

PAPER



Cite this: *J. Mater. Chem. A*, 2017, 5, 10442

Charge separation in a nanostep structured perovskite-type photocatalyst induced by successive surface heterojunctions†

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Formation of surface heterojunctions in photocatalysts through tailoring the exposed crystal facets is an efficient strategy to boost charge separation. In this work, successive surface heterojunctions with large space-charge separation were achieved in a nanostep structured $\text{La}_2\text{Ti}_2\text{O}_7$ (LTO NSP) single crystal exposed periodically with (010) and (012) facets. The three-dimensional (3D) nanosteps were found to enhance the photocatalytic hydrogen generation performance 35 and 74 times, compared with LTO nanosheets and nanoparticles with the same surface area, respectively. The ultrahigh superficial charge accumulation in LTO NSP verified by surface photovoltage (SPV) measurements suggested the efficient migration of photogenerated charge carriers to the surface. Femtosecond time-resolved diffuse reflectance (TDR) spectroscopy provided direct evidence that the electrons generated from the excited sites of LTO NSP were effectively delivered to the high energy (012) facets and temporarily stored there for further reduction reactions, originating from the successive (010) and (012) surface heterojunctions.

Received 17th March 2017

Accepted 23rd April 2017

DOI: 10.1039/c7ta02379k

rsc.li/materials-a

Introduction

Photocatalysis that directly converts solar light into chemical energy has attracted significant attention for effective utilization of solar energy in water splitting for hydrogen (H_2) production.^{1–4} The recombination of photogenerated electrons and holes is one of the most important features limiting the efficiency of photocatalytic water splitting.^{5–7} Recently, crystal facet engineering of semiconductor-based photocatalysts has been demonstrated to be effective in separating photogenerated carriers where electrons and holes may be driven to different crystal facets.^{8–11} For example, Li *et al.* found that much higher photocatalytic activities were observed in BiVO_4 crystals with reduction and oxidation co-catalysts selectively deposited on the {010} and {110} facets than those with randomly deposited co-catalysts.¹² Using fluorescence measurements with single-molecule redox sensors, Majima's group showed that in the TiO_2 single crystal, reaction sites for probe molecules are selectively located on the {101} facets rather than on the {001} facets with higher surface energy.¹³ Besides having different

adsorption capacities for electrons and holes, the adjacent crystal facets often form a surface heterojunction, which enables fast separation of photo-generated electrons and holes and thus enhances the photocatalytic performance. Yu *et al.* reported that the ratio of the exposed {101} and {001} facets greatly affected the photocatalytic activity of anatase TiO_2 owing to the formation of a surface heterojunction within a single TiO_2 particle.¹⁴ When adjacent different crystal facets (A and B) within a single particle exhibit different band structures and band edge positions, a surface heterojunction is formed. In surface heterojunction band alignment, the positions of the conduction band (CB) and valence band (VB) of the A facet are both higher than those of the B facet. The band bending at the interface of A and B facets due to the difference of chemical potential between the co-exposed crystal surfaces induces a built-in field, which promotes the photoexcited electrons to facilitate move from the CB of the A facet to the B facet, and holes move from the VB of the B facet to the A facet. Accordingly, fabrication of photocatalysts with surface heterojunctions through tailoring the exposed crystal facets is an effective approach to boosting charge separation.

However, advances in surface heterojunction steering receive limited success because most crystal facet engineering work is focused on microscale crystals, where the charge carrier diffusion length usually ranges from several to several tens of nanometers.¹⁵ As a result, the photogenerated electrons and holes easily recombine before reaching the reactive surface to participate in the redox reaction. Reducing the material size can diminish the inner charge recombination, but the increased

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† Electronic supplementary information (ESI) available: Additional results and discussion. See DOI: 10.1039/c7ta02379k

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specific surface area will distinctly raise the surface and interfacial charge recombination.^{16,17} Therefore, it is imperative to develop catalyst structures with an ideal-sized surface heterojunction that has a short charge carrier diffusion length as well as low surface charge recombination.

Herein, we report for the first time a successive surface heterojunction with large space-charge separation and a shortened charge transport distance using a nanostep structured $\text{La}_2\text{Ti}_2\text{O}_7$ (LTO) single crystal with periodically coexposed (010) and (012) facets. The photocatalytic H_2 generation performance of this nanostep-like LTO is 35 and 74 times that of the LTO nanosheets (NS) and nanoparticles (NP) with the same surface area, respectively. The structure-induced electron generation, trapping, recombination and accumulation processes investigated using time-resolved diffuse reflectance spectroscopy demonstrated the substantially extended lifetime of the electrons in the nanostep structured LTO.

Experimental and computational details

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification.

