Band gap tuning of $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$ solid solutions for visible light photocatalysis

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Monophase solid solutions $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$ ($x=0-0.25$) were prepared with conventional solid state reactions method. The band gaps of the solid solutions can be tuned to effectively absorb visible light, with varying x value. The $\text{Na}_{0.9}\text{La}_{0.1}\text{Ta}_{0.9}\text{Co}_{0.1}\text{O}_3$ photocatalyst exhibited the highest performance of H_2 evolution ($4.34 \mu\text{mol/h}$) under visible light irradiation ($\lambda > 420 \text{ nm}$), whereas no H_2 evolution is observed for NaTaO_3 under the same conditions. The first principles calculation using generalized gradient approximation revealed that the band gap alteration and the photocatalytic activities of $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$ are mainly due to the hybridization of Co $3d$ and O $2p$ orbitals. © 2007 American Institute of Physics. [DOI: 10.1063/1.2826277]

Photocatalysis is one approach to utilize solar energy and one of the key issues is to develop high performance photocatalysts active under visible light irradiation.¹⁻⁴ Numerous studies had attempted, however, it is very difficult to get a satisfied one and the efforts have recently been extended to solid solutions.^{5,6} In this letter, we study the solid solutions of $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$ in view of the superior photocatalysis of NaTaO_3 under UV light and the strong visible light absorbability of LaCoO_3 .^{4,7} It was found that the solid solutions can be tailored to evolve H_2 under visible light irradiation and the Co $3d$ orbitals play an important role for the band structures alteration.

The powder samples of $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$ ($x=0.00, 0.05, 0.10, 0.15, 0.20, 0.25$) were prepared by conventional solid-state reaction method. Appropriate amounts of high purity raw materials (in which excess NaHCO_3 of 2 mol % out of the stoichiometry was added to compensate for the volatilization of sodium during sintering at high temperatures) were first mixed and presintered at 1223 K for 10 h, then remilled and calcined at 1423 K in air for 10 h. The crystal structures of the prepared samples were identified by x-ray diffraction (XRD) method with $\text{Cu K}\alpha$ radiation (Rigaku, RINT-2100). The UV-visible diffuse reflectance spectrum was measured using the diffuse reflection method with a Shimadzu UV-2500 spectrometer. The photocatalytic H_2 evolution were measured in a closed gas circulation system. The photocatalyst powders (0.5 g) were dispersed in a methanol aqueous solution (220 mL distilled H_2O , 50 mL CH_3OH) by a magnetic stirrer in a cell with a side-window made of quartz. The platinum cocatalysts (0.2 wt %) were deposited onto the photocatalyst surface from H_2PtCl_6 aqueous methanol solution by *in situ* photodeposition. The light source was an ozone-free 300 W Xe illuminator (ILC Technology, CE-MAX LX-300). The cutoff filter of 420 nm was employed for the visible light irradiation. The evolved gases were determined using a gas chromatograph (Shimadzu, GC-8A, TCD, Ar carrier), which is connected to the gas circulation system. The plane-wave-based density functional theory calculations were performed with the CASTEP program.⁸ All calculations were carried out using the generalized gradient ap-

proximation with gradient corrected functional Perdew-Burke-Ernzerhof (PBE). Ultrasoft pseudopotentials were applied with a plane wave cutoff energy of 370 eV. The valence electronic configurations for Na, La, Ta, Co, and O were $2s^2 2p^6 3s^1$, $5s^2 5p^6 5d^1 6s^2$, $5d^3 6s^2$, $3d^7 4s^2$, and $2s^2 2p^4$, respectively. The crystal parameters of NaTaO_3 were taken from Ref. 9, whereas virtual crystal approximation was employed for the calculation of the solid solution $\text{Na}_{0.9}\text{La}_{0.1}\text{Ta}_{0.9}\text{Co}_{0.1}\text{O}_3$ (two pairs of atoms, Na-La and Ta-Co, were considered as the virtual atoms). The calculations were carried out with primitive unit cells.

