PAPER

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View Journal | View Issue Cite this: *J. Mater. Chem. A*, 2019, 7, 17053Porous NiTiO₃/TiO₂ nanostructures for photocatalytic hydrogen evolution†Congcong Xing,^a Yongpeng Liu,^c Yu Zhang,^a Junfeng Liu,^a Ting Zhang,^d Pengyi Tang,^d Jordi Arbiol,^{de} Lluís Soler,^b Kevin Sivula,^c Néstor Guijarro,^c Xiang Wang,^a Junshan Li,^a Ruifeng Du,^a Yong Zuo,^a Andreu Cabot^{ae} and Jordi Llorca^{id}*^b

We present a strategy to produce porous NiTiO₃/TiO₂ nanostructures with excellent photocatalytic activity toward hydrogen generation. In a first step, nickel-doped TiO₂ needle bundles were synthesized by a hydrothermal procedure. Through the sintering in air of these nanostructures, porous NiTiO₃/TiO₂ heterostructured rods were obtained. Alternatively, the annealing in argon of the nickel-doped TiO₂ needle bundles resulted in NiO_x/TiO₂ elongated nanostructures. Porous NiTiO₃/TiO₂ structures were tested for hydrogen evolution in the presence of ethanol. Such porous heterostructures exhibited superior photocatalytic activity toward hydrogen generation, with hydrogen production rates up to 11.5 mmol h⁻¹ g⁻¹ at room temperature. This excellent performance is related here to the optoelectronic properties and geometric parameters of the material.

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Introduction

Since the first reports on photocatalytic water splitting, TiO₂ has been considered one of the most attractive photocatalysts.^{1–3} Among others, its interest resides on its excellent optoelectronic properties, high resistance to photocorrosion, natural abundance, low-cost and safety.^{4–6} However, TiO₂ optimization for solar photocatalysis requires maximizing its surface area.⁷ It also requires the introduction of dopants, additional phases or structural defects that allow this wide band gap semiconductor to take advantage of a larger spectral range of the solar radiation.^{8–13}

To maximize surface area, the production of hollow and porous TiO₂ nanostructures has recently drawn growing attention.^{14–16} Besides, Ti-based mixed oxides and particularly perovskite titanates MTiO₃ (M = Ba, Sr, Ca and Ni) have been pointed out as a new exciting class of photoactive materials.^{17–19} Additionally heterostructured oxides, such as SrTiO₃/TiO₂ and

NiTiO₃/TiO₂ have been demonstrated to promote charge-separation, hole-transportation and visible-light-driven photocatalytic performance over TiO₂.^{20–23}

To cite some examples in this direction, Wu *et al.* demonstrated an enhancement of the charge separation and hole transportation in TiO₂/SrTiO₃ nano-heterostructures to be at the origin of an improved photoelectrochemical performance.²⁰ When combined with TiO₂, several other oxides and chalcogenides have demonstrated to be able to enhance its photocatalytic activities.^{23–26} In particular, Ni-based materials have been proven especially effective to improve TiO₂ photocatalytic activity. Rawool *et al.* demonstrated pn heterojunctions in NiO/TiO₂ produced by sol gel to promote photocatalytic H₂ generation.²⁷ Wei *et al.* showed Ni(HCO₃)₂ produced through a hydrothermal method to be an excellent co-catalyst to boost photocatalytic hydrogen evolution of mesoporous TiO₂.²⁸ Enhanced photocatalytic H₂ production was also reported with the introduction of Ni(OH)₂ clusters to commercially available TiO₂ (ref. 29) and in Ni/NiO/N-TiO_{2-x} heterostructures produced from a NH₃ plasma treatment of sol-gel derived Ti-Ni precursors.³⁰ Besides, Qu *et al.* prepared porous NiTiO₃ nano-rods with enhanced photocatalytic performance toward the degradation of nitrobenzene.²¹

While excellent results have been obtained to date, the synthesis of such mixed oxides and oxide heterostructures in the form of high surface area materials remains as an extremely challenging endeavor, what has limited further advances in this direction.^{31–33}

To overcome this limitation, we present here a simple, high throughput and scalable hydrothermal-based strategy to

