ heterostructure. It could be seen from the FESEM results that pure KNbO$_3$ with orthorhombic geometry and smooth surface was prepared as shown in the inset of Figure 3a. Also, the particle size distribution histogram of KNbO$_3$ is shown in the inset of Figure 3a having particle size distribution centered between 50 and 250 nm. Figure 3b depicts highly agglomerated polygonal morphologies of $\alpha$-Fe$_2$O$_3$ nanoparticles. The morphology of as-synthesized $\alpha$-Fe$_2$O$_3$ is similar to that reported in the literature, which shows that aggregated bundles of small nanoparticles are formed due to the magnetic dipolar interaction of $\alpha$-Fe$_2$O$_3$ nanoparticles.$^{52}$ There is an increase in the texture of pure KNbO$_3$ by the presence of $\alpha$-Fe$_2$O$_3$ over the smooth surface of KNbO$_3$. From the TEM results, as evident from the inset of Figure 2c, it was observed that interface morphology has been developed, which can have a significant influence on the PEC and photocatalytic activity of the heterostructure.

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2.3. X-ray Photoelectron Spectroscopy (XPS) Analysis. XPS technique was used to estimate and analyze the surface composition, electronic structure, and oxidation state of different constituents of pristine KNbO$_3$, $\alpha$-Fe$_2$O$_3$, and their heterostructure. Figure 5a shows the full-range XPS spectrum of KNbO$_3$, $\alpha$-Fe$_2$O$_3$, and KNbO$_3$/ $\alpha$-Fe$_2$O$_3$ heterostructure. From the survey scan of XPS spectrum, peaks corresponding to K, Nb, and O were observed in pure KNbO$_3$ and peaks present in pure $\alpha$-Fe$_2$O$_3$ demonstrate the presence of Fe and O. Similarly, peaks corresponding to K, Nb, Fe, and O were
present in the XPS spectrum of the KNbO$_3$/α-Fe$_2$O$_3$ heterostructure. The high-resolution and deconvoluted XPS scans of K 2p, Nb 3d, Fe 2p, and O 1s in pure KNbO$_3$, α-Fe$_2$O$_3$, and their heterostructure are shown in Figure 5b–e. The peaks having binding energies of 291.2, 294.04, 206.47, 209.22, and 529.5 eV correspond to K$^+$ 2p$^{3/2}$, K$^+$ 2p$^{1/2}$, Nb$^{5+}$ 3d$^{5/2}$, Nb$^{5+}$ 3d$^{3/2}$, and O$^{2-}$ 1s of pure KNbO$_3$ (Figure 5a). Similarly, the peaks at 711.16, 724.47, and 718 eV correspond to Fe$^{3+}$ 2p$^{3/2}$, Fe$^{3+}$ 2p$^{1/2}$, and satellite peaks, while the peak at 530 eV corresponds to O$^{2-}$ 1s of pure α-Fe$_2$O$_3$. From Figure 5a, it was also observed that the as-prepared heterostructure shows a similar XPS pattern to pure KNbO$_3$ except the peaks corresponding to Fe. Figure 5b shows the high-resolution XPS spectra of Nb 3d present in pure KNbO$_3$ and KNbO$_3$/α-Fe$_2$O$_3$ heterostructure. The gap between the two Nb peaks at 206.47 and 209.22 eV is 3 eV, which may be associated with the +5 oxidation state of Nb. The XPS spectra of K$^{+}$ 2p present in pure KNbO$_3$ and KNbO$_3$/α-Fe$_2$O$_3$ heterostructure, which demonstrates that K is present in +1 oxidation state in both pure and heterostructured KNbO$_3$. The peaks at 291.2 and 294.04 eV correspond to K 2p$^{1/2}$ and K 2p$^{3/2}$, respectively. The peaks at 206.47 and 209.22 eV are associated with Fe 2p$^{3/2}$ and Fe 2p$^{1/2}$, respectively. The high-resolution spectra of Fe (Figure 5d) showed that the peaks centered at 710 and 724.6 eV are associated with Fe 2p$^{3/2}$ and Fe 2p$^{1/2}$, respectively. The peaks at 210 eV represent the characteristic feature for Fe$^{3+}$ in α-Fe$_2$O$_3$. The high-resolution spectra of Fe also show that a small satellite peak is present at 718 eV. Figure 5e shows high-resolution XPS spectra of O in which the peak at 530 eV corresponds to O 1s. The XPS results also demonstrate that after development of α-Fe$_2$O$_3$ over the surface of KNbO$_3$, the peaks corresponding to K, Nb, and O are shifted positively toward higher binding energies compared to pure KNbO$_3$.

Figure 3. FESEM micrographs of (a) KNbO$_3$, (b) α-Fe$_2$O$_3$, and (c) KNbO$_3$/α-Fe$_2$O$_3$. EDX spectra of (d) KNbO$_3$, (e) α-Fe$_2$O$_3$, and (f) KNbO$_3$/α-Fe$_2$O$_3$. The inset in (a) shows the particle size distribution histogram of KNbO$_3$. 

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whereas the peaks corresponding to Fe in the heterostructure are shifted to lower binding energies compared to Fe peaks present in pure $\alpha$-Fe$_2$O$_3$. Such shifting in peaks indicates a strong interaction between KNbO$_3$ and $\alpha$-Fe$_2$O$_3$ as well as electron transfer process taking place between KNbO$_3$ and $\alpha$-Fe$_2$O$_3$, which is highly beneficial for the catalytic processes.$^{54}$ From the XPS analysis, it was clearly demonstrated that successful deposition of $\alpha$-Fe$_2$O$_3$ was carried out on the surface of KNbO$_3$ in the KNbO$_3$/$\alpha$-Fe$_2$O$_3$ heterostructure.

2.4. Diffuse Reflectance Spectroscopy (DRS) Studies. UV-visible diffuse reflectance spectroscopy (DRS) was employed to investigate the optical properties of as-synthesized bare nanoparticles and heterostructure catalyst. The optical band gap was determined using the Kubelka–Munk equation as expressed in eq 1.

