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Photocatalytic Performance of the Perovskite and Metal–Organic Framework Hybrid Material for the Reduction of N₂ to Ammonia

Masoumeh Chamack, Madjid Ifires, Sayed Ali Akbar Razavi, Ali Morsali,* Ahmed Addad, Afsanehsadat Larimi,* Sabine Szunerits, and Rabah Boukherroub*

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ABSTRACT: The orthorhombic phase of KNbO₃ perovskite has been applied for nitrogen (N₂) photoreduction to ammonia (NH₃). However, this material suffers from a low surface area and low ammonia production efficiency under UV light irradiation. To eliminate these barriers, we used a metal–organic framework (MOF), named as TMU-5 (with formula [Zn(OBA)(BPDH)₅]ₓ·1.5DMF, where H₂OBA = 4,4’-oxybis(benzoic acid) and BPDH = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene), for the synthesis of the KNbO₃@TMU-5 hybrid material. KNbO₃@TMU-5 achieved a NH₃ production rate of 39.9 μmol·L⁻¹·h⁻¹·g⁻¹ upon UV light irradiation, as compared to 20.5 μmol·L⁻¹·h⁻¹·g⁻¹ recorded for KNbO₃ under similar experimental conditions. Using different characterization techniques especially gas adsorption, cyclic voltammetry, X-ray photoelectron spectroscopy, photocurrent measurements, and Fourier transform infrared spectroscopy, it has been found that the higher photoactivity of KNbO₃@TMU-5 in ammonia production is due to its higher surface area, higher electron–hole separation efficiency, and higher density of negative charges on Nb sites. This work shows that hybridization of conventional semiconductors (SCs) with photoactive MOFs can improve the photoactivity of the SC@MOF hybrid material in different reactions, especially kinetically complex reactions like photoconversion of nitrogen to ammonia.

1. INTRODUCTION

Increasing world population and consequent demand for growing agricultural products have led to an increase in demand for ammonia (NH₃), as it represents a basic building block for fertilizer industry. NH₃ is generally produced through the Haber–Bosch process using pure H₂ and N₂ gases under high temperature (>500 °C) and pressure (>200 bar) conditions. Therefore, industrial-scale production of NH₃ requires consumption of large amounts of fossil fuels. In addition to utilizing a large amount of world’s energy, industrial production of NH₃ also emits a lot of greenhouse gases every year. In order to address these issues, the last decade has witnessed a huge increase of investigations on the development of low-cost and sustainable photocatalytic processes for NH₃ production. One of the prominent candidates for N₂ fixation reaction is perovskite oxide compounds. However, there are only a few reports on this class of materials for the photocatalytic reduction of N₂. In this regard, the only reported perovskite oxide compounds are KNbO₃, LaCoO₃, SrTiO₃, BiFeO₃, LiNbO₃, and layered Bi₂WO₆. Therefore, more investigations are required to understand the aptitude of perovskite oxide materials in the photocatalytic production of NH₃ from N₂.

As a perovskite, KNbO₃ can be regarded as a promising photocatalyst for N₂ photoreduction reaction, owing to its proper conduction and valence band positions. The conduction band (CB) and valence band (VB) of KNbO₃ are located at around −0.8 and +2.39 eV versus standard hydrogen electrode, respectively (https://doi.org/10.1016/j.apcata.2019.06.001). However, the band gap of KNbO₃ is in the 3.08–3.24 eV range. Therefore, the best activity for this
photocatalyst is achieved under UV irradiation. Furthermore, the specific surface area value, recorded for KNbO₃, by means of the N₂ adsorption–desorption technique, is in the range of 0.68 to 3.9 m² g⁻¹. Such a low surface area might be due to the weak interactions between nitrogen gas molecules and the surface atoms of solid KNbO₃, which restricts its photocatalytic applicability in N₂ fixation reaction. To address this hurdle, metal/nonmetal ion doping, noble metal loading, and coupling with SCs have been investigated as approaches for tuning the band gap and surface area of perovskite oxides including KNbO₃.

