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Constructing cubic-orthorhombic surface-phase junctions of NaNbO₃ towards significant enhancement of CO₂ photoreduction

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NaNbO₃ photocatalyst with cubic-orthorhombic surface-junctions was synthesized by a polymerized-complex method. Compared with cubic and orthorhombic NaNbO₃, the activity of mix-phase NaNbO₃ is enhanced by 30% and 200% in reducing CO₂ into CH₄, respectively. The enhancement of photoactivity over mix-phase NaNbO₃ was attributed to the cubic-orthorhombic surface-junctions which improved the charge separation.

Photocatalysis using semiconductor has attracted particular interests in the past decades because of its ability in directly converting the solar energy into chemical fuels.¹ The performances of photocatalyst are strongly affected by various parameters, such as crystallinity, surface area, surface state, and especially the crystal structure, which is usually the most important factor.² Generally, TiO₂ in anatase phase exhibits much better performances than those in the other phases in many photocatalytic reactions.³ However, a commercial photocatalyst P25, which consists of anatase and rutile, shows higher activities than either pure anatase or rutile in water splitting and gaseous pollutant degradation.⁴ In mixed-phase TiO₂, the previous reports revealed that the recombination of photo-generated electron-hole pairs in rutile is suppressed through electron transferring to lower energy anatase lattice trapping sites.⁵ However, besides TiO₂, there are only a few reports about the mix-phase junction to enhance photocatalytic performance over the other semiconductors.⁶

Alkaline and alkaline earth metal niobate materials are typical environmentally friendly photocatalysts with high activities in water splitting because of their unique crystal structures containing a network of corner-shared octahedral units of [NbO₆] metal cations, which enhance the charge migration in the crystals.⁷ More recently, NaNbO₃ attracts extensive attentions due to its higher stability and narrower band gap than the other Nb-based photocatalysts.⁸ In both of photocatalytic water splitting and CO₂ reduction, NaNbO₃ has the excellent performances.⁹ Among a series of crystal structures, NaNbO₃ in cubic and orthorhombic phases are more important for photocatalysis as the cubic NaNbO₃ has the better activities and the orthorhombic NaNbO₃ is the most stable phase at room temperature.¹⁰

In this study, the NaNbO₃ samples were synthesized from 400 to 600°C based on the polymerized complex method. Pure cubic and orthorhombic NaNbO₃ were respectively obtained at 400 and 600°C, while the NaNbO₃ samples with mixed phases were formed at the temperature ranging from 400 to 600°C. The crystal structures, optical properties, and microstructures of the prepared materials were differentiated by X-ray diffractometer (XRD) combined with ultraviolet-visible (UV-vis) spectroscopy and high-resolution transmission electron microscopy (HR-TEM). The photocatalytic performances of the NaNbO₃ samples were evaluated by CO₂ reduction in gaseous phase. Compared with pure cubic and orthorhombic NaNbO₃, the NaNbO₃ samples in mixed phases showed the enhanced activities. The surface junction between cubic and orthorhombic NaNbO₃ plays a significant role to enhance the separation of electron-hole pairs and therefore improve the photocatalytic performances.

According to the thermo-gravimetric/differential thermal analyzer (TG/DTA) measurement (as shown in Fig. S1), the polymerized precursor was selectively oxidized at different temperatures for 10 hours (the final products were named as
All the samples have similar intense absorption edges, the orthorhombic crystal structures. Fig. 1b plots the content of the desorption of surface carbonate releases the Na NbO\textsubscript{3} generated from the oxidation of surface coordinated polymer. This is attributed to the surface coordinated carbonates, which are oxidized from the surface coordinated polymer. The desorption of surface carbonate releases the Na NbO\textsubscript{3} surface and induces the growth of orthorhombic Na NbO\textsubscript{3} when the oxidation temperature rises from 400 to 600°C.\textsuperscript{3}

Fig. 1 (a) XRD patterns of the as-prepared NaNbO\textsubscript{3} samples. (■: orthorhombic; ●: cubic) (b) Dependence of cubic and orthorhombic NaNbO\textsubscript{3} contents on the oxidation temperature. (c) UV-Vis absorption spectra of the as-prepared NaNbO\textsubscript{3} samples and the inset in figure is the corresponding (ahv)\textsuperscript{1/2} ∼ hv curves.

