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Synthesis and Optimization of Ti/Li/Al Ternary Layered Double Hydroxides for Efficient Photocatalytic Reduction of CO₂ to CH₄

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A series of Ti/Li/Al ternary layered double hydroxides (TiLiAl-LDHs) with different Ti:Li:Al molar ratios were prepared by a coprecipitation method for photocatalytic CO₂ reduction. It was demonstrated that the contents of anions between the layers of Ti/Li/Al-LDHs greatly determined the photocatalytic activity for CO₂ reduction. With Ti:Li:Al molar ratios optimized to be 1:3:2, the largest contents of CO₃²⁻ anion and hydroxyl group were obtained for the Ti₁Li₃Al₂-LDHs sample, which exhibited the highest photocatalytic activity for CO₂ reduction, with CH₄ production rate achieving 1.33 mmol h⁻¹ g⁻¹. Moreover, the theoretical calculations show that Ti₁Li₃Al₂-LDHs is a p-type semiconductor with the narrowest band gap among all the obtained TiLiAl-LDHs. After calcined at high temperatures such as 700 °C, and the obtained TiLiAl-700 sample showed much increased photocatalytic activity for CO₂ reduction, with CH₄ production rate reaching about 1.59 mmol h⁻¹ g⁻¹. This calcination induced photocatalytic enhancement should be related to the crystal structure transformation from hydrotalcite to mixed oxides containing high reactive oxygen species for more efficient CO₂ reduction.

The greenhouse effect caused by greenhouse gases has seriously affected people's life and social development^{1,2}. CO₂ has been believed as a major greenhouse gas, and its emission controlling has become a key problem faced by our human society^{3,4}. Physical adsorption and photocatalytic reduction have been considered to be the most promising methods for CO₂ emission reduction^{5,6}. However, photoreduction of CO₂ is a complex and difficult reaction with a lot of carbon species produced⁷, the searching for high efficiency adsorbents and photocatalysts is the key priority to the technological breakthrough⁸. Until now, different kinds of semiconductors, including oxides, sulfides and nitrides, have been developed for photocatalytic CO₂ reduction, and yet shown unsatisfying activity and selectivity⁹.

In recent years, hydrotalcite like compounds (i.e., layered double hydroxides, LDHs) have been widely used in the study of CO₂ adsorption and photocatalysis, because of its unique physical and chemical properties as well as excellent catalytic properties. Recently, the use of hydrotalcite as CO₂ adsorbent or photocatalyst has been reported in many literatures, aiming at the enhancement of adsorption and catalytic properties. For instance, Chang *et al.*¹⁰ found that in the Ca/Al based hydrotalcite the highly dispersed inert alumina calcium oxide coated on the surface of calcium oxide could effectively prevent the aggregation of calcium oxide particles, thereby improving the stability of adsorbent, and enhancing the hydrotalcite adsorption performance. Iguchi *et al.*¹¹ prepared Al-LDHs composite by a co-precipitation method, which showed considerable photocatalytic activity for converting CO₂ to CO. Through co-precipitation method, hydrothermal method and roasting recombination method, Zhao *et al.*¹² obtained a series of TiO₂/MgAlTi-LDHs and found that the photocatalytic properties of the composite were related to the crystal shape and the crystal form of TiO₂ loaded on hydrotalcite and the adsorption surface area.

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Sample	Ti ₁ Li ₃ Al ₁ -LDHs	Ti ₁ Li ₃ Al ₂ -LDHs	Ti ₁ Li ₃ Al ₃ -LDHs	Ti ₁ Li ₃ Al ₄ -LDHs
Precursor solution	1:3:1	1:3:2	1:3:3	1:3:4
Solid sample	0.98:2.12:1.13	0.99:2.37:2.14	0.96:2.62:3.10	1.02:2.72:3.96

Table 1. The atomic ratios of Ti:Li:Al in the precursor solution and in the obtained solid samples.

