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Enhancement of the conversion of mechanical energy into chemical energy by using piezoelectric  $KNbO_{3-x}$  with oxygen vacancies as a novel piezocatalyst

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# Abstract

Synthesis of new piezoelectric materials to harness the vibrational and thermal energies may contribute to solve the current increasing energy demands. KNbO<sub>3</sub> is a known piezo- electric material that exhibits poor piezocatalytic activity owing to the scarcity of charge carriers in it. In order to enhance the charge carrier density in KNbO<sub>3</sub>, extra electrons were added to KNbO<sub>3</sub> lattice. Extrinsic piezoelectric KNbO<sub>3-x</sub> having extra electrons in the lattice was synthesized via the reaction between Nb<sub>2</sub>O<sub>5</sub> and KBH<sub>4</sub> at elevated temperatures. The KNbO<sub>3</sub> nanostructures formed at 450 and 550 °C contained feebly piezoelectric KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> and piezoelectric KNbO<sub>3-x</sub> respectively. The enhanced piezocatalytic activity of KNbO<sub>3-x</sub> is demonstrated by the production of hydrogen from water by harnessing the mechanical vibrations and the observed hydrogen production rates are 0.05 and 3.19 ml h<sup>-1</sup> g<sup>1</sup> for KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> and KNbO<sub>3-x</sub> respectively. The enhanced piezocatalytic activity of the enhancement of the charge carrier density resulting from the creation of oxygen vacancies in KNbO<sub>3</sub> that lead to enhancing the electronic conductivity as well as charge carrier separation. It is demonstrated that the piezocatalytic activity can be boosted by augmenting the charge carrier density in piezoelectric materials by synthesizing them under highly reducing reaction conditions.

## 1. Introduction

Harvesting of waste energy is one of the most promising technologies to address contemporary energy shortage in which the waste energy such as heat, wind, vibrational and mechanical energies is converted into electrical or chemical energies [1–4]. Recently, there is a keen interest in the use of piezoelectric materials for the harvesting of waste energy as a promising alternative energy harvesting method. The piezoelectric materials having a non-centrosymmetric structure possess a piezoelectric potential due to spontaneous electrical polarization. The piezoelectric effect has been successfully employed to convert waste energy into electrical energy. The piezoelectric effects have been applied in piezoelectric nanogenerators optoelectronics, sensors, piezoelectric transducers, transparent conductor and nanogenerators successfully. Though catalysis/photocatalysis is an emerging technology, the piezoelectric effect has not been exploited fully in catalysis/photocatalysis to produce chemical energy such as hydrogen due to lack of suitable piezoelectric materials [5–8].

The first use of piezoelectric materials in the production of chemical energy from the waste energy was reported by Hong *et al* in 2010 in which the authors demonstrated the production of H<sub>2</sub> and O<sub>2</sub> by direct water splitting with ZnO nanofibers and BaTiO<sub>3</sub> micro dendrites under vibrations [9]. The charge generation and separation processes in piezoelectric materials under mechanical stress have been discussed in detail by

Strass *et al* [10] and Liang *et al* [2] When piezoelectric materials are subjected to mechanical stress, positive and negative charges that are generated due to the asymmetries in their crystal structures create an electrical potential within the piezoelectrical material. The newly created internal electrical potential within the piezoelectrical material drives the positive and negative charges towards opposite directions of the crystal surfaces resulting in spatially separated charges. These separated positive and negative charges could participate in reduction and oxidation reactions respectively, i.e. free charges generated that are having potential higher than the 1.23 eV react with water and produces H<sub>2</sub> and O<sub>2</sub> by water splitting [11]. I.e. Tan *et al* [12] reported the semiconductor-piezoelectric hetero-junction in photo-electrochemical (PEC) water splitting device while Wu *et al* [13] reported the water splitting with nano-flowers of MoS<sub>2</sub>. Despite the hydrogen production by the piezoeatalytic process via scavenging waste energy is simple as well as cost-effective, little or no attention has been paid to this important research owing to the lack of suitable piezoelectric materials. Finding appropriate piezoelectric materials for piezoeatalytic applications is an uphill task as the generation and the separation of charges in piezoelectric materials are highly controlled by the crystal structure, the electronic states of the material, the number of electric dipoles present within these materials and also depends on the reaction medium.

Among the available piezoelectric materials, lead zirconatetitanate (PZT) is still the most commonly used material for piezoelectric harvesting of waste energy. Recently, Pb-free piezoelectric sodium potassium niobate  $(Na_{0.5}K_{0.5}NbO_3, piezoelectric constant (d33) \sim 240 pC/N)$ , potassium niobate (KNbO<sub>3</sub>, d33 ~ 120 pC/N), lithium niobate (LiNbO<sub>3</sub>, d33 ~ 31 pC/N) and sodium niobate (NaNbO<sub>3</sub>, d33 ~ 160 pC/N) gained much interest in piezoelectric materials for harvesting waste energy, especially via piezotronic devices [8, 14, 15]. Perovskite potassium niobate (KNbO<sub>3</sub>) that exhibits the unique physicochemical properties in acoustic-optic, electro-optic and nonlinear optic is a good lead-free piezoelectric material for piezoelectric applications. Despite their excellent piezoelectric properties, the piezocatalytic activity of unpolarized KNbO<sub>3</sub> nanostructures was found to be poor [16, 17]. In piezocatalysis, the presence of free charges in these materials is essential to induce the piezocatalytic activity and it has been demonstrated that the intrinsic charge carrier density but not the piezoelectric charges in piezoelectric materials is the key factor in the piezocatalysis process [18]. Hence, piezocatalytic activity can be enhanced by regulating the intrinsic charge carrier density by defect doping. Once free charge carriers are created in these materials, they can be effectively separated under the influence of piezoelectric potential generated under stress and could involve in redox reactions. In this investigation, a modified solid-state reaction was employed to synthesize the piezoelectric KNbO<sub>3-x</sub>. The free charge carrier density in KNbO<sub>3-x</sub> was increased by creating a large number of oxygen vacancies by maintaining highly reducing reaction conditions during KNbO3-x synthesis and an excellent piezocatalytic activity of KNbO3 was demonstrated by harnessing waste energy to produce H<sub>2</sub>. The important fact in this investigation is that the piezocatalytic activity of KNbO3-x can be initiated via introducing soft-stress generated via mechanical stirring of the reaction medium rather than using high-intensity ultrasonic vibrations.

# 2. Experimental section

#### 2.1. Preparation of the catalyst

The piezoelectric KNbO<sub>3-x</sub> (KN) was synthesized via the solid-state reaction method. The potassium borohydride (KBH<sub>4</sub>) (AR, 98%, Macklin Biochemical Co., Ltd, China) and Nb<sub>2</sub>O<sub>5</sub> (AR, 99.9%, Macklin Biochemical Co., Ltd, China) were weighed at a molar ratio of  $[Nb_2O_5]$ : $[KBH_4] = 1.0$ :2.5, and mixed using an agate mortar and pestle for 30 min followed by sintering at 350, 450, 550 °C for 4 h in Ar(95%):H<sub>2</sub>(5%) with a heating rate of 5 °C min<sup>-1</sup>. After sintering, samples were cooled naturally to room temperature and washed thoroughly with ample distilled water to remove unreacted reactants if any and dried at 100 °C in air. The pristine KNbO<sub>3</sub> was either a commercial grade (Sigma-Aldrich) or synthesized via the modified solid-state reaction method [19]. The starting compounds, potassium oxalate  $[K_2C_2O_4.3H_2O]$  (99%), Nb<sub>2</sub>O<sub>5</sub> (99.9%) and urea  $[CO(NH_2)_2]$  (99%) were weighed at a molar ratio of [K]:[Nb]: $[CO(NH_2)_2] = 1$ :1:1 and mixed well using an agate mortar and calcined in air at 600 °C for 4 h.