Preparation of LTO NSP *via* a molten-salt method

A stoichiometric mixture of commercial P25, AR grade La_2O_3 , and KCl (molar ratio = 2 : 1 : 10) was ground together with ~1 mL of ethanol. After evaporation of the ethanol, the reactant mixture was placed inside an alumina crucible and heated at 1100 °C inside a box furnace for 3 h with a graded heating and cooling rate (Scheme S1†). The resulting products were washed with hot deionized water to remove the flux and then dried at 80 °C for 12 h.

Preparation of LTO NS *via* a hydrothermal method

2 mmol of $\text{Ti}(\text{SO}_4)_2$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 10 mL of deionized water followed by addition of 10 mL of 2 M NaOH aqueous solution dropwise. After magnetically stirring for 4 h, the reactant precursors were poured into a Teflon cup in a stainless steel autoclave and then heated at 240 °C for 24 h. The white precipitates were collected after centrifugation, washed and dried in air at 80 °C for 12 h.^{18–21}

Preparation of LTO NP *via* a solution combustion method

Stoichiometric $\text{Ti}(\text{SO}_4)_2$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and citric acid (molar ratio = 1 : 1 : 2) were dissolved in 10 mL of distilled water in a crucible, which was then transferred to a preheated furnace maintained at 500 °C. Within a few minutes, the solution was boiled and ignited to produce a self-propagating combustion, yielding a black product. The product obtained was ground in a mortar and then annealed in air at 1000 °C for 3 h.²²

Characterization of materials

The samples were characterized using X-ray diffraction (XRD) (Bruker D/max-V2500; operated at 40 kV and 200 mA, Cu K α source), field emission scanning electron microscopy (FE-SEM) (Zeiss), transmission electron microscopy (TEM) (Zeiss EM 912 Ω instrument or Hitachi H-800; operated at 200 kV), atomic force microscopy (AFM) (Keyence VN-8010), X-ray photoelectron spectroscopy (XPS) (Shimadzu AXIS-165X), and nitrogen sorption (BEL Japan, BEL-SORP max). The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area. The steady-state UV-vis diffuse reflectance spectra were measured using UV-vis-NIR spectrophotometers (Jasco V-770) at room temperature. The zeta potentials of the samples suspended in aqueous solution (pH = 7.2) were measured using an electrophoretic light-scattering spectrophotometer (Nano ZS90).

Photocatalytic H_2 generation tests

3.0 wt% of Pt co-catalyst was loaded on the photocatalysts by a photoreduction method. A tight-fitting 60 mL quartz glass tube containing an aqueous suspension of 30 mg of photocatalyst and 30 mL of 20% methanol solution was irradiated under a 300 W xenon lamp (BOFEILAI Co., PLS-SXE300C). The solution was stirred vigorously during the reaction. Prior to hydrogen generation, the mixture was deaerated with Ar. During the photocatalytic process, the evolved gases were analyzed with Ar as the carrier gas by using a gas chromatograph (Jingkeruida SP6900, China) equipped with a thermal conductivity detector (TCD). Apparent quantum yields (AQE) for hydrogen generation at 365 nm of monochromatic light were measured using a UV-LED source (Asahi Spectra, POT-365; 100 mW cm⁻²) and calculated *via* the following equation: $\text{AQE} = (2 \times \text{number of hydrogen molecules/number of incident photons}) \times 100\%$.

Electrochemical and photoelectrochemical measurements

LTO thin film electrodes were prepared by electrophoretic deposition of LTO powder on FTO conductive glass supports. The electrophoretic deposition was carried out in an acetone solution (50 mL) containing LTO powder (30 mg) and iodine (10 mg), which was dispersed by sonication for 30 min. Two FTO electrodes (4 × 2 cm) were immersed parallelly in the solution 8 mm apart, and then 10 V of bias was applied between them for 10 min using a potentiostat (DH1715 Model Dual Regulated Power Supply). The LTO-coated area was controlled to be *ca.* 2 × 2 cm. The electrode was dried and then calcined at 400 °C for 2 h in air. A three-electrode photoelectrochemical cell (PEC) was constructed and its performance was measured with a 660E electrochemical station (Shanghai Chenhua Co., China). Pt wire, a saturated calomel electrode (SCE) and the photoelectrodes acted as the counter electrode, the reference electrode and the working electrode, respectively. 0.1 M Na_2SO_4 aqueous solution was employed as the electrolyte (pH = 7.0). The light source for the PEC was the same as that used in photocatalysis. The electrochemical impedance spectroscopy

(EIS) data and photocurrent (I) as a function of the time (t) were obtained under a bias of 1.23 V *vs.* the RHE. The potential (*vs.* the SCE) was converted to the reversible hydrogen electrode (RHE) according to the Nernst equation: $E_{\text{RHE}} = E + 0.05916 \text{ pH} + E_0$, where E_{RHE} is the potential *vs.* the RHE, $E_0 = 0.1976 \text{ V}$ at 25 °C, and E is the measured potential *vs.* the SCE.