Figure 1. XRD patterns of (a) Ti/Li/Al-LDHs with different Ti:Li:Al molar ratios, (1) Ti₁Li₃Al₄-LDHs, (2) Ti₁Li₃Al₃-LDHs, (3) Ti₁Li₃Al₂-LDHs, (4) Ti₁Li₃Al₁-LDHs and (b) Ti₁Li₃Al₂-LDHs calcined at different temperatures (180 °C, 300 °C, 500 °C and 700 °C), (1) not calcined (Ti₁Li₃Al₂-LDHs), (2) Ti₁Li₃Al₂-180, (3) Ti₁Li₃Al₂-300, (4) Ti₁Li₃Al₂-500, (5) Ti₁Li₃Al₂-700.

Given the fact of low conversion and utilization of CO₂, in our previous study¹³, a new type of lithium aluminum hydroxalate (Ti/Li/Al-LDHs) was developed for its utilization in efficient CO₂ adsorption. Ti/Li/Al-LDHs with chemical composition optimized showed quite high efficiency for CO₂ absorption and capture, and moreover the calcined Ti/Li/Al-LDHs exhibited much increased performance towards CO₂ adsorption. As inspired by these observations, herein, a series of Ti/Li/Al-LDHs with different Ti/Li/Al molar ratios were prepared by co-precipitation method and further calcined at different temperatures. It was found that the photocatalytic activity for CO₂ reduction was greatly on the dependence of the Ti/Li/Al molar ratios, and high temperature calcination could further increase the activity for photocatalytic conversion of CO₂ to CH₄. In this study, the chemical compositions were optimized and the reaction active sites were modulated to elucidate the relationship between the structure and the photocatalytic activity, which provides new ideas and theoretical guides for the further design of high efficiency photocatalyst for CO₂ reduction.

Results

In this study, a series of Ti/Li/Al ternary hydroxalates (TiLiAl-LDHs) with different Ti:Li:Al molar ratios was obtained by co-precipitation method, and further calcined at different temperatures, with Ti/Li/Al molar ratios determined and summarized in Table 1. One will observe that with the increasing Al contents in the precursor solution, the Ti/Li/Al molar ratios in the obtained TiLiAl-LDHs samples could be well tuned, which display the same tendency as the Ti/Li/Al molar ratios in precursor solutions. Figure 1a shows the XRD patterns of Ti/Li/Al-LDHs with different Ti:Li:Al molar ratios. One can easily observe that all samples exhibit sharp and clear peaks corresponding to the crystal indexes of (003), (006), (009), (105), (108), (110), and (113), respectively, which are matching well with the layered structure of LDHs. No other peaks appear, indicating the single crystalline phase for these synthesized hydroxalate samples. It is also easily noted that the (006) peak appears a doublet peak character, which is similar to Li/Al-LDHs reported in the previous literature¹⁴, indicating that monovalent Li⁺ ions exist between the layers. However, because of the small quantity of Li⁺ charge, the crystal cell structure is deformed due to the uneven charge density with Li⁺ entering the laminate, leading to the splitting of the (006) peak¹⁵. Further comparison will find that the XRD peak intensity of Ti/Li/Al-LDHs decreases gradually with the Al³⁺ content decreasing. It is clear that the decreased contents of interlayer Al³⁺ will lead to the increased proportion of Ti⁴⁺. Thus, these Ti⁴⁺ could produce more positive charges, which cause repulsion between the neighbouring layers, resulting in the deformation of crystal structures and thus the decreased crystallinity¹⁶.

Figure 1b shows the XRD patterns of Ti₁Li₃Al₂-LDHs calcined at different temperatures. With the calcination temperatures increasing, the XRD peaks assigned to hydroxalate show gradual decrease in peak intensity, and the (003) and (110) diffraction peaks even disappear with the calcination temperature higher 300 °C. At the same time, some new peaks with crystal indexes of (211), (311), (400) and (440) emerge, which could be assigned to mixed oxides such as Al₂TiO₅ and spinel Li₄Ti₅O₁₂. This observation demonstrates that high temperature calcination will destroy the layer structure of hydroxalate, giving rise to the crystal structure transformation from hydroxalate to oxides and spinel^{17,18}.

Figure 2. FTIR spectra of $\text{Ti}_1\text{Li}_3\text{Al}_2$ -LDHs calcined at different temperatures.