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

where $F(R)$, $a$, $s$, and $R$ are the Kubelka–Munk function, absorption coefficient, scattering factor, and reflectance of the material, respectively. Figure S2a shows the reflectance spectra using DRS analysis, and Figure S2b shows the plot of energy versus $(F(R_\infty)\hbar\nu)^{1/2}$, which allows us to calculate the band gap by linear extrapolation of $(F(R_\infty)\hbar\nu)^{1/2}$. KNbO$_3$ shows the absorption band in the UV region of the spectrum. The absorption band represents the electron excitation from the valance band (VB) of the semiconductor to the conduction band (CB). Similarly, $\alpha$-Fe$_2$O$_3$ shows the pronounced absorption band in the visible region of the solar spectrum. The development of $\alpha$-Fe$_2$O$_3$ over the KNbO$_3$ nanocube surface results in a considerable red shift of absorption band of KNbO$_3$, which also demonstrate the interfacial interaction between KNbO$_3$ and $\alpha$-Fe$_2$O$_3$ nanoparticles. The heterostructure shows the absorption peak at 460 nm. The change in the band gap was also visible from the color change from white KNbO$_3$ powder to reddish-brown, as shown in the inset of Figure S2a. The dark brown image in the inset of Figure S2a corresponds to the synthesized $\alpha$-Fe$_2$O$_3$ nanoparticles. Using the Kubelka–Munk equation, the calculated band gaps (Figure S2b) for KNbO$_3$, $\alpha$-Fe$_2$O$_3$ nanoparticles, and KNbO$_3$/($\alpha$-Fe$_2$O$_3$) heterostructure were 3.14, 2.1, and 2.75 eV, respectively. From the obtained results, it was observed that the KNbO$_3$/($\alpha$-Fe$_2$O$_3$) heterostructure shows substantial absorption in visible light; therefore, it was expected to show better PEC and photocatalytic activity compared to the individual counterparts.

2.5. Brunauer–Emmett–Teller (BET) Surface Area Studies. Surface area of a material plays an important role in its physical and chemical properties. High surface area of material provides large surface active adsorption and reaction sites for PEC and photocatalysis. Also, the charge-carrying ability of the materials is also enhanced due to the improved surface area, which results in the enhanced PEC and photocatalytic activity. Therefore, before evaluation of PEC and the photocatalytic activity of the synthesized bare KNbO$_3$, $\alpha$-Fe$_2$O$_3$, and heterostructured KNbO$_3$/($\alpha$-Fe$_2$O$_3$) systems, it becomes necessary to analyze the surface area of the as-synthesized nanoparticles. The Brunauer–Emmett–Teller (BET) theory was used to ascertain the surface area of the synthesized samples. Figure 6 shows the BET surface area plots of the as-prepared nanoparticles. Figure 6a shows the normalized BET isotherm of KNbO$_3$, $\alpha$-Fe$_2$O$_3$, and heterostructured KNbO$_3$/($\alpha$-Fe$_2$O$_3$). KNbO$_3$ and heterostructured KNbO$_3$/($\alpha$-Fe$_2$O$_3$) show type I isotherm according to IUPAC classification, therefore confirming the microporous characteristic of the samples, as shown in Figure 6a. The BET isotherm of $\alpha$-Fe$_2$O$_3$ demonstrates that it possesses type IV isotherm with H3 hysteresis from $P/P_0 = 0.5$ to 1.0, which is a characteristic feature of mesoporous materials. Surface areas calculated from the BET studies of KNbO$_3$, $\alpha$-Fe$_2$O$_3$, and KNbO$_3$/($\alpha$-Fe$_2$O$_3$) were 4, 100, and 20 m$^2$/g, respectively. It was also observed that the development of $\alpha$-Fe$_2$O$_3$ on the smooth surface of KNbO$_3$ nanoparticles results in the enhancement of the surface area of the heterostructure. The enhanced surface area arising from the development of a rough surface could give rise to more active sites, which would be conducive to improved PEC and photocatalytic activity of the KNbO$_3$/($\alpha$-Fe$_2$O$_3$) heterostructure. The estimation of pore size distribution was carried out using the Barrett–Joyner–Halenda (BJH) method using desorption points of the isotherm, as shown in Figure 6b. The KNbO$_3$ and KNbO$_3$/($\alpha$-Fe$_2$O$_3$) heterostructure show a mesoporous structure.

Figure 4. Elemental mapping of KNbO$_3$/$\alpha$-Fe$_2$O$_3$ heterostructure for (a) K, (b) Nb, (c) Fe, and (d) O.
(α-Fe₂O₃) pores possess bimodal size distribution centered at 18 and 36 nm for KNbO₃ and at 18 and 47 nm for KNbO₃/(α-Fe₂O₃), whereas pure α-Fe₂O₃ shows the BJH size distribution between 20 and 60 nm, as shown in Figure 6b.

2.6. Photoelectrocatalytic (PEC) Studies. PEC measurements of bare KNbO₃, α-Fe₂O₃, and KNbO₃/(α-Fe₂O₃) heterostructure were carried out by utilizing as-synthesized samples deposited on fluorine tin oxide (FTO) conducting glass substrates as working electrodes in PEC cell with a 0.1 M KOH electrolyte solution. The PEC current density–potential characteristics of bare KNbO₃, α-Fe₂O₃, and KNbO₃/(α-Fe₂O₃) heterostructure were determined by linear sweep voltammetry (LSV) measurements. LSV measurements were carried out under both dark (D) and light (L) conditions for pristine KNbO₃, α-Fe₂O₃, and KNbO₃/(α-Fe₂O₃) heterostructure, as shown in Figure 7a. It is seen that both bare KNbO₃ and α-Fe₂O₃ show negligible current densities. However, from the DRS measurements, KNbO₃ absorbs at lower wavelengths of solar spectrum; therefore, it shows

![Figure 5](image5.png)

Figure 5. (a) Full-range XPS spectra of KNbO₃, α-Fe₂O₃, and KNbO₃/(α-Fe₂O₃) heterostructure, and high-resolution XPS spectra of (b) Nb, (c) K, (d) Fe, and (e) O in pure KNbO₃, α-Fe₂O₃, and KNbO₃/(α-Fe₂O₃) heterostructure.