Surface photovoltage measurements

The lock-in amplifier-based surface photovoltage spectroscopy (SPS) measurement system is constituted of a source of monochromatic light, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), a photovoltaic cell, and a computer. Monochromatic light was provided by passing light from a 500 W Xe lamp (CHF-XM-500 W, Global Xe Lamp Power) through a grating monochromator (Omni-5007, Zolix). A low chopping frequency of 23 Hz was used in the conventional testing. The constructed SPS sample cell has a sandwich-like structure of ITO-mica-sample-ITO. The ITO electrode has a resistance of $20 \text{ } \Omega \text{ sq}^{-1}$, and a high transmittance of 80% in the visible spectral range (with a glass substrate). SPS measurements were carried out in an air atmosphere at room temperature.²³

Time-resolved diffuse reflectance measurements

The femtosecond diffuse reflectance spectra were measured by the pump and probe method using a regeneratively amplified titanium sapphire laser (Spectra-Physics, Spitfire Pro F, 1 kHz) pumped by a Nd:YLF laser (Spectra-Physics, Empower 15). The seed pulse was generated by a titanium sapphire laser (Spectra-Physics, Mai Tai VFSJW; fwhm 80 fs). The fourth harmonic generation (310 nm, 3 mJ per pulse) of an optical parametric amplifier (Spectra-Physics, OPA-800CF-1) was used as the excitation pulse. A white light continuum pulse, which was generated by focusing the residual of the fundamental light on a sapphire crystal after the computer controlled optical delay, was divided into two parts and used as the probe and the reference lights, of which the latter was used to compensate the laser fluctuation. Both probe and reference lights were directed towards the sample powder coated on the glass substrate, and the reflected lights were detected by a linear InGaAs array detector equipped with a polychromator (Solar, MS3504). The pump pulse was chopped by the mechanical chopper synchronized to one-half of the laser repetition rate, resulting in a pair of spectra with and without the pump, from which the absorption change (% Abs) induced by the pump pulse was estimated. All measurements were carried out at room temperature.²¹

Computational details

All calculations were carried out using the density functional theory (DFT) within the generalized-gradient approximation (GGA) with the exchange-correlation functional of Perdew–Burke–Ernzerhof (PBE). This has been implemented in the Vienna Ab Initio Simulation Package (VASP), which spans reciprocal space with a plane-wave basis and uses the projector-augmented wave (PAW) method.^{24,25} For the plane-wave basis set, a cutoff of $E_{\text{cut}} = 500 \text{ eV}$ has been used. We have used a $2 \times$

1×3 Monkhorst–Pack k -point mesh for bulk $\text{La}_2\text{Ti}_2\text{O}_7$, $3 \times 2 \times 1$ for (010) slabs and $3 \times 1 \times 1$ for (012) slabs for the energy calculations. During the relaxations, both lattice parameters and atoms of the bulk structures are allowed to relax with an energy convergence of 10^{-4} eV and a force convergence of $0.03 \text{ eV } \text{\AA}^{-1}$. The lattice parameters of the supercell including the slab and vacuum are fixed and only atoms near the surface are allowed to relax. In the case of slabs, the vacuum space is $15 \text{ } \text{\AA}$.^{26,27}

Results and discussion

Characterization of $\text{La}_2\text{Ti}_2\text{O}_7$ nanosteps

As a member of perovskite-type layer-structured photocatalysts, LTO has received much attention because of its high photocatalytic activity induced by the unique perovskite-layered structure that separates H_2 and O_2 evolution sites.^{18–21} However, the layer-structured perovskite materials are readily formed into a 2D plate structure thus exposing the O-terminated inactive (010) surfaces as shown in Fig. S1 (ESI†). To conquer this problem, a modified molten-salt growth method was employed to synthesize single crystalline LTO nanosteps (NSP) with 3D step-like surface topography. LTO NS and NP were also prepared as controls.

Fig. S2† shows SEM images of inter-connected polygonal nanoparticles with typical structural units in the range of hundreds of nanometers (Fig. S2a†), rectangle nanosheets with 300–800 nm size and 10 nm thickness (Fig. S2b†), and rod-like nanocrystals in a polygonal cross profile with an average diameter of around 100 nm and an aspect ratio of 3–5 (Fig. S2c†) obtained through solution combustion synthesis, hydrothermal processing and the molten-salt growth method, respectively. From the XRD patterns of the three products (Fig. S3†), all diffraction peaks are indexed to the monoclinic phase LTO with a perovskite structure belonging to the P21 space group (JCPDS No. 70-0903). The XRD peaks located at 27.71° , 29.85° , 32.26° , and 33.01° are indexed to the (040), (211), (002), and (012) crystal planes of the LTO phase, respectively. The half-peak widths of the diffraction peaks of the two samples synthesized *via* molten-salt and solution combustion methods are much smaller than that of the hydrothermally processed one, revealing the high crystallinity of products treated at high temperature ($\geq 1000^\circ \text{C}$). The small particle size with a high crystallinity is advantageous to increase the probability of the photoreaction.^{28,29}