The calcination induced crystal structure transformation was further investigated by FTIR analysis. As shown in Fig. 2, both $\text{Ti}_1\text{Li}_3\text{Al}_2$ -LDHs and $\text{Ti}_1\text{Li}_3\text{Al}_2$ -T ($T = 180, 300, 500$ and 700) show two broad and strong absorption peaks located at ca. 3430 cm^{-1} and 1630 cm^{-1} , respectively, which belong to the superposition of the hydrogen bond stretching vibration $\nu(\text{O-H})$ absorption band of the hydroxyl group of interlayer water molecule and the bending vibration peak of O-H bond¹⁹. It can be seen that the hydroxyl peak decreases gradually with the increase in calcination temperatures, indicating the dehydration of the interlayer hydroxyl groups. The absorption peaks at 1389 cm^{-1} and 1038 cm^{-1} , which are characteristic of the telescopic CO_3^{2-} carbon oxygen bond and carbon oxygen bond vibration absorption peak, respectively²⁰, shows gradually weakened intensities and even disappears, implying the removal of CO_3^{2-} during high temperature calcination. The absorption peaks located at 540 cm^{-1} and 744 cm^{-1} should be related to the Ti-O bond and the Li-O bond²¹, both of which gradually fuse into a wide absorption peak with intensities weakened depending on the increasing calcination temperatures. All these observations suggest the destroyed layered structure of hydrotalcite and the crystal structure transformation from hydrotalcite to mixed oxides of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and spinel Al_2TiO_5 during high temperature calcination²².

The morphology of Ti/Li/Al -LDHs was investigated by SEM images. With very similar morphology obtained for those Ti/Li/Al -LDHs with different Ti:Li:Al molar ratios, herein, the morphology of $\text{Ti}_1\text{Li}_3\text{Al}_2$ -LDHs was analyzed as the typical sample in details. Clearly, the $\text{Ti}_1\text{Li}_3\text{Al}_2$ -LDHs sample shows morphology in cluster-like coral reefs with serious particles agglomeration (Fig. 3a), due to the large free energy of the nanoparticles system²³. One could also easily observe that the $\text{Ti}_1\text{Li}_3\text{Al}_2$ -LDHs particles are comprised of numerous petal-like nanosheets with thickness estimated to be tens of nanometers (Fig. 3b), which evidences the layered structure of the obtained tenary hydrotalcites. When calcined at different temperatures, the $\text{Ti}_1\text{Li}_3\text{Al}_2$ -LDHs shows a significant change in morphology, as shown in Fig. 3c–f. In comparison to $\text{Ti}_1\text{Li}_3\text{Al}_2$ -180 with layer structure well maintained (Fig. 3c), $\text{Ti}_1\text{Li}_3\text{Al}_2$ -300 shows slight deformation in the lamellar structure (Fig. 3d), and further increase in calcination temperatures brings significant morphology change to $\text{Ti}_1\text{Li}_3\text{Al}_2$ -500 and $\text{Ti}_1\text{Li}_3\text{Al}_2$ -700 with lamellar structure almost completely destroyed (Fig. 3e,f). It is well known that the increase in free energy of nanoparticle system will lead to nanoparticles agglomeration. After dehydration, $\text{Ti}_1\text{Li}_3\text{Al}_2$ -LDHs particles are more easily to agglomerate, especially after high temperature calcination, as induced by the increasing free energy of nanoparticles, which should be the main reason for the morphology change. Moreover, high temperature calcination gives rise to the crystal structure transformation from hydrotalcite to LiO , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Al_2TiO_5 and other mixed oxides with low crystallization as supported by XRD and FTIR analysis.

