

Journal of Materials Chemistry A

Materials for energy and sustainability

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Zhang, Y. Wang, J. Liu, M. Thangamuthu, Y. Yue, Z. Yan, J. Feng, D. Zhang, H. Zhang, S. Guan, M. Titirici, I. Abrahams, J. Tang, Z. Zhang, S. Dunn and H. Yan, *J. Mater. Chem. A*, 2021, DOI: 10.1039/D1TA04131B.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ARTICLE

Facile one-step synthesis and enhanced photocatalytic activity of WC/ferroelectric nanocomposite

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Man Zhang^a, Yaqiong Wang^b, Jianguo Liu^c, Madasamy Thangamuthu^d, Yajun Yue^e, Zhongna Yan^{e,g}, Jingyu Feng^f, Dou Zhang^g, Hongtao Zhang^h, Shaoliang Guanⁱ, Maria-Magdalena Titirici^f, Isaac Abrahams^e, Junwang Tang^d, Zhen Zhang^j, Steve Dunn^{b*}, Haixue Yan^{a*}

The development of noble-metal-free co-catalysts is seen as a viable strategy for improving the performance of semiconductor photocatalysts. Although the photocatalytic efficiency of ferroelectrics is typically low, it can be enhanced through incorporation of co-catalyst into nanocomposites. Here, we demonstrate the influence of ferroelectricity on the decolorization of Rhodamine B under simulated solar light using RbBi₂Ti₂NbO₁₀ and compared the performance with non-ferroelectric RbBi₂Nb₅O₁₆. The decolorization rate for RbBi₂Ti₂NbO₁₀ was 5 times greater than RbBi₂Nb₅O₁₆. This behaviour can be explained in terms of ferroelectric polarization, which drives separation of the charge carriers. The photocatalytic activity of the RbBi₂Ti₂NbO₁₀ was further enhanced to over 30 times upon preparing nanocomposite with tungsten carbide (WC) through high energy ball milling. This enhancement was not only attributed to the increased specific surface area, but also to the incorporated WC co-catalyst which also serves as source of plasmonic hot electrons and extends the photocatalytic activity into the visible light range. The WC/RbBi₂Ti₂NbO₁₀ nanocomposite shows interesting water oxidation property and evolves O₂ with a rate of 68.5 μmol h⁻¹ g⁻¹ and the quantum yield of 3% at 420 nm. This work demonstrates a simple route for preparing WC containing nano ferroelectric composites for solar energy conversion applications.

1. Introduction

The development of low cost photocatalyst materials with high photocatalytic efficiency that are also environmental benign is viewed as a matter of global urgency.¹ In this respect, direct use of natural solar energy through photocatalysts represents an important area of technology. When refined the approach could be used to provide useful chemicals,² reduce CO₂ in the atmosphere³ or using narrow band-gap materials to produce fuels.⁴ Despite abundant studies on semiconductors, including a variety of inorganic metal oxides (such as TiO₂, ZnO, WO₃ and SnO)^{5–9} and sulfides (ZnS and CdS),^{10–14} and the development of a variety of structures¹⁵ their photocatalytic efficiency is still far from satisfactory. A key challenge for efficiency improvement is to suppress the recombination of photo-induced charge carriers and prolong their lifetime.^{10,16–18} One important strategy to address this problem is to use the ferroelectric materials. Their switchable spontaneous polarization produces internal electric fields,^{19–22} resulting in the spatial separation of photo-induced electron-hole pairs.^{23,24}

Morris *et al.*²⁵ tested the charge carrier lifetime in films of cubic (paraelectric) and tetragonal (ferroelectric) BaTiO₃ using transient absorption spectroscopy and found that the charge carrier lifetime

in ferroelectric BaTiO₃ was four orders of magnitude longer than in paraelectric BaTiO₃. The prolonged charge carrier lifetime is also reported in Aurivillius ferroelectric, Bi_{6-x}Sr_xTi_{3+x}Fe_{2-x}O₁₈.²⁶ This clearly demonstrates that the presence of internal fields can reduce recombination of charge carriers, leading to enhanced photocatalytic efficiency. Moreover, the ferroelectric domains cause band bending of the electronic states and induce spatially selective reactivity for photochemical reactions, as demonstrated in perovskites, such as BiFeO₃,²⁷ BaTiO₃²⁸ and Pb(Zr_{0.3}Ti_{0.7})O₃.²⁹ Among various ferroelectric photocatalysts with perovskite-like structure, bismuth-containing niobates are reported promising candidates^{30–32} due to the high energy of the Nb 4d conduction band³² and the O 2p orbitals hybridized by Bi 6s in the valence band.^{33,34} Moreover, depending on the Bi/Nb ratio, these compounds can adopt complex crystal structures, such as pyrochlore, layered perovskite or fluorite related structures, and thus exhibit different dielectric properties.³⁵ Although previous studies have reported the ferroelectricity of bismuth-containing niobates with layered perovskite structures, the effect of their polarization on photocatalysis has been barely studied.³⁶

Besides, loading a co-catalyst onto a ferroelectric material has been proved to be an effective strategy to further boost the photocatalytic efficiency.^{37–39} The co-catalyst not only provides the catalytic sites, but also suppresses the recombination of photo-induced charge carriers in the photocatalyst.^{40,41} The most popular co-catalysts are

E-mail: h.x.yan@qmul.ac.uk
dunns4@lsbu.ac.uk

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



ARTICLE

Journal of Materials Chemistry A

noble metals, such as Au, Pt, Rh, and Ru. However, their high cost and scarcity hamper large-scale commercial applications, and thus the development of earth-abundant and inexpensive alternatives is extremely essential. Both tungsten (W) and carbon (C) are earth-abundant, while tungsten carbide (WC) exhibits high electronic conductivity and have Pt-like *d*-band electronic density states.⁴² Since Levy and Boudart's first report on WC in the catalysis of hydrogenolysis,⁴³ it has been intensively studied as an electrocatalyst support for methanol oxidation, oxygen reduction, nitrophenol oxidation and hydrogen evolution.^{44,45} Hence, it is extremely desirable to prepare nanocomposites of ferroelectric photocatalyst particles with WC to enhance the photocatalytic activity. The intimate interfacial contact between WC and ferroelectric particles maximizes the reaction active sites and facilitates the charge transfer between the different phases. Different processing routes have been employed to produce WC particles,^{46,47} such as direct carburization of tungsten powder, solid-state metathesis, reduction carburization,⁴⁸ mechanical grinding,⁴⁹ thermal pyrolysis of tungsten-containing organic acid,⁴⁷ polymeric precursor routes using metal alkoxides, hydrothermal method,⁵⁰ etc. However, these processing routes are limited due to complicated apparatus and procedures, long processing time, high temperatures, and high-energy consumption.⁵¹ Depending on the processing conditions, the obtained nanocomposites can have inhomogeneous distribution of constituent phases, uncontrollable size, and weak interaction between the semiconductor and WC phases.⁵² Thus, the efficient production of WC containing nanocomposite using low cost approaches remains a scientific and technological challenge. Traditionally, ball-milling method is used to prepare sub-micron sized particles, and high energy ball milling can be used to prepare nano-sized particles. Using the high energy ball milling approach, the ball milled material, for instance, the photocatalyst, would be coated with secondary or foreign material which can be introduced from both the milling balls and milling jar. In this study, two Rb- and Bi-containing niobates, ferroelectric RbBi₂Ti₂NbO₁₀⁵³ and non-ferroelectric RbBi₂Nb₅O₁₆⁵⁴ materials were prepared to investigate the impact of ferroelectric polarization on photocatalytic properties. To enhance the photocatalytic performance of ferroelectric RbBi₂Ti₂NbO₁₀, WC co-catalyst was loaded onto the RbBi₂Ti₂NbO₁₀ nanopowders by facile one-step high-energy ball milling processing technique. The ferroelectric RbBi₂Ti₂NbO₁₀ has larger bandgap (3.25 eV) with lower specific surface area (7.72 m²/g) compared to the values of (3.02 eV and 13.85 m²/g) for non-ferroelectric RbBi₂Nb₅O₁₆. However, the decolorization rate for RbBi₂Ti₂NbO₁₀ was 5 times greater than for RbBi₂Nb₅O₁₆. The prepared WC/RbBi₂Ti₂NbO₁₀ nanocomposite, produced using a facile route in only 40 min, showed over 30 times higher photocatalytic activity than the non-ferroelectric RbBi₂Nb₅O₁₆. Overall, this work demonstrates a novel approach to produce noble-metal-free co-catalyst loaded nanocomposites in an efficient and ultra-fast way for photocatalytic applications.