The regular strip-like structures observed on the surface of particles prepared by the molten-salt method are the edge/boundary of steps as shown in the enlarged SEM image (Fig. 1a). This ordered nanostructure seems to be self-constructed by stacking layered plates along the [010] direction. The surface topography of steps was further clarified by closer examination of the single-particle from the TEM images. Fig. 1b and c disclose that the nanostep is a single crystal and enclosed by several well-defined terraces through internal and external stairways. To examine the thickness (in the [010] direction) of LTO NSP, AFM was used to image individual pieces. Fig. S4a and b† reveal that well-organized multilayers stack together and

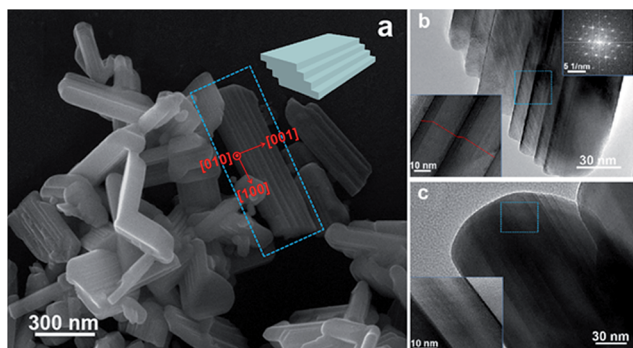


Fig. 1 SEM image of LTO NSP (a). TEM images of LTO NSP from the side view (b) and top view (c). Insets in the bottom-left corner of (b) and (c) indicate HRTEM images enlarged from the blue square after rotating 10 degrees. Inset in the top-right corner of (b) indicates the FFT pattern.

construct the up-and-down step structure. From profile analysis in Fig. S4c,[†] the thicknesses of the component nanosheets were determined to be ~ 45 nm. Particle size distribution tests provide an average size of 340 nm for the LTO NSP (Fig. S5[†]). The LTO NSP crystal growth process is proposed in Fig. S6[†] based on considerations of the layered crystal structure.

Photocatalytic activity of $\text{La}_2\text{Ti}_2\text{O}_7$ nanosteps

The photocatalytic activities of LTO with different morphologies in the reductive generation of H_2 were examined under simulative solar light irradiation. In Fig. 2a, the H_2 generation rate of nanostep structured LTO ($5.1 \text{ mmol g}^{-1} \text{ h}^{-1}$) was 4 and 154 times higher than that of LTO NS and NP, respectively. In order to eliminate the size effect, the specific H_2 generation rates over different samples were calibrated using their specific surface

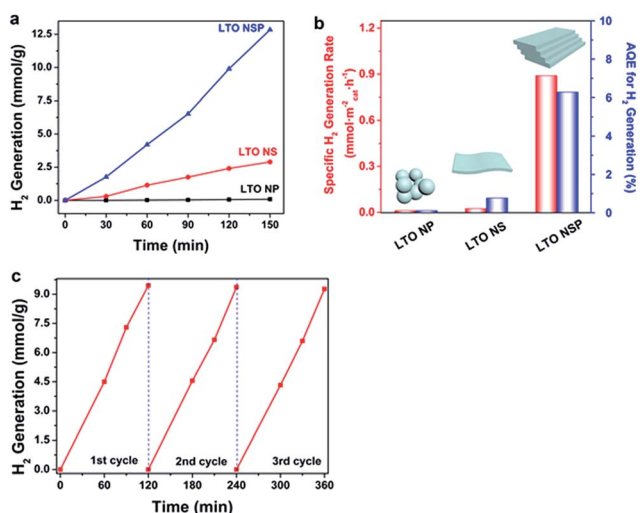


Fig. 2 Time-dependent profiles of H_2 generation in the presence of LTO NP, NS, and NSP under simulative solar light irradiation (a). Comparison of the specific H_2 generation rate (left axis) and AQE for H_2 generation (right axis) under simulative solar light irradiation and 365 nm light irradiation, respectively (b). Cycling runs for H_2 generation over LTO NSP under 365 nm of monochromatic light irradiation (c).

areas as shown in Fig. S7.[†] The specific surface areas of the LTO NP and NSP were far below that of the LTO NS, while the specific H_2 generation rate over LTO NSP ($0.89 \text{ mmol m}_{\text{cat}}^{-2} \text{ h}^{-1}$) was 35 and 74 times that of LTO NS and NP, respectively (Fig. 2b left axis). The apparent quantum efficiency (AQE) for H_2 generation at 365 nm using the LTO NSP photocatalyst reached 6.3% (Fig. 2b right axis). The stability of LTO NSP was further tested by recycling the catalyst three times under 365 nm light irradiation (Fig. 2c). In the test runs, the catalyst did not show any loss of activity, indicating its reusability in the photocatalytic reaction.