The optical properties of Ti/Li/Al -LDHs with different Ti:Li:Al molar ratios were investigated by UV-vis diffuse reflectance spectra. As shown in Fig. 4a, all the Ti/Li/Al -LDHs samples show strong optical absorption in the ultraviolet light region. With optical absorption onsets (λ_0) determined to be 397 nm , 413 nm , 401 nm and 408 nm , respectively, the band gaps (E_g) could be calculated to be 3.23 eV , 3.10 eV , 3.14 eV and 3.13 eV for $\text{Ti}_1\text{Li}_3\text{Al}_1$ -LDHs, $\text{Ti}_1\text{Li}_3\text{Al}_2$ -LDHs, $\text{Ti}_1\text{Li}_3\text{Al}_3$ -LDHs and $\text{Ti}_1\text{Li}_3\text{Al}_4$ -LDHs, by the $E_g \sim \lambda_0$ relationship (i.e., $E_g = hc/\lambda_0 = 1240/\lambda_0$), herein, h is the Planck constant, and c is the speed of light²⁴. It is clear that with the increase of Al^{3+} content, Ti/Li/Al -LDHs shows very similar band gaps, which might not be determinative to their different photocatalytic activities. Given O 2p states mainly comprising the valence band of the hydrotalcites^{25–27}, the conduction band of the Ti/Li/Al -LDHs samples should be negative enough for driving the CO_2 reduction reaction, as deduced from their band gaps ($>3.0\text{ eV}$)²⁸. However, all the Ti/Li/Al -LDHs samples possess band gap much smaller than the previously reported $(\text{Cu})/\text{Zn}(\text{Fe})/\text{Al}$ -LDHs (about 4.10 – 4.50 eV)^{29,30}. Thus, it could be deduced that these obtained Ti/Li/Al -LDHs could efficiently utilize ultraviolet light to excite electrons from valence band to conduction band to trigger photocatalytic conversion of CO_2 to CH_4 . After calcined at different temperatures,

Figure 3. SEM images of (a,b) $\text{Ti}_1\text{Li}_3\text{Al}_2$ -LDHs and (c–f) $\text{Ti}_1\text{Li}_3\text{Al}_2$ -T, (c) $T = 180$, (d) $T = 300$, (e) $T = 500$, and (f) $T = 700$.

Figure 4. UV-Vis spectra of (a) Ti/Li/Al -LDHs with different Ti:Li:Al molar ratios and (b) $\text{Ti}_1\text{Li}_3\text{Al}_2$ -LDHs calcined at different temperatures.

the $\text{Ti}_1\text{Li}_3\text{Al}_2$ -LDHs shows obvious change in optical absorption. As shown in Fig. 4b, the $\text{Ti}_1\text{Li}_3\text{Al}_2$ -T ($T = 180, 300, 500$, and 700) samples show optical absorption onsets at 404 nm , 398 nm , 414 nm and 427 nm , respectively, with band gaps determined to be 3.07 eV , 3.12 eV , 3 eV and 2.90 eV . Comparative analysis demonstrates that the band gap of $\text{Ti}_1\text{Li}_3\text{Al}_2$ -T is widened first and then narrowed, depending on the increasing calcination temperature. These results imply that the conductivity of hydrotalcite decreases first and then increased, with the gradual deformation of the layered structure and the crystal structure transformation from hydrotalcite to mixed metal oxides during high temperature calcination. For instance, with the calcination temperature higher than 500°C , the lamellar structure of $\text{Ti}_1\text{Li}_3\text{Al}_2$ -T ($T = 500$ and 700) collapses completely, with hydrotalcite transformed to $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Al_2TiO_5 and other spinel mixed oxides, which should give rise to the obvious red shift in optical absorption and then benefit the photocatalytic CO_2 reduction reaction for the $\text{Ti}_1\text{Li}_3\text{Al}_2$ -700 sample as discussed in the following sections.

Given the narrowest band gap of $\text{Ti}_1\text{Li}_3\text{Al}_2$ -LDHs benefiting the photocatalytic process, the crystal structure and electronic structure of $\text{Ti}_1\text{Li}_3\text{Al}_2$ -LDHs were further optimized and calculated by Density Functional Theory³¹. As shown in Fig. 5a, the 2H model is adopted in the Al-LDHs structure and the $[\text{Al}_6(\text{OH})_{16}]_2\text{CO}_3$ fundamental model is constructed. The CO_3^{2-} unit in the hcp-Al position is located in the middle of two parallel plates (The triangle formed by the three oxygen atoms on the top of the CO_3^{2-} is located in the interior of the three hydroxyl oxygen of the aluminum atom of the laminated plate). Based on the structure of Al-LDHs, three representative structures of $\text{Ti}_1\text{Li}_3\text{Al}_2$ -LDHs were constructed by atomic substitution, as shown in Fig. 5b–d. In all the three structures, the CO_3^{2-} species tends to locate in the middle of the two adjacent layers, and does not appear to