To improve the photocatalytic properties of KNbO₃, metal–organic frameworks (MOFs) can be appropriate candidates. MOFs, classified as highly porous materials with remarkable potential in adsorption of gas molecules including N₂, can play important roles in enhancing the capability of photocatalysts in N₂ reduction reactions. However, to date, no investigations highlighting the effect of MOF coupling on the photocatalytic properties of KNbO₃ have been reported. Furthermore, there are still no studies about the effect of coupling of MOFs with perovskite oxides on their photocatalytic operation in N₂ fixation reactions. In spite of increasing gas molecule adsorption, MOFs with the appropriate structure can also improve light absorption, charge separation, and reactant activation, which are expected to lead to superior photocatalytic performance. In this regard, TMU-5 ([Zn₂(OBA)₂(BPDH)]·(DMF)) has been described as one of the promising materials with desirable porosity, band gap (2.25 eV) in the visible region, and high specific surface area (591 m² g⁻¹ based on N₂ adsorption–desorption analysis). Additionally, it has been demonstrated that coupling of photactive TMU-5 to MoO₃ (band gap: 3.2 eV) led to improvement of photodegradation of dibenzothiophene over MoO₃.

In this work, a hybrid material consisting of MOF (TMU-5) and perovskite oxide (KNbO₃) is synthesized and applied as a photocatalyst for N₂ fixation reaction, and the effect of coupling of the MOF on the structural properties and photocatalytic performance of the KNbO₃ perovskite oxide material has been investigated.

2. EXPERIMENTAL SECTION

2.1. Materials and Instrumentation. 2.1.1. Materials and Methods. Sodium dodecyl sulfate (SDS, ≥97%), niobium(V) oxide (Nb₂O₅, 99.9%), potassium hydroxide (KOH, 99.99%), 4,4'-oxybisbenzic acid (oba, ≥99%), and zinc(II) acetate dihydrate (Zn(CH₃COO)₂·2H₂O, ≥99.0%) were commercially available from Sigma-Aldrich company. Acetonitrile (CH₃CN) and dimethylformamide (DMF, ≥99.9%) were obtained from Merck Company. All materials were used without further purification unless otherwise stated. The ligand 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (BPDH) was synthesized according to a previously reported method. The synthesized samples were characterized using various analytical tools. X-ray powder diffraction (XRD) measurements were performed using a Philips Xpert diffractometer with monochromated Cu Kα radiation. N₂ adsorption–desorption isotherms were measured on a Nova Station A instrument at 77 K. The specific surface area was calculated in accordance to the Brunauer–Emmett–Teller (BET) method. The sample for Raman analysis was prepared by dispersing the sample in ethanol by sonication. 50 μL of the solution was drop-cast on a clean silicon wafer and dried. Micro-Raman spectroscopy measurements were recorded on a HORIBA Jobin Yvon LabRam HR micro-Raman system combined with a 473 nm laser diode as the excitation source. Visible light was focused by a 100X objective. The scattered light was collected by the same objective in backscattering configuration, dispersed by an 1800 mm focal length monochromator, and detected by a charge-coupled device (CCD) camera. Scanning electron microscopy (SEM) images were recorded by a Hitachi S-4160 FESEM instrument. Transmission electron microscopy (TEM) images were acquired on a FEI TITAN Themis 300 operating at 300 kV, equipped with a Schottky FEG electron gun and a goniometer. Energy-dispersive X-ray spectroscopy (EDX) analysis was performed with a Philips CM30 microscope operating at 300 kV and equipped with a Brucker EDX detector. X-ray photoelectron spectroscopy (XPS) measurements were recorded with an ESCALAB 220 XL spectrometer from Vacuum Generators, featuring a monochromatic Al Kα X-ray source (1486.6 eV) and a spherical energy analyzer operated in the CAE (constant analyzer energy) mode (CAE = 100 eV for survey spectra and CAE = 40 eV for high-resolution spectra), using the electromagnetic lens mode. No flood gun source was needed due to the conducting character of the substrates. The angle between the incident X-rays and the analyzer was 88°. The detection angle of the photoelectrons was 30°.

2.2. Synthesis Procedures. 2.2.1. Synthesis of KNbO₃. A reported hydrothermal method was used to prepare the KNbO₃ material. In short, 36 g of KOH was dissolved in 80 mL of distilled water. 1 g of Nb₂O₅ was added to the alkaline solution and stirred at 80 °C for 30 min. Subsequently, 2.88 g of SDS was added to the mixture and stirred at 80 °C for an additional 30 min. The obtained white color suspension was poured into a 150 mL Teflon-lined stainless-steel autoclave and heated at 180°C for 48 h. After that, a white solid was formed, separated by centrifugation, and washed with distilled water and ethanol. The obtained KNbO₃ powder was dried at 80 °C overnight.