![Figure 6](image6.png)

Figure 6. (a) BET surface area isotherm and (b) BJH pore size distribution plots of KNbO₃, α-Fe₂O₃, and KNbO₃/(α-Fe₂O₃) heterostructure.

![Figure 7](image7.png)

Figure 7. (a) LSV plots in dark (D) and light (L) and (b) Tafel slopes of PEC reaction in the presence of KNbO₃, α-Fe₂O₃, and KNbO₃/(α-Fe₂O₃) catalysts.
activity in the UV region due to which a low current density was observed. Further, α-Fe₂O₃ is visible active material and widely used as photovoltaic material, but large recombination rate of charge carriers and short diffusion length of holes are the main drawbacks that hinder the practical application of α-Fe₂O₃. While heterostructured KNbO₃/(α-Fe₂O₃) shows little improved current density under dark conditions, the dark current density for heterostructured KNbO₃/(α-Fe₂O₃) was found to be 1.22 mA/cm² at 1.68 V along with a decreased onset potential with respect to the reversible hydrogen electrode (RHE). It is worth noting that under white-light illumination, an increase in the current density of KNbO₃/(α-Fe₂O₃) heterostructured catalyst was observed, which was close to 3.5 mA/cm² with respect to RHE at 1.68 V. Thus, under white-light illumination, the heterostructure shows a highly enhanced (almost 3-fold) current density with a low onset potential, compared to the pristine counterparts. A comparison of PEC activities of bare KNbO₃ and α-Fe₂O₃ with heterostructure is presented in Table 1. Therefore, the obtained results reveal that compared to bare KNbO₃ and α-Fe₂O₃, the developed heterostructure shows superior PEC activity with enhanced current densities and low onset potential versus RHE under both dark and light conditions. The results clearly demonstrate that the development of KNbO₃/(α-Fe₂O₃) heterostructure improves the ability to harvest light more efficiently, and the charge segregation property is also improved compared to the bare KNbO₃ and α-Fe₂O₃. As we know, Fe and Nb show variable oxidation states, thus the two small peaks at 0.7 and 1.2 V in LSV could be ascribed to change in their oxidation state. The Tafel slope for PEC of the as-synthesized photocatalysts is shown in Figure 7b. The value of the Tafel slope determines the kinetics of the PEC reactions. The smaller the Tafel slope, the faster the electrode reaction. Figure 7b shows that bare KNbO₃ and α-Fe₂O₃ exhibit higher values of Tafel slope of 415 and 272 mV/dec for the OER, respectively. On the other hand, the nanoheterostructure photoanode shows a lower value of Tafel slope (97 mV/dec), which represents faster reaction kinetics of PEC-OER. The increase in charge separation and low recombination rate is envisioned as the reason for enhanced PEC activity and decreased Tafel slope for heterostructured photocatalyst.

Electrochemical impedance spectroscopy (EIS) studies were carried out to understand and validate the photogenerated charge transfer process and impedance behavior of as-synthesized nanostructured materials. The EIS Nyquist electrochemical characteristics of KNbO₃, α-Fe₂O₃, and KNbO₃/(α-Fe₂O₃) heterostructure are demonstrated in Figure 8a. The radius of the arc in the EIS Nyquist plot is the evidence of electron transport resistance related to the electrochemical surface. The smaller the arc radius, the lower the charge transfer resistance and hence the better the charge transfer efficiency. EIS studies were carried out in the frequency range of 0.1 Hz to 200 kHz under white-light irradiation at a DC potential of 1.23 V (thermodynamic potential for the OER) and an AC potential amplitude of ±5 mV. From the results, it is observed that the resistance offered

Table 1. Comparison of Photoelectrocatalytic OER Activity of KNbO₃, α-Fe₂O₃, and KNbO₃/(α-Fe₂O₃) Heterostructure

| Material            | Current Density (mA/cm²) | Onset Potential (V) | Overpotential (V) | Photocurrent Density (mA/cm²) I₁ – I₀ | Tafel Slope mV/dec |
|---------------------|--------------------------|---------------------|-------------------|----------------------------------------|-------------------|
| K NbO₃              | 0.0057                   | 0.0057              | 0.37              | 0.27                                   | 0.00              | 415 |
| Fe₂O₃               | 0.325                    | 0.325               | 0.88              | 0.81                                   | 0.31              | 0.15 | 272 |
| KNbO₃/(α-Fe₂O₃)     | 1.25                     | 3.56                | 0.74              | 0.6                                    | 0.01              | 0.005 | 2.31 | 97 |

Figure 8. (a) EIS Nyquist plots and (b) Mott–Schottky (MS) plots for bare core material KNbO₃, α-Fe₂O₃, and KNbO₃/(α-Fe₂O₃) heterostructure in the presence of light.
to the flow of charge carriers by KNbO3 and α-Fe2O3 is high compared to KNbO3/(α-Fe2O3) heterostructure under white-light illumination, which proves that more charge carriers are found at the KNbO3/(α-Fe2O3) electrode interface compared to bare KNbO3 and α-Fe2O3. EIS plots reveal that fostering of interface charge transfer and inhibition of charge recombination occur efficiently in the heterostructure between KNbO3 and α-Fe2O3. Therefore, it is reasonable to prove that development of a heterostructure between KNbO3 and α-Fe2O3 enhances the photocurrent density, which takes place because of OER kinetics offered by α-Fe2O3 and easy transfer of photogenerated holes.