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produce porous NiTiO₃/TiO₂ heterostructures. This strategy is based on the synthesis of needle bundles of Ni-doped TiO₂ (TiO₂ : Ni) and their posterior sintering in air to produce highly crystalline NiTiO₃/TiO₂ heterostructures with a significant level of porosity reminiscent of the large density of interfaces within the needle bundles. We further demonstrate here that these preliminarily optimized materials are excellent photocatalysts for hydrogen generation. We choose hydrogen generation as test reaction owing to the excellent performances of Ni-based photocatalysts in this direction.^{27–30,34–36}

Experimental

Chemicals

Titanium(IV) isopropoxide (97%, Sigma-Aldrich), nickel(II) nitrate hexahydrate (98%, Fluka), ethanol (96%, PanReac AppliChem), hexadecylamine (HDA, 90%, Sigma-Aldrich), potassium chloride (Sigma-Aldrich), and ammonium hydroxide solution (28–30%, Sigma-Aldrich) were used without further purification.

Synthesis of NiTiO₃/TiO₂ heterostructures

A solution of KCl (1.9 mg) in MilliQ water (0.99 g) was added dropwise to a HDA (0.45 g) solution in ethanol (20 mL) under stirring at room temperature. To this solution, a proper amount of Ni(NO₃)₂·6H₂O was added (0 mg, 22.5 mg, 45 mg, 90 mg, and 225 mg to reach 0, 0.5, 1, 2, and 5 mol% concentrations, respectively). Then, 4.7 mL of titanium(IV) isopropoxide was added. After stirring for 1 h at room temperature, we kept the solution 16 h without stirring, and afterward the solution was washed with ethanol three times using centrifugation to recover the product. This product was then dissolved in a solution containing 20 mL of MilliQ water, 40 mL of ethanol and 2.2 mL of ammonium hydroxide. This solution was stirred for 1 h and it was subsequently transferred to a 100 mL Teflon-lined hydrothermal reactor. The reactor was heated at 170 °C and maintained at this temperature for 17 h. Afterward, it was cooled down to room temperature and the product was washed three times with ethanol. Dried materials were finally annealed in a tube furnace under synthetic air flow at 650 °C for 8 h.

Characterization

X-ray diffraction analyses (XRD, 2 θ : 20–80°; scanning rate: 5° min^{−1}) were carried out on a Bruker AXS D8 Advance X-ray diffractometer with Ni-filtered Cu-K α radiation (λ = 0.15406 Å), operating at 40 mA and 40 kV. The morphology and size of the particles were characterized by transmission electron microscopy (TEM, ZEISS LIBRA 120), working at 120 kV and field-emission scanning electron microscopy (SEM, Zeiss Auriga) operating at 5.0 kV. High resolution transmission electron microscopy (HRTEM) images and scanning transmission electron microscopy (STEM) studies were conducted on a FEI Tecnai F20 field emission gun microscope operated at 200 kV with a point-to-point resolution of 0.19 nm, which was equipped with high angle annular dark field (HAADF) and a Gatan Quantum electron energy loss spectroscopy (EELS) detectors. Elemental analysis was carried out using an Oxford

energy dispersive X-ray spectrometer (EDX) combined with the Zeiss Auriga SEM working at 20.0 kV. X-ray photoelectron spectroscopy (XPS) was examined on a SPECS system equipped with a Phoibos 150 MCD-9 detector, working at 150 mW with an Al anode XR50 source. Fourier transform infrared spectroscopy (FTIR, Alpha Bruker) was carried with a platinum attenuated total reflectance single reflection module. Nitrogen sorption measurements were collected on a MicroActive 3.00 at 77.3 K.

Photocatalytic hydrogen evolution tests

In a typical experiment, a cellulose paper impregnated with 2.0 mg of the photocatalyst was placed inside a photocatalytic reactor that was equipped with a UV LED (Fig. S1†). An Ar gas stream was saturated with a water : ethanol vapour mixture (90 : 10 ratio on a molar basis) by bubbling dry Ar gas at a flow rate of 20 mL min^{−1} through a saturator (Dreschel bottle) containing a liquid mixture of 87.5 g of H₂O and 9.92 g of ethanol.^{37,38} This Ar stream was introduced into the photoreactor and passed through the cellulose paper loaded with the photocatalyst. The photoreactor effluent was monitored on-line every 4 min using gas chromatography (GC) (Agilent 3000A MicroGC) using three columns: MS 5 Å, Plot U and Stabilwax. The LED UV light source (from SACOPA, S.A.U.) consisted of four LEDs at 365 ± 5 nm and a synthetic quartz glass cylindrical lens that transmitted the light to the photocatalyst. Light irradiation was measured directly with a UV-A radiation monitor from Solar Light Co. and was 79.1 ± 0.5 mW cm^{−2} at the sample position. At the beginning of each experiment, the UV light was off, and the reaction system was purged by entering 20 mL min^{−1} of saturated Ar gas with the water–ethanol vapour mixture, to remove oxygen in the line. After 30 min, the UV light was turned on and we monitored all photoreaction products during ca. 20–40 min by GC. Control experiments were carried out with only the cellulose paper support and no photoactivity was measured.