#### 2.2. Characterization of the catalyst

The crystal structures of the various phases of the powder catalysts were studied using a PANalyticalX'pert diffractometer (X'Pert PRO MPD, PW3040/60) with Cu K $\alpha$  ( $\lambda = 0.154\ 060\ nm$ ) radiation with a scanning step of 10 (deg/min). The sample morphologies were characterized by a Hitachi S-4800 field emission scanning electron microscope (SEM). Transmission electron microscopy (TEM) and high-resolution TEM images were obtained using JEM-2100 microscopes operating at 200 kV. Raman spectroscopy measurements were conducted using a HORIBA JY, LabRAM HR800 Raman Spectroscopy System with a 514 nm laser. Fourier transform infrared (FTIR) spectra were obtained on a BRUKER, TENSOR27 FTIR with KBr and mixed powders and twenty scans in a range of 4000–400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> were carried out. Brunauere

EmmetteTeller (BET) specific surface area was measured using a Quantachrome, QUADRASORB SI-MP-10 apparatus. XPS analyses were conducted through a Thermo ESCALAB 250XI multifunctional imaging electron spectrometer (Thermo Fisher Scientific Inc.) equipped with an Al K $\alpha$  radiation source. Monochromatic 150 W Al K $\alpha$  radiation was utilized with a pass energy of 30 eV and the binding energies were referenced to the C1s signal at 284.8 eV. All binding energies (BE) were corrected for the charging of the sample by calibration in the C1s signal. For the investigation of the change of chemical composition with the depth, a spot size of 2 mm × 2 mm was sputtered with Ar plasma (4 keV energy ions and 0.36 mA cm<sup>-2</sup> current beam). Avantage XPS software was used to analyze the experimentally obtained spectra. The fitting of spectra was performed after subtraction of a Shirley background and in all fits, the peak separation and the peak area ratios between the Nd3d<sub>5/2</sub> and the Nd3d<sub>3/2</sub> components were constrained to 2.75 eV and 3:2 respectively. The piezoelectricity of KNbO<sub>3-x</sub> was directly probed using piezoresponse force microscopy (Asylum Research MFP-3D-SA). A conductive Pt-coated Si probe, i.e. HA-FM01/Pt, was used in contact mode to apply an alternating voltage to the sample and induce piezoelectric surface oscillations and the imaging contact force set-points were carefully controlled. For domain imaging, AC signals (amplitude VAC = 1 V) were used to excite the surface oscillations.

#### 2.3. Piezocatalytic activity of the catalyst

The piezocatalytic activity was performed using a reactor designed in our laboratory as shown in figure S1 (available online at stacks.iop.org/NANOX/1/030036/mmedia) in SI. For piezocatalytic activity, 0.40 g the ground catalyst was suspended in 400 ml of distilled water in a 600 ml Pyrex reactor and sonicated for 30 min to enhance the suspension of the catalyst. A round shape magnetic stirrer (2 cm length, 0.25 cm diameter) was placed at the bottom of the reactor and stirred at a specific rpm. To detect the gaseous products *in situ*, the reactor was connected to the Gas Chromatography (GC, Techcomp (China) GC7890II) with a steel packed (TDX-01) column and a thermal conductivity detector (TCD) where Argon or Helium was used as the carrier gas. The concentration of the OH radicals in the reaction solution was detected using both H<sub>2</sub>O<sub>2</sub> test strips (Quantofix<sup>R</sup> peroxide test sticks) or by colorimetrically based on the oxidation of iodide in the presence of ammonium molybdate and photometry of the resulting blue starch-iodine complex [20].

#### 2.4. Electrochemical methods

Mott-Schottky analyses were performed with three-component system in which platinum as the counter electrode, Ag/AgCl (0.01 M), saturated KCl as the reference electrode and KNbO<sub>3</sub> catalyst coated FTO (fluorine doped tin oxide) as the working electrode at 10 mV amplitude ac signal and 1KHz frequency by using Zahner Zannium universal electrochemical work station equipped with a frequency response analyzer (Thalas) under ambient light. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a Zahner Zannium electrochemical interface analysis instrument after sandwiching the catalyst coated electrode with Pt counter electrode, an electrolyte solution (0.1 M KCl) was added in between the two electrodes. Finally, the impedance measurement was performed with Zahner Zannium universal electrochemical work station equipped with a frequency response analyzer (Thalas) at 10 mV amplitude ac signal and in the frequency range from 0.1 Hz to 1 MHz under dark conditions without any vibrations at open-circuit voltage.

# 3. Results and discussion

#### 3.1. Materials synthesis and characterization

Highly reduced and black colored piezoelectric KNbO<sub>3-x</sub> powder was synthesized by the solid-state reaction in which Nb<sub>2</sub>O<sub>5</sub> and KBH<sub>4</sub> powders were mixed and heated at different temperatures under H<sub>2</sub>:Ar stream. The XRD diffraction patterns of the initial Nb<sub>2</sub>O<sub>5</sub> when sintered with KBH<sub>4</sub> under H<sub>2</sub>:Ar stream at 350, 450 and 550 °C are shown in figure 1. The diffraction peaks of the pristine Nb<sub>2</sub>O<sub>5</sub> can be indexed to orthorhombic phase (JCPDS Card No. 30-0873) with the typical diffraction peaks located at  $2\theta$  of 22.7°(001), 28.5° (100), 36.7° (101), 46.2° (002), 50.6° (110), 55.1° (102) [21]. In the case of the sample heated to 350 °C, the formation of blue-colored Nb<sub>2</sub>O<sub>5</sub> was noticed while the diffraction patterns are similar to that of the initial orthorhombic Nb<sub>2</sub>O<sub>5</sub> indicating that the Nb<sub>2</sub>O<sub>5</sub> is partially reduced with the generation of oxygen vacancies in the Nb<sub>2</sub>O<sub>5</sub> lattice [22].