2.2.2. Synthesis of TMU-5. 0.26 g of 4,4'-oxybisbenzic acid (H₂OBA) was added to 25 mL of DMF and stirred at 80 °C for 30 min. Subsequently, 0.22 g of Zn(CH₃COO)₂·2H₂O and 0.24 g of BPDH were separately dissolved in 15 mL of DMF. The two solutions were added to the abovementioned mixture and kept under stirring at 80 °C for 72 h. The obtained yellow powder was washed several times with DMF and dried at 80 °C for 24 h. Finally, the prepared MOF was activated by washing it several times with acetonitrile and dried at 120 °C for 72 h. Scheme S1 depicts the structure of TMU-5.

2.2.3. Synthesis of KNbO₃@TMU-5. The co-precipitation method was used for the synthesis of the KNbO₃@TMU-5 composite. 1 g of KNbO₃ powder was added to 50 mL of DMF and sonicated for 5 min. Afterward, 0.5 g of H₂OBA was added to the suspension and the resulting mixture was stirred (500 rpm) at 80 °C for 30 min. Subsequently, 0.44 g of Zn(CH₃COO)₂·2H₂O and 1 g of BPDH, separately dissolved in 20 mL of DMF, were added to the mixture and the reaction pot was completely sealed. The mixture was stirred at 80 °C for 72 h. The obtained pale yellow powder was washed several times with DMF, and dried at 80 °C for 24 h. Finally, this sample was activated by the same method as applied for TMU-5. The scheme of the synthesis method is depicted in Scheme S2.

2.3. Preparation of the Modified Electrode. 1 mg of KNbO₃@TMU-5 powder was dispersed in 100 μL of ethanol using an ultrasonic bath for 10 min. 3 μL of the dispersed mixture was dripped onto the glassy carbon (2 mm diameter) electrode surface and allowed to dry under the IR lamp. Then, 1 μL of nafion solution was added on the surface and allowed to dry by the same method. The counter electrode and reference electrode were platinum disk (2 mm diameter) and calomel electrodes, respectively. 10 mL of Na₂SO₄ (0.2 M) was used as the electrolyte solution.

2.4. N₂ Photoreduction Test. 2.4.1. General photocatalytic Process. The nitrogen (N₂) photoreduction experiments were performed in a quartz tube. 10 mg of the photocatalyst was added to 10 mL of water and 0.789 mL of ethanol as a hole scavenger. The mixture was dispersed using an ultrasonicator for 10 min, and the resulting suspension was saturated with N₂. During photoreduction under UV irradiation (power of lamp (P) = 0.2 W), N₂ was bubbled into the solution. At certain time intervals, 2 mL of the reaction mixture was collected and immediately centrifuged to separate the liquid sample from the solid catalyst. The concentration of NH₃ was determined using a chemical analyzer.
measured using the indophenol method via UV–vis absorption
spectra recorded using a Safas Bio-UVmc spectrophotometer in
quartz cuvettes with an optical path of 10 mm. The wavelength range
was 200–800 nm. UV–vis curves of indophenol assays with $\text{NH}_4^+$
ions and the calibration curve used for estimation of $\text{NH}_3$ by $\text{NH}_4^+$
ion concentration are illustrated in Figure S1.

2.4.2. Photocatalytic Stability of $\text{KNbO}_3@\text{TMU-5}$. The cycling
stability of the $\text{KNbO}_3@\text{TMU-5}$ photocatalyst for $\text{N}_2$ reduction was
assessed under UV irradiation. After each cycle, the catalyst was
collected by centrifugation, dried in the oven at 60 °C overnight, and
reused in the subsequent experiment.

3. RESULTS AND DISCUSSION

techniques including powder X-ray diffraction (PXRD),
nitrogen adsorption at 77 K, XPS, transmission electron
spectroscopy (TEM), Fourier transform infrared spectroscopy
(FT-IR), Raman spectroscopy, and SEM were applied to
classify the structure of $\text{KNbO}_3@\text{TMU-5}$.
Combination of PXRD patterns for $\text{KNbO}_3@\text{TMU-5}$ and
its components clearly shows that the structure of both
components is identical in their pristine and composite
materials (Figure 1). In detail, the PXRD pattern of the

Figure 1. Combination of PXRD patterns of $\text{KNbO}_3@\text{TMU-5}$ and
its components.