Electrochemical impedance spectroscopy (EIS)

EIS analyses were performed using a Bio-Logic SP-300 potentiostat in a 3-electrode configuration employing a Cappuccino-type PEC cell, wherein the photocatalyst was deposited as a thin film in a conductive substrate (FTO) to be used as working electrode, whereas a Ag/AgCl electrode and a Pt wired were used as a reference and a counter electrode, respectively. The applied potential on the working electrode was sinusoidally modulated with an amplitude of 25 mV using frequencies ranging from 100 kHz to 50 mHz. The analysis of the impedance response was undertaken using ZView (Scribner Associates).

The apparent quantum yield (AQY) was estimated using the following equation:

$$\text{AQY} = \frac{2n_{\text{H}_2}}{n_p} 100 = \frac{nN_A}{E_T/E_p} 100$$

where n_{H_2} is the number of molecules of H₂ generated and n_p is the number of incident photons reaching the catalyst. The number of incident photons can be calculated by $n_p = E_T/E_p$, where E_T is the total energy reaching the catalyst and E_p is the

energy of a photon. $E_T = PSt$, where P (W m^{-2}) is the power density of the incident monochromatic light, S (m^2) is the irradiation area and t (s) is the duration of the incident light exposure. $E_p = hc/\lambda$, where h is the Planck's constant, c the speed of light and λ (m) is the wavelength of the incident monochromatic light. The number of hydrogen molecules can be calculated as $n_{\text{H}_2} = nN_A$, where n are H_2 moles evolved during the time of light exposure (t), and N_A is the Avogadro constant.^{39–41} In our experimental conditions, the wavelength of the incident light was $\lambda = 365$ nm, the power density of the incident light at the paper surface was $P = 79.1$ mW cm^{-2} and the irradiation area was $S = 2.27$ cm^2 .

Results and discussion

Characterization of the photocatalysts

Ni-doped TiO_2 ($\text{TiO}_2 : \text{Ni}$) nanostructures were produced from the hydrothermal decomposition of titanium(IV) isopropoxide in the presence of proper amounts of nickel(II) nitrate hexahydrate, HDA as a shape-directing agent and KCl to control the ionic strength of the solution (see experimental section for details and Fig. S2† for SEM images).⁴² As shown by TEM characterization, the size and shape of the nanostructures obtained from this hydrothermal reaction strongly depended on the amount of Ni introduced (Fig. S3†). In the absence of Ni, nanoparticles with an average size around 50 nm and mostly irregular shapes, although some elongated, were obtained. When introducing increasingly higher amounts of Ni, more and more elongated nanostructures were obtained. In the presence of a nominal 5% of Ni, most structures resembled nanorods with a length in the range from 100 nm to 200 nm and thickness of 30–60 nm (Fig. 1b, 2b and S3†). A closer look to these nanorods allowed discerning that they consisted of needle-shaped nanostructures assembled in bundles (Fig. 2b).

XRD analyses showed the crystal structure of these needle bundles to match that of anatase TiO_2 . Diffraction peaks shifted to lower angles with the introduction of increasing amounts of Ni (Fig. 1a), which pointed at the presence of Ni ions within the TiO_2 anatase lattice. Besides anatase TiO_2 , no additional crystallographic phase could be discerned from XRD patterns.

EDX analysis showed the Ni atomic concentration to be systematically higher than the nominal amount introduced, pointing at a higher yield of reaction of the nickel(II) nitrate than

Fig. 2 (a) XRD patterns of $\text{NiTiO}_3/\text{TiO}_2$ (0, 1%, 2%, 5%) nanopowders obtained by annealing in air. (b) TEM micrograph of $\text{TiO}_2 : \text{Ni}$ (5%) needle bundles. (c and d) TEM micrographs of $\text{NiTiO}_3/\text{TiO}_2$ (5%) porous structures obtained after annealing in air. (e) HAADF micrograph of a $\text{NiTiO}_3/\text{TiO}_2$ (5%) rod and corresponding EELS elemental maps for Ti, O, Ni and Ti–O–Ni.