On the other hand, in the sample heated to 450 °C, the blue colored Nb<sub>2</sub>O<sub>5</sub> turned into black color and additional new diffraction peaks at 2 $\theta$  of 22.2°, 31.2°, 45.2°, 50.2°, 56.2° ( $\star$  marked peaks) also appeared together with the diffraction peaks assigned to the Nb<sub>2</sub>O<sub>5</sub>. These new diffraction peaks can be indexed to orthorhombic KNbO<sub>3</sub> crystalline structure (space group Amm2, JCPDS card 32-0822) with lattice constants of a = 0.5695, b = 0.5721 and c = 0.3973, which could be produced from the reaction between KBH<sub>4</sub> and Nb<sub>2</sub>O<sub>5</sub> under H<sub>2</sub>:Ar stream as KBH<sub>4</sub> decomposes to KH, B and H<sub>2</sub> at 450 °C. Hence the sample heated to 450 °C contained both Nb<sub>2</sub>O<sub>5</sub> and KNbO<sub>3</sub>. As shown in figure 1, when the reaction temperature increases to 550 °C, diffraction peaks assigned to Nb<sub>2</sub>O<sub>5</sub> completely disappeared with the concomitant increase in the intensities of



diffraction peaks of orthorhombic KNbO<sub>3</sub> at 22.2°,  $31.2^\circ$ ,  $45.0^\circ$ ,  $45.5^\circ$ ,  $50.2^\circ$  and  $56.2^\circ$  owing to complete conversion of Nb<sub>2</sub>O<sub>5</sub> into KNbO<sub>3</sub> crystalline form. The standard XRD patterns from the orthorhombic perovskite KNbO<sub>3</sub> phase (figure 1(e), JCPDS file No. 32-0822) [23] are well matched with the newly formed black orthorhombic KNbO<sub>3</sub> suggesting that the KNbO<sub>3</sub> is formed due to the solid-state reaction between Nb<sub>2</sub>O<sub>5</sub> and KBH<sub>4</sub>. The BET specific surface area of the products formed at 450 °C (KNbO<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub> mixture) and 550 °C (i.e. KNbO<sub>3</sub>) are 22.3 and 19.2 m<sup>2</sup> g<sup>-1</sup> respectively.

The appearance of blue and black color respectively in the Nb<sub>2</sub>O<sub>5</sub> and KNbO<sub>3</sub> synthesized at 550 °C could be due to the presence of Nb<sup>4+</sup> cation and oxygen vacancies (V<sub>O</sub>) and hence the black colored KNbO<sub>3</sub> formed at 550 °C and Nb<sub>2</sub>O<sub>5</sub> are labeled as KNbO<sub>3-x</sub> and NbO<sub>5-x</sub> as they possess a large number of vacant oxygen sites. The presence of Nb<sup>4+</sup> cation and V<sub>O</sub> sites in NbO<sub>5-x</sub> and KNbO<sub>3-x</sub> was confirmed by the XPS analysis and discussed under XPS analysis, accurate quantification of V<sub>O</sub> sites cannot be carried out in powdered samples. Also, in the XRD pattern of KNbO<sub>3-x</sub> (pattern d in figure 1), the weak peaks (marked by arrows) cannot be assigned to KNbO<sub>3-x</sub>, however, the secondary phase was found to be matched with the polyniobate K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> (JCPDS 076- 0977) [24]. As the polyniobate K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> is unstable and hence the presence of a small amount of K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> as a secondary phase might not affect the piezoelectric properties of KNbO<sub>3-x</sub> [25].

Based on the crystalline structures formed during the reaction between  $Nb_2O_5$  and  $KBH_4$  and considering the chemical properties of both  $Nb_2O_5$  and  $KBH_4$ , the following reaction path is proposed for the solid-state synthesis of highly reduced  $KNbO_{3-x}$ 

$$Nb_2O_5 \xrightarrow{H_2:Ar (350-400 \ ^{\circ}C)} Nb_2O_{5-x} + H_2O$$
(1)

$$KBH_4 \xrightarrow{H_2:Ar (450-500 \ ^{\circ}C)} KH + B + \frac{3}{2}H_2$$
(2)

$$Nb_2O_{5-x} + KH \xrightarrow{H_2:Ar (450 \ ^\circ C)} KNbO_{3-x} + Nb_2O_{5-x} + xH_2O$$

$$(3)$$

$$Nb_2O_{5-x} + KH \xrightarrow{H_2:Ar (550 \ ^{\circ}C)} KNbO_{3-x} + xH_2O$$
(4)

$$Nb_2O_5 + KBH_4 \xrightarrow{H_2:Ar(550\ ^{\circ}C)} KNbO_{3-x} + xH_2O$$
(5)

As given in reactions (1) to (5), when the reaction temperature was around 350 °C, the O atom leaves with the H atom in form of H<sub>2</sub>O by transferring electrons from the H atoms to the O atoms in the lattice of Nb<sub>2</sub>O<sub>5</sub> creating oxygen vacancies (V<sub>O</sub>) with concomitant formation of blue-colored Nb<sub>2</sub>O<sub>5-x</sub> [26, 27]. The electron is trapped in a Nb<sup>5+</sup> lattice site to form Nb<sup>4+</sup> ions. When the reaction temperature was increased to 450 °C, more oxygen vacancies are generated due to drastic interaction between H<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> leading to the formation of more reduced Nb states (i.e. Nb<sup>4+</sup> and Nb<sup>3+</sup>) in the Nb<sub>2</sub>O<sub>5</sub> lattice due to the transfer of excess electrons from oxygen vacancies to Nb<sup>5+</sup> ions turning the blue-Nb<sub>2</sub>O<sub>5-x</sub> into black-color Nb<sub>2</sub>O<sub>5-x</sub> [28]. Meantime, as KBH<sub>4</sub> melts at 450 °C–550 °C and decomposes to KH [29] and the KH formed could react with Nb<sub>2</sub>O<sub>5-x</sub> to form KNbO<sub>3-x</sub> at temperature ~450 °C and the Nb<sub>2</sub>O<sub>5-x</sub> is fully converted to KNbO<sub>3-x</sub> at ~550 °C. As described earlier, the origin of the black color in KNbO<sub>3-x</sub> synthesized at ~550 °C could be mainly due to the presence of

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highly reduced states of Nb such as  $Nb^{3+/+4}$  and oxygen vacancies in  $KNbO_{3-x}$  [30]. The presence and qualitative analysis of  $Nb^{3+/+4}$  and Vo sites in  $KNbO_{3-x}$  were performed by XPS technique.

As mentioned earlier, in this investigation, the free charge carrier density of KNbO<sub>3</sub> was increased by generating a large number of oxygen vacancies in KNbO<sub>3</sub> by maintaining reducing reaction conditions (H<sub>2</sub>:Ar and KBH<sub>4</sub>) during the synthesis of KNbO<sub>3</sub>. The presence of oxygen vacancies and reduced Nb states in KNbO<sub>3</sub> structures were confirmed by XPS analysis. The chemical states of pristine Nb<sub>2</sub>O<sub>5</sub> and the reaction products (Nb<sub>2</sub>O<sub>5-x</sub> and KNbO<sub>3-x</sub>) were examined by XPS after sputtering (10 Å) to remove all surface dust or contamination are shown in figure 2.