To further understand the effect of heterostructure development on the charge carrier density and to investigate the type of conductivity and flat-band potential (Vfb) Mott–Schottky (MS) analysis was carried out. MS analysis of all of the three electrodes was carried out in a three-electrode system at a frequency of 100 mHz, as shown in Figure 8b. The linear slope and intercept of the MS plot were used to determine the conductivity type and charge carrier concentration and to calculate the flat-band potential of the prepared catalysts.

\[
1/C^2 = \left(2/q_0\varepsilon_0\varepsilon_d\right)(V_{app} - V_{fb} - k_BT/q) \tag{2}
\]

where \(\varepsilon\) corresponds to the dielectric constant of the material, \(\varepsilon_0\) is the permittivity of vacuum (8.85 \times 10^{-14} \text{ F/cm}), \(N_d\) is the density of donor, \(V_{app}\) represents the applied voltage, \(V_{fb}\) corresponds to flat-band potential, and \(k_BT/q\) represents the temperature-dependent term of the MS equation, in which \(K\) represents the Boltzmann constant (1.38 \times 10^{-23} \text{ J/K}), \(T\) represents room temperature, and \(q\) corresponds to the electronic charge (1.60 \times 10^{-19} \text{ C}). The value of the intercept at 1/C² gives the flat-band potential of the semiconductor. The positive slope in the MS plot of KNbO3 and α-Fe2O3 semiconductor determined that electrons are the majority charge carriers showing n-type characteristics of the semiconductors. The smaller slope of the heterostructure determines the high density of charge carriers. From the MS plot, it was observed that the developed heterostructures have the smallest slope among the three (KNbO3, α-Fe2O3, and KNbO3/α-Fe2O3) PEC catalysts. The observed charge carrier concentration follows the order KNbO3/(α-Fe2O3) > α-Fe2O3 > KNbO3, as shown in Figure 8b. The increase in charge carrier concentration results in the increase in the conductivity and electron–hole separation in the space charge region, which has a significant impact on the PEC properties of the material. The band bending is measured by the flat-band potential. The flat-band potential of the synthesized material is in the order of KNbO3/(α-Fe2O3) > α-Fe2O3 > KNbO3. A comparative analysis of different parameters of pure α-KNbO3, α-Fe2O3, and KNbO3/(α-Fe2O3) heterostructure is given in Table 2, which clearly shows that the conductivity and charge density of pristine KNbO3 is enhanced by development of its heterostructure with α-Fe2O3.

### 2.7. Photocatalytic Studies

Dyes are widely used in textile industries, and their expulsion into water bodies creates a unique environmental problem. In addition to deforming the aesthetic shape of natural ecosystem, these dyes can transform into carcinogenic amines due to degradation under anaerobic conditions. To remove these demonized dyes from industrial waste waters, several techniques, including physical, chemical, and biological methods, have been developed. However, for removal of such notorious dyes from industrial effluents, semiconductor photocatalysis attracted tremendous attention. Thus, for investigating the application of KNbO3/(α-Fe2O3) heterostructure as an efficient semiconductor photocatalyst under natural climatic conditions like solar radiation, methylene blue (MB) was employed as a model pollutant. The photocatalytic activity of bare KNbO3 and α-Fe2O3 nanoparticles as well as KNbO3/α-Fe2O3 heterostructure semiconductor catalysts was elucidated. It was observed that no photolysis or degradation took place in the absence of catalyst and solar radiation. The change in the intensity of the characteristic absorption peak present at 663 nm was considered to determine the photocatalytic activity of as-synthesized semiconductor photocatalysts. The results of photodegradation in the presence of visible light and semiconductor catalysts and the efficiency of methylene blue dye removal after 90 min are shown in Figure 9. Figure 9a shows the percentage degradation of MB in the presence of different photocatalysts, and it was observed that after 90 min, bare KNbO3 nanocubes show negligible photocatalytic activity under visible light irradiation and α-Fe2O3 nanoparticles remove only 49% of the MB dye from the solution, whereas

### Table 2. Comparative Analysis of Charge Carrier Concentration and Flat-Band Potential Using MS Plots of KNbO3, α-Fe2O3, and KNbO3/(α-Fe2O3) Heterostructure

| Material          | Charge Carrier Concentration (cm⁻²) | Flat-Band Potential (V) versus (Hg/HgO) |
|-------------------|-------------------------------------|----------------------------------------|
| KNbO3             | 1.715 \times 10^{21}                | −0.339                                 |
| Fe₂O₃             | 2.540 \times 10^{21}                | −0.512                                 |
| KNbO₃/(α-Fe₂O₃)   | 6.443 \times 10^{21}                | −0.833                                 |

### Figure 9

(a) Percentage removal efficiency and (b) kinetics of photocatalytic reaction using bare KNbO₃, α-Fe₂O₃, and KNbO₃/(α-Fe₂O₃) heterostructure.
KNbO3/α-Fe2O3 photocatalysts show an 89% removal of dye from the solution, which is much higher than pure KNbO3 and α-Fe2O3 nanoparticles, respectively. Figure 9b displays the kinetic plot of pristine KNbO3, α-Fe2O3 nanoparticles, and the heterostructured photocatalyst. Kinetic analysis of the photocatalytic degradation was carried out using eq 3, which follows pseudo-first-order kinetics.

\[
\ln \frac{C_0}{C} = kt
\]

where \( C_0 \), \( C \), \( k \), and \( t \) represent the initial concentration of the MB dye, concentration of the dye solution after time \( t \), rate constant of the degradation reaction, and time intervals of the reaction, respectively. The rate constant of the reaction in the presence of different photocatalysts was obtained from the slope of the plot of \( \ln \frac{C_0}{C} \) versus time \( t \). The calculated rate constants and percentage degradation were employed to have a comparison among the photocatalytic activities of the bare synthesized nanoparticles, heterostructure, and previously reported catalysts (Table 3). The kinetic results obtained demonstrated that the synthesized heterostructure shows enhanced rate of the photocatalytic degradation process due to the low recombination of charge carriers effective transport mechanism and efficient separation of charges, as shown in Figure S3a,b.