Fig. 1 (a) XRD patterns of TiO_2 and $\text{TiO}_2 : \text{Ni}$ (1%, 2%, 5%) nanopowders. (b) TEM image of $\text{TiO}_2 : \text{Ni}$ (5%) nanopowder.

the titanium(IV) isopropoxide under the hydrothermal conditions used for the synthesis (Table S1†).

$\text{TiO}_2 : \text{Ni}$ nanopowders were annealed under synthetic air flow at 650 °C during 8 h. Upon this thermal treatment, the color of the material changed from the original blueish, characterizing $\text{TiO}_2 : \text{Ni}$ samples, to yellow (Fig. S4†). TEM micrographs of the annealed powder showed it to still consist on elongated nanostructures. However, on the contrary to the starting nanoneedle bundles, the annealed nanostructures displayed a crystallographic continuity (Fig. 2c) and presented numerous holes all over them (Fig. 2d). In contrast, undoped TiO_2 nanopowders annealed in the same conditions did not present such porous structure (Fig. S5†).

XRD analysis showed that the porous nanostructures obtained after the annealing of $\text{TiO}_2 : \text{Ni}$ in air consisted mainly on anatase TiO_2 (Fig. 2a). With the annealing process, the shift of the XRD peaks observed in the precursor $\text{TiO}_2 : \text{Ni}$ material disappeared, pointing at the outward diffusion of the Ni ions from the TiO_2 lattice. Besides the anatase phase, XRD patterns displayed the presence of a second crystal structure, which was

identified as NiTiO_3 .⁴³ The relative intensity of the peaks associated to this NiTiO_3 phase clearly increased with the nominal amount of Ni (Fig. 2a). Rietveld analysis showed the relative amount of the NiTiO_3 phase to correspond to a 4.6 mol%, 9.0 mol% and 15 mol%, for samples obtained from nominal Ni concentration of 1 mol%, 2 mol% and 5 mol%, respectively (Fig. S6 and Table S1†).⁴⁴ Within its experimental error, EDX analysis showed the Ni molar concentrations to be maintained after the annealing process (Table S1†).

HRTEM analysis confirmed the annealed material to contain mostly anatase TiO_2 (Fig. S7†).⁴⁵ EELS elemental maps of the annealed materials showed Ni, Ti and O to be evenly distributed throughout the nanostructures (Fig. 2e). The lack of HRTEM evidences of the presence of large NiTiO_3 crystal domains and the homogeneous distribution of Ni throughout the material observed by EELS and EDX analyses pointed at the growth of small NiTiO_3 domains as a discontinuous shell on the surface of the porous TiO_2 nanostructures.⁴⁶

XPS analyses of the annealed samples displayed only one chemical state for Ti, assigned to Ti^{4+} , and one for Ni, assigned to Ni^{2+} , consistently with XRD, HRTEM, EELS and EDX characterization (Fig. S8 and S9†).⁴⁷ XPS analyses also showed the amount of Ni to be almost a twofold of that measured by EDX, pointing at its preferential surface location (Table S1†).

When Ni-doped materials were annealed under Ar instead of air, the sample color changed from blue to black, instead of yellow (Fig. S4†), but the elongated geometry of the initial structures was conserved. In contrast to the annealing in air, the nanostructuring of the original nanoneedle bundles partially persisted after annealing in argon. The particles annealed in argon did not show full crystallographic continuity and contained a lower density of holes compared with the material obtained from the annealing in air (Fig. S10†). XRD patterns of materials annealed under argon showed anatase TiO_2 as the main phase, with no evidence of the presence of NiTiO_3 , but with a small XRD peak at $2\theta = 28.6^\circ$ that we associated to a NiO_x phase (Fig. S11†). The black nanopowder annealed under argon showed certain magnetization, which further pointed toward the formation of a NiO_x phase (Fig. S4†).⁴⁸