Both the crystal structures of NaTaO_3 and LaCoO_3 can be depicted as corner-sharing MO_6 ($M=\text{Ta, Co}$) octahedra with perovskitelike structure. The XRD patterns of $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$ powders in Fig. 1 reveal that no second phases were detected, however, with the increase of LaCoO_3 content, the diffraction peaks shifted toward lower 2θ values and, at the same time, their intensities varied. A further analysis of lattice parameters of the solid solutions (see EPAPS in Ref. 10) using program UNITCELL¹¹ indicates that, with the increase of the x values, the lattice constants of the solid solutions increased substantially due to the larger lattice constants of LaCoO_3 under monoclinic symmetry,^{7,9} whereas

FIG. 1. (Color online) X-ray diffraction patterns of $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$ powders ($x=0.00-0.25$) at room temperature.

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FIG. 2. UV-visible diffusive reflectance spectra of solid solutions $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$.

there is no apparent changes for the β values. The lattice volumes of the solid solutions are substantially increased with increasing x . These information indicate that the $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$ solid solutions were obtained.

Figure 2 shows the UV-visible diffuse reflectance spectra of the $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$ solid solutions. The absorption edge extended gradually to the whole visible light range with increasing x values, which reflects the band structures evolution and is an important attribute required for visible light sensitive materials. Too low LaCoO_3 content ($x=0.05$) could only introduce local levels without altering the band gap of NaTaO_3 , that is why there is a hump at ~ 350 nm, whereas no apparent differences for the main absorption edges in the UV-visible absorption spectra. When more LaCoO_3 incorporated, the band gap narrowing becomes apparent and, thus, influences the main absorption edges. Correspondingly, the color of the samples varied gradually from original white of NaTaO_3 , to interim yellow gray, and to final black of $\text{Na}_{0.75}\text{La}_{0.25}\text{Ta}_{0.75}\text{Co}_{0.25}\text{O}_3$. These results demonstrate clearly that the optical response of the solid solutions $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$ can be tuned effectively and, thereby, have potential applications in visible light range.

The water splitting experiments under visible light irradiation ($\lambda > 420$ nm) were carried out to test the photocatalytic activities of the solid solutions. It is known that the photocatalytic water splitting using semiconductors involves photogenerated electrons and holes migrating to the surface and serving as redox sources that react with absorbed water and sacrifice reagents, leading to the splitting of water, provided the potential difference of the reaction exceeds 1.23 eV and the potential is dictated by the standard potential E^0 of water being -1.23 (standard hydrogen electrode, $\text{pH}=0$).^{2,3} Both NaTaO_3 and LaCoO_3 are inactive to split water under visible light irradiation because of their inappropriate band gaps. However, as shown in Fig. 3, there is H_2 evolution activities under visible light irradiation, due to the alteration of optical response of the solid solutions $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$. The inset in Fig. 3 shows the long time courses of H_2 evolution for the solid solution $\text{Na}_{0.9}\text{La}_{0.1}\text{Ta}_{0.9}\text{Co}_{0.1}\text{O}_3$ with the highest performance. Within three times of repeated experiments it is quite stable for the H_2 evolution performance, whereas no gases were evolved upon turning off the light. The solid solutions can not evolve O_2 due to inappropriate potential of local levels or valance band top.

FIG. 3. H_2 evolution rates of the initial stage of second run from methanol aqueous solution (50 mL $\text{CH}_3\text{OH}+220$ mL H_2O) over Pt-loaded (0.2 wt %) photocatalysts $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$ (0.5 g), under visible light irradiation ($\lambda > 420$ nm). Inset shows the time courses of H_2 evolution for the solid solution $\text{Na}_{0.9}\text{La}_{0.1}\text{Ta}_{0.9}\text{Co}_{0.1}\text{O}_3$ with the highest performance.