Liquid chromatography–mass spectrometry (LC–MS) analysis was also carried to find the possible intermediates and final degradation fragments formed during the process of photocatalysis. The mass spectra of methylene blue dye after photocatalytic reaction using as-synthesized heterostructured photocatalysts are shown in Figure S4a. Using LC–MS spectra, the possible degradation fragments formed during photocatalysis are given in Figure S4b.

2.8. Proposed Mechanism for Enhanced Photocatalytic and Photocatalytic Performance. Generally, migration of photogenerated charge carriers occurs at the interface and photocatalytic reaction takes place between the adsorbed reactants over the surface of photocatalysts. The reason for enhanced photocatalytic and photocatalytic activity of the KNbO3/α-Fe2O3, composite nanoparticles might be the rapid interfacial transfer of charge carriers. The band edge position plays a crucial role in the charge transfer mechanism of semiconductor photocatalysts as well as in their photocatalytic activity. The relative positions of the valance band (VB) and conduction band (CB) of the two semiconductors (KNbO3 and α-Fe2O3) were investigated on the basis of band gap using the following equations

\[
E_{CB} = X - E_0 - 1/2E_g \quad \text{and} \quad E_{VB} = E_{CB} + E_g
\]

where \( E_{CB} \), \( E_g \), \( X \) and \( E_{VB} \) have their own significance and represent the conduction band, geometrical mean of absolute electronegativities of atoms present in a semiconductor, band gap, and valance band, respectively. \( E_g \) represents the scale factor, which relates the redox level of the reference electrode to the absolute vacuum scale. For normal hydrogen electrode (NHE), \( E_0 = 4.5 \) eV. From the band gap and band edge calculations, the positions of the VB and CB of the two semiconductors (KNbO3 and α-Fe2O3) were determined, and the corresponding values are tabulated in Table 4.

Based on the band gap calculation, α-Fe2O3 absorbs solar radiation in the visible range and electrons get excited from the valance band to the conduction band. Similarly, the electrons in the valance band are being excited to the conduction band of KNbO3 in the ultraviolet region of the solar spectrum. The band structure of both bare semiconductor nanoparticles before contact is depicted in Figure S3a,bb1. It is observed that the conduction band of α-Fe2O3 lies below the conduction band of KNbO3. Similarly, the valance band of KNbO3 lies above the valance band of α-Fe2O3. After contact with each other in the heterostructure, the transfer of charge carriers took place through the interface. After irradiation of the heterostructure with white light, the electrons get excited from the valance band of α-Fe2O3 to the conduction band and the holes created in the valance band are transferred to the valance band of KNbO3 via the interface formed between KNbO3 and α-Fe2O3; therefore preventing the recombination of charge carriers, which in turn results in the enhanced PEC and photocatalytic activity of the heterostructured photocatalyst.55–57

Another possible reason for the enhanced PEC and photocatalytic activity in the heterostructure photocatalyst is the configuration of band gap, which leads to a local electric field. This developed local electric field has the ability to separate the photoexcited charge carriers and thus reduces the recombination. As tabulated in Table 4, the conduction band and valance band of KNbO3 are located at -1.23 and 2.17 eV, respectively, whereas for α-Fe2O3, the conduction and valance bands have values equal to 0.19 and 2.49 eV with respect to RHE, respectively, as shown in Figure S3b1. The values of band edge positions obtained in this report are in good agreement with previous reports.51,59–61 According to the Watanabe models proposed for ferroelectric/semiconductor heterostructure, the ferroelectric polarization induced band bending, which superimposes the band bending induced due to the development of heterostructure. A model was developed based on the configuration of bands in the heterostructure, as

| Table 3. Comparison of Percentage Photocatalytic Activity/Rate Constant of KNbO3, α-Fe2O3, and KNbO3/(α-Fe2O3) Heterostructure as Photocatalysts with Reported Works |
|---------------------------------|----------------|-----------------|-----------------|
| sample                        | % degradation | rate constant, \( k \) (min\(^{-1}\)) | reference     |
|------------------              |----------------|-----------------|-----------------|
| KNbO3 nanorods       | 0.00108        | 55              |
| α-Fe2O3             | 0.162 \times 10^{-3} | 56              |
| g-C3N4/KNbO3        | 1.5 \times 10^{-3} | 57              |
| KNbO3              | 6.79 \times 10^{-4} | this report |
| α-Fe2O3             | 3.54 \times 10^{-3} | this report |
| KNbO3/(α-Fe2O3)     | 9.70 \times 10^{-3} | this report |

| Table 4. Band Gap and Position of Valance Band/Conduction Band of KNbO3, α-Fe2O3, and KNbO3/(α-Fe2O3) Heterostructure |
|-------------------------------------------------|-----------------|-----------------|-------------------|
| sample                        | band gap (eV) | conduction band (eV) | valance band (eV) |
|------------------              |----------------|-----------------|-----------------|
| KNbO3              | 3.4            | -1.23           | 2.17             |
| α-Fe2O3             | 2.3            | 0.19            | 2.49             |
| KNbO3/(α-Fe2O3)     | 2.5            | 0.93 (KNbO3), 0.19 (α-Fe2O3) | 2.41 (KNbO3), 2.49 (α-Fe2O3) |

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shown in Figure S3b. A similar model was developed previously to explain the photocatalytic activity of different heterostructured photocatalysts. As depicted in Figure S3bb2,bb3, due to internal ferroelectric polarization, the holes and electrons are moved toward the interface with negative and positive polarization, respectively. Based on the band bending and band configuration in heterostructure, a possible charge transfer process at the interface was proposed, as shown in Figure S3bb2,bb3. Therefore, it is speculated that these photogenerated electrons accumulate at the interface and directly take part in the photocatalytic reactions. Another important factor that influences the catalytic activity of the catalyst is the surface area of the material. As observed from the BET surface area analysis, the development of α-Fe₂O₃ over the surface of KNbO₃ enhances its surface area. Therefore, the improved surface area of the heterostructure could result in the enhanced PEC and photocatalytic activity of the heterostructure.