Figure 5. Model of (a) Al-LDHs, (b) Ti₁Li₃Al₂-LDHs-(I), (c) Ti₁Li₃Al₂-LDHs-(II), (d) Ti₁Li₃Al₂-LDHs-(III), and The energy band diagram of (e) Ti₁Li₃Al₄-LDHs-(I), (f) Ti₁Li₃Al₄-LDHs-(II), (g) Ti₁Li₃Al₄-LDHs-(III).

come closer towards one layer. To understand the electronic structure changes caused by atomic replacement of Al with Ti and Li, the electronic structures were calculated with the three optimized structures of Ti₁Li₃Al₂-LDHs-(I), Ti₁Li₃Al₂-LDHs-(II), and Ti₁Li₃Al₂-LDHs-(III). As shown in Fig. 5e–g, with Al atoms substituted by Ti and Li atoms, the obtained Ti₁Li₃Al₂-LDHs shows band gaps calculated to be 1.489 eV, 2.427 eV and 1.464 eV, for the three representative structures. Moreover, all three structures show the Fermi level across the valence band in the calculated band structures, indicating the characteristics of p-type semiconductor for Ti₁Li₃Al₂-LDHs.

The photocatalytic activity for the reduction of CO₂ with water vapor was measured on the obtained Ti/Li/Al-LDHs under ultraviolet light irradiation. Without light irradiation or CO₂, there is no product detected. As shown in Fig. 6a, all the Ti/Li/Al-LDHs samples display good photocatalytic activity for CO₂ reduction with CH₄ obtained as the main product; while other products can be hardly detected, meaning the high selectivity of CH₄ generation from CO₂ photoreduction. For all the samples, with the photocatalytic reaction proceeding, the CH₄ production rates increase first and then stabilize after ca. 2 hours. This could be explained by the adequate illumination condition which is necessary to ensure the photocatalytic CO₂ conversion reaction, and help Ti/Li/Al-LDHs generate enough electrons to drive the reaction of CO₂ with H₂O, producing H• and •CO₂[−] as the two main intermediates for CH₄ generation³². It is observable that the photocatalytic activities for CO₂ reduction is of great dependence on the Ti:Li:Al molar ratios. In comparison, the Ti₁Li₃Al₂-LDHs sample shows the highest photocatalytic activity for CO₂ reduction, with CH₄ production rate achieving as high as 1.33 mmol h^{−1} g^{−1}. As confirmed in our previous study¹³, all the obtained Ti/Li/Al-LDHs samples contain a large amount of H₂O and CO₃^{2−}. Moreover, the contents of H₂O and CO₃^{2−} in Ti₁Li₃Al₂-LDHs are the highest, which should contribute to the highest photocatalytic activity for CO₂ reduction, given the inherent adsorption of water and CO₃^{2−} between hydroxalate layers for efficient photocatalytic CO₂ reduction reaction. The optical absorption property and the density functional calculation results suggest the characteristics of p-type semiconductor for Ti₁Li₃Al₂-LDHs with the narrowest band gap among all the Ti/Li/Al-LDHs samples, which are also favorable for photocatalytic CO₂ reduction.

With the Ti₁Li₃Al₂-LDHs sample undergoing high temperature calcination, the photocatalytic CO₂ reduction activity is decreased first and then increased, depending on the increasing calcination temperatures, as shown in Fig. 6b. The highest photocatalytic CO₂ reduction activity is achieved over the Ti₁Li₃Al₂-700 sample, with CH₄ production rate reaching 1.59 mmol h^{−1} g^{−1}. As demonstrated by the XRD, FTIR and SEM analysis, high temperature calcination will cause the deformation of the layered structure and more importantly the crystal structure transformation from hydroxalate to mixed metal oxides such as Li₄Ti₅O₁₂ and Al₂TiO₅. Especially for the samples calcined at temperatures higher than 500 °C, for instance, Ti₁Li₃Al₂-700, the mixed oxides with high reactive oxygen species is generated in a large amount, which benefits the photocatalytic decomposition of H₂O to produce active hydrogen species, activating the photocatalytic CO₂ reduction for CH₄ production³³.