The spectrum of pristine Nb<sub>2</sub>O<sub>5</sub> (figure 2(a)) showed Nb  $3d_{5/2}$  and Nb  $3d_{3/2}$  doublet peaks at binding energies of 207.21 and 210.11 eV respectively, which refer to two peaks for Nb<sup>5+</sup> [31, 32]. However, in the spectrum of the blue Nb<sub>2</sub>O<sub>5-x</sub> (figure 2(b)), the Nb  $3d_{5/2}$  peaks were shifted by ~0.15 eV to the lower binding



Figure 3. O 1 s x-ray photoelectron spectra of: (a) pristine Nb<sub>2</sub>O<sub>5</sub>, (b) Nb<sub>2</sub>O<sub>5-x</sub> reduced at 350  $^{\circ}$ C, (c) bulk of KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> and (d) bulk of KNbO<sub>3-x</sub>.

energy side compared with the pristine Nb<sub>2</sub>O<sub>5</sub>. These shifts indicate the formation of Nb<sup>4+</sup> or oxygen vacancies in the nanocrystals [33]. The shift is more pronounced in the etched blue Nb<sub>2</sub>O<sub>5-x</sub> sample (figure 2(c)) and could be attributed to differences in the surface bonding state of Nb<sub>2</sub>O<sub>5</sub>. The peaks can be resolved to two peaks for Nb<sup>5+</sup> (207.00, 209.6 eV) and Nb<sup>4+</sup> (205.16, 208.02 eV) [34]. However, the observation of the absence of Nb<sup>4+</sup> peak in the case of etched pristine Nb<sub>2</sub>O<sub>5</sub> indicates that the hydrogen treatment caused an increase in oxygen vacancies leading to the formation of Nb<sup>4+</sup> state just below the surface of Nb<sub>2</sub>O<sub>5-x</sub> sample in the 350 °C heated Nb<sub>2</sub>O<sub>5</sub> sample during the reduction reaction.

The XPS spectra of the products of reactions (4) (KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub>) and 5 (KNbO<sub>3-x</sub>) are demonstrated in figures 2(d) and (e) respectively. As shown in figure 2(d), the XPS spectrum of KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> clearly shows three different spin-orbital pairs that could be assigned to Nb<sup>5+</sup> (207.01 and 209.9 eV), Nb<sup>4+</sup> (204.00 and 207.00 eV) and Nb<sup>3+</sup> (202.48 and 205.65 eV) [31, 32, 35, 36]. As discussed earlier, in the blue Nb<sub>2</sub>O<sub>5-x</sub> sample, only Nb<sup>5+</sup> and Nb<sup>4+</sup> states are present while the Nb<sup>3+</sup> state is not observed. However, in the case of  $KNbO_{3-x}/Nb_2O_{5-x}$  sample (unetched sample), the presence of  $Nb^{3+}$  state even on the surface layer suggesting that oxygen vacancies and highly reduced Nb states are present in the outer layer of  $KNbO_{3-x}/Nb_2O_{5-x}$ samples. Similar XPS results were observed with the KNbO<sub>3-x</sub> in which Nb<sup>5+</sup>, Nb<sup>4+</sup> and Nb<sup>3+</sup> states were observed on the outer layer of KNbO<sub>3-x</sub> samples. The relative higher peak intensity ratios of Nb<sup>4+</sup>/Nb<sup>5+</sup> and  $Nb^{3+}/Nb^{5+}$  in XPS analysis of KNbO<sub>3-x</sub> than that of KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> samples indicated the presence of a greater number of reduced Nb states and oxygen vacancies in  $KNbO_{3-x}$  than the  $KNbO_{3-x}/Nb_2O_{5-x}$ . As shown in figure 2(f), the depth profile XPS analysis of KNbO3-x after etching of the KNbO3-x with Ar plasma indicated the presence of more Nb<sup>3+</sup> sites below the surface of KNbO<sub>3-x</sub> particles. Detailed relative quantification of the Nd 3d spectrum of  $KNbO_{3-x}$  surface layer and the etched  $KNbO_{3-x}$ , suggested the presence of Vo and reduced Nb states even on the surface of  $KNbO_{3-x}$ , and higher concentrations of  $V_O$  and the  $Nb^{4+}/Nb^{3+}$  states just below the surface of KNbO<sub>3-x</sub>. Notably, the reduction of Nb<sub>2</sub>O<sub>5</sub> in the conditions of the XPS experiment can be



excluded considering the fact that neither Nb<sup>3+</sup> nor Nb<sup>4+</sup> species were detected in the as-prepared sample after Ar pre-sputtering.

The curve-fitting of the O 1 s line is very complex and as shown in figure 3(a), in the O1s XPS spectra of the topmost layer of pristine Nb2O5, the O1s peak can be deconvoluted into two components with binding energies at 531.21 and 532.29 eV, which corresponds to lattice O<sup>2-</sup> ions and hydroxylated OH in Nb<sub>2</sub>O<sub>5</sub>[31, 32, 35]. The Ols peak at BE of 533.10 eV in the topmost film layer of Nb<sub>2</sub>O<sub>5</sub> is due to H<sub>2</sub>O (chemisorbed water). In the Ols spectrum of the surface layer of the reduced Nb<sub>2</sub>O<sub>5-x</sub> (figure 3(b)), the lattice  $O^{2-}$  ions in Nb<sub>2</sub>O<sub>5-x</sub> has been shifted to the lower binding energy of 529.88 eV compared with that of pristine Nb<sub>2</sub>O<sub>5</sub>. The peak shift could be attributed to differences in the surface bonding state of Nb<sub>2</sub>O<sub>5-x</sub> than the Nb<sub>2</sub>O<sub>5</sub> while the hydroxylated OH and adsorbed H<sub>2</sub>O peaks appear at binding energies of 531.22 and 532.22 eV respectively. In the case of black KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> (figure 3(c)) and KNbO<sub>3-x</sub> (figure 3(d)) samples, the O1s XPS spectra taken from the topmost layer contain peaks at binding energies of 530.07, 531.28, 532.28 and 533.00 eV which could be assigned to the lattice  $O^{2-}$  ions, oxygen vacancies, hydroxylated OH and H<sub>2</sub>O (chemisorbed water) respectively [36, 37]. Hence, the origin of V<sub>O</sub> and the generation of lower Nb oxidation states in KNbO<sub>3-x</sub> and Nb<sub>2</sub>O<sub>5-x</sub> can be explained as follows. As given in the reaction (1), Vo is created when the O atom leaves with the H atom in form of H<sub>2</sub>O by transferring electrons from the H atoms to the O atoms in the lattice of Nb<sub>2</sub>O<sub>5</sub>. In order to compensate for the charge balance in  $Nb_2O_5$ , these extra electrons are captured by  $Nb^{5+}$  atoms and generate  $Nb^{4+}$  states in  $Nb_2O_5$  with the concomitant formation of blue-colored  $Nb_2O_{5-x}$  [26, 38]. Hence, the  $KNbO_{3-x}$ produced from the reaction between Nb<sub>2</sub>O<sub>5</sub> and KBH<sub>4</sub> at 550  $^{\circ}$ C under Ar:H<sub>2</sub> conditions resulted in a greatly increased amount of donor states, leading to the improved electronic conductivity. These generated shallow donor levels of  $Nb^{4+/3+}$  and oxygen vacancies in the  $KNbO_{3-x}$  could also contribute to increasing the electron concentration, and the inter-valence charge transition from Nb<sup>5+</sup> to Nb<sup>4+/3+</sup> [39].