2. Results and discussion

Fig. 1a and b show the fitted room temperature X-ray diffraction (XRD) patterns of the calcined RbBi₂Ti₂NbO₁₀ and RbBi₂Nb₅O₁₆

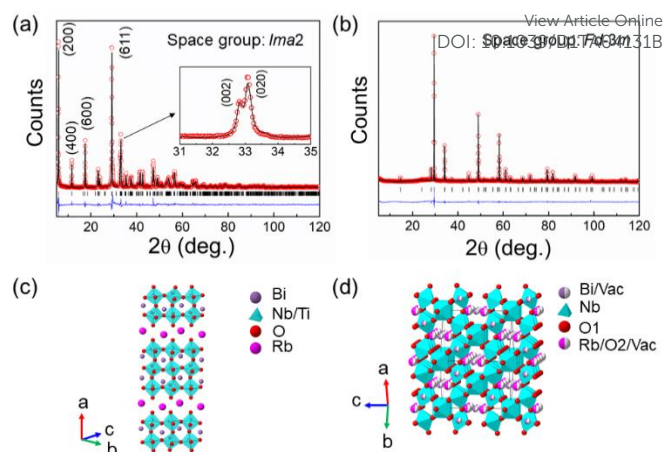


Fig. 1 Fitted X-ray diffraction patterns for (a) RbBi₂Ti₂NbO₁₀ and (b) RbBi₂Nb₅O₁₆. The observed and calculated profiles represented by red open circles and a black solid line, respectively. The difference profile (blue line) and reflection position (black markers) are also shown. Crystal structures of (c) RbBi₂Ti₂NbO₁₀ and (d) RbBi₂Nb₅O₁₆.

powders. These two materials appear to be a single phase with no detectable impurities. The atomic coordinates for RbBi₂Ti₂NbO₁₀ and RbBi₂Nb₅O₁₆ as reported by Kim *et al.*⁵³ and Ehlert *et al.*⁵⁴ were selected as the initial model for refinement. RbBi₂Ti₂NbO₁₀ is a 3-layer Dion-Jacobson phase, with orthorhombic symmetry and a polar space group of *Ima2*.⁵³ The peak splitting of (002) and (020) planes is related to the orthorhombic ferroelectric lattice distortion (Fig. 1a inset). RbBi₂Nb₅O₁₆ has a cubic defect pyrochlore structure with a non-polar space group of *Fd-3m*. Fig. 1c and d show schematic crystal structures of the studied compounds. RbBi₂Ti₂NbO₁₀ consists of 3-layers of corner sharing Ti/NbO₆ octahedra with Bi³⁺ cations in the A-sites. These perovskite blocks are separated by a layer of Rb⁺ cations. On the other hand, RbBi₂Nb₅O₁₆ consists of a 3-dimensional network of corner sharing NbO₆ octahedra. While Bi³⁺ cations sit in the normal 8-coordinate pyrochlore sites (the actual coordination is lowered due to partial occupancy of one of the oxygen sites), the Rb⁺ cations are shifted away from the normal pyrochlore position to adopt an octahedral geometry with oxygen. Fitted parameters and unit cell parameters for the samples are summarized in Table 1.

Table 1 Crystal and refinement parameters for RbBi₂Ti₂NbO₁₀ and RbBi₂Nb₅O₁₆.

Composition	Crystal parameters	Refinement parameters
RbBi ₂ Ti ₂ NbO ₁₀	Orthorhombic (<i>Ima2</i>) $a = 30.5499(1) \text{ \AA}$ $b = 5.4255(3) \text{ \AA}$ $c = 5.4656(3) \text{ \AA}$ $V = 905.9(1) \text{ \AA}^3$	$\chi^2 = 3.92$ $R_{wp} = 0.0987$ $R_p = 0.072$ $R_{ex} = 0.0502$ $R_{F2} = 0.1292$
RbBi ₂ Nb ₅ O ₁₆	Cubic (<i>Fd-3m</i>) $a = 10.5268(1) \text{ \AA}$ $V = 1166.52(1) \text{ \AA}^3$	$\chi^2 = 4.286$ $R_{wp} = 0.1032$ $R_p = 0.08$ $R_{ex} = 0.0500$ $R_{F2} = 0.1003$



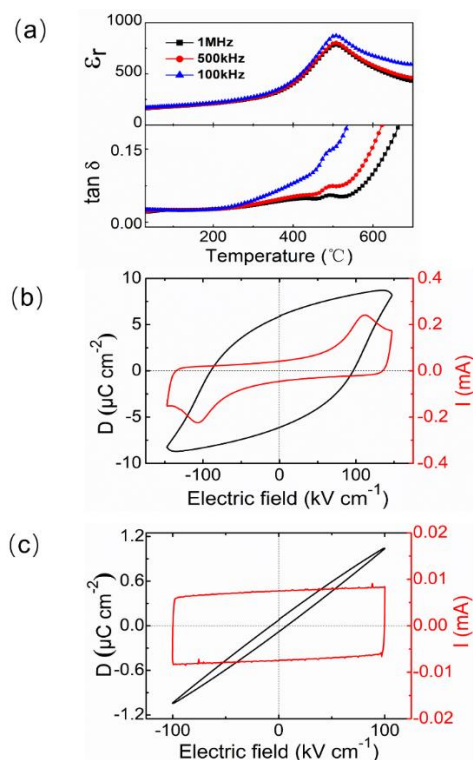


Fig. 2. (a) Temperature dependencies of dielectric permittivity (ϵ_r) and loss ($\tan \delta$) for $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$; I-E and D-E loops of (b) $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ ceramic at 100 °C and (c) $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$ ceramic at room temperature.

The relative densities of the sintered $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ and $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$ ceramics were 92% and 95%. The morphological characterization of $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ ceramic shows the plate-like grains (Fig. S1a), whereas $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$ ceramic was observed to have densely arranged grains in a polygonal pattern (Fig. S1b). The temperature dependence of dielectric permittivity and loss of $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ ceramic are presented for the first time (Fig. 2a). A frequency independent peak is observed at around 506 °C in the dielectric permittivity plots, implying that $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ is ferroelectric with a Curie point (T_c) at this temperature. The loss peak appears a few degrees below T_c , which has been attributed to ferroelectric domain wall movement.⁵⁵ Although ferroelectric polarization - electrical field loops have been reported,⁵³ there was no evidence to show domain switching in the loops. The published loops show a dominant contribution from conductivity and highest polarization less than 0.3 $\mu\text{C cm}^{-1}$. It is considered a requirement of ferroelectricity to have a measured switchable polarisation loop. As such our measured loops are the first definitive evidence of ferroelectricity in the system.

The current - electric field (I - E) and displacement - electric field (D - E) loops of $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ were first measured at room temperature at a frequency of 20 Hz. At this temperature ferroelectric domain switching was not observed due to a large coercive field. The measurement was then carried out at 100 °C at the same frequency to facilitate domain switching at a reduced coercive field, shown in Fig. 2b. The current peaks associated with ferroelectric domain

Table 2 Properties of sub-micron sized $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ and $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$ powders

Catalyst	$\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$	$\text{RbBi}_2\text{Nb}_5\text{O}_{16}$
Band gap (eV)	3.25	3.02
Specific surface area ($\text{m}^2 \text{g}^{-1}$)	7.72	13.85
Decolorization rate (min^{-1})	3.8×10^{-3}	7.4×10^{-4}

switching are clearly observed in the I - E loop.^{56,57} Moreover, when the $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ ceramics were poled at 100 °C, a piezoelectric constant (d_{33}) value of $14.7 \pm 0.2 \text{ pC N}^{-1}$ was detected. All these dielectric, ferroelectric, and piezoelectric property results provide powerful evidence for the existence of ferroelectricity in $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$. Similarly, I - E and D - E loops were tested for $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$ at room temperature and 20 Hz (Fig. 2c). In contrast to $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$, no current peaks were observed in the I - E loop of $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$ ceramic suggesting that this materials has linear dielectric behaviour^{56,57}. This is consistent with its non-polar structure.