It is well recognized that photocatalytic CO₂ reduction process must be involved with several steps, including CO₂ adsorption, light absorption and photoexcitation, charge separation and transfer, surface CO₂ reduction reaction, and each step could determine the CO₂ photoreduction activity. In this study, Ti/Li/Al-LDHs was used as photocatalyst for CO₂ reduction. Given the almost the same band gaps of Ti/Li/Al-LDHs with different Ti:Li:Al molar ratios (Fig. 4a), light absorption and photoexcitation should not be the determinant for their different photocatalytic activities. Interestingly, as shown in Fig. 7a, with the increasing Ti:Li:Al molar ratios, both the surface area and the CO₂ adsorption capacity reach the highest for Ti₁Li₃Al₂-LDH, which corresponds well with its highest photocatalytic activity. This observation implies that the CO₂ adsorption capacity should greatly determine the photocatalytic CO₂ reduction activities of these obtained Ti/Li/Al-LDHs samples. For Ti₁Li₃Al₂-LDHs calcined at different temperatures, depending on the increasing calcination temperatures, one can hardly find any relationship between the surface area and the CO₂ adsorption capacity (Fig. 7b). It is somewhat surprising that Ti₁Li₃Al₂-700 display the smallest CO₂ adsorption capacity, despite of the highest surface area. More importantly,

Figure 6. Photocatalytic CH_4 yields of (a) Ti/Li/Al-LDHs with different Ti:Li:Al molar ratios, (b) $\text{Ti}_1\text{Li}_3\text{Al}_2\text{-LDHs}$ calcined at different temperatures, (c) $\text{Ti}_1\text{Li}_3\text{Al}_2\text{-LDHs}$ and (d) $\text{Ti}_1\text{Li}_3\text{Al}_2\text{-700}$ during 10 reaction cycles.

Figure 7. Surface area and the CO_2 adsorption capacity of (a) Ti/Li/Al-LDHs with different Ti:Li:Al molar ratios, (b) $\text{Ti}_1\text{Li}_3\text{Al}_2\text{-LDHs}$ calcined at different temperatures.

$\text{Ti}_1\text{Li}_3\text{Al}_2\text{-700}$ shows the highest photocatalytic activity for CO_2 reduction, which indicates that in this case some other reasons rather than the CO_2 adsorption capacity should be decisive to the CO_2 photoreduction activity. Given the band gap determining the light absorption ability and then the electron photoexcitation, the highest CO_2 photoreduction activity achieved over $\text{Ti}_1\text{Li}_3\text{Al}_2\text{-700}$ should be then mainly due to its reduced band gap harvesting more light for photoexcitation (Fig. 4b).

As an excellent photocatalyst, except for the high photocatalytic activity, good stability is also highly required. Herein, the photocatalytic stabilities of $\text{Ti}_1\text{Li}_3\text{Al}_2\text{-LDHs}$ and $\text{Ti}_1\text{Li}_3\text{Al}_2\text{-700}$ were measured during a 10-cycle photocatalytic reaction. As shown in Fig. 6c and d, both $\text{Ti}_1\text{Li}_3\text{Al}_2\text{-LDHs}$ and $\text{Ti}_1\text{Li}_3\text{Al}_2\text{-700}$ exhibit considerable photocatalytic stability during the 10-cycle photocatalytic measurement (ca. 2500 min), with photocatalytic CH_4 production rates decreased by only 19% and 12%, respectively. Given the almost unchanged XRD patterns of the samples after the CO_2 photoreduction reaction (data not shown), such decrease in photocatalytic activity

Figure 8. Schematic of the apparatus for CO₂ adsorption and photocatalytic CO₂ reduction.

of Ti₁Li₃Al₂-LDHs should be due to the inactivation of photoactive sites in the layered structure of hydrotalcite, while high temperature calcination will turn these active sites to high reactive oxygen species in mixed oxides, which should be more stable for photocatalytic CO₂ reduction, ensuring the better stability of Ti₁Li₃Al₂-700. Therefore, to obtain a high efficiency LDHs photocatalyst, it is highly desired to optimize the cation molar ratio and then identify the photocatalytic active sites to elucidate the photocatalytic mechanism for CO₂ reduction with high activity, selectivity and stability.