Additionally, the micro-Raman spectra of black  $KNbO_{3-x}/Nb_2O_{5-x}$  and  $KNbO_{3-x}$  samples displayed in figure 4 provide surface composition identification. The amorphous  $KNbO_{3-x}/Nb_2O_{5-x}$  structures formed at 450 °C has very weak Raman bands at maximums centered ~230 and 675 cm<sup>-1</sup> (figure 4-spectra a). The weak Raman scattering of  $KNbO_{3-x}/Nb_2O_{5-x}$  structure could be due to molecular charge disorder or a minimum asymmetry [40]. However, comparatively sharp Raman scatterings were noted with the  $KNbO_{3-x}$  sample as shown in figure 4-spectra b. The prominent Raman scattering in oxygen-deficient and deeply reduced  $KNbO_{3-x}$  could arise as a result of a greater asymmetry in the molecular charge which leads to an enhancement of the polarizability. The bands 256, 288, 301 cm<sup>-1</sup> can be ascribed to F2g symmetric bending mode of Nb–O–Nb and those around 538–603 cm<sup>-1</sup> could be due to the symmetric stretching mode of NbO<sub>6</sub> octahedra, particularly due to the large contribution of longer Nb–O bonds [36, 41, 42]. The broad and strong band centered at ca. 602 cm<sup>-1</sup> represents the O–Nb–O stretching vibration (n3 mode) in the corner-shared NbO<sub>6</sub> and the band around 534 cm<sup>-1</sup> can be due to the edge-shared NbO<sub>6</sub> octahedron. Additionally, the Raman band associated with the vibrational mode of Nb–O in KNbO<sub>3-x</sub> appeared at about 874 cm<sup>-1</sup>. The observed shift in Raman peaks in a highly reduced KNbO<sub>3-x</sub> sample could be due to the deformation of the NbO<sub>6</sub> framework as a result of the formation of Vo and shifting of the natural position of the oxygen atom in the lattice KNbO<sub>3-x</sub> structures.







The SEM and HR-TEM measurements were performed to investigate the morphological and structural changes in the formation of perovskite KNbO<sub>3</sub> nanocrystals. The SEM image of pristine Nb<sub>2</sub>O<sub>5</sub> is shown in figure 5(a) while the SEM images of the products Nb<sub>2</sub>O<sub>5-x</sub>/KNbO<sub>3-x</sub> and KNbO<sub>3-x</sub> formed at 450 °C and 550 °C are shown in figures 5(b) and (c) respectively. In the SEM image of pristine Nb<sub>2</sub>O<sub>5</sub> shown in figure 5(a), distorted microcube Nb<sub>2</sub>O<sub>5</sub> particles with a size of about ~0.5–1.0  $\mu$ m can be clearly noticed. In the case of SEM image of Nb<sub>2</sub>O<sub>5-x</sub>/KNbO<sub>3-x</sub> cubical shaped particles with ~0.5  $\mu$ m size and few spherical particles with 50 nm size can be distinguished clearly and these particles could be assigned to the Nb<sub>2</sub>O<sub>5-x</sub> and KNbO<sub>3-x</sub> particles





Table 1. Measured  $R_{ct}$  and  $C_{sc}$  parameters of  $Nb_2O_5$ ,  $KNbO_3$ ,  $KNbO_{3-x}/Nb_2O_{5-x}$  and  $KNbO_{3-x}$  by EIS analysis.

anarysis.		
$R_{ct}(k\Omega)$	$C_{sc}(\mu F)$	
2.94	$3.68 \times 10^{-5}$	
10.48	$3.99 \times 10^{-5}$	
5.58	$3.12 \times 10^{-5}$	
4.65	$2.93 \times 10^{-5}$	
	R <sub>ct</sub> (kΩ) 2.94 10.48 5.58 4.65	

respectively. However, in the SEM image of  $KNbO_{3-x}$ , even smaller particles were seen (40 nm) which could be assigned to  $KNbO_{3-x}$  nanostructures as evidenced by XRD analysis.

The detailed structural features of the pristine Nb<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5-x</sub>/KNbO<sub>3-x</sub> and KNbO<sub>3-x</sub> were investigated via high-resolution TEM analysis and the HRTEM images of the pristine Nb<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5-x</sub>/KNbO<sub>3-x</sub> and KNbO<sub>3-x</sub> are shown in figures 5(d)–(f) respectively. The well-defined lattice fringes which are shown in figure 5(d) for the pristine Nb<sub>2</sub>O<sub>5</sub> suggest the good crystallinity of the initial Nb<sub>2</sub>O<sub>5</sub> sample and the lattice fringe separation of 0.39 nm corresponding with the (001) crystal plane of pristine Nb<sub>2</sub>O<sub>5</sub> [43]. However, in the HRTEM image of Nb<sub>2</sub>O<sub>5-x</sub>/KNbO<sub>3-x</sub> shown in figure 5(e), clear fringe patterns could not be observed owing to amorphous nature of Nb<sub>2</sub>O<sub>5-x</sub>/KNbO<sub>3-x</sub> formed at 450 °C. Yet, by a careful inspection of the fringe patterns, weak lattice fringes with 0.21 and 0.36 nm lattice spacing could be identified which do not exactly correspond with fringe patterns reported for KNbO<sub>3</sub> or Nb<sub>2</sub>O<sub>5</sub> indicating these materials could be due to some intermediate compounds formed during the reaction between Nb<sub>2</sub>O<sub>5</sub> and KBH<sub>4</sub> at 450 °C. However, in the high-resolution TEM image of KNbO<sub>3-x</sub> (figure 5(f)), the HRTEM image indicates that the lattice fringe 0.29 nm corresponds to

the (111) plane of the orthorhombic phase of KNbO<sub>3</sub> and together with the selected area electron diffraction (SAED) patterns (inset in figure 5(f)), confirm the crystalline nature of KNbO<sub>3-x</sub> formed at 550 °C [44].

Having firmly established the characteristic properties of  $KNbO_{3-x}$  and  $Nb_2O_{5-x}$  nanostructures by XRD, HRTEM, XPS and Raman analyses, the piezoelectric properties of  $KNbO_{3-x}$  and  $KNbO_{3-x}/Nb_2O_{5-x}$  were investigated by the PEM analysis. It is known that the  $KNbO_3$  is a piezoelectric material which belongs to space group Amm2 (identified from the Inorganic Crystal Structure Database (ICSD No. 9533) and Crystallography Open Database—an open-access collection of crystal structures) [45]. It is known that the perovskite  $KNbO_3$  nanocrystals possess piezoelectric properties as it belongs to Amm2 space group which has no center of symmetry and to confirm its piezoelectric properties, PFM analysis was carried out. The piezoelectric properties of both  $KNbO_{3-x}/Nb_2O_{5-x}$  and  $KNbO_{3-x}$  were directly probed using piezoresponse force microscopy (PFM).