The as-calcined $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ and $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$ powders were first milled in nylon milling jars at 180 rpm for 24 h to obtain sub-micron sized powders (Fig. S2). The sub-micron sized $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ powder is ferroelectric in nature as confirmed by the PFM images shown in Fig. S3. The specific surface area of sub-micron sized $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ and $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$ powders were 7.72 and 13.85 $\text{m}^2 \text{g}^{-1}$ (Table 2). The light absorption properties of both powders were characterized by using UV-Vis spectroscopy (Fig. 3a). It is assumed that $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ and $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$ are direct band gap materials, based on analogy with the 2-layer Dion-Jacobson phase $\text{CsBi}_{1-x}\text{Eu}_x\text{Nb}_2\text{O}_7$.⁵⁸ The band gaps (E_g) of $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ and $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$, which were calculated by the Tauc equation,⁵⁹ are 3.25 eV and 3.02 eV (Fig. 3b).

The photocatalytic activity of the $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ and $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$ powder was tested through the photodecomposition of RhB and the degradation profiles are shown in Fig. 3c. It can be seen that the ferroelectric $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ degrades about 60% of the dye within 4 h, whereas the non-ferroelectric $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$ degrades about 12% at the same duration. The decolorization rate of was calculated according to the following equation:

$$\ln\left(\frac{C_0}{C_t}\right) = k_{obs}t$$

where C_0 and C_t are the concentration of RhB at time 0 and t , respectively, and k_{obs} is the observed pseudo-first-order reaction rate constant.⁶⁰ The ratio $C_0/C_t = A_0/A_t$ are corresponding to the measured absorbances. As shown in Table 2, the decolorization rate constants of sub-micron sized $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ and $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$ powders are 3.8×10^{-3} and $7.4 \times 10^{-4} \text{ min}^{-1}$, respectively. Although the $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ powder has a slightly larger bandgap and a smaller specific surface area, it shows 5 times higher decolorization rate compared to $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$. The higher photocatalytic activity shown by $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ can be attributed to its ferroelectric nature^{60,61} that the internal field generated by spontaneous polarization promotes the separation of charge carriers and reduces their recombination. It should be noted that orthorhombic phase of $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ contributes additional opportunity to support charge separation by anisotropic surface potentials in layered structure.⁶²



ARTICLE

Journal of Materials Chemistry A

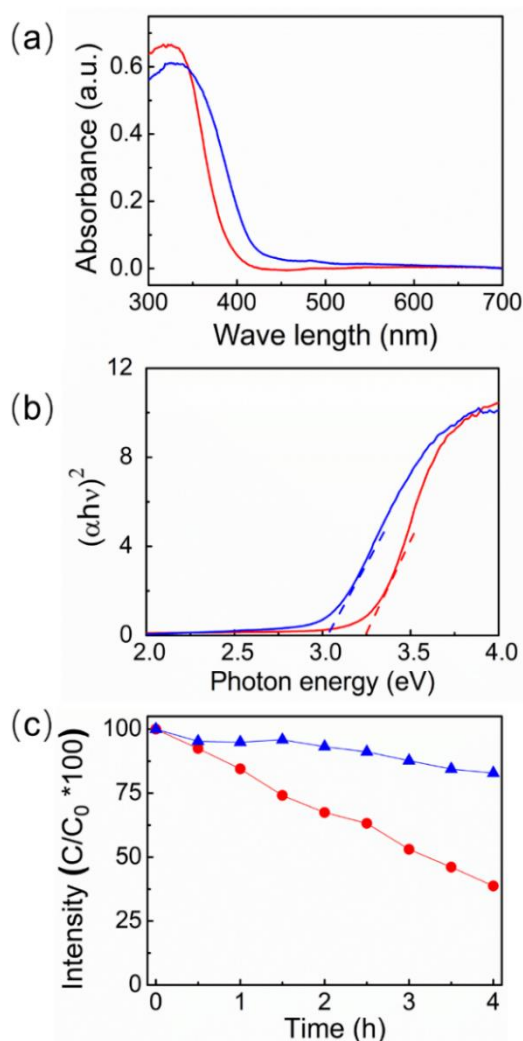


Fig. 3 Light absorption and photocatalytic property characterisation of sub-micron sized $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ (red curves) and $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$ powders (blue curves): (a) UV-Vis absorption spectra; (b) illustration of $(\alpha h\nu)^2$ versus photon energy (the optical bandgaps can be determined by extrapolation of the linear portion); (c) photodegradation efficiencies of RhB as a function of irradiation time under simulated sunlight, where the lines serve as a guide to the eye.

It was reported by Levy and Boudart⁴³ that WC has platinum-like behaviour and facilitate redox reactions. In order to study the effect of WC on photocatalytic activity of $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ material, the calcined $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ powder was ball milled at higher rotation speed of 600 rpm for 40 min using same ZrO_2 milling balls. For this control experiment, two different types of milling jars, which are made of ZrO_2 and WC, were used in an attempt introduce WC to the surface of $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ powder. The ZrO_2 jar was used for comparison. The XRD patterns of the ball milled powders are shown in Fig. S4. Diffraction peaks for both $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ and ZrO_2 are present, which indicates the introduction of ZrO_2 from the milling balls into $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ powder due to intense collision between the milling balls/jar and the ceramic powder. Photocatalytic degradation of RhB under stimulated solar light irradiation using these two composite powders was studied and the results are shown in Fig. S5 and Table 3. Although the composite powder ball milled in a ZrO_2 jar has larger specific surface area (Table 3), a lower photodegradation

Table 3 Photocatalytic properties of $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanopowders prepared by using different milling jars at 600 rpm for 40 min DOI: 10.1039/D1TA04131B

Jar type	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	Degradation rate (min^{-1})
WC	19.47	0.016
ZrO_2	21.99	0.009

rate was observed. The composite prepared in WC jar shows almost 100% dye degradation within 3 h, whereas the composite prepared in ZrO_2 jar made dye degraded about 90% in 4 h. Considering that the composite powders prepared in WC jar and ZrO_2 jar have similar specific surface area, the enhance photocatalytic activity of the composite powder made in the WC jar is attributed to the contribution from WC. The control experimental results indicated a route to optimize the preparation conditions for further enhancing the photocatalytic activity of $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$. As such the calcined $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ powder was ball milled in WC jar under different rotation speed and duration, details of which are listed in Table S1. The XRD patterns of the powder are shown in Fig. S6. With increasing rotation speed and ball milling time, diffraction peaks of the powders become broader, which indicates that the particle sizes of the powder are becoming smaller. Photodegradation of RhB was carried out to characterize the photocatalytic behaviour of the obtained powders (Fig. S7). The ball milling parameters, specific surface areas, and photodegradation rate of RhB of the obtained nanocomposites are shown in Table S1. For easier comparison, the powder ball milled in a WC jar at 600 rpm for 40 min (Table 3) is also shown in Table S1. It is clear that at 600 rpm, the degradation rate of RhB firstly increase and then decrease with increasing ball-milling time. The initial increase in photodegradation rate is attributed to the increased specific surface area, however, further reduction in particle size reduced the photocatalytic activity. It can be possibly attributed to the blocking effect of ZrO_2 from milling balls and/or decreased polarization in powders with smaller particle size, which will be discussed below. The best photocatalytic activity was observed with a ball milling speed of 800 rpm with 40 min milling time.