Determination of co-exposed crystal facets

In order to elucidate the effects of morphology on the photocatalytic activity, we first measured the optical absorption of the LTO materials. The absorption of all samples is limited in the UV light region due to their intrinsic band gap (Fig. 3a). The derived electronic band gap of LTO NP, NS, and NSP is 3.27, 3.34, and 3.23 eV, respectively, indicating that the nanostep structure causes slight band gap narrowing (Fig. 3b). Next, photoelectrochemical and electrochemical measurements confirmed the efficient charge carrier transfer process on LTO NSP. The LTO thin film electrodes used in this study were prepared using an electrophoretic deposition method where LTO particles were electrodeposited on an FTO substrate followed by annealing treatment (see photographs in Fig. S8a[†]). SEM images of the three electrodes are demonstrated in Fig. S8b–c,[†] showing their continuously covered film surfaces. Under intermittent simulative solar light irradiation, the time-dependent photocurrent generation of the LTO photoelectrodes presented in Fig. S9[†] followed the same order as that observed for photocatalytic performance in Fig. 2. The highest photocurrent over LTO NSP indicates the efficient separation of charge carriers, certifying that the lifespan of electron-hole pairs is prolonged by the strategy of morphological regulation. Fig. S10[†] is the EIS Nyquist plots of the LTO electrodes. The smaller the arc radius of an EIS Nyquist plot, the smaller the charge transfer resistance.^{30,31} Thus, in LTO NSP, the photoinduced electron-hole pairs are more easily separated and transferred to the surface due to the existence of the novel step structure.

To verify whether there are activated sites in the LTO nanostep crystals, we designed a photo-deposition experiment to produce Pt

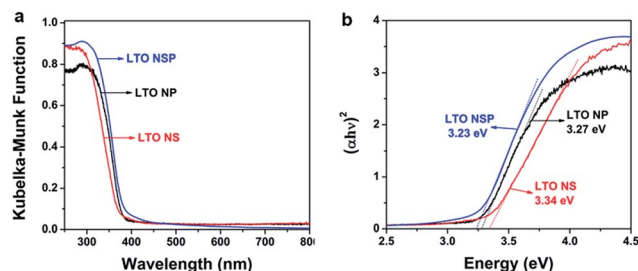


Fig. 3 Diffuse reflectance spectra of the different LTO samples (a), and the derived optical band gap energies (b).

metals from Pt^{4+} through a reductive reaction. If free electrons are accumulated in a certain region of the step structure, metals are formed selectively on that particular area.^{28,32,33} The results clearly show that the Pt nanoparticles were selectively deposited on the side facets parallel to the [010] direction (Fig. 4a and b). STEM-EDS elemental mapping images in Fig. S11† also demonstrate that Pt nanoparticles are formed selectively in certain regions of the nanostep. To determine the crystal indices of the exposed active and inactive surface of the nanosteps, HRTEM analysis as well as the corresponding selected area electron diffraction (SAED) analysis was performed on individual LTO NSP loaded with Pt. During observation, the direction of incident electrons is parallel to the reactive facets of the step by adjusting the perspective until Pt particles aligned in a row (Fig. 4c inset). Two sets of SAED patterns were observed in Fig. 4d, which correspond to the monoclinic phase LTO crystal diffraction pattern along the [0–21] zone axis (Fig. S12a†) overlapped with the hexagonal phase Pt along the [110] zone axis (Fig. S12b†). The atomic planes with lattice spacing of 0.19, 0.23, and 0.26 nm observed in the HRTEM image in Fig. 4c correspond to (100), (212), and (012) lattice planes of LTO, respectively. Fig. S13† displays the lattice fringes of LTO NS with a spacing of about 0.26 nm corresponding to the (012) plane. Among the three lattice planes, (100), (112), and (012), only the (012) planes are parallel to the side facets of the step. Thus, the high-index (012) and low-index (010) facets are co-exposed in the as-prepared LTO NSP. According to the TEM observation and the symmetry of perovskite LTO single crystals, the geometry models of the step are schematically described in Fig. 4e. The projection

angle between the (010) and (012) facets was calculated to be 78.0° , and the exposed (012) facet was terminated with unsaturated Ti atoms.