In PFM measurements, even though a feeble PFM response was noted for  $KNbO_{3-x}/Nb_2O_{5-x}$ nanostructures, a clear image could not be plotted due to very weak piezoelectric response. Nevertheless, a distinct PFM response was observed for  $KNbO_{3-x}$  and figures 6(a)-(c) present the PFM topography, amplitude and phase images of KNbO3-x respectively. In the PFM topography image, the KNbO3-x can be detected while from the phase image, a clear phase contrast between different regions can be observed and these different contrast regions represent the domain with opposite out-of-plane polarization orientation [46, 47]. At the same time, in the amplitude image also the presence of piezoelectric domains can be identified. The observation of PFM response in KNbO<sub>3-x</sub> is a clear indication of that the KNbO<sub>3-x</sub> synthesized at 550 °C is more piezoelectrically active than the KNbO3-x/Nb2O5-x synthesized at 450 °C. As mentioned earlier and the PFM analysis confirmed the low piezoelectric properties of KNbO3-x/Nb2O5-x and the low piezoelectric nature of  $KNbO_{3-x}/Nb_2O_{5-x}$  could be due to lack of intrinsic charge carriers as it was the case with piezoelectric  $MoS_2$ and BaTiO<sub>3</sub> [18, 48]. However, as explained earlier, the KNbO<sub>3-x</sub> nanostructures are present in their highly reduced state and increase in intrinsic charge carrier can be expected in KNbO3-x owing to presence of a large number of defect states and oxygen vacancies in KNbO3-x. Hence, the piezoelectric properties in highly reduced  $KNbO_{3-x}$  particles could arise due to the significant increase in charge carrier density in  $KNbO_{3-x}$  which was confirmed by the Mott-Schottky measurement.

The charge carrier density and electrons transport properties of KNbO<sub>3-x</sub> nanostructures were investigated by the Mott–Schottky and EIS measurements respectively. In Mott–Schottky plots, the capacitance (C) of the space charge region as a function of the electrode potential is displayed and the flat band potential (V<sub>FB</sub>) was determined by extrapolating the linear part of the curve to the *y*-axis (1/C2) = 0 and the carrier densities in terms of the gradient dV/d(1/C2) can be calculated as follows: Nd =  $2 e_0 \varepsilon \varepsilon_0 dV d(1/C2)$  where e0 is the electronic charge,  $\varepsilon$  is the dielectric constant of Nb<sub>2</sub>O<sub>5</sub> which is found to be 41,  $\varepsilon$ 0 is the vacuum permittivity, N<sub>d</sub> is the donor density, and V is the applied voltage. The positive slopes in the Mott-Schottky plots of the pristine Nb<sub>2</sub>O<sub>5</sub>, KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> and KNbO<sub>3-x</sub> shown in figure 7(a) indicated the n-type semiconducting behavior of Nb<sub>2</sub>O<sub>5</sub>, KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> and KNbO<sub>3-x</sub>. However, as given in table 1, the calculated N<sub>d</sub> indicates the increased electron carrier density in the following order Nb<sub>2</sub>O<sub>5</sub> < KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> < KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> < magnitude higher than those of Nb<sub>2</sub>O<sub>5</sub> and KNbO<sub>3</sub> respectively suggesting the presence of increased donor states and more electrically conductive KNbO<sub>3-x</sub>. Furthermore, computed flat-band potentials of KNbO<sub>3</sub>, KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> and KNbO<sub>3-x</sub>. Furthermore, computed flat-band potentials of KNbO<sub>3</sub>, KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> and KNbO<sub>3-x</sub>. However, as ection in the Mott-Schottky curves to the potential axis are respectively -0.49, -0.30 and -0.18 V versus NHE.

These results were further proven by the EIS Nyquist plot, as exhibited in figure 7(b) for Nb<sub>2</sub>O<sub>5</sub>, KNbO<sub>3</sub>, KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> and KNbO<sub>3-x</sub>. EIS analyses were performed in the frequency range 10 kHz to 0.1 Hz in 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte in which the EIS results were fitted with the equivalent circuit given in the insert in figure 7(b) and the fitted parameters are summarized in table 2. In the equivalent circuit, R<sub>S</sub>, R<sub>Ct</sub> and C<sub>SC</sub> represent the electrode resistance (including the FTO substrate, the resistance relating to the ionic conductivity in the electrolyte, and the external contact resistance), R<sub>Ct</sub> at high-frequency conveyed the interfacial charge-transfer resistance in the semiconductor depletion layer (semiconductor catalyst /electrolyte interface), and the space-charge capacitance (C<sub>SC</sub>) corresponding to the ability to store charge in the double layer of the semiconductor/electrolyte interface respectively. It is known that a smaller arc size in the Nyquist plot usually means a lower charge transfer resistance on the surface of materials [49]. Compared to the pristine Nb<sub>2</sub>O<sub>5</sub> and KNbO<sub>3</sub>, the reduced Nb<sub>2</sub>O<sub>5-x</sub> and KNbO<sub>3-x</sub> exhibited smaller radiuses, indicating the lower interfacial charge-transfer resistance (or faster interfacial electron transfer) in Nb<sub>2</sub>O<sub>5-x</sub> and KNbO<sub>3-x</sub>. As, both R<sub>SC</sub> and R<sub>Ct</sub> values were greatly decreased in reduced KNbO<sub>3-x</sub> than the KNbO<sub>3</sub>, fast charge-separation and transport process could be greatly enhanced in KNbO<sub>3-x</sub> nanostructures which is favorable for higher piezocatalytic activity.





**Table 2.** Estimated charge carrier density of different samples from Mott-Schottky analysis.

Sample	$N_{\rm d}/{\rm cm}^{-3}$
Nb <sub>2</sub> O <sub>5</sub> KNbO <sub>3</sub> KNbO <sub>3-x</sub> /Nb <sub>2</sub> O <sub>5-x</sub> KNbO <sub>3-x</sub>	$9.69 \times 10^{17} \\ 1.63 \times 10^{18} \\ 2.44 \times 10^{18} \\ 2.74 \times 10^{18}$

## 3.2. Piezocatalytic activity of $KNbO_{3-x}$

The piezocatalysis is the direct conversion of mechanical energy into chemical energy by the charge carriers (positive and negative charges) generated in the strain state of a piezoelectric material [1, 2]. The piezocatalysis is a new approach that enables or enhances the electrochemical processes by making use of the strain state of a piezoelectric material. The process is strongly resemblance to that of the conventional electrocatalysis process wherein the former, the electrical potential that drives the electron is in-built potential while in the latter it is an external power source [1, 10]. Once these charges are separated, hydrogen is produced via the reduction reaction  $(H^+ + e^- \rightarrow H_2)$  while the positive charges could react with adsorbed OH or directly with water to produce  $O_2$  or OH radicals. These water redox reactions are possible with Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub>-based piezoelectric materials as their CB positions are more negative than the proton reduction reaction [8]. Similarly, as the CB positions of KNbO<sub>3-x</sub> (i.e. -0.18 V versus NHE) is more negative than the proton reduction reaction  $(H^+/H_2, -0.0 \text{ V} \text{ versus NHE})$ , the hydrogen production by the electrons accumulate in the CB of KNbO<sub>3-x</sub> can be justified.