We hypothesize that the porous geometry of the $\text{NiTiO}_3/\text{TiO}_2$ structures obtained after annealing $\text{TiO}_2 : \text{Ni}$ in air was created by the sintering of the nanoneedle bundles. The large density of interfaces of the initial bundles translated in the formation of a large density of holes on the sintered material, which could be aided by the simultaneous outward diffusion of Ni ions to form NiTiO_3 domains. On the contrary, annealing in argon did not allow a similar level of sintering of the nanostructures, which was promoted in air by the ubiquitous presence of oxygen. Thus, the material obtained from the annealing process in argon maintained smaller crystal domains and presented a less porous structure. The BET specific surface areas of $\text{NiTiO}_3/\text{TiO}_2$ and $\text{NiO}_x/\text{TiO}_2$ were 40.8 and 28.0 $\text{m}^2 \text{g}^{-1}$, respectively, supporting the higher porosity of the former (Fig. S12†). With the annealing process in air, pure TiO_2 nanopowders did not result in porous materials as those obtained from $\text{TiO}_2 : \text{Ni}$ because they did not present a proper initial nanostructuring.

Photogeneration of hydrogen

To test their photocatalytic properties toward hydrogen evolution, the annealed materials were supported on a conventional filter paper and placed on a reactor containing a UV LED light source. An Ar flow saturated with a water-ethanol vapor mixture was flowed through this reactor. Exhaust gases were analyzed using GC, being acetaldehyde and hydrogen the main reaction products (Fig. S1†).

Fig. 3a shows the accumulated hydrogen production during a 32 min reaction for $\text{NiTiO}_3/\text{TiO}_2$ hetero-nanostructures having different nominal Ni concentrations. Data for bare TiO_2 and pure NiTiO_3 (Fig. S13 and S14†) prepared following the same procedure (see experimental section for details†) were also plotted in Fig. 3a as reference. $\text{NiTiO}_3/\text{TiO}_2$ hetero-nanostructures with a nominal 1% of Ni systematically provided the highest hydrogen production rates, with values up to 11.5 $\text{mmol h}^{-1} \text{g}^{-1}$ and an AQY of 11.6% at 365 nm, well above those previously reported for other Ni-Ti-O systems (Table S2†). The hydrogen production rate of $\text{NiTiO}_3/\text{TiO}_2$ (1%) was almost a fourfold higher than that of bare TiO_2 and 60 times larger than that of pure NiTiO_3 (Fig. 3b, S15†). The presence of larger amounts of Ni did not improve the evolution rate with respect to $\text{NiTiO}_3/\text{TiO}_2$ (1%). We associate this experimental evidence with the blocking of the TiO_2 surface active sites when too large amounts of NiTiO_3 were grown on the TiO_2 surface. SEM characterization showed the morphology of the $\text{NiTiO}_3/\text{TiO}_2$ hetero-nanostructures to remain unmodified after the catalytic test (Fig. 3c).

We believe the enhancement of the photocatalytic properties of TiO_2 with the NiTiO_3 introduction to be related with an improvement of three fundamental parameters: (i) surface area; (ii) light absorption; and (iii) charge separation. We estimate that the introduction of Ni had associated a factor 3 increase of

Fig. 3 (a) H_2 production of TiO_2 , $\text{NiTiO}_3/\text{TiO}_2$ (1%, 2%, 5%), $\text{NiO}_x/\text{TiO}_2$ (1%) and NiTiO_3 . (b) H_2 production rate of TiO_2 , $\text{NiTiO}_3/\text{TiO}_2$ (1%, 2%, 5%), $\text{NiO}_x/\text{TiO}_2$ (1%) and NiTiO_3 . (c) Optical and SEM images of $\text{NiTiO}_3/\text{TiO}_2$ (5%) before and after 30 min photocatalytic test.

the surface area with respect to pure TiO_2 through the formation of the porous $\text{NiTiO}_3/\text{TiO}_2$ hetero-nanostructures during the annealing process. Additionally, the presence of NiTiO_3 provided a higher light absorption coefficient at the used excitation wavelength. In case of using solar radiation, the presence of NiTiO_3 would provide an even larger improvement with respect to pure TiO_2 , as it would allow absorbing a larger portion of the solar spectra due to its smaller band gap (Fig. S16†). Besides, the proper band alignment of TiO_2 and NiTiO_3 allowed an efficient spatial charge separation that significantly reduced recombination of the photogenerated charge carriers before reaction.