The role of WC in the nanocomposite prepared under this condition was studied in detail. The obtained nanocomposite consisted of three nanocrystalline phases ($\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$, ZrO_2 , and WC), but as discussed later, ZrO_2 give no contribution to photocatalytic response under the irradiation condition used here. Hence, we use the term "WC/ $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanocomposite" for simplicity. Compared with the sub-micron sized powder the width of the $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ diffraction peaks in the nanocomposite is broader indicating the average crystallite size is smaller. The introduction of WC from the WC milling jar into the $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ could not be confirmed by XRD due to the lack of detectable diffraction peaks (Fig. S6). Fig. 4a show detail of the (002) and (020) peaks in the XRD patterns of sub-micron sized $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ and WC/ $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanocomposite. These peaks were modelled using a simple pseudo-Voigt peak shape. The peak splitting is clearly discernible in the sub-micron sized sample and less clear in the nanocomposite due to the peak broadening. Nevertheless, asymmetry in the distribution is obvious and the two peaks were successfully fitted indicating that the ferroelectric distortion is maintained, albeit slightly reduced in magnitude in the nanocomposite. The spontaneous polarisation P_s in $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$



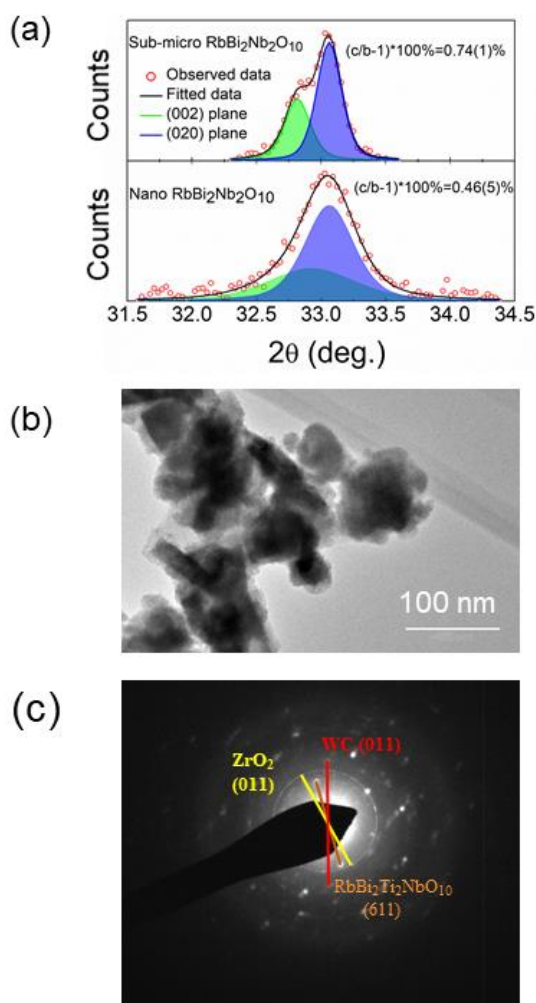


Fig. 4 (a) Detail of X-ray diffraction patterns for sub-micron $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ and $\text{WC/RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanocomposite showing pseudo-Voigt fit to (020) and (002) diffraction peaks; (b) TEM image of $\text{WC/RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanocomposite and (c) corresponding SAED pattern.

depends on the extent of the orthorhombic distortion, which can be quantified by the orthorhombicity, $(c-b)/b$, where b and c are lattice parameters.

According to the fitted results, the orthorhombicity values for sub-micron sized $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ and $\text{WC/RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanocomposite are 0.74% and 0.46%, respectively. The smaller orthorhombicity value in the $\text{WC/RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanocomposite suggests the P_s is reduced compared to that in the sub-micron sized powder.^{24,63} This can be attributed to the size effect on the ferroelectric domain structure.^{64,65} When the sizes of ferroelectric particles/grains are in the micrometre range, domain walls are generated to minimize the internal stresses induced by phase transition from the paraelectric to the ferroelectric phase at the Curie point. In this case, P_s and orthorhombicity are insensitive to changes in the particle/grain size. When the particle/grain size of ferroelectric powders is reduced to the nanometre range, the orthorhombic distortion reduces. Therefore, there is no necessity for domain wall formation to minimize the internal stresses which are already reduced as the P_s is decreased.^{66,67}

Fig. 4b shows a TEM image of the $\text{WC/RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanocomposite. Granular powders with an average particle size of ca. 80 nm can be observed. The specific surface area tested by the BET method was $19.77 \text{ m}^2 \text{ g}^{-1}$ (Table S1). The selected area electron diffraction (SAED) image (Fig. 4c) shows the diffraction spots from the (611) plane of $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$. Although ZrO_2 and WC particles were not noticeable from the TEM images, the diffraction spots from (011) plane of WC⁶⁸ and (011) plane of ZrO_2 ⁶⁹ are visible. This confirms the existence of WC and ZrO_2 nanoparticles within the nanocomposite.

UV absorption (Fig. 5a) and valence band X-Ray photoelectron spectroscopy (XPS) (Fig. S9) were used to foresee the band structure of the $\text{WC/RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanocomposite. ZrO_2 was expected to have no contribution to photocatalytic response under simulated solar irradiation with wavelength longer than 280 nm due to its large band gap ($\sim 5.7 \text{ eV}$)⁷⁰ and therefore the discussion below is focused on the photocatalytically active components. The $\text{WC/RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanocomposite not only showed strong absorption at wavelength shorter than 400 nm, but also showed weak but broad absorption at longer wavelength range (Fig. 5a), which indicates the absorption of visible light. The band gap for the $\text{WC/RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanocomposite was calculated as 3.25 eV (Fig. S8), confirming that the powder particle size reduction in $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ does not alter the band gap value. The valence band XPS spectrum in Fig. S9a confirms the metal like behaviour of WC.⁷¹ By comparing Fig. S9a and S9b, it is concluded that Fermi level of WC is lower than the conduction band level of $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ (Fig. S9c). The morphological characterization via TEM reveals that the WC nanoparticles were homogeneously distributed within the $\text{WC/RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanocomposite (Fig. S10).

Photodegradation of RhB using the $\text{WC/RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanocomposite under simulated sun light and visible light irradiations were investigated, and the results are shown in Fig. 5b. Almost 100% of the RhB dye degraded within 2 hours while irradiated using simulated sunlight with a rate of $2.3 \times 10^{-2} \text{ min}^{-1}$ (Table 4), which is 6 times higher than the sub-micron sized $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ and over 30 times higher than the non-ferroelectric $\text{RbBi}_2\text{Nb}_5\text{O}_{16}$. As discussed above, the driving force for charge carrier separation in $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ powders would reduce with decreasing particle size down to the nanoscale owing to the reduced orthorhombicity and P_s . The size reduction of $\text{RbBi}_2\text{Ti}_2\text{NbO}_{10}$ is expected to compromise the photocatalytic activity to some extent. However, the positive contribution from greater specific surface area of the ferroelectric nanoparticles, the efficient charge separation and transport by the WC incorporation and possibly severe plastic deformation produced by high-speed ball milling⁷² overwhelm the decreased ferroelectric contribution in $\text{WC/RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanocomposite and contribute to the enhanced photocatalytic activity.

To prove the above claim and see the role of WC, we further characterized the nanocomposite of $\text{WC/RbBi}_2\text{Ti}_2\text{NbO}_{10}$. Under visible light irradiation, $\text{WC/RbBi}_2\text{Ti}_2\text{NbO}_{10}$ nanocomposite photocatalytically degrades the 32% of the RhB within 4 h (Fig. 5b),



ARTICLE

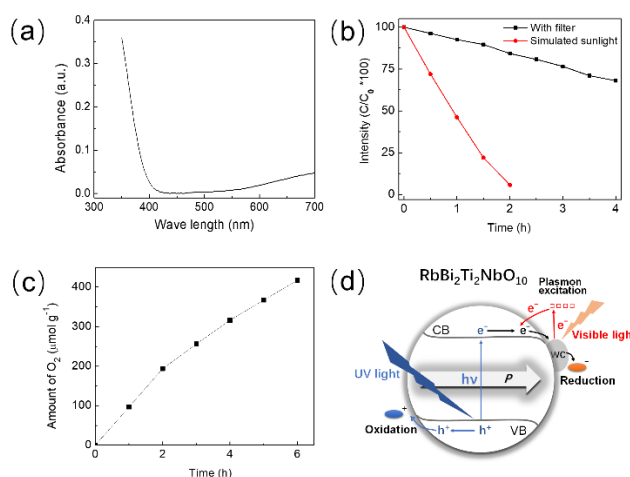


Fig. 5 (a) Light absorption and photocatalytic property characterisation of WC/RbBi₂Ti₂NbO₁₀ nanocomposite; (b) Degradation of RhB with WC/RbBi₂Ti₂NbO₁₀ nanocomposite under simulated sunlight (red) and visible light (black) (lines serve as a guide to the eye); (c) O₂ evolution from water (pH 7.0) using 30 mg of RbBi₂Ti₂NbO₁₀ containing 10 mM AgNO₃, as an electron scavenger under full arc condition for 6 h; (d) schematic of redox reaction on the surface of a WC/RbBi₂Ti₂NbO₁₀ nanocomposite particle.