areas, calculated from nitrogen adsorption–desorption iso-
therms, are about 2 and 172 m$^2$·g$^{-1}$ for $\text{KNbO}_3$ and $\text{KNbO}_3@\text{TMU-5}$
samples, respectively. Therefore, compared to pristine
$\text{KNbO}_3$, the adsorption capacity of the $\text{KNbO}_3@\text{TMU-5}$
hybrid material for adsorption of $\text{N}_2$ gas molecules was
significantly increased. This is a structurally critical improve-
ment for observation enhancement in photocatalytic efficiency
of $\text{KNbO}_3@\text{TMU-5}$ compared to pristine $\text{KNbO}_3$, and it can
be concluded that $\text{TMU-5}$ can act like a gas cylinder for $\text{N}_2$
storage. $\text{TMU-5}$ can adsorb and store $\text{N}_2$ gas molecules and
inject them to the SC surface where the photocatalytic reaction
occurs.

XPS was performed to investigate the elemental composition
and electronic state of the $\text{KNO}_3$ surface atoms before and
after coupling with $\text{TMU-5}$. The full-scan XPS spectra of
$\text{KNbO}_3$, $\text{TMU-5}$, and $\text{KNbO}_3@\text{TMU-5}$ are displayed in Figure
3. The XPS spectrum of $\text{KNbO}_3$ confirms the presence of

Figure 3. Full-scan XPS spectra of $\text{KNbO}_3$, $\text{TMU-5}$, and $\text{KNbO}_3@\text{TMU-5}$.

potassium, niobium, and oxygen elements. The XPS spectrum
of $\text{TMU-5}$ shows the presence of zinc, carbon, oxygen, and
nitrogen corresponding to metal ions and linker organic
ligands of the MOF. For the $\text{KNbO}_3@\text{TMU-5}$ spectrum, all
peaks related to component elements of both $\text{KNbO}_3$ (K, Nb,
and O) and $\text{TMU-5}$ (Zn, C, N, and O) are observed.

Besides XPS analysis for $\text{KNbO}_3@\text{TMU-5}$ and its
components, SEM and TEM analyses have been applied to
elucidate the morphological structure and structural composi-

tion of KNbO$_3$@TMU-5 and its components. SEM images clearly show that KNbO$_3$ particles have rod morphology (Figure 4a), while TMU-5 particles are of plate morphology (Figure 4b) in the applied synthesis conditions. These components retain their morphology in the structure of the composite (Figure 4c). TEM elemental mapping images (Figures 5 and S2) display that potassium and niobium elements of KNbO$_3$ are distributed only on the region of tiny rod particles, while the zinc element, originating from TMU-5, is distributed on big blocks' region with plate morphology. The superposition of K and Zn reveals better contrast about the posture of TMU-5 blocks (orange color) and KNbO$_3$ rod particles (green color). 

FT-IR spectra of KNbO$_3$, TMU-5, and KNbO$_3$@TMU-5 are depicted in Figure 6. For KNbO$_3$, the sharp broad band below 800 cm$^{-1}$ belongs to Nb–O stretching vibration mode. The FT-IR spectrum of the TMU-5 sample shows vibration modes at 1240 and 1160 cm$^{-1}$ related to C–O–C vibrations. The weak band at 1299 cm$^{-1}$ and the band ranging from 1320 to 281...
1420 cm$^{-1}$ can be attributed to the asymmetric stretching mode of C–O bonds. The peak centered at 1498 cm$^{-1}$ can be assigned to C≡N pyridine stretching vibration. The bands centered at 1553 and 1573 cm$^{-1}$ may be due to C≡C stretching vibration modes. The bands at 1613 and 1595 cm$^{-1}$ are related to C≡N–N≡C (azine) and C≡N (azomethine) stretching vibration modes, respectively. For KNbO$_3$@TMU-5, all vibration bands of both KNbO$_3$ and TMU-5 are detected with very slight shifts (Figure 6a). Furthermore, a new vibration band appeared at 1640 cm$^{-1}$, which may be attributed to new C≡N vibration mode resulting from interaction between azomethine groups of TMU-5 with the KNbO$_3$ structure (Figure 6b). Deconvolution of IR bands ranging from 1450 to 1700 cm$^{-1}$ also displays these details with more clarity (Figure S3).