2.9. Dielectric Properties. Compressed pellets of the synthesized materials were used to carry out dielectric studies. The capacitance (C) obtained from LCR meter was used to calculate the dielectric constant of the material using the expression \( \varepsilon = C d / \varepsilon_0 A \), where \( \varepsilon \), \( C \), \( d \), and \( A \) represent dielectric constant of the synthesized material, capacitance, thickness, and cross-sectional area of pellet, respectively, and \( \varepsilon_0 \) (8.8554 × 10⁻¹² F/m) is the dielectric permittivity of free space.

The frequency-dependent dielectric permittivity and dielectric loss of pristine KNbO₃, α-Fe₂O₃, and their heterostructure at 50 °C are given in Figure 10a–c, respectively. Dielectric constant and dielectric loss of both the pure and heterostructured compounds shows strong dependence on frequency, which have high values of dielectric constant and dielectric loss at low frequencies, which decreases with increase in frequency and remains constant at higher frequencies. The reason behind such type of behavior is the existence of polarization mechanisms present in the materials. Figure 10 shows the change in dielectric loss with frequency at 50 °C. The dielectric loss behavior also shows a similar dispersion at low frequency to dielectric constant. The main reason for the dielectric loss is the motion of domain walls and electric dipole rotation under the influence of external electric field. However, at high frequencies, inhibition of motion of domain walls takes place and polarization effect comes into action. The rotation of polarization forces causes inconsequential response to the applied electric field, thus little heat is produced during the rotation process and therefore remains constant at higher frequencies. The main reason for the increase in dielectric constant of the heterostructure at low frequencies is dipolar and interfacial polarization. Similar results were also reported by Yu and Ang in 1 − x(BaTiO₃) − x(NiₓZn₁₋ₓFe₂O₄) ceramic composites, in which the increase in dielectric constant at lower frequencies was attributed to the electron relaxation mode coupling phenomenon. During this mechanism, charge carriers like protons, polarons, and so on show coupling with the dielectric modes, which are already present in the material.

Figure 11 illustrates the variation of dielectric constant and dielectric loss of pristine KNbO₃, α-Fe₂O₃, and their heterostructure with temperature at 500 kHz. One can observe that with increase in temperature, the dielectric constant of KNbO₃ shows a small increase in dielectric constant up to 250 °C, and above this temperature, an abrupt increase in dielectric constant was observed up to 450 °C, which corresponds to the Curie temperature \( T_c \), as observed in Figure 11a. Above Curie temperature, dielectric constant shows a decreasing trend. At 450 °C, KNbO₃ shows phase transition from cubic to tetragonal \( (T_{c2}) \). The dielectric constant of α-Fe₂O₃ shows gradual increase up to 300 °C, as shown in Figure 11b; however, an abrupt increase in dielectric constant was observed above 300 °C. The variation of dielectric properties with temperature at 500 kHz of the KNbO₃/α-Fe₂O₃ composite is illustrated in Figure 11c. The heterostructure shows a similar behavior in dielectric properties to KNbO₃ however, with the development of heterostructure, \( T_c \) shifts toward lower temperatures. In the case of heterostructure, \( T_c \) and \( T_{c2} \) correspond to 400 °C, which is lower than pristine KNbO₃. The dielectric loss of all of the three synthesized materials follows the same pattern with temperature at 500 kHz. With increase in temperature, dielectric loss increases for all of the samples. The increase in dielectric loss is due to the electronic and ionic charge domination at higher temperatures. Notably, the heterostructure shows a proportionate increase in permittivity at higher temperatures. Intrinsic and extrinsic effects are responsible for the change in the dielectric behavior.

![Figure 10. Variation of dielectric constant and dielectric loss with frequency at 50 °C for (a) KNbO₃, (b) α-Fe₂O₃, and (c) α-Fe₂O₃-modified KNbO₃ heterostructure.](https://dx.doi.org/10.1021/acsomega.0c02646)
of the materials. Herein, the intrinsic effect in the heterostructure arises from the volume effect, which causes domain wall shifting and thus results in a high dielectric constant of the heterostructure. Surface and grain boundary defects are probably caused by space charge polarization. Due to these defects under the influence of an external electric field, charge accumulation occurs at the interface, therefore resulting in a higher dielectric constant due to change of defect-trapped negative and positive space charges at the interface. The values of dielectric constant were found to be of 250.2, 65.2, and 251.5 at 500 kHz for KNbO3, α-Fe2O3, and KNbO3/α-Fe2O3, respectively.

2.10. AC Conductivity. AC conductivity of the as-prepared samples was measured using the pellets of the samples. The variation of conductivity with frequency ranging from 20 Hz to 1 MHz at different temperatures is shown in Figure S5. It can be seen that at lower temperatures, there is no reasonable change in conductivity with respect to frequency; however, KNbO3 and its heterostructure with α-Fe2O3 shows increase in conductivity with increase in frequency above 400 and 250 °C, respectively. In the case of the α-Fe2O3 sample, there occurs less change in conductivity with respect to frequency and temperature. The increase in conductivity with increase in temperature is due to the creation of huge oxygen vacancies in the crystal lattice. The conductivity behavior of the samples was further explained using power law fitting according to the expression $\sigma = A\omega^\eta$, where $\sigma$ represents the AC conductivity of the samples, $\omega$ represents the angular frequency, and $\eta$ shows the type of conductivity. Depending on the variation of $\eta$ with respect to temperature and frequency, different theoretical models have been used previously to explain the mechanism of AC conductivity behavior of the materials.

A conduction band hopping model is used to explain the behavior of the material when exponent $\eta$ decreases with rise in temperature. When $\eta$ shows an increasing trend with increase of temperature, a nonoverlapping small polaron tunneling conduction model is employed to explain the behavior of the material. If the value of exponent $\eta$ is dependent on both frequency and temperature and decreases up to a minimum value and then increases with increase in temperature, a large polaron overlapping tunneling model is used. Another model used to explain the conduction behavior is the quantum mechanical tunneling model, in which $\eta$ is equal to 0.8 and increases slightly with increase in temperature or remains constant with temperature.