To probe the piezocatalytic activity of  $KNbO_{3-x}$ , the hydrogen production rate of  $KNbO_{3-x}$  nanoparticles in dist. H<sub>2</sub>O at a pH of 6.5 was carried out at a stirring speed of 200 rpm. To distinguish the piezocatalytic activity of KNbO3-x, as control experiments, hydrogen production rates with the weakly piezoelectric  $KNbO_{3-x}/Nb_2O_{5-x}$ , pristine  $KNbO_3$  (commercial and synthesized) and non-piezoelectric  $Nb_2O_5$  (as the starting material used in synthesizes of  $KNbO_{3-x}$ ) were investigated under similar reaction conditions. As shown in figure 8(a), after two hours of continuous reaction under the same reaction conditions, the formation of hydrogen was observed only with  $\rm KNbO_{3-x}/\rm Nb_2O_{5-x}$  and  $\rm KNbO_{3-x}$  nanoparticles and the observed hydrogen production rates were 0.05 and 3.149 ml  $h^{-1}g^{-1}$  respectively. The normalized hydrogen production rates against the specific surface areas would even provide a slightly higher hydrogen production rate for the KNbO3-x as the BET surface area of KNbO3-x is slightly less than that of KNbO3-x/Nb2O5-x catalyst. (i.e. BET surface areas of KNbO<sub>3</sub>/Nb<sub>2</sub>O<sub>5</sub> and KNbO<sub>3</sub> are 22.3 and 19.2 m<sup>2</sup>g<sup>-1</sup> respectively) In contrast, pristine KNbO<sub>3</sub> or non-piezoelectric Nb<sub>2</sub>O<sub>5</sub> and slightly reduced blue colored Nb<sub>2</sub>O<sub>5-x</sub> as control samples did not display hydrogen production at all under similar reaction conditions. Furthermore, hydrogen formation was not observed with the control experiments carried out in the presence of KNbO3-x/Nb2O5-x or KNbO3-x catalysts but in the absence of agitation or without KNbO3-x/Nb2O5-x or KNbO3-x in the presence of agitation. Hence, it is strongly suggested the observed hydrogen production with the piezocatalyst  $KNbO_{3-x}$  under stirring is originating from the piezoelectric effect.



Figure 9. Schematic illustration of the piezocatalytic reactions of  $KNbO_{3-x}$  under mechanical force. Left and right images show the  $KNbO_{3-x}$  particle without and with mechanical force respectively.

 $\begin{array}{l} \textbf{Table 3. Estimated charge carrier density from} \\ Mott-Schottky analysis of KNbO_{3-x} synthesized \\ by varying the Nb_{2}O_{5}: KBH_{4} \mbox{ molar ratio, sample} \\ A 1.00:0.50, Sample B 1.0:2.5, Sample C 1.00:3.75 \\ and Sample D 1.00:5.00. \end{array}$ 

Samples	$N_{\rm d}/{ m cm}^{-3}$
KNbO3	$1.63 \times 10^{18}$
А	$1.95  imes 10^{18}$
В	$2.74\times10^{18}$
С	$3.15 \times 10^{18}$
D	$3.65 \times 10^{18}$

On the other hand, one could argue that the observed hydrogen production could arise due to thermochemical hydrogen production via reduced metal oxides in which the reduced metal oxide oxidizes and releases H<sub>2</sub> from water [50]. However, hydrogen production by oxidation of reduced metal oxides takes place at high temperatures such as 673–873 K and hence the observed hydrogen production by KNbO<sub>3-x</sub> cannot be due to thermochemical hydrogen production via the reduced KNbO<sub>3-x</sub> as the reaction was carried out at room temperature. Furthermore, the total production of hydrogen from piezocatalytic KNbO<sub>3-x</sub> over a period of 200 h is more than 1.95 mol H<sub>2</sub> per mol catalyst and this number is greater than the theoretically possible hydrogen amount (~0.35 mol H<sub>2</sub> per mol catalyst) from the oxidation of the KNbO<sub>3-x</sub> (x = 0.35) catalyst through a water reduction reaction. (for calculation details, refer the SI) This observation that the total hydrogen produced amount is greater than that of the expected hydrogen amount through the oxidation of the reduced catalyst i.e. KNbO<sub>3-x</sub>, (x = 0.35) is strong evidence for the catalytic nature of the piezocatalyst. It was also observed the concomitant formation of oxygen and OH by water oxidation reactions given in reactions 6 and 7 with the piezoelectric-induced holes.

$$H_2O + h^+ \to OH + H^+ \tag{6}$$

$$H_2O + 2h^+ \rightarrow \frac{1}{2}O_2 + 2H^+$$
 (7)

However, the amounts of O<sub>2</sub> and OH generated were smaller than the amount of hydrogen yield and the exact reason for not observing the stoichiometric amount of O<sub>2</sub>/OH is not clear at this stage but could be due to the fact that the positive charges are not freely diffused to the interface of the catalyst or due to some additional reactions. As the only energy supplier of the hydrogen production experiment carried out with KNbO<sub>3-x</sub> is the mechanical energy, the observed hydrogen production with KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> and KNbO<sub>3-x</sub> under mechanical energy could be assigned to the piezocatalytic activity of KNbO<sub>3-x</sub>/Nb<sub>2</sub>O<sub>5-x</sub> and KNbO<sub>3-x</sub>. Though a small amount of K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> is present as a secondary phase in KNbO<sub>3-x</sub>, it would not affect the

piezocatalytic activity of  $KNbO_{3-x}$  as it has been reported to be weak ferroelectric/piezoelectric material despite  $K_4Nb_6O_{17}$  belongs to  $P2_1$ nb space group having non-centrosymmetry [51].

It was observed that the piezocatalytic hydrogen production of  $KNbO_{3-x}$  was highly dependent on the catalyst loading, the solution pH and stirring speed and figures S2–S4 demonstrate the hydrogen production rates with  $KNbO_{3-x}$  with the variation of catalyst loading, the solution pH and the stirring speed respectively. According to figure S2, the hydrogen production rate increases with the catalyst loading amount up to 1.5 g l<sup>-1</sup> and a further increase in catalyst loading resulted in a decrease in hydrogen production. Similarly, the optimum pH was found to be ~4.0 and highly basic or highly acidic solutions, the hydrogen production rates decrease. As shown in figure S4, it was noted that hydrogen yield increases with the increase of mechanical energy. The long-term stability of the catalyst was investigated by analyzing the hydrogen production with time. Figure S5 shows the variation of hydrogen production rates with time for the catalyst KNbO<sub>3-x</sub> with catalyst loading 1.5 g l<sup>-1</sup>, pH<sup>-1</sup> 6.5 and stirring speed of 200 rpm. Under these conditions, it was clearly noticeable that the initial hydrogen production rates decrease within 24 h and subsequent continuous formation of hydrogen up to 168 h indicates the stability of the catalyst. The exact reason(s) for the decrease in hydrogen rates during 24 h is not clear and needs to be investigated.