Discussion

In this study, a series of ternary Ti/Li/Al-LDHs with different Ti:Li:Al molar ratios was synthesized by a simple co-precipitation method, and investigated for photocatalytic CO₂ reduction. It was found that the Ti/Li/Al-LDHs sample with Ti:Li:Al molar ratio optimized to be 1:3:2 displayed the highest photocatalytic activity for CO₂ reduction, with CH₄ production rate achieving 1.33 mmol h⁻¹ g⁻¹, which should be related to the interlayer anion content and the narrowest band gap, as supported by both experimental and theoretical evidences. After calcined at different temperatures, the photocatalytic activity for CO₂ reduction could be further improved. Especially, for the sample calcined at 700 °C, the photocatalytic CH₄ production rate was increased to be 1.58 mmol h⁻¹ g⁻¹, and the activity was well maintained during a 10-cycle measurement. Such photocatalytic enhancement should be mainly attributed to the crystal structure transformation from hydrotalcite to mixed oxides containing high reactive oxygen species for more efficient CO₂ reduction. This study successfully developed a facile approach to prepare multiple cations contained LDHs as efficient and stable photocatalysts for CO₂ reduction, and demonstrated that the composition optimization and reactive site evolution could be pivotal to the high efficiency photocatalytic CO₂ reduction.

Methods

Materials preparation. A series of Ti/Li/Al-LDHs was prepared by a co-precipitation method. Typically, a 200 mL of aqueous solution prepared by mixing 0.03 mol of LiCl and desired amounts of TiCl₄ and AlCl₃ in a flask. Under stirring, a mixed solution of KOH and NaCO₃ was dropped into the as-prepared mixture solution in flask to adjust the pH value at 7~8. After stirred for another 1 h, the mixture solution was kept at 75 °C for 36 h, and then filtered and washed with distilled water for several times to completely remove Cl⁻ in the solution. Then Ti/Li/Al-LDHs was obtained after dried at 80 °C for 24 h. With molar ratios of Ti:Li:Al in the mixture solutions set to be 1:3:1, 1:3:2, 1:3:3, and 1:3:4, a series of Ti/Li/Al-LDHs with different Ti:Li:Al molar ratios was successfully obtained, and labeled as Ti₁Li₃Al₁-LDHs, Ti₁Li₃Al₂-LDHs, Ti₁Li₃Al₃-LDHs, and Ti₁Li₃Al₄-LDHs, respectively.

The Ti₁Li₃Al₂-LDHs sample was further calcined for 30 min in air at different temperatures (180 °C, 300 °C, 500 °C and 700 °C), and the obtained samples were labeled as Ti₁Li₃Al₂-T (T = 180, 300, 500 and 700).

Characterizations. The molar ratios of the samples were determined by Atomic Absorption Spectrometer (AAS Various 6, Analytik Jena AG, German). X-ray diffraction (XRD) patterns were collected on a MiniFlex600 desktop X-ray diffractometer operated at 30 kV and 10 mA using Cu Kα irradiation (Wavelength = 1.5406 Å). Scanning electron microscopy (SEM) images were recorded on a S-4800 scanning electron microscope at an accelerating voltage of 200 kV. Fourier transform infrared (FTIR) spectra were recorded on a Brook Tensor 27 Fourier transform infrared spectrometer) using the KBr pellet technique. UV-vis diffuse reflectance spectra were recorded on a Perkin Elmer Lambda 950 ultraviolet spectrophotometer. N₂ adsorption-desorption isotherms were conducted at 77 K using an Accelerated Surface Area and Porosimetry Analyzer (ASAP2010, Micromeritics) after degassing the samples at 100 °C for 4 h. The specific surface areas were determined by the Brunauer-Emmett-Teller (BET) methods. The CO₂ adsorption capacity was calculated from the weights of the samples before and after CO₂ adsorption in a home-made quartz fixed bed reactor (Fig. 8).