Compared to the XRD technique, Raman spectroscopy is more sensitive to lattice disorder. Therefore, lattice perturbations in the local structure of NbO$_6$ octahedra of KNbO$_3$ coupled to TMU-5 were investigated by Raman spectroscopy. Figure 7 depicts the corresponding Raman spectra of KNbO$_3$ and KNbO$_3$@TMU-5 samples. For KNbO$_3$, all the characteristic peaks corresponding to the NbO$_6$ octahedra appear at the same pattern of the orthorhombic phase reported in literature. For KNbO$_3$@TMU-5, several new bands are detected above 900 cm$^{-1}$, which can be related to TMU-5 structure vibration modes. Furthermore, vibration modes of the potassium niobate phase detected in the KNbO$_3$@TMU-5 Raman spectrum revealed slight shifts, as compared to the pristine KNbO$_3$ spectrum. The Raman signal at 191.1 cm$^{-1}$, attributed to the internal bending vibration mode of the NbO$_6$ octahedron, experienced a slight shift to 192.7 cm$^{-1}$ for the KNbO$_3$@TMU-5 sample. Also, the shift of O–Nb–O symmetric stretching vibration mode of NbO$_6$ from 591.5 to 589 cm$^{-1}$ implies its softening due to lowering the bond force constant. In contrast, no shift was observed for the band at 536.9 cm$^{-1}$ ascribed to the stretching vibration mode of NbO$_6$. Moreover, the Raman spectrum of KNbO$_3$@TMU-5 is more broaden than that of KNbO$_3$, suggesting that the lattice disorder of KNbO$_3$ is increased upon coupling with TMU-5. Subsequently, evaluation of Raman spectra suggests the presence of interaction between the TMU-5 and KNbO$_3$ structure in the KNbO$_3$@TMU-5 sample, which affects NbO$_6$ octahedron vibration modes.

3.2. Photocatalytic Reduction of N$_2$. The photocatalytic reduction of N$_2$ to NH$_3$ comprises several steps. First, like for any other photocatalytic reaction, the photocatalyst absorbs light of appropriate wavelength to generate electron–hole pairs (eq 1). Afterward, a fraction of the photogenerated electrons and holes recombine together, while some holes (h$^+$) oxidize water into H$^+$ and O$_2$ (eq 2) and electrons reduce N$_2$ to NH$_3$ (eq 3). Therefore, NH$_3$ is synthesized from water and N$_2$ using light as the energy source (eq 4).

$$\text{Photocatalyst} + h\nu \rightarrow h^+ + e^-$$
$$3\text{H}_2\text{O} + 6h^+ \rightarrow \frac{3}{2}\text{O}_2 + 6\text{H}^+$$
$$\text{N}_2 + 6\text{H}^+ + 6e^- \rightarrow 2\text{NH}_3$$

$$\text{h}^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$$

$$\text{e}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2$$

$$\text{N}_2 + \text{e}^- + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{OH}^-$$

$$\text{N}_2 + \text{H}_2 + \text{e}^- + \text{H}_2\text{O} \rightarrow 2\text{NH}_3$$
Even though any photocatalyst having a band gap energy larger than 1.2 eV with proper CB and VB positions can thermodynamically promote the reaction of eq 3, this half-reaction is kinetically more challenging because of the required six electrons. Furthermore, the adsorption of N₂ gas molecules over the photocatalyst surface and cleavage of the highly stable N≡N bond are also regarded as remarkable challenges. To address these issues, coupling of the photocatalyst with MOFs having high capacity for N₂ gas molecule adsorption, which can modify the electron transfer mechanism in the photocatalyst, could represent a promising strategy. Apart from enhancement in adsorption capacity, many investigations demonstrated that coupling of a SC with MOFs can modify the electronic structure of the SC, leading to enhanced performance for various photocatalytic reactions including water splitting, CO₂ reduction, and organic pollutant degradation. Nevertheless, for N₂ photo-reduction reaction, there are still a few reports about the role of MOFs in improving the SCs’ photocatalytic activity. Hence, for improvement of the operation of KNbO₃ through enhancement in adoption capacity and photocatalytic activity, it has been coupled to TMU-5 to synthesize the KNbO₃@TMU-5 hybrid material.