In order to optimize and to investigate the effect of charge carrier density in piezoelectric KNbO<sub>3-x</sub>, the charge carrier density of KNbO<sub>3-x</sub> was regulated via the deep reduction of KNbO<sub>3-x</sub> by varying the Nb<sub>2</sub>O<sub>5</sub> to KBH<sub>4</sub> molar ratios ([Nb<sub>2</sub>O<sub>5</sub>]:[KBH<sub>4</sub>] = 1.0:0.5, 1.0:2.5, 1.0:3.75 and 1.0:5.0 and labeled as sample A, B, C and D respectively) during the synthesis process and piezocatalytic activity was monitored against the initial Nb<sub>2</sub>O<sub>5</sub> to KBH<sub>4</sub> ratio. As shown in figure 7(b), the observed hydrogen production rates were 0.21, 3.19, 2.61 and 2.01 ml h<sup>-1</sup> g<sup>-1</sup> for A, B, C and D samples respectively. The Mott-Schottky plots of samples A, B, C and D are shown in figure S6 and the calculated N<sub>d</sub> are given in table 3. According to table 3, the calculated charge carrier densities by Mott-Schottky analysis of different KNbO<sub>3-x</sub> formed with the variation of the initial Nb<sub>2</sub>O<sub>5</sub> to KBH<sub>4</sub> molar ratio indicates the increase in the charge carrier density (hence the number of defective sites) in KNbO<sub>3-x</sub> with the increase of Nb<sub>2</sub>O<sub>5</sub>: KBH<sub>4</sub> molar ratio. As shown in figure 8(b), the observed piezocatalytic hydrogen production rates were 0.21, 3.19, 2.61 and 2.01 ml h<sup>-1</sup> g<sup>-1</sup> for A, B, C and D are since a correlation between the piezocatalytic activity and the charge carrier density in KNbO<sub>3-x</sub> with the increase of Nb<sub>2</sub>O<sub>5</sub>: KBH<sub>4</sub> molar ratio activity and the charge carrier density in KNbO<sub>3-x</sub> in which the hydrogen production rate was increased with the increase of Nb<sub>2</sub>O<sub>5</sub> to KBH<sub>4</sub> molar ratio was found to be 1.0:2.5 and further increase in Nb<sub>2</sub>O<sub>5</sub> to KBH<sub>4</sub> molar ratio resulted in the decrease in hydrogen production rates.

Hence, the enhance in piezocatalytic activity of KNbO<sub>3-x</sub> with the increase in the initial Nb<sub>2</sub>O<sub>5</sub> to KBH<sub>4</sub> molar ratio could be mainly attributed to the increase in charge carrier density and hence the number of defective sites in KNbO<sub>3-x</sub> structures as the crystalline structure of KNbO<sub>3-x</sub> remains the same with different Nb<sub>2</sub>O<sub>5</sub> to KBH<sub>4</sub> molar ratio which was confirmed by XRD analysis. The dependence of hydrogen production with the charge of charge carrier density in piezoelectric KNbO<sub>3-x</sub> can be explained as follows; It is known that the charges generated in piezoelectric KNbO<sub>3</sub> by the piezoelectric effect are not free-state and cannot be migrated as they are formed by the relative displacement of positive and negative charges under the mechanical stress (still under bound state) and would not involve in the reaction [52]. Nevertheless, On the other hand, free charge carriers generated in KNbO<sub>3-x</sub> can be effectively separated under the influence of piezoelectric potential generated by stress and could involve in redox reactions. Hence, piezoelectric KNbO<sub>3-x</sub> having high intrinsic charge carrier densities are the most appropriate piezocatalysts. However, it appeared that at higher charge carrier densities, the piezocatalytic activity decreases slightly from the optimized piezocatalytic rate which could be due to enhanced scatterings of charges during mechanical stress.

Based on the hydrogen production rates and the physical as well as electronic properties of KNbO<sub>3-x</sub>, the overall piezocatalytic activity of KNbO<sub>3-x</sub> is schematically illustrated in figure 9. It is known that the piezocatalysis is a catalytic effect driven by the stress-induced (i.e. ultrasonic vibrations) piezoelectric charges (positive and negative ones) in piezoelectric materials through the piezoelectric effect. As in this investigation, stress was introduced to the piezoelectric KNbO<sub>3-x</sub> by water stirring which is similar to the piezoelectric field induced by discrete fluid mechanical energy [53, 54]. The flow-induced vibrations are widely distributed in nature and piezoelectric energy harvesting from the flow-induced vibration is a hot topic [5, 54–56]. In the fluid mechanical energy harvesting technology, it was demonstrated the generation of piezoelectric field in piezoelectric material due to fluid eddies formation when the solution is stirred by the magnetic stirring [54]. When KNbO<sub>3-x</sub> structures undergo different stress by water stirring, the piezoelectric field in KNbO<sub>3-x</sub> will be originated. Due to the polarization, the intrinsic charges in KNbO<sub>3-x</sub> could rapidly transport through the highly conductive KNbO<sub>3-x</sub> nanostructures into the interfacial region thereby enhanced charge separation, resulting in remarkably enhanced piezocatalytic activity. Once these positive and negative charges could react with

adsorbed OH or directly with water to produce  $O_2$  or OH radicals. The enhanced charge carrier density in  $KNbO_{3-x}$  nanostructures and higher stirring rates will further enhance the piezoelectric effect and hence piezocatalytic activity. The important factor in this investigation is the ability to create a piezoelectric field in  $KNbO_{3-x}$  by the low-frequency mechanical force rather than by the high-frequency ultrasonic vibrations will pave the way to wider applications in piezoelectric KNbO<sub>3-x</sub> in catalysis. Despite hydrogen formation has been reported for the pristine  $KNbO_3$  under high-stress introduced by ultrasonic vibration, the hydrogen formation was not observed with the pristine  $KNbO_3$  under mild stress (figure 8(a)) originated by flow-induced vibrations due to lack of intrinsic charge carrier density in the pristine  $KNbO_3$  further substantiate the role of the intrinsic charge carrier density is.

# 4. Conclusion

Piezoelectric KNbO<sub>3-x</sub> nanostructures with a large number of oxygen vacancy sites can be synthesized via the reaction between Nb<sub>2</sub>O<sub>5</sub> and KBH<sub>4</sub> at 550 °C under reducing reaction conditions. These piezoelectric KNbO<sub>3-x</sub> materials are a good piezoelectric material that can be used to harness mechanical energy and produce hydrogen from water splitting via piezocatalysis. The origin of the piezoelectric field and the piezocatalysis in KNbO<sub>3-x</sub> materials is found to be the stress introduced by water stirring in which piezoelectric field is generated in KNbO<sub>3-x</sub> materials due to fluid eddies formation when the solution is stirred by magnetic stirring. The intrinsic charge carrier density in KNbO<sub>3-x</sub> is enhanced significantly by the formation of oxygen vacancies by the deep reduction of KNbO<sub>3-x</sub>. The observed piezocatalytic activity of KNbO<sub>3-x</sub> could be assigned to the enhancement of intrinsic charge carrier density that leads to enhancing the electronic conductivity and hence charges generated by the piezoelectric effect could rapidly be transported and separated in KNbO<sub>3-x</sub> resulting in remarkably enhanced piezocatalytic activity. Hence, creating a large number of oxygen vacancy sites in piezoelectric materials could be a better approach to enhance the piezocatalytic performance of piezoelectric materials.

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