By applying nonlinear fitting power law to the conductivity data, it was observed that all of the synthesized nanoparticles show $\eta > 1$, which confirms that ($M-W$) conduction is followed by KNbO3, α-Fe2O3, and their heterostructure. Also, the exponent $\eta$ shows an increase with increase in temperature; therefore, the nonoverlapping small polaron tunneling conduction model is appropriate to explain the conduction behavior of the synthesized KNbO3, α-Fe2O3, nanoparticles, and their heterostructure. From Figure S5a–c, it was also observed that conductivity increases with increase in frequency and temperature. With an increase in frequency, the space charge polarization is reduced, therefore resulting in the increase of conductivity, and at lower frequency, more charges are accumulated at the interface of the electrode and electrolyte, which therefore results in a decrease in the conductivity of the materials.

3. CONCLUSIONS

Nanocrystalline KNbO3, α-Fe2O3, and KNbO3/α-Fe2O3 heterostructure were developed by employing a wet environmentally friendly chemical route. XRD, TEM, FESEM, XPS,
and UV–vis DRS studies showed the formation of monophasic KNbO₃, α-Fe₂O₃, and KNbO₃/α-Fe₂O₃ heterostructure. The as-prepared heterostructure shows enhanced PEC activity under white-light irradiation compared to bare KNbO₃ and α-Fe₂O₃ nanoparticles. Similarly, under visible light, the heterostructure shows improved photocatalytic activity toward degradation of methylene blue. The improved photocatalytic response is attributed to the increase in the absorption range of solar spectrum of KNbO₃ and reduced charge recombination of the photogenerated charge carriers in the developed heterostructure. The dielectric properties were also investigated as a function of frequency and temperature, which show dielectric constant of as high as 251 in heterostructure. The present study offers a new strategy to develop highly efficient materials for energy generation, energy storage, and environment remediation purposes.

4. EXPERIMENTAL SECTION

4.1. Synthesis of Bare KNbO₃ Nanoparticles. The synthesis of KNbO₃ nanoparticles was carried out by a simple low-temperature hydrothermal route. All of the chemicals used during the reaction process were of analytical grade, commercially available, and used as received with no further purification. During a typical synthesis process, a 15 M solution of KOH was prepared and 0.025 moles of Nb₂O₅ was added to the solution. The whole reaction mixture was placed in a 50 mL Teflon-lined autoclave and was treated at 150 °C in a vacuum oven for 4 h. Then, the reaction mixture was cooled naturally followed by centrifugation. Figure S6 represents the flowchart and pictorial representation of the hydrothermal experimental setup used during the synthesis. During centrifugation, the obtained product was washed several times with distilled water and then with ethanol. The obtained white powder was kept in an oven and dried overnight at 80 °C. The dried powder was used for further characterization and application.

4.2. Synthesis of α-Fe₂O₃ and Heterostructured KNbO₃/α-Fe₂O₃. To develop the heterostructure, a solvent evaporation method was employed as reported in the literature. For the synthesis of the KNbO₃/α-Fe₂O₃ heterostructure, 1.5 g of as-prepared KNbO₃ was dispersed by ultrasonication in 30 mL of 0.001 M ethanolic solution of Fe(NO₃)₃·9H₂O. The optimization of a precursor for α-Fe₂O₃ was done using three different concentrations of 0.0005, 0.001, and 0.01 M. However, based on better photoelectrochemical (PEC) performance, only the sample with 0.001 M precursor concentration is discussed throughout the manuscript. At 0.0005 M concentration, PEC current density was insignificant, whereas at 0.01 M concentration, the prepared electrode was not stable and was peeling off from the substrate. The reaction mixture was ultrasonicated for 30 min followed by vigorous stirring for another 30 min on a magnetic stirrer at room temperature. After vigorous stirring, the reaction mixture was heated at 50 °C to evaporate whole ethanol. The final powder was collected and annealed at 300 °C for 10 min followed by washing with ethanol. After washing with ethanol, the powder was further annealed for 6 h at 300 °C. Similarly, monophasic pristine α-Fe₂O₃ nanoparticles were synthesized by the same method except addition of KNbO₃.

4.3. Characterization. Powder X-ray diffraction (PXRD) technique was employed to analyze the phase composition, crystal structure, purity, and crystallinity of powder samples. An X-ray diffractometer (Rikagu) having Cu Kα radiation (λ = 1.5406 Å) was used to carry out the X-ray diffraction studies of the as-prepared samples in a 2θ range of 10–80°. The scan rate used to record the diffraction pattern was 5°/min. Crystallite size of the samples was also calculated by employing the Scherrer formula D = 0.9λ/βcosθ, where β, λ, and θ represent the full width at half-maximum of the diffraction peak, wavelength of Cu Kα radiation, and diffraction angle, respectively.

Transmission electron microscopy (TEM) was employed to give insight into the size and shape of the as-prepared nanoparticles. An FEI Technai G² 20 HRTEM with 200 kV accelerating voltage was used to obtain the TEM micrographs of the samples. For TEM analysis, the dispersion of the as-prepared samples in ethanol was prepared with the aid of ultrasonication. The dispersed samples were mounted by drop-casting on a copper grid coated with carbon. To study the morphology and chemical composition of the as-synthesized samples Field-emission scanning electron microscopy (FESEM) was employed using FEI NOVA NanoSEM 450. X-ray photoelectron spectroscopy (XPS) was used to evaluate the binding energy and oxidation state of different elements present in as-synthesized samples. XPS measurement was performed using a Thermo Scientific XPS instrument with Al Kα radiation having hν = 1486.6 eV. All of the measurements were carried out in survey mode having XPS instrument equipped with surface charge neutralization operating flood gun. The step size and pass energy of the flood gun for XPS analysis were 0.1 and 30 eV, respectively. The corrections, shifting, and calibration of all peak positions were done with reference to C 1s peak positioned at 284.8 eV.