The photocatalytic activity of the as-synthesized KNbO₃ and KNbO₃@TMU-5 samples for the reduction of N₂ to NH₃ in the presence of water is illustrated in Figure 8. Without light irradiation (blank test), no NH₃ was formed by adding KNbO₃ or KNbO₃@TMU-5 catalysts to N₂-saturated aqueous solution (Figure S4). Under UV light irradiation, the NH₃ generation rate reaches 20.5 μmol·L⁻¹·h⁻¹·g⁻¹ in the presence of the KNbO₃ photocatalyst, while by applying KNbO₃@TMU-5, the NH₃ generation rate increased to 39.9 μmol·L⁻¹·h⁻¹·g⁻¹. To examine the reusability of the KNbO₃@TMU-5 photocatalyst, the N₂ reduction system was recycled five times (Figure 9). During the first three cycles of the reaction, NH₃ production efficiency was not changed. However, after the fifth run, the NH₃ production rate is 37.9 μmol·L⁻¹·h⁻¹·g⁻¹, confirming the high stability of the developed photocatalyst. Table S1 compares the rate of nitrogen reduction for KNbO₃@TMU-5 with some of other MOF-based photocatalysts applied in this area.

To investigate the effect of coupling of TMU-5 on the charge transfer and recombination behavior of KNbO₃, photoluminescence measurements were employed at an excitation wavelength of 325 nm. As shown in Figure S5, the KNbO₃ sample exhibited a strong blue luminescence emission in the 350–455 nm range, which may be attributed to the emission connected with charge transfer from oxygen atoms to the central niobium atom in the NbO₅ octahedra. The luminescence emission was observed for the KNbO₃@TMU-5 sample with relatively lower intensity compared to pristine KNbO₃, suggesting that TMU-5 hybridization with KNbO₃ reduces the recombination rate of photogenerated electron–hole pairs, which may be due to the internal charge transfer between the KNbO₃ and TMU-5 component. A complementary study on electron–hole separation by photocurrent measurement demonstrates that the rate of charge recombination is significantly diminished upon hybridization of KNbO₃ with TMU-5 (Figure S6). These results clearly show that the photoactivity of the KNbO₃@TMU-5 composite is highly improved compared to pristine KNbO₃.

To investigate the effect of TMU-5 on the optical properties of KNbO₃, UV–vis analysis was performed (Figure S7). The optical band gap (E(bg)) of KNbO₃ and KNbO₃@TMU-5 samples was determined using the following equation (eq 5):

\[
(\alpha h \nu)^n = A (h \nu - E(bg))
\]

where α, h, ν, A, and E(bg) represent the absorption coefficient, Planck constant, light frequency, proportionality constant, and band gap, respectively. The value of n depends on the nature of the electronic transition and assumed to be 1/2 for KNbO₃, which has an indirect band gap. By plotting \((\alpha h \nu)^{1/2}\) versus \((h \nu - E(bg))\), one can estimate the band gap from the intercept of the tangent to the x-axis. Accordingly, an E(bg) value of 3.2 eV (387.45 nm) was calculated for KNbO₃, which is in good agreement with previous reports. After hybridization of KNbO₃ with TMU-5, the E(bg) value decreased slightly to 3.1 eV (399.95 nm).

In the next step, the Mott–Schottky diagram has been drawn to calculate the flat band potentials \(E(F_b)\) of TMU-5 and KNbO₃ components to calculate their CB and VB energy levels (Figure S8). The calculated E(F_b) values for TMU-5 and KNbO₃ were determined as -4.12 eV and -4.02 eV, respectively.
3.3. Mechanism of Nitrogen Reduction. XPS analysis is an ideal technique for characterization of a material before and after coupling with another component in a composite. In this regard, XPS analysis is applied to understand the electronic state of the KNbO$_3$ atoms before and after coupling with TMU-5. The core-level XPS spectra for Zn, C, K, and O, especially Nb and N atoms, were collected.

The core-level XPS spectra of the KNbO$_3$@TMU-5 samples are illustrated in Figure S12c. As shown in Figure 12, for the TMU-5 sample, the N 1s XPS peak can be fitted to the C=N group (397.9 eV). The C=N peak is shifted to 397.1 eV in the KNbO$_3$@TMU-5 hybrid material. The weak peaks centered at 399.2 eV for both TMU-5 and KNbO$_3$@TMU-5 samples can be ascribed to pyridine nitrogen of the BPDH ligand of TMU-5. These results show that upon formation of the KNbO$_3$@MU-5 composite, it is possible to say that the electronic properties of N atoms of coordinating pyridine groups did not change, while an alteration in electronic properties of N atoms of azine function (−C=N−N=N=−C−) is observed.