whereas sub-micron sized RbBi₂Ti₂NbO₁₀ shows no photocatalytic activity. These results suggest that the observed photocatalytic activity under visible light is originated from the WC. It is worth noting that the nanoparticles of WC show the surface plasmon property.⁷³ Various plasmonic properties such as plasmonic scattering, near-field coupling, and hot electron have been reported for photocatalysis.^{74,75} However, in the present case, we expect that the plasmonic hot electrons generated from the WC nanoparticles may transfer into the RhB molecule directly to degrade or enter into the conduction band (CB) of the RbBi₂Ti₂NbO₁₀, which is later reducing the RhB molecule. The broad visible absorption peak observed for WC/RbBi₂Ti₂NbO₁₀ (Fig. 5a), in the range of 500 nm to 700 nm is attributed to the plasmonic WC particles with various sizes.^{73,76}

To verify the stability of the material, 3 cycles of RhB degradation reaction were performed under simulated sunlight (Fig. S11) and observed no significant changes suggesting that the WC/RbBi₂Ti₂NbO₁₀ nanocomposite is stable enough under the present experimental conditions.

The photocatalytic water oxidation activity of the WC/RbBi₂Ti₂NbO₁₀ nanocomposite was studied in the presence of Ag as electron scavenger under full arc (similar to solar light) condition. A significant O₂ evolution was observed at pH 7.0 with an average gas evolution rate of 68.5 μmol h⁻¹ g⁻¹ (Fig. 5c). In the absence of photocatalyst as well as in the absence of electron scavenger no O₂ evolution was observed, in addition to the no activity under dark condition. It can be seen from Fig. 5c that the rate of O₂ evolution was higher during the early hours of the reaction, which may be due to the

prearrangements of the photocatalytic system to produce the O₂ with a steady rate after 3 h of irradiation. It exhibits the apparent quantum yield (AQY) of 3% at 420 nm. This value is significant because the photocatalytic water oxidation using the present ferroelectric material is relatively new, and competitive to the conventional water oxidation photocatalysts. These results encouraging us to use the ferroelectric material for solar-driven photocatalysis.

Fig. 5d schematically describes the redox reaction on the surface of the WC/RbBi₂Ti₂NbO₁₀ nanocomposite. Under UV light, electrons produced from RbBi₂Ti₂NbO₁₀ participate in the degradation reactions with WC acting as cocatalysts to enhance the charge carrier separation and transfer. In addition, it is expected that the Fermi energy of WC with Pt-like electronic features would be lower than the conduction band of RbBi₂Ti₂NbO₁₀.⁷⁶ The plasmonic hot electrons generated in the WC nanoparticles contribute the photodegradation in visible light range. The approach used here for enhanced semiconductor visible light photocatalysis using nano-sized WC could be applied to a broad range of semiconductor/cocatalyst materials for high performance photocatalysis.

Although the ferroelectric RbBi₂Ti₂NbO₁₀ material has a larger band gap it can be used for photocatalytic application using the present facile one step high speed ball milling method. Table 4 lists the photocatalytic properties of ferroelectric photocatalysts. The photodegradation rate of RhB and O₂ production are much higher than the reported ferroelectric photocatalysts (Table 4).



Table 4. Comparison of photocatalytic performance over ferroelectric photocatalysts

Photocatalyst	Band gap/eV	Catalytic condition	Catalytic application	Catalytic activity	ref
KNbO ₃ nanowire	3.25	UV light	RhB degradation	$K_{\text{obs}} = 4.2 \times 10^{-3} \text{ min}^{-1}$	77
Au/KNbO ₃ nanowire	3.81	UV light	RhB degradation	$K_{\text{obs}} = 1.6 \times 10^{-2} \text{ min}^{-1}$	78
Bi ₂ WO ₆ nanoparticle	2.9	Visible light	RhB degradation	$K_{\text{obs}} = 1.2 \times 10^{-2} \text{ min}^{-1}$	79
Ag/Bi ₂ WO ₆ nanoparticle	2.9	Visible light	RhB degradation	$K_{\text{obs}} = 3.3 \times 10^{-2} \text{ min}^{-1}$	79
Ag/Bi ₄ Ti ₃ O ₁₂	2.9	UV light	RhB degradation	$K_{\text{obs}} = 1.3 \times 10^{-2} \text{ min}^{-1}$	80
Pt/Bi ₄ Ti ₃ O ₁₂	2.9	UV light	RhB degradation	$K_{\text{obs}} = 1.5 \times 10^{-2} \text{ min}^{-1}$	80
Ag/BaBi ₄ Ti ₄ O ₁₅	3.2	Simulated solar light	RhB degradation	Complete within 3.5 h	81
Ag/BaBi ₂ Nb ₂ O ₉	3.2	Simulated solar light	RhB degradation	Complete within 3 h	82
Ag/Ca ₂ Bi ₄ Ti ₅ O ₁₈	3.2	Simulated solar light	RhB degradation	50% degraded within 4 h	83
Ag/RbBiNb ₂ O ₇ nanosheet	3.45	UV-light	RhB degradation	$K_{\text{obs}} = 8.7 \times 10^{-3} \text{ min}^{-1}$	84
Ag/Ba _{0.8} Sr _{0.2} TiO ₃	3.24	Simulated solar light	RhB degradation	$K_{\text{obs}} = 0.18 \text{ min}^{-1}$	67
WC/RbBi ₂ Ti ₂ NbO ₁₀	3.25	Simulated solar light	RhB degradation	$K_{\text{obs}} = 2.3 \times 10^{-2} \text{ min}^{-1}$	This work
Pt/LiNbO ₃ nanowire	-	UV-light	O ₂ evolution	19 $\mu\text{mol g}^{-1} \text{ h}^{-1}$	85
WC/RbBi ₂ Ti ₂ NbO ₁₀	3.25	Simulated solar light	O ₂ evolution	68.5 $\mu\text{mol g}^{-1} \text{ h}^{-1}$	This work

3. Experimental

RbBi₂Ti₂NbO₁₀ and RbBi₂Nb₅O₁₆ powders were synthesized by conventional solid-state reaction. Rb₂CO₃ (99.8%), Bi₂O₃ (99.9%), Nb₂O₅ (99.5%), and TiO₂ (99%) powders were mixed in stoichiometric ratio (with 4 wt% excess of Rb₂CO₃) by planetary ball milling (Fritsch Pulverisette 6) in ethanol using nylon milling jars and ZrO₂ balls with diameter of 10 mm for 4 h at a speed of 180 rpm. The resulting slurry was dried overnight at 80 °C. The dried powders were calcined at 920 °C for 4 h for RbBi₂Ti₂NbO₁₀ and 980 °C for 4 h for RbBi₂Nb₅O₁₆ followed by dry grinding using an agate mortar and pestle.

The calcination and grinding processes were carried out three times. Calcination at high temperature resulted in an agglomeration of powders. In order to reduce agglomerate size and to facilitate subsequent sintering, the calcined powders were re-milled by planetary ball milling in ethanol for 4 h. The resulting powders were pressed into cylindrical discs of 10 mm diameter and ca. 2 mm thickness, with poly (ethylene glycol) (PEG) as a binder, at 200 MPa. The pressed pellets were sintered at 950 °C for RbBi₂Ti₂NbO₁₀ and 1050 °C for RbBi₂Nb₅O₁₆ for 2 h in air. The surfaces of the sintered ceramics were polished and coated with Pt paste for dielectric measurements and Ag paste for ferroelectric and piezoelectric measurements.