To gain additional insight into the band structure alignment and the interfacial charge carrier dynamics at the $\text{NiTiO}_3/\text{TiO}_2$ heterostructure, EIS analyses were carried out on TiO_2 , $\text{NiTiO}_3/\text{TiO}_2$ (1%) and NiTiO_3 thin films in dark conditions. Representative impedance responses in the form of Nyquist plot for TiO_2 and $\text{NiTiO}_3/\text{TiO}_2$ (1%) are displayed in Fig. 4a. Responses typically feature a single semicircle. Interestingly, the size of the semicircle obtained for the TiO_2 sample was reduced with the incorporation of Ni. A more quantitative description of the EIS data can be provided by modelling the electrical response with an equivalent circuit, such as a Randles circuit (Fig. 4a inset), which has been previously reported to successfully describe nanostructured TiO_2 and other photocatalysts.^{22,50,54} This circuit consists of a resistor R_s in series with a bulk capacitance C_{bulk} , attributed to the space charge region, and a second resistor $R_{\text{ct,bulk}}$ that represents the charge transport resistance, both in parallel. At a first glance, the decrease in the size of the semicircle with the incorporation of Ni in TiO_2 suggests the reduction in the charge transport resistance,^{49,50} which is further confirmed with the decrease of $R_{\text{ct,bulk}}$ from 15.4 kΩ to 9.8 kΩ pointing out the amelioration of the charge transport process. In addition, the electron lifetime τ_n can be calculated as the inverse of the angular frequency at the maximum of the Nyquist plot ($2\pi f_{\text{max}}$),²² highlighted in Fig. 4a. Results reveal that τ_n increases from 4.5 ms to 6.6 ms when the heterostructure is formed. In general, τ_n is considered a metric of electron recombination, *i.e.*, the longer the value the lesser the charge recombination. The lengthening of τ_n when TiO_2 is interfaced with NiTiO_3 underpins the effective charge carrier separation

across the n-n heterojunction and thus the enhanced photocatalytic activity of the composite with respect to TiO_2 . Similar behavior was reported by Wei and co-workers on $\text{NiTiO}_3/\text{TiO}_2$ composite for inorganic sensitized solar cells.²²

In an attempt to further interrogate the energy band positions, Mott-Schottky (M-S) plots were constructed from C_{bulk} values extracted from EIS measurements on TiO_2 and NiTiO_3 and further analyzed using the M-S equation:

$$C_{\text{bulk}}^{-2} = \frac{2}{qA^2\epsilon\epsilon_0N_D} \left(V - V_{\text{fb}} - \frac{kT}{q} \right)$$

where q is elementary charge, A is taken as the geometric area (assuming a low surface roughness spin-coated thin film), ϵ is relative permittivity (taken to be 55 and 15 for TiO_2 (ref. 51) and NiTiO_3 ,⁵² respectively), ϵ_0 is vacuum permittivity, N_D is donor density, V is applied potential, V_{fb} is flat band potential, k is Boltzmann constant, and T is absolute temperature. The positive slope in the linear region (dashed line in Fig. 4b) unambiguously confirmed the n-type character of both NiTiO_3 and TiO_2 , whereas V_{fb} values of -0.186 V and -0.276 V vs. RHE were obtained for TiO_2 and NiTiO_3 , respectively. Likewise, N_D shows values of $1.1 \times 10^{18} \text{ cm}^{-3}$ for TiO_2 and $5.5 \times 10^{17} \text{ cm}^{-3}$ for NiTiO_3 . Similar values have also been reported by Thimsen *et al.* on nanocrystalline anatase TiO_2 ,⁵¹ and by Trari and co-workers on nanostructured NiTiO_3 .⁵³ We note that the depletion width is estimated to be 20 nm in the linear region of M-S plot for both TiO_2 and NiTiO_3 so that M-S analysis can be reasonably applied in the case of not fully depleted feature.⁵⁴ Considering the density-of-state effective mass for electrons m_{de} for nanocrystalline anatase TiO_2 is $9.1 \times 10^{-30} \text{ kg}$,⁵¹ and for nanostructured NiTiO_3 is $1.9 \times 10^{-30} \text{ kg}$,⁵⁵ the effective density of states in the conduction band N_C is:^{54,56}

$$N_C \equiv 2 \left(\frac{2\pi m_{\text{de}} kT}{h^2} \right)^{\frac{3}{2}}$$

where h is Planck constant. N_C is estimated to be $7.7 \times 10^{20} \text{ cm}^{-3}$ for TiO_2 , and $7.5 \times 10^{19} \text{ cm}^{-3}$ for NiTiO_3 . Since the ratio between N_D and N_C is in all cases less than 0.05, both TiO_2 and NiTiO_3 could be treated as nondegenerate semiconductors, and therefore, the Boltzmann statistics can be applied.^{54,56}