The wavelength dependence of the H_2 evolution was further conducted to prove whether the reaction was really driven by light irradiation.^{5,6} Figure 4 shows the diffusive reflectance spectroscopy of $\text{Na}_{0.9}\text{La}_{0.1}\text{Ta}_{0.9}\text{Co}_{0.1}\text{O}_3$ and the variation of evolved H_2 concentration with wavelength after light irradiation for 2 h. The evolved H_2 concentration decreased with increasing wavelength and the longest wavelength suitable for H_2 evolution is within 500 nm, which is coincided with the absorption characteristic of the photocatalyst $\text{Na}_{0.9}\text{La}_{0.1}\text{Ta}_{0.9}\text{Co}_{0.1}\text{O}_3$. This indicated that the present catalytic reaction was indeed driven by light and that the light absorption property of the photocatalyst governed the reaction rate. In other words, the H_2 evolution herein originates from an intrinsic photocatalytic process.

To further understand the behavior of the photocatalysts, the first principles density functional calculations⁸ were performed to demonstrate the band gap narrowing and the visible light photocatalysis of $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$. According to the crystal field theory, the $3d$ orbitals of Co^{3+} would split into the lower t_{2g} (d_{xy} , d_{yz} , d_{zx}) states and the higher e_g ($d_{x^2-y^2}$, d_{z^2}) states under an octahedrally coordinated field. For the compound LaCoO_3 , due to the low energy difference

FIG. 4. UV-visible diffusive reflectance spectroscopy of $\text{Na}_{0.9}\text{La}_{0.1}\text{Ta}_{0.9}\text{Co}_{0.1}\text{O}_3$ and the variation of amount of evolved H_2 with wavelength, after light irradiation for 2 h, from methanol aqueous solution (50 mL $\text{CH}_3\text{OH}+220$ mL H_2O) over Pt-loaded (0.2 wt %) photocatalyst $\text{Na}_{0.9}\text{La}_{0.1}\text{Ta}_{0.9}\text{Co}_{0.1}\text{O}_3$ (0.5 g).

FIG. 5. (Color online) Density of states (DOS) of (a) NaTaO_3 and (b) $\text{Na}_{0.9}\text{La}_{0.1}\text{Ta}_{0.9}\text{Co}_{0.1}\text{O}_3$.

between the high and low spin states the ground state can vary from low-spin state to intermediate-spin state and high-spin state when temperature fluctuates and, thereby, the full particulars of its electronic structure are still under debate.¹² The quantitative description of the electronic structure of $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$ would be more complex and, for conciseness, Fig. 5 shows only the density of states (DOS) of NaTaO_3 and $\text{Na}_{0.9}\text{La}_{0.1}\text{Ta}_{0.9}\text{Co}_{0.1}\text{O}_3$ without regard to spin polarization. The top of the valence band [highest energy occupied molecular orbital (HOMO)] and the bottom of the conduction band [lowest energy unoccupied molecular orbital (LUMO)] of the compound NaTaO_3 are mainly composed of O 2p and Ta 5d, respectively, whereas for the solid solution $\text{Na}_{0.9}\text{La}_{0.1}\text{Ta}_{0.9}\text{Co}_{0.1}\text{O}_3$, Co 3d states mix with O 2p states and, the hybridization makes predominantly contributions to both the HOMO and the LUMO and, thus, results in narrower band gap. Therefore, it is concluded that the band

gap of solid solutions $\text{Na}_{1-x}\text{La}_x\text{Ta}_{1-x}\text{Co}_x\text{O}_3$ can be tuned with varying cobalt content. Too low cobalt concentration is not sufficient to induce enough density of states needed for maximum H_2 evolution whereas, too high cobalt concentration would change completely the band structures of NaTaO_3 and, thereby, result in inappropriate redox potentials. The aforementioned experiments indicate that x value of 0.10 is the optimum concentration of cobalt. In other words, the photocatalytic H_2 evolution activity can be attributed to the suitable band structures that yield an active photocatalyst with optimal band gap for significant absorption of visible light. The role of La is still unclear; it has no contribution to either HOMO or LUMO.

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