For photocatalytic studies, the calcined RbBi₂Ti₂NbO₁₀ and RbBi₂Nb₅O₁₆ powders were milled in ethanol using ZrO₂ milling balls with a diameter of 10 mm in nylon milling jars at a rotation speed of 180 rpm for 24 h, producing sub-micron sized powders. In order to investigate the effect of WC on the photocatalytic performance of RbBi₂Ti₂NbO₁₀, control experiments, which were designed to load the RbBi₂Ti₂NbO₁₀ powder with WC using high energy ball milling, were carried out. The high energy ball milling machine used is a Fritsch Premium line P7 planetary ball milling machine. The difference in the two parallel control experiments is the milling jars, with one experiment using WC jar and the other using ZrO₂ jar for comparison. Same amount of calcined RbBi₂Ti₂NbO₁₀ powder was loaded into milling jar and ball milled at a speed of 600 rpm for 40 min. The milling media is DI water and milling ball was 1 mm ZrO₂ balls. Although attempts were made to use WC milling balls in the WC jar to give better composition, they were not successful due to the limited commercial availability of small diameter WC milling balls (high rotation speed and hard milling balls with small diameter are required for the production of nanopowders via planetary ball milling⁸⁶). Moreover, to optimize the property of WC/RbBi₂Ti₂NbO₁₀ composite powder, the RbBi₂Ti₂NbO₁₀ powder was high energy ball milled in WC jar for different duration (20 min, 120min) and different rotation speed (800 rpm).

Room temperature X-ray powder diffraction measurements were performed on a PANalytical X'Pert Pro diffractometer using Ni filtered Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). Data were collected in flat plate Bragg-Brentano geometry over the 2θ range 5 to 120° in steps



ARTICLE

Journal of Materials Chemistry A

of 0.033°, with a count time of 200 s per step. Structure refinement was carried out by Rietveld analysis using the GSAS suite of programs.⁸⁷ Morphologies and microstructures of the samples were observed using scanning electron microscopy (FEI Inspect-F) and transmission electron microscopy [TEM, FEI Titan Themis (200 kV)], equipped with energy dispersive X-ray spectroscopy (EDX). Piezoresponse Force Microscopy (PFM) (NT-MDT, Ntegra sys-tems, Russia) was used to characterize the domain structure. The specific surface area of the powders was tested using the Brunauer-Emmett-Teller (BET) (Gemini VII) method. The temperature dependencies of dielectric permittivity and loss were measured using an LCR meter (Agilent Technologies Ltd, 4284A, Kobe, Hyogo, Japan) connected to a furnace. The current - electric field (*I-E*) and displacement - electric field (*D-E*) loops were measured at selected temperatures using a ferroelectric hysteresis measurement tester (NPL, UK) at 20 Hz. A triangular voltage waveform was used. For piezoelectric measurements, ceramic samples were immersed in a silicone oil bath and poled under a DC field of 130 kV cm⁻¹ at 100 °C. The piezoelectric coefficient, *d*₃₃, was measured on a quasi-static *d*₃₃ meter (CAS, ZJ-3B) at room temperature.

The band structures of WC and RbBi₂Ti₂NbO₁₀ were measured using valance band X-Ray photoelectron spectroscopy (Nexsa, XPS system). The photocatalytic activity of the samples was evaluated by photodegradation of Rhodamine B (RhB) under simulated sunlight with wavelengths longer than 280 nm and visible light using an AM 1.5 filter. 150 mg catalyst was added to 50 ml aqueous RhB solution (10 ppm). The suspension was stirred continuously in the dark for 0.5 h before it was exposed to a solar simulator (Newport, class ABB). Under irradiation, 2 ml of solution was collected at intervals of 30 min. The ceramic particles were removed from the solution using a centrifuge before testing the change in the concentration of RhB by recording the absorbance at 554 nm using a UV-vis spectrophotometer. Recyclability experiments were carried out to test stability of the WC/ RbBi₂Ti₂NbO₁₀ nanocomposite. Quantity of photocatalyst and RhB solution used were same as pervious photodegradation experiments. After 1.5 hours of first photocatalytic test, the WC/ RbBi₂Ti₂NbO₁₀ nano composite was washed and centrifuged three times for second 1.5-hour cycle. This producer was repeated for a third time before being centrifuged and measuring the light absorbance.

The photocatalytic water splitting was carried out in a custom-made glass batch reactor with a quartz top window. A 30 mg of the photocatalyst was dispersed in 70 mL DI water containing 10 mM AgNO₃ using ultrasonication for 15 min. The reactor was sealed and purged with high purity Argon gas for 1 h to remove the air/dissolved oxygen in solution and headspace. The reactor was irradiated using 300 W Xe lamp (Newport, USA). The reactor was placed in a water bath during irradiation to eliminate the influence of heat. The production of O₂ gas was quantified at regular intervals using a gas chromatography (Varian 430-GC, TCD, argon carrier gas) equipped with a molecular 5A column using Ar as the carrier gas. The apparent quantum yield (AQY) was determined by performing photocatalytic experiments using 420 nm bandpass filter ($\lambda \pm 10$ nm at 10% of peak height, Comar Optics). The AQY was calculated using the following equation:

$$\text{AQY (\%)} = \frac{\alpha \times \text{amount of gas molecules evolved}}{\text{Total number of incident photons}} \times 100\%$$

where $\alpha = 4$ for O₂ evolution.

4. Conclusions

In summary, we have successfully demonstrated the ferroelectric material RbBi₂Ti₂NbO₁₀ for enhancing the photocatalytic RhB degradation compared to the non-ferroelectric RbBi₂Nb₅O₁₆. The observed higher activity is due to the effective charge carrier separation by ferroelectric polarisation induced internal field. Furthermore, the photocatalytic activity of the RbBi₂Ti₂NbO₁₀ is increased significantly by incorporating the WC, which also extended the activity to the visible range. The WC/RbBi₂Ti₂NbO₁₀ nanocomposite shows 6 times higher RhB degradation rate under simulated solar light than the sub-micron sized RbBi₂Ti₂NbO₁₀. It is attributed to the greater specific surface area, and the better charge carrier separation by the WC co-catalyst. The visible light photocatalytic activity of the WC/RbBi₂Ti₂NbO₁₀ nanocomposite is due to the plasmonic hot electron generation from WC. More importantly, the present nanocomposite shows water oxidation activity suggesting that it can be used for solar fuel synthesis application. Our promising results indicate the feasibility to use the earth abundant WC as a competitive co-catalyst to replace expensive noble metals. The novel approach for the incorporation of WC into semiconductor materials is a facile and low-cost way of producing noble-metal-free photocatalyst composites, and the strategy could be readily adapted to other classes of materials for a variety of applications.

Author Contributions

M. Zhang: Conceptualization, Data curation, Formal Analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft;

Y. Wang: Data curation, Formal Analysis, Investigation, Methodology, Writing – review & editing;

J. Liu: Data curation, Formal Analysis, Writing – review & editing;

M. Thangamuthu: Data curation, Formal Analysis, Writing – review & editing;

Y. Yue: Data curation, Formal Analysis, Writing – review & editing;

Z. Yan: Data curation, Formal Analysis, Writing – review & editing;

J. F.: Data curation, Formal Analysis, Writing – review & editing;

D. Zhang: Supervision, Funding acquisition, Writing – review & editing;

H. Zhang: Data curation, Formal Analysis, Supervision, Writing – review & editing;

S. G.: Data curation, Formal Analysis, Writing – review & editing;

M. Titirici: Data curation, Formal Analysis, Writing – review & editing;

I. Abrahams: Formal Analysis, Supervision, Writing – review & editing;

J. Tang: Data curation, Formal Analysis, Writing – review & editing;

Z. Zhang: Data curation, Formal Analysis, Writing – review & editing;



S. Dunn: Conceptualization, Formal Analysis, Investigation, Methodology, Supervision, Writing – review & editing;

H. Yan: Conceptualization, Formal Analysis, Investigation, Methodology, Funding acquisition, Supervision, Writing – review & editing.