Fig. 4 (a) Representative impedance response of TiO_2 (black sphere) and $\text{NiTiO}_3/\text{TiO}_2$ (1%) (orange sphere) with the corresponding fit (solid lines) in Nyquist plot. The maximum point of the Nyquist plot is highlighted (hollow), and the equivalent circuit used is included as an inset. (b) Mott-Schottky plot of TiO_2 (black sphere) and NiTiO_3 (red sphere) including a linear fit (dashed lines). (c) Schematics of the electronic band structures of a Z-scheme $\text{NiTiO}_3/\text{TiO}_2$ heterojunction.

$$E_{\text{CB}} - E_{\text{F}} = kT \ln(N_{\text{C}}/N_{\text{D}})$$

where E_{CB} is the bottom of the conduction band (CB) and E_{F} is the Fermi level position. E_{CB} is found to be around 168 mV and 126 mV above V_{fb} for TiO_2 and NiTiO_3 , respectively.

Based on the aforementioned results, Fig. 4c displays a scheme of the electronic band structures. The relative band alignment between NiTiO_3 and TiO_2 allows the formation of a direct Z-scheme heterojunction. In such Ni- TiO_2 system, while photogenerated electrons in the CB of TiO_2 recombine with photogenerated holes in the valance band (VB) of NiTiO_3 , photogenerated electrons with strong reduction ability remain in the CB of NiTiO_3 ready to reduce water into hydrogen and photogenerated holes with strong oxidation abilities in the VB of TiO_2 could drive ethanol dehydrogenation to acetaldehyde and hydrogen. Therefore, the formation of a direct Z-scheme $\text{NiTiO}_3/\text{TiO}_2$ heterojunction can promote photogenerated carriers with strong redox abilities to drive photocatalytic reaction.⁵⁷ As a result, $\text{NiTiO}_3/\text{TiO}_2$ composites at optimal NiTiO_3 loading condition shows a significantly increased photocatalytic activity. Similar Z-scheme photocatalytic systems have also been reported such as TiO_2/Rh ,⁵⁸ TiO_2/CdS ,⁵⁹ and $\text{CdS}/\text{cobalt-benzimidazole}$.⁶⁰

Conclusions

Porous $\text{NiTiO}_3/\text{TiO}_2$ heterostructures were prepared from the annealing in air of TiO_2 : Ni nanoneedle bundles obtained from a hydrothermal route. Pores were generated during the sintering of the nanostructured bundles due to the presence of a large density of interfaces on the precursor material. $\text{NiTiO}_3/\text{TiO}_2$ heterostructures were used for photocatalytic hydrogen generation from ethanol–water solutions at room temperature. $\text{NiTiO}_3/\text{TiO}_2$ hetero-structures provided unprecedented H_2 production rates up to $11.5 \text{ mmol h}^{-1} \text{ g}^{-1}$ and an AQY of 11.6%. This excellent performance was associated to the improvement of three parameters, surface area, light absorption and charge separation. We estimated a factor 3 increase of the surface area with the introduction of Ni through the formation of porous $\text{NiTiO}_3/\text{TiO}_2$ hetero-nanostructures during the annealing in air. Additionally, the presence of NiTiO_3 , with a lower band gap energy, provided a higher light absorption coefficient at the excitation wavelength. Besides, TiO_2 and NiTiO_3 presented a proper band alignment that allows an efficient spatial charge separation of the photogenerated charge carriers before reaction, as confirmed by EIS analysis.

Author contributions

The manuscript was prepared through the contribution of all authors. A. C. and J. L. guided the project and supervised the work. C. C. X., Y. P. L., Y. Z., Y. P. L., J. L., and A. C. conceived and prepared the manuscript. L. S. and J. L. designed the hydrogen production experiments. C. C. X., Y. Z., and J. F. L. produced the samples. Y. P. L., K. S., N. G., and Y. Z. performed the electrochemical measurements and analyzed the results. J. S. L. and R. F. D. performed XRD measurements and discussed

these results. T. Z., P.-Y. T., and J. A. performed HRTEM and STEM-EELS and discussed these results. X. W., performed BET results. L. S. and J. L. performed XPS measurements and discussed these results. The manuscript was corrected and improved by all authors.

Conflicts of interest

There are no conflicts of interest to declare.

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