To obtain further insight into the high photocatalytic performance of LTO NSP, the surface structures and surface energies were investigated by density functional theory (DFT) calculations. Our surface models and computational results are described in Fig. S14 and Table S1,† respectively. The results show that the surface energy of the unsaturated Ti-terminated (012) facet (1.846 J m^{-2}) is much higher than that of the O-terminated (010) facet (0.538 J m^{-2}), indicating that the (012) facet is more reactive.³⁴

XPS and zeta potential results experimentally verified the existence of unsaturated Ti-terminated (012) surfaces on LTO NSP. As shown in the Ti 2p spectra (Fig. S15a†), LTO NS exhibits a symmetric Ti $2p_{3/2}$ peak at 458.0 eV, which is assigned to the Ti–O bonds in the TiO_6 octahedral slabs.³⁵ In contrast, the Ti $2p_{3/2}$ peak of LTO NSP is asymmetric and is deconvoluted into two components. The additional peak at 458.4 eV is assigned to the unsaturated Ti in TiO_5 structures at the terminal site of the (012) surface. In addition, the peak of Ti $2p_{3/2}$ in LTO NSP shifts to a higher binding energy, indicating that the electron density around partial Ti becomes lower.^{36,37} Both LTO NS and NSP have typical O 1s spectra with two peaks respectively located at 532.5 eV (adsorbed oxygen) and 530.7 eV (Ti–O bonds in the TiO_6 octahedron), whereas for LTO NSP, there is an additional peak at 530.0 eV which corresponds to the Ti–O bonds in TiO_5 slabs (Fig. S15b†).³⁵ There is no difference in the La 3d doublet peak of LTO NS and NSP (Fig. S15c†), suggesting the retained La arrangement in the (010) and (012) surfaces. Fig. S16† demonstrates the zeta potentials of each sample suspended in aqueous solution at a pH of 7.2. The surface zeta potential of the LTO NSP (-36.2 mV) was more negative than that of LTO NP (11.3 mV) and NS (7.4 mV), which indicated that the surface of LTO NSP was negatively charged in neutral aqueous solution. Fig. S17† shows a possible surface structure for the (010) and (012) surfaces. The O-terminal sites in octahedral TiO_6 and Ti-terminal sites in TiO_5 respectively adsorb the ionized H^+ and OH^- ions from water, giving rise to a differently charged particle surface. The strength of Ti– OH^- bonding is much stronger than that of the O– H^+ bonding since the Ti in the positively charged TiO_5 structure is unsaturated, whereas the O in the TiO_6 structure is saturated.³⁸ The results of zeta potentials obtained in the present study suggest that unsaturated Ti atoms play an important role in controlling the surface adsorptive properties.

Determination of successive surface heterojunctions

Mott–Schottky measurements were analyzed to elucidate the flat-band potential V_{fb} of LTO NSP with coexposed (010) and (012) facets (Fig. 5a). Interestingly, two determined V_{fb} values, -0.72 and $-0.52 \text{ eV vs. the RHE}$, were observed for LTO NSP, implying the multiple donor energy levels.^{39,40} The VB XPS in Fig. 5b reveal that LTO NSP and NS possess the same VB edge positions, suggesting the VB edge of the (010) surface. Because the VB edge potential of the (010) surface is more negative than

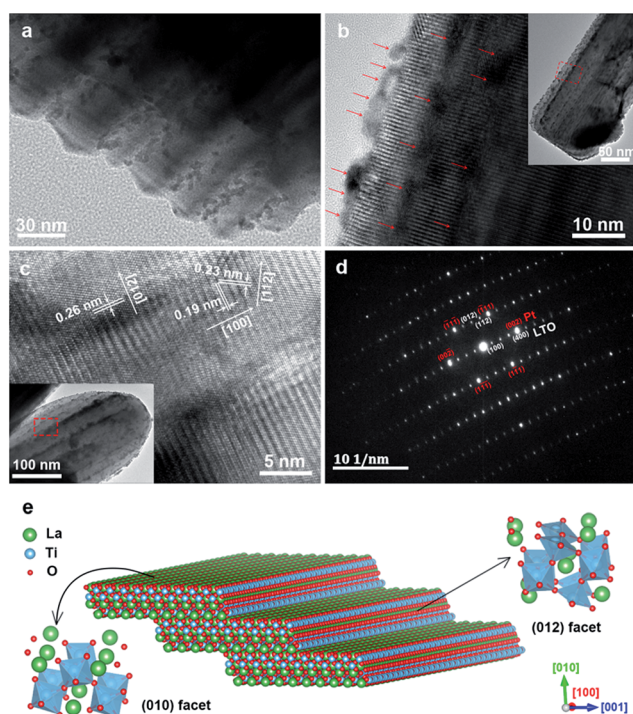


Fig. 4 TEM images of the Pt selectively deposited LTO NSP from the side view (a) and top view (b). HRTEM image (c) and corresponding SAED pattern (d) of the Pt selectively deposited LTO NSP enlarged from the red square in the inset TEM image. Structural model of LTO NSP (e). Red arrows in (b) indicate the Pt nanoparticles.