Author addresses

^a School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London E1 4NS, UK

^b School of Engineering, London South Bank University
103 Borough Road, London, SE1 0AA, UK

^c School of Environment, Tsinghua University
1 Qinghuayuan, Beijing, 100084, China

^d Department of Chemical Engineering, University College London,
Torrington Place, London, WC1E 7JE, UK

^e School of Biological and Chemical Science, Queen Mary University of London, Mile End Road, London E1 4NS, UK

^f Department of Chemical Engineering, Imperial College London
South Kensington Campus, London SW7 2AZ, UK

^g State Key Laboratory of Powder Metallurgy, Central South University
South Lushan Road, Changsha, 410083, China

^h Department of Materials, Loughborough University
Leicestershire, LE11 3TU, UK

ⁱ School of Chemistry, Cardiff University
Main Building, Park Place, Cardiff, CF10 3AT

^j Division of Solid State Electronics, Department of Engineering Science, Uppsala University
Lagerhyddsvägen 1, Uppsala, Sweden

Conflicts of interest

The authors declare no competing interests.

Acknowledgements

The authors are grateful for financial support from the China Scholarship Council (CSC, 201706370172, 201608060162) and Guangzhou Guangdong Technology Group Co. Ltd. Dr. Yaqiong Wang was partly funded by London South Bank University. The X-ray photoelectron (XPS) data collection was performed at the EPSRC National Facility for XPS ("HarwellXPS"), operated by Cardiff University and UCL, under Contract No. PR16195.

Notes and references

View Article Online

DOI: 10.1039/D1TA04131B

- H. Tong, S. Ouyang, Y. Bi, N. Umezawa, M. Oshikiri and J. Ye, *Adv. Mater.*, 2012, **24**, 229–251.
- C. Y. Toe, C. Tsounis, J. Zhang, H. Masood, D. Gunawan, J. Scott and R. Amal, *Energy Environ. Sci.*, 2021, **14**, 1140–1175.
- S. C. Shit, I. Shown, R. Paul, K. H. Chen, J. Mondal and L. C. Chen, *Nanoscale*, 2020, **12**, 23301–23332.
- J. Zheng, H. Zhou, Y. Zou, R. Wang, Y. Lyu, S. P. Jiang and S. Wang, *Energy Environ. Sci.*, 2019, **12**, 2345–2374.
- C. Shifu, C. Lei, G. Shen and C. Gengyu, *Mater. Chem. Phys.*, 2006, **98**, 116–120.
- R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 2001, **293**, 269–271.
- P. M. Rao, L. Cai, C. Liu, I. S. Cho, C. H. Lee, J. M. Weisse, P. Yang and X. Zheng, *Nano Lett.*, 2014, **14**, 1099–1105.
- Q. Wu, F. Huang, M. Zhao, J. Xu, J. Zhou and Y. Wang, *Nano Energy*, 2016, **24**, 63–71.
- S. Sun, X. Yu, Q. Yang, Z. Yang and S. Liang, *Nanoscale Adv.*, 2019, **1**, 34–63.
- R. Macquart, B. J. Kennedy, T. Kamiyama and F. Izumi, *J. Phys. Condens. Matter.*, 2004, **16**, 5443.
- Z. Xie, X. Liu, W. Wang, X. Wang, C. Liu, Q. Xie, Z. Li and Z. Zhang, *Nano Energy*, 2015, **11**, 400–408.
- Q. Sun, N. Wang, J. Yu and J. C. Yu, *Adv. Mater.*, 2018, **30**, 1–7.
- Z. Zhang, Q. Qian, B. Li and K. J. Chen, *ACS Appl. Mater. Interfaces*, 2018, **10**, 17419–17426.
- L. Cheng, Q. Xiang, Y. Liao and H. Zhang, *Energy Environ. Sci.*, 2018, **11**, 1362–1391.
- X. Li, J. Yu and M. Jaroniec, *Chem. Soc. Rev.*, 2016, **45**, 2603–2636.
- J. Li, L. Cai, J. Shang, Y. Yu and L. Zhang, *Adv. Mater.*, 2016, **28**, 4059–4064.
- H. Lei, M. Wu, Y. Liu, F. Mo, J. Chen, S. Ji, Y. Zou and X. Dong, *Chinese Chem. Lett.*, 2021, **32**, 2317–2321.
- M. Wang, B. Wang, F. Huang and Z. Lin, *Angew. Chemie - Int. Ed.*, 2019, **58**, 7526–7536.
- X. Huang, K. Wang, Y. Wang, B. Wang, L. Zhang, F. Gao, Y. Zhao, W. Feng, S. Zhang and P. Liu, *Appl. Catal. B Environ.*, 2018, **227**, 322–329.
- B. Dai, Y. Yu, Y. Chen, H. Huang, C. Lu, J. Kou, Y. Zhao and Z. Xu, *Adv. Funct. Mater.*, 2019, **29**, 1–9.
- B. Dai, Y. Chen, S. M. Hao, H. Huang, J. Kou, C. Lu, Z. Lin and Z. Xu, *J. Phys. Chem. Lett.*, 2020, **11**, 7407–7416.
- B. Dai, J. Fang, Y. Yu, M. Sun, H. Huang, C. Lu, J. Kou, Y. Zhao and Z. Xu, *Adv. Mater.*, 2020, **32**, 1–9.
- R. Su, Y. Shen, L. Li, D. Zhang, G. Yang, C. Gao and Y. Yang, *Small*, 2015, **11**, 202–207.
- L. Li, P. A. Salvador and G. S. Rohrer, *Nanoscale*, 2014, **6**, 24–42.
- M. R. Morris, S. R. Pendlebury, J. Hong, S. Dunn and J. R. Durrant, *Adv. Mater.*, 2016, **28**, 7123–7128.
- J. Malik, S. Kumar, P. Srivastava, M. Bag and T. K. Mandal, *Mater. Adv.*, 2021, **2**, 4832–4842.
- H. T. Yi, T. Choi, S. G. Choi, Y. S. Oh and S. W. Cheong, *Adv. Mater.*, 2011, **23**, 3403–3407.
- J. L. Giocondi and G. S. Rohrer, *J. Phys. Chem. B*, 2001, **105**, 8275–8277.
- Y. Inoue, K. Sato and K. Sato, *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases*, 1989, **85**, 1765–1774.
- J. Chen, H. Lu, H. J. Liu, Y. H. Chu, S. Dunn, K. Ostrikov, A. Gruverman and N. Valanoor, *Appl. Phys. Lett.*, 2013, **102**, 1–5.
- H. G. Kim, D. W. Hwang and J. S. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 8912–8913.
- L. Wang, W. Wang, M. Shang, S. Sun, W. Yin, J. Ren and J. Zhou, *J. Mater. Chem.*, 2010, **20**, 8405–8410.