To assess the photocatalytic property of as-prepared NaNbO\textsubscript{3}, the CO\textsubscript{2} photoreduction experiments were carried out in gaseous phase. Since in the gas-phase CO\textsubscript{2} photoreduction experiments, CH\textsubscript{4} is the main organic product, we measured the amounts of CH\textsubscript{4} evolution to judge the reaction activities. Fig. 3a exhibits the CH\textsubscript{4} evolutions over the series of NaNbO\textsubscript{3} samples (0.1 g) with 0.5 wt% Pt loading under the irradiation of full-arc Xe lamp (λ > 300 nm). All of the NaNbO\textsubscript{3} samples can reduce CO\textsubscript{2} into CH\textsubscript{4} under light irradiation but show different activities. For the pure phase NaNbO\textsubscript{3}, the sample in cubic phase has the higher activity than that in orthorhombic phase, and the samples in mix-phase prepared between 450 and 525°C show better performance than the pure cubic or orthorhombic sample. The higher activities of mix-phase samples were also observed in photocatalytic water splitting (Supporting Information). Because the surface area is an important factor in gaseous CO\textsubscript{2} photoreduction, the surface-area specific rates of CH\textsubscript{4} evolution over the NaNbO\textsubscript{3} samples in 8 hours were calculated and are
shown in Fig. 3b. Different from the total CH\textsubscript{4} evolution, NaNbO\textsubscript{3.525} has the highest efficiency in reducing CO\textsubscript{2} into CH\textsubscript{4}. This difference is attributed to the rapid decrease of surface area along with the oxidation temperature increasing from 400 to 600°C. However, all the mix-phase samples are still more efficient in CO\textsubscript{2} reduction than the two pure phases. A reference isotope experiment over NaNbO\textsubscript{3-500} was carried out in the present of D\textsubscript{2}O to verify the source of hydrogen in the product. The GC-MS spectrum (as shown in Fig. S5) shows that CD\textsubscript{4} is the majority in the CH\textsubscript{4} product. Combined with our previous isotope experiment using \textsuperscript{13}CO\textsubscript{2} as a carbon source,\textsuperscript{10(b)} the CH\textsubscript{4} molecules are generated from CO\textsubscript{2} and H\textsubscript{2}O.

The junctions between two phases could promote the spatial charge separation in the surface region, and the surface-phase junctions between anatase and rutile particles, which are formed in P25, are responsible to its high photocatalytic activity.\textsuperscript{10} The same charge transfer process may also happen in the mix-phase NaNbO\textsubscript {3}. Our previous investigation proved that due to the asymmetric reformation of [NbO\textsubscript{5}] octahedral ligand field, the energy level of the O 2p orbitals raises, which induces the larger band gap of orthorhombic NaNbO\textsubscript{3} and the higher energy levels of valence band (VB) and conduction band (CB) in orthorhombic NaNbO\textsubscript{3}.\textsuperscript{9} To confirm the electronic structural differences between cubic and orthorhombic NaNbO\textsubscript{3}, VBs of NaNbO\textsubscript{3-400} and NaNbO\textsubscript{3-600} were measured by X-ray photoelectron spectroscopy (XPS). As shown in Fig 4a, the energy level of VB top in NaNbO\textsubscript{3-600} is 0.1 eV higher than that in NaNbO\textsubscript{3-400}. From Fig. 1c, the band gaps of pure cubic and orthorhombic NaNbO\textsubscript{3} are determined as 3.27 and 3.43 eV, respectively. Thus, it can be deduced that the energy level of CB bottom in orthorhombic is 0.26 eV higher than that in cubic NaNbO\textsubscript{3}, which thus induces the charge separation similar to P25. Fig. 4b plots the proposed electron transfer mechanism in cubic-orthorhombic junctions and the surface photocatalytic reactions. The phase junctions between cubic and orthorhombic NaNbO\textsubscript{3} can facilitate the transfer of the photo-excited electrons from the conduction band of the orthorhombic phase to the trapping sites on the cubic surface, thus avoiding the electron-hole recombination in orthorhombic NaNbO\textsubscript{3} and improving the charge separation efficiency in the mix-phase NaNbO\textsubscript{3} samples. Since the charge migration in cubic NaNbO\textsubscript{3} is easier than in orthorhombic NaNbO\textsubscript{3} and the photocatalytic activities over cubic NaNbO\textsubscript{3} is significantly higher than those over orthorhombic NaNbO\textsubscript{3},\textsuperscript{10(a)} the enhanced photocatalytic performances over the mix-phase NaNbO\textsubscript{3} are understandable. After all, this obvious increase in the photocatalytic activity can be attributed to the formation of the surface cubic-orthorhombic junctions.

In conclusion, this work demonstrates that the photocatalytic activities of NaNbO\textsubscript{3} are greatly affected by the crystal structure, which can be selectively synthesized by a simple low temperature oxidation with the surface organic ligands assisted. More interestingly, the activities of photocatalytic CO\textsubscript{2} reduction and H\textsubscript{2} evolution could be greatly enhanced by forming the surface-phase junctions between the cubic and orthorhombic NaNbO\textsubscript{3} nanoparticles. The results and discussion in this study reveal that the surface/interface engineering of semiconductor photocatalyst is a feasible and efficient approach to promote the photocatalytic performance.

Notes and references


Fig. 3 (a) CH\textsubscript{4} evolution in gaseous phase reaction over the as-prepared NaNbO\textsubscript{3} samples with 0.5 wt% Pt loading under the irradiation of 300 W Xe lamp (λ > 300 nm). (b) The surface-area specific CH\textsubscript{4} evolution rates over the as-prepared NaNbO\textsubscript{3} samples.

Fig. 4 (a) Valence band XPS curves of NaNbO\textsubscript{3-400} and NaNbO\textsubscript{3-600}. (b) The proposed electron transfer in cubic-orthorhombic junctions and the surface photocatalytic reactions. (C: cubic NaNbO\textsubscript{3}, O: orthorhombic NaNbO\textsubscript{3}, D: electron donor)