The surface area of each sample was analyzed by a Brunauer–Emmett–Teller BET surface area analyzer (Nova 2000e, Quantachrome Limited) at liquid nitrogen temperature (77 K). Before carrying out the analysis, all of the samples were degassed under vacuum conditions at 150 °C for 12 h to remove the surface-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. UV–visible diffuse reflectance spectroscopy (DRS) was used to measure the reflectance and band gap of the samples. DRS studies of all samples were carried out using BaSO₄ as a reflectance standard. The DRS study was carried out using a PerkinElmer Lambda 365 spectrophotometer in the wavelength range of 200–800 nm. The DRS plot was used to determine the band gap of the samples using the Tauc plot, which was obtained using the following Tauc equation

\[(αhν)^{1/n} = A(hν - E_g)\]

where α, h, ν, and E_g represent the absorption coefficient, Planck’s constant, frequency of vibrations, and band gap of the material, respectively. The type of transition is determined by the value of n. For direct and indirect transitions, n = 1/2 and 2, respectively.

4.4. Photoelectrochemical (PEC) and Photocatalytic (PC) Measurements. During all PEC measurements, as-synthesized α-Fe₂O₃, KNbO₃, and KNbO₃/α-Fe₂O₃ heterostructure catalyst-coated electrodes were employed as the working electrode, Pt wire as the counter electrode, and Hg/HgO as the reference electrode. All of the working electrodes were prepared by the drop-casting method. Typically, fluorine tin oxide (FTO)-coated glass substrates (resistance, ca. 15–20
3.5% polyvinyl alcohol PVA in a mixture of 90 μL of isopropanol and 10 μL of Nafion solution (5 wt%; Sigma-Aldrich) was ultrasonicated to prepare a uniform dispersion. This dispersion (10 μL) was deposited onto 1 × 1 cm² area of the cleaned FTO substrate. Electrical contacts were made through copper wires attached by silver conductive paint (RS components, U.K.). The entire substrate without the deposited film was sealed via Hysol epoxy resin (RS components, U.K.) to avoid any interference from the substrate. The electrolyte used to carry out the PEC reaction was 0.1 M KOH solution. To carry out the PEC analysis, white light from a 150 W xenon arc lamp of optosolar GmbH was used as the light source in CH1660 workstation. Photocurrent was measured by linear sweep voltammetry (LSV). Equation 4 was used to convert the reference potential into the potential corresponding to the reversible hydrogen electrode (RHE). LSV measurements were done under both dark and white-light illumination conditions. The Mott—Schottky study was carried out in the voltage range of −1.0–1.0 V versus RHE at a 100 MHz frequency. Electrochemical impedance studies (EIS) were carried out at an applied potential of 1.23 V and over a frequency ranging from 200 kHz to 100 MHz with respect to the RHE reference electrode.

\[ E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \times \text{pH} + 0.118 \]  

(4)

Photocatalytic measurements of all of the samples were elucidated by carrying out degradation of methylene blue (MB) dye using a xenon lamp with wavelength equal to 400 nm. During the photocatalytic reaction, 100 mL of a 1 × 10⁻⁵ M dye solution with 50 mg of dispersed as-prepared catalyst was first kept in the dark for 60 min to check the adsorption–desorption equilibrium. Similarly, dye solution without catalyst was exposed to light to evaluate the photolysis of the MB dye. Finally, the dye solution having as-prepared dispersed nanocatalysts was exposed to visible light, and after every 10 min, a sufficient quantity of dye solution was taken to evaluate the change in characteristic absorption maximum of the MB dye centered at 663 nm. The change in the intensity of the MB dye was examined using a PerkinElmer 365 UV–visible spectrophotometer. Equation 5 was used to measure the percentage removal of MB dye from aqueous solution.

\[ \text{percentage removal} (\%) = \frac{C_i - C_f}{C_i} \times 100 \]  

(5)

where \( C_i \) and \( C_f \) represent the concentration of the MB dye before exposure to light and concentration after time "t", respectively. The degradation products of the MB dye after photocatalytic reaction was determined by liquid chromatography–mass spectroscopy (LC–MS). LC–MS analysis of the dye solution having least intensity in UV–visible spectra was carried out by an API2000 Applied Biosystem LCMS/MS/MS instrument.

4.5. Dielectric Measurements. The dielectric properties of the as-prepared samples were analyzed by an HF-LCR meter (model 6505 P) procured from Wayne Kerr Electronics, U.K., at 50 °C and frequency ranging from 20 Hz to 1 MHz. To study the dielectric properties of the synthesized samples, a parallel-plate capacitor was developed using an 8 mm sample disk having 0.8 mm thickness coated with a silver conducting surface, which acts as an electrode. All of the synthesized samples were mixed with 5% polyvinyl alcohol PVA in a mortar and pestle, and pellets were formed by applying a pressure equal to 5 tons using Technosearch model M-5. All of the pellets were annealed at 800 °C before dielectric measurements were carried out.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02646.

Figure S1: XRD patterns of heterostructure with high-concentration precursor for Fe₂O₃; Figure S2: (a) diffuse reflectance spectra and (b) Tauc’s plot of as-prepared samples; Figure S3: (a) relative band positions of KNbO₃ and α-Fe₂O₃ and (b) band position and Fermi level before contact (b1), band configuration after contact with negative (b2) and positive (b3) polarization; Figure S4: (a) LC–MS plot of methylene blue dye after photocatalytic reaction and (b) possible intermediates and fragments of methylene blue dye formed after photocatalytic degradation process using heterostructure as photocatalyst. Figure S5: variation of conductivity with frequency at different temperatures for (a) KNbO₃ṣ, (b) α-Fe₂O₃, and (c) α-Fe₂O₃-modified KNbO₃ heterostructure; and Figure S6: flowchart and pictorial representation of the experimental setup used during the hydrothermal reaction (PDF)

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The authors declare no competing financial interest.

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