The O 1s XPS spectra of KNbO$_3$ and KNbO$_3$@TMU-5 are displayed in Figure S12. For KNbO$_3$, the spectrum can be deconvoluted into three components at 529.4, 530.2, and 531.7 eV due to oxygen of perovskite lattice, oxygen deficient bonding, and weakly bound O−H−O surface species, respectively (Figure S12a). The O 1s XPS spectrum of TMU-5 is fitted with two components at 529.8 and 531.4 eV, which can be assigned to carboxylate and ether groups of the OBA$_2$ ligand of TMU-5, respectively. Overall, based on the observed shifts in XPS analysis of TMU-5 and KNbO$_3$@TMU-5 samples, a new peak centered at 531.7 eV due to oxygen of perovskite lattice, oxygen deficient bonding, and weakly bound O−H−O surface species, respectively (Figure S12a). The O 1s XPS spectrum of TMU-5 is fitted with two components at 529.8 and 531.4 eV, which can be assigned to carboxylate and ether groups of the OBA$_2$ ligand of TMU-5, respectively (Figure S12a). The spectrum of the KNbO$_3$@TMU-5 sample can be curve-fitted with four components at 527.2, 529.2, 531.1, and 531.9 eV (Figure S12b). Compared to the O 1s XPS spectra of KNbO$_3$ and TMU-5 samples, a new peak centered at 527.2 eV (O* atom in Figure S12c) is observed for KNbO$_3$@TMU-5.

Overall, based on the observed shifts in XPS analysis of TMU-5 and KNbO$_3$ samples before and after hybridization in the KNbO$_3$@TMU-5 composite, it is possible to say that the significant changes in oxidation numbers are observed in the case of Nb and N atoms. These changes are discussed in detail as follows. For this purpose, the required information from FT-IR and XPS analyses is gathered here and discussed together.

As is mentioned, Nb(3d) core-level XPS analysis shows that the BE for Nb atoms shifts is equal to 2 eV after synthesis of KNbO$_3$@TMU-5, while the value of spin−orbit coupling (2.8 eV) does not alter. Because such a shift in the BE of Nb atoms occurs after hybridization of KNbO$_3$ with TMU-5, it is rational to hypothesize that there is some kind of interactions between Nb atoms and the other components of the composite.
these two materials in the final composite. Based on N(1s) core-level XPS, it has been observed that there is a positive shift equal to 0.8 eV in the BE of the azine $-\text{C}==\text{N}$− site, while the binding energy of pyridine $-\text{C}==\text{N}$− is completely unchanged. Based on core-level XPS analysis of N and Nb atoms, it is possible to state that Nb sites of KNbO3 and azine functions ($-\text{C}==\text{N}==\text{N}==\text{C}==$) of TMU-5 are potential interactive sites after the formation of the KNbO3@TMU-5 photocatalyst.

The mentioned assumption, possible interaction between Nb$^{5+}$ centers and azine sites in the composite, can be witnessed using FT-IR spectroscopy specifically in the 1450−1700 cm$^{-1}$ region. Based on the literature, this region belongs to observation of $-\text{C}==\text{N}$− bonds. As can be seen in Figure 6b, there is a new peak centered at 1640 cm$^{-1}$ after the formation of the KNbO3@TMU-5 composite, while other peaks (related to pyridine C$==$N, aromatic C$==$C, azomethine $-\text{C}==\text{N}==\text{N}==\text{C}==$ and azine $-\text{C}==\text{N}==\text{N}==\text{C}==$− bonds) are almost identical. According to the literature, FT-IR analysis of aromatic azine function shows a singlet peak at the 1600−1635 cm$^{-1}$ region, similar to what we observed here, 1613 cm$^{-1}$ for TMU-5 and 1615 cm$^{-1}$ for the composite. In the cases that there is a specific interaction between azine $-\text{C}==\text{N}==\text{N}==\text{C}==$− and metal, a new peak can be observed in the 1630−1652 cm$^{-1}$ region. Therefore, according to shifts in XPS peaks of Nb atoms along with the formation of a new band at 1640 cm$^{-1}$ in FT-IR, we reason that there is specific kind of interaction between azine functions of TMU-5 and Nb$^{5+}$ sites of KNbO3 in the composite. Based on principles of XPS measurement, the BE of a specific atom will decrease if the density of negative charges is increased on that specific atom. Therefore, due to the shift in the BE of Nb$^{5+}$ sites to the lower values, it can be speculated that the density of negative charges is increased on Nb$^{5+}$ sites. The final values of BE of Nb sites in the composite is relatively similar to Nb$^{4+}$ species published in the literature. This higher negative charge density on Nb sites is another reason for improvement of N2 reduction efficiency in case of KNbO3@TMU-5 compared to pristine KNbO3. Cyclic voltammetry has been conducted to compare the reducing strength of KNbO3 before and after hybridization (Figure S13). The results show that the reduction reaction on KNbO3@TMU-5 shifts to more positive reduction potentials as equal as 60 mV (from $-770$ to $-710$ mV), which indicates that the KNbO3@TMU-5 composite has higher affinity to reduction reactions compared to KNbO3.