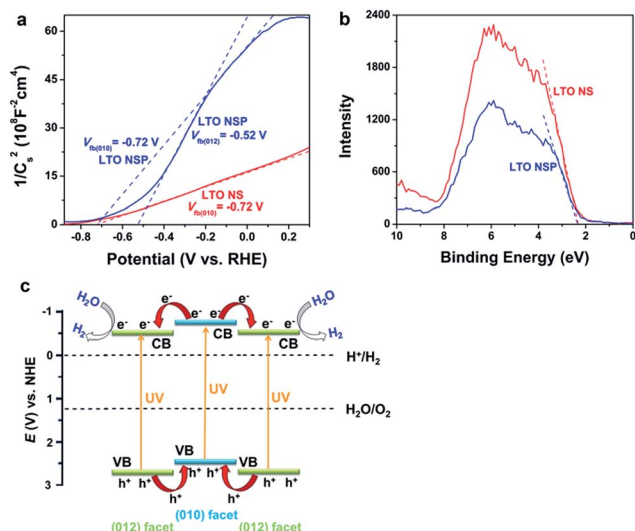


Fig. 5 Mott–Schottky plots (a) and valence-band XPS (b) of LTO NS and NSP. Schematic illustration of the energetic distribution of electrons and holes in the successive (010) and (012) surface heterojunctions of LTO NSP (c).

that of the (012) surface, the electrons excited from the VB of the (010) surface are preferentially detected by VB XPS. Having the same V_{fb} value as the (010) facet exposed LTO NS, the former donor energy level (-0.72 eV) of LTO NSP was considered to be the CB edge of the (010) surface. Considering the narrowed band gap of LTO NSP (see Fig. 3), the latter donor energy level (-0.52 eV) was attributed to the CB edge of the (012) surface. Accordingly, as proposed in Fig. 5c, the successive (010) and (012) surface heterojunctions formed in LTO NSP are beneficial to the transfer and separation of photogenerated electrons and holes.¹³ As discussed in Fig. S18 and Table S2,† when compared with conventional surface heterojunctions, the charge transport distance from the excited sites to nearby reactive surfaces is significantly shortened by successive surface heterojunctions in the nanostep, thus decreasing the recombination possibility of photogenerated electrons and holes during migration.

Investigation of charge transfer dynamics

Surface photovoltage spectrum (SPS) measurements were further performed to examine the photo-induced carrier separation and transfer behaviors in the samples. When photogenerated charge carriers are separated in space under 320 nm laser irradiation, a photovoltage arises.⁴¹ In a semiconducting material, the formation of a surface photovoltage (SPV) signal is determined by the fundamental properties of light absorption and transport of excess carriers.^{23,42,43} As exhibited in Fig. 6a, positive SPV signals were detected for all samples as expected in the n-type semiconductors, where positive charges migrate to the surface.²³ As compared to LTO NS (9.3 μV) with exposed (010) facets and LTO NP with uncertain exposure (5.0 μV), a much higher SPV signal observed for LTO NSP (180 μV) suggests that more photogenerated charge carriers migrate to the surface of LTO NSP before recombination, derived from the successive surface heterojunctions.

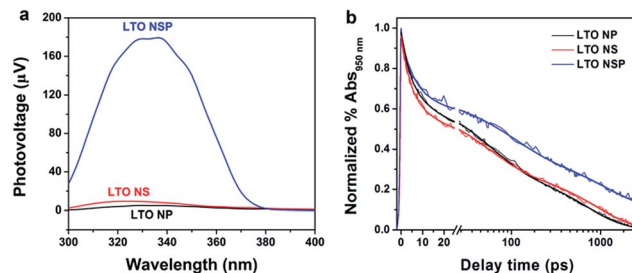


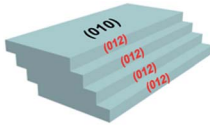
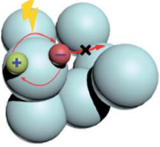
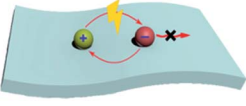
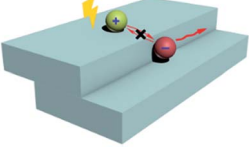
Fig. 6 Surface photovoltage spectra (a) and normalized transient absorption traces observed at 950 nm (b) for the different LTO samples. Bold lines in (b) indicate multiexponential curves fitted to kinetic traces.