ARTICLE

Journal of Materials Chemistry A

- 33 A. Kudo, K. Ueda, H. Kato and I. Mikami, *Catal. Letters*, 1998, **53**, 229–230.
- 34 A. Kudo, K. Omori and H. Kato, *J. Am. Chem. Soc.*, 1999, **121**, 11459–11467.
- 35 W. Zhou, D. A. Jefferson and J. M. Thomas, *J. Solid State Chem.*, 1987, **70**, 129–136.
- 36 C. Chen, H. Ning, S. Lepadatu, M. Cain, H. Yan and M. J. Reece, *J. Mater. Chem. C*, 2015, **3**, 19–22.
- 37 I. M. Arabatzis, T. Stergiopoulos, M. C. Bernard, D. Labou, S. G. Neophytides and P. Falaras, *Appl. Catal. B Environ.*, 2003, **42**, 187–201.
- 38 V. Subramanian, E. Wolf and P. V. Kamat, *J. Phys. Chem. B*, 2001, **105**, 11439–11446.
- 39 C. G. Silva, R. Juárez, T. Marino, R. Molinari and H. García, *J. Am. Chem. Soc.*, 2011, **133**, 595–602.
- 40 J. Yang, D. Wang, H. Han and C. Li, *Acc. Chem. Res.*, 2013, **46**, 1900–1909.
- 41 J. S. Jang, D. J. Ham, N. Lakshminarasimhan, W. Yong Choi and J. S. Lee, *Appl. Catal. A Gen.*, 2008, **346**, 149–154.
- 42 A. Y. Liu, R. M. Wentzcovitch and M. L. Cohen, *Phys. Rev. B*, 1988, **38**, 9483–9489.
- 43 R. B. Levy and M. Boudart, *Science (80-)*, 1973, **181**, 547–549.
- 44 Y. Wang, S. Song, V. Maragou, P. K. Shen and P. Tsiakaras, *Appl. Catal. B Environ.*, 2009, **89**, 223–228.
- 45 K. He, J. Xie, Z. Yang, R. Shen, Y. Fang, S. Ma, X. Chen and X. Li, *Catal. Sci. Technol.*, 2017, **7**, 1193–1202.
- 46 V. G. Pol, S. V. Pol and A. Gedanken, *Eur. J. Inorg. Chem.*, 2009, **2009**, 709–715.
- 47 S. Shanmugam, D. S. Jacob and A. Gedanken, *J. Phys. Chem. B*, 2005, **109**, 19056–19059.
- 48 F. H. Ribeiro, R. A. D. Betta, G. J. Guskey and M. Boudart, *Chem. Mater.*, 1991, **3**, 805–812.
- 49 Y. Oosawa, *J. Chem. Soc. Chem. Commun.*, 1982, **4**, 221–222.
- 50 M. J. Jacinto, P. K. Kiyohara, S. H. Masunaga, R. F. Jardim and L. M. Rossi, *Appl. Catal. A Gen.*, 2008, **338**, 52–57.
- 51 Z. Zhang, Y. Ma, X. Bu, Q. Wu, Z. Hang, Z. Dong and X. Wu, *Sci. Rep.*, 2018, **8**, 1–11.
- 52 A. T. Garcia-Esparza, D. Cha, Y. Ou, J. Kubota, K. Domen and K. Takanabe, *ChemSusChem*, 2013, **6**, 168–181.
- 53 H. G. Kim, T. T. Tran, W. Choi, T. S. You, P. S. Halasyamani and K. M. Ok, *Chem. Mater.*, 2016, **28**, 2424–2432.
- 54 M. K. Ehlert, J. E. Greedan and M. A. Subramanian, *J. Solid State Chem.*, 2016, **28**, 2424.
- 55 H. Yan, H. Zhang, M. J. Reece and X. Dong, *Appl. Phys. Lett.*, 2005, **87**, 1–4.
- 56 J. Wu, A. Mahajan, L. Riekehr, H. Zhang, B. Yang, N. Meng, Z. Zhang and H. Yan, *Nano Energy*, 2018, **50**, 723–732.
- 57 L. Jin, F. Li and S. Zhang, *J. Am. Ceram. Soc.*, 2014, **97**, 1–27.
- 58 H. G. Kim, J. S. Yoo and K. M. Ok, *J. Mater. Chem. C*, 2015, **3**, 5625–5630.
- 59 J. Tauc, R. Grigorovici and A. Vancu, *Phys. status solidi*, 1966, **15**, 627.
- 60 Y. Cui, J. Briscoe and S. Dunn, *Chem. Mater.*, 2013, **25**, 4215–4223.
- 61 Q. Fu, X. Wang, C. Li, Y. Sui, Y. Han, Z. Lv, B. Song and P. Xu, *RSC Adv.*, 2016, **6**, 108883–108887.
- 62 R. Li, F. Zhang, D. Wang, J. Yang, M. Li, J. Zhu, X. Zhou, H. Han and C. Li, *Nat. Commun.*, 2013, **4**, 1432–1437.
- 63 S. C. Abrahams, S. K. Kurtz and P. B. Jamieson, *Phys. Rev.*, 1968, **172**, 551–553.
- 64 G. Viola, K. Boon Chong, M. Eriksson, Z. Shen, J. Zeng, Q. Yin, Y. Kan, P. Wang, H. Ning, H. Zhang, M. E. Fitzpatrick, M. J. Reece and H. Yan, *Appl. Phys. Lett.*, 2013, **103**, 0–4.
- 65 Q. Jiang, H. Ning, Q. Zhang, M. Cain, M. J. Reece and H. Yan, *J. Mater. Chem. C*, 2013, **1**, 5628.
- 66 Z. Zhao, V. Buscaglia, M. Viviani, M. T. Buscaglia, L. Mitoseriu, A. Testino, M. Nygren, M. Johnsson and P. Nanni, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2004, **70**, 1–8.
- 67 Y. Wang, M. Zhang, J. Liu, H. Zhang, F. Li, C. W. Tseng, B. Yang, G. Smith, J. Zhai, Z. Zhang, S. Dunn and H. Yan, *Adv. Energy Mater.*, 2020, **10**, 6–11.
- 68 K. Page, J. Li, R. Savinelli, H. N. Szumila, J. Zhang, J. K. Stalick, T. Proffen, S. L. Scott and R. Seshadri, *Solid State Sci.*, 2008, **10**, 1499–1510.
- 69 B. Bondars, G. Heidemane, J. Grabis, K. Laschke, H. Boysen, J. Schneider and F. Frey, *J. Mater. Sci.*, 1995, **30**, 1621–1625.
- 70 A. Liibert and B. Leibold, 1992, **8**, 253–256.
- 71 L. H. Bennett, J. R. Cuthill, A. J. Mcalister, N. E. Erickson and R. E. Watson, *Science*, 1974, **184**, 563–565.
- 72 I. Fujita, P. Edalati, Q. Wang, M. Watanabe, M. Arita, S. Munetoh, T. Ishihara and K. Edalati, *Scr. Mater.*, 2020, **187**, 366–370.
- 73 W. Huang, H. Meng, Y. Gao, J. Wang, C. Yang, D. Liu, J. Liu, C. Guo, B. Yang and W. Cao, *J. Mater. Chem. A*, 2019, **7**, 18538–18546.
- 74 M. Thangamuthu, C. Santschi and O. J. F. Martin, in *Faraday Discussions*, 2019, **214**, 339.
- 75 M. Wang, M. Ye, J. Iocozzia, C. Lin and Z. Lin, *Adv. Sci.*, 2016, **3**, 1600024.
- 76 S. Linic, P. Christopher and D. B. Ingram, *Nat. Mater.*, 2011, **10**, 911–921.
- 77 T. Zhang, W. Lei, P. Liu, J. A. Rodriguez, J. Yu, Y. Qi, G. Liu and M. Liu, *Chem. Sci.*, 2015, **6**, 4118.
- 78 J. Lan, X. Zhou, G. Liu, J. Yu, J. Zhang, L. Zhi and G. Nie, *Nanoscale*, 2011, **3**, 5161.
- 79 A. Phuruangrat, A. Maneechote, P. Dumrongrojthanath, N. Ekthammathat, S. Thongtem and T. Thongtem, *Mater. Lett.*, 2015, **159**, 289–292.
- 80 G. Yuan, G. Zhang, K. Li, F. Li, Y. Cao, J. He, Z. Huang, Q. Jia, S. Zhang and H. Zhang, *Nanomaterials*, 2020, **10**, 1–15.
- 81 J. D. Bobić, M. M. Vijatović, S. Greičius, J. Banyš and B. D. Stojanović, *J. Alloys Compd.*, 2010, 499, 221.
- 82 W. Qi, Y. Wang, J. Wu, Z. Hu, C. Jia, G. Viola, H. Zhang and H. Yan, *J. Am. Ceram. Soc.*, 2020, **103**, 28.
- 83 Y. Wang, M. Zhang, J. Wu, Z. Hu, H. Zhang and H. Yan, *J. Am. Ceram. Soc.*, 2021, **104**, 322–328.
- 84 W. Xiong, H. Porwal, H. Luo, V. Araullo-Peters, J. Feng, M. M. Titirici, M. J. Reece and J. Briscoe, *J. Mater. Chem. A*, 2020, **8**, 6564–6568.
- 85 K. Saito, K. Koga and A. Kudo, *Dalt. Trans.*, 2011, **40**, 3909.
- 86 C. Suryanarayana, *Prog. Mater. Sci.*, 2001, **46**, 1–184.
- 87 A. C. Larson and R. B. Von Dreele, *LAUR*, 1994, **86**, 748.