Therefore, KNbO3@TMU-5 is a more efficient photocatalyst for reductive photoconversion of nitrogen molecules to ammonia. Overall, there are three major reasons that assist KNbO3@TMU-5 to show higher efficiency compared to pristine KNbO3, which are (I) increased porosity and surface area, (II) higher efficiency in photoinduced electron−hole separation, and (III) higher density of negative charges on Nb sites in the composite. Based on these reasons, the mechanism of nitrogen photoreduction by KNbO3@TMU-5 can be described in detail as follows. In the first step, N2 molecules access the surface of KNbO3 through diffusion in the three-dimensional interconnected pores of TMU-5. In this condition, it can be stated that the pores of TMU-5 act as nanocylinders to accumulate the surface of KNbO3 with nitrogen molecules. Due to the higher surface area of KNbO3@TMU-5 than pristine KNbO3, it is anticipated that the concentration of N2 molecules on the surface of KNbO3 is more than that on pristine KNbO3. In the next step, upon light irradiation, the organic framework of TMU-5 is used as antenna and absorbs light photons, which improves the electron−hole separation efficiency of KNbO3@TMU-5, becoming higher than that of pristine KNbO3. The higher charge carrier separation, the higher will be the photocatalytic efficiency. In the final step, it is anticipated that the rate of N2 reduction will increase due to the changes in BEs and higher affinity of Nb sites to the reduction reaction in the composite after hybridization of KNbO3 with TMU-5 in the composite. Therefore, the rate of ammonia production will increase for KNbO3 in the composite form when compared to the pristine form.

**CONCLUSIONS**

KNbO3 is one of the perovskite-based SCs that was used for photocatalytic nitrogen reduction. However, it has some disadvantages like no porosity and band gap in the UV region. To overcome these challenges, we have synthesized a hybrid material based on KNbO3 and one of our TMU MOFs named as TMU-5 because it is porous to nitrogen molecules and its optical band gap lies in the visible region. Experimental analyses suggest that there are three reasons for improved photocatalytic activity of KNbO3 in the KNbO3@TMU-5 composite when compared to the pristine material. The higher surface area and porosity of the composite compared to pristine KNbO3, higher affinity of Nb sites to reduction reaction in the composite due to the changes in BEs after hybridization, and higher efficiency in electron−hole separation in the composite are the major reasons for improved photocatalytic activity of the KNbO3@TMU-5 composite when compared to pristine KNbO3.
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c03622.

AUTHOR INFORMATION

Corresponding Authors

Ali Morsali — Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, Tehran 14117-13116, Islamic Republic of Iran; orcid.org/0000-0002-1828-7287; Phone: (+98) 21-82884416; Email: morsali_a@modares.ac.ir
Afsanehsadat Larimi — Department of Chemical and Process Engineering, Niroo Research Institute, Tehran 14686-13113, Iran; orcid.org/0000-0001-5566-171X; Email: Alarimi@nri.ac.ir
Rabah Boukherroub — University of Lille, CNRS, Centrale Lille, Université Polytechnique Hauts-de-France, UMR 8520, IEMN, Lille F-S9000, France; Email: rabah.boukherroub@univ-lille.fr

Authors

Masoumeh Chamack — Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, Tehran 14117-13116, Islamic Republic of Iran
Madjid Ilifes — University of Lille, CNRS, Centrale Lille, Université Polytechnique Hauts-de-France, UMR 8520, IEMN, Lille F-S9000, France; Research Center of Semiconductor Technology for Energy, Mervelles 16038, Algeria
Sayed Ali Akbar Razavi — Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, Tehran 14117-13116, Islamic Republic of Iran
Ahmed Addad — University of Lille, CNRS, UMR 8207 — UMET, Lille F-S9000, France
Sabine Szunerits — University of Lille, CNRS, Centrale Lille, Université Polytechnique Hauts-de-France, UMR 8520, IEMN, Lille F-S9000, France; orcid.org/0000-0002-1567-4943

Complete contact information is available at:
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Notes

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