As a powerful analytical tool for investigating ultrafast processes in photocatalysis under various conditions, femto-second time-resolved diffuse reflectance (TDR) spectroscopy was employed to measure the lifetime of the injected electrons, which in turn provides the direct evidence for electron transfer over the excited LTO nanocrystals.^{44–46} Soon after the 320 nm laser excitation of the samples in ambient air, a broad absorption was observed in the whole wavelength region (Fig. S19†), which is considered to be superimposed on that of the trapped electrons (600–1000 nm) and free electrons (increasing monotonically from the visible to the near infrared region) in LTO.⁴⁷ For a time period of 0–1000 ps, the concentration of the electrons in LTO decreases in a multiexponential fashion due to the charge recombination of electrons with holes. At 1000 ps, the surviving electron concentration in LTO NSP was 24% of the maximum, while <12% for the LTO NS and NP. To evaluate the decay kinetics of trapped electrons, the time profiles of absorption probed at 950 nm were fitted using a multiexponential function as displayed in Fig. 6b, and their lifetimes are summarized in Table 1. The transient absorption trace on the LTO NSP was fitted to a three-exponential function with time constants of 6.0 ps (29%), 95 ps (28%), and 1100 ps (43%). In the same manner, three decay lifetimes for the nanoparticles were obtained: 4.5 ps (30%), 53 ps (38%), and 680 ps (32%), indicating a faster charge recombination process. As compared to step structured LTO, the LTO NS also exhibited shortened electron lifetimes (4.3 ps (33%), 52 ps (33%), and 890 ps (34%)). Because of the poor crystallization and the inactive (010) exposed surface of the nanosheets, the photogenerated electrons readily recombine with holes during the short-distance migration from the photoexcited sites to the (010) surface, reducing the charge carrier lifetime. On the basis of the above analysis, we speculate that each single-crystalline LTO NSP

Table 1 Lifetimes of the transient absorption decays observed for the LTO samples

Sample	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
LTO NP	4.5 ± 0.2 (30%)	53 ± 2 (38%)	680 ± 30 (32%)
LTO NS	4.3 ± 0.2 (33%)	52 ± 2 (33%)	890 ± 50 (34%)
LTO NSP	6.0 ± 0.3 (29%)	95 ± 8 (28%)	1100 ± 100 (43%)

Table 2 Photocatalytic activity of the LTO samples

Sample	LTO NP	LTO NS	LTO NSP
Structure			
AQE for H ₂ generation, %	0.091	0.75	6.3
Specific H ₂ generation rate, mmol m _{cat} ⁻² h ⁻¹	0.12	0.025	0.89
Surface photovoltage, μV	5.0	9.3	180
Electron lifetime, ps	680 (32%)	890 (34%)	1100 (43%)
Surviving electron concentration at 1 ns, %	8.4	11	24
Electron transfer process			

possesses at least ten (012) facets (SEM and AFM observations) and a high density of corners, edges, and dangling bonds (theoretical calculations), which may markedly increase the number of catalytically active sites on their surfaces and facilitate the adsorption of water molecules on these sites. When LTO NSP is irradiated with light, the VB electrons are excited to the CB level, while holes remain in the VB (see Fig. 5c). Driven by unsaturated Ti atoms which act as reduction sites, the electrons can efficiently migrate to the (012) facets. The TDR measurements over a wide range of time scale demonstrate that a substantial part of electrons in the step structured nanocrystal directionally migrate from photoexcited sites to the nearby (012) facets and are temporarily stored there for further reactions. The mean free path of this anisotropic electron flow is significantly prolonged in LTO NSP by unsaturated Ti, while the charge recombination process is retarded owing to the successive surface heterojunctions. The unique step structure thus boosts charge separation and exhibits a very high photocatalytic activity for H₂ generation.

Conclusions

In summary, we demonstrated that successive surface heterojunctions constituted by two periodically arranged facets in a nanostep structure can efficiently boost space-charge separation. As summarized in Table 2, although the well-crystallized LTO NSP periodically coexposed with high-energy (012) facets and low-energy (010) facets was found to have a lower surface area, its H₂ generation performance was much higher than that of LTO NP and NS. The accumulation of surface charges in the nanosteps (180 μV) was significantly larger than those in the nanoparticles and nanosheets (<10 μV). More than 40% electrons in LTO NSP have a prolonged electron lifetime of 1100 ps, whereas the electrons in LTO NP and NS recombine with the holes within several hundred ps. With respect to the LTO NS which only expose the inactive (010) surfaces, the electrons

generated from the excited sites of nanosteps are effectively transferred to the high energy (012) facets of the crystal, derived from the unsaturated Ti-terminated (012) surfaces. Compared with conventional surface heterojunctions, the charge transport distance from excited sites to nearby reactive surfaces is significantly shortened by successive surface heterojunctions in the nanostep. These significantly reduce the charge recombination probability, thus enhancing the photocatalytic performance.

Acknowledgements

This project is financially supported by the National Natural Science Foundation of China (NSFC) No. 51472013 and 51672106, and the China Scholarship Council (CSC). We are thankful for the help of the Comprehensive Analysis Center of SANKEN, Osaka University, and Jilin University. This work has been partly supported by a Grant-in-Aid for Scientific Research (Project 25220806 and others) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

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