Computation methods. The crystal structure and electronic structure of $\text{Ti}_1\text{Li}_3\text{Al}_2\text{-LDHs}$ were optimized and calculated by Density Functional Theory. Based on the structure of Al-based hydrotalcite, the structure of $\text{Ti}_1\text{Li}_3\text{Al}_2\text{-LDHs}$ was constructed by atomic substitution, and built by Statistical Disorder included in Materials Studio. Statistical Disorder can build all possible structural models in an exhaustive way. The final structure model has 13186 structures, and each containing 144 atoms. Herein, we choose three representative structures, and calculated them in arithmetic average. Three structures are named as $\text{Ti}_1\text{Li}_3\text{Al}_2\text{-LDHs-(I)}$, $\text{Ti}_1\text{Li}_3\text{Al}_2\text{-LDHs-(II)}$, and $\text{Ti}_1\text{Li}_3\text{Al}_2\text{-LDHs-(III)}$, which will be described in Results and Discussion.

In order to predict the stable structure of hydrotalcite with specific measurement ratio, the structure is optimized. All calculations are performed using the CASTEP module in the Materials Studio package. By using Broyden-Fletcher-Goldfarb-Shanno structure optimization (BFGS) algorithm, the atomic positions and cell parameters are optimized at the same time, the convergence of standard energy is $5.0 \times 10^{-6} \text{ eV} \cdot \text{atom}^{-1}$, the convergence criteria for each atomic force is less than $0.01 \text{ eV}/\text{\AA}$, the displacement deviation is $5 \times 10^{-4} \text{ \AA}$, and the pressure deviation is 0.02 GPa. The exchange correlation functionals are LDA-CA-PZ, the pseudopotential uses the OTFG form of the super soft pseudopotential, and the electron minimization method uses the Pulay density mixing method (Density, Mixing). The mixed error self-consistent field calculation is $5 \times 10^{-7} \text{ eV} \cdot \text{atom}^{-1}$, the truncation kinetic energy is 630 eV, while the Brillouin zone K vector is selected for the $5 \times 5 \times 2$. The total charge number is 0, and the inter layer has a weak interaction, such as van Edward force.

Photocatalytic CO_2 reduction. The activity of photocatalytic conversion of CO_2 to CH_4 was tested in a continuous entry type system (Fig. 8), including a home-made quartz fixed bed reactor equipped with an on-line gas detection system (Agilent 7890 A gas chromatograph). For photocatalytic CO_2 reduction, 1.0 g of photocatalyst was loaded in the middle part of the quartz tube reactor, with temperature heated up to 60°C . CO_2 gas with the flow of 80 mL/min was continuously passed through the water vapor generator and then introduced into the photocatalytic reactor. CO_2 photocatalytic reduction was triggered under UV irradiation, with produced gas analyzed by on-line gas chromatograph with the temperature of the injector, column and detector set at 120°C , 50°C , 100°C , respectively.

References

1. IPCC. Special Report on Renewable Energy Sources and Climate Change Mitigation, <http://www.ipcc.ch/report/srren/2011>.
2. Tang, L. Q. *et al.* $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ tunable band structure-directing photocatalytic activity and selectivity of visible-light reduction of CO_2 into liquid solar fuels. *Nanotechnology* **29**, 064003 (2018).
3. Buursink, M. L. Significance of carbon dioxide density estimates for basin-scale storage resource assessments. *Energy Proced.* **63**, 5130–5140 (2014).
4. Bhowan, A. S. & Freeman, B. C. Analysis and status of post-combustion carbon dioxide capture technologies. *Environ. Sci. Technol.* **45**, 8624–8632 (2011).
5. Olah, G. A., Goeppert, A. & Prakash, G. K. S. Chemical recycling of carbon dioxide to methanol and dimethyl ether. From greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons. *J. Org. Chem.* **74**, 487–498 (2009).
6. Wang, B. *et al.* Oxygen-Vacancy-Activated CO_2 splitting over amorphous oxide semiconductor photocatalyst. *ACS Catal.* **8**, 516–525 (2018).
7. Rao, H. *et al.* Visible-light-driven methane formation from CO_2 with a molecular iron catalyst. *Nature* **548**, 74–77 (2017).
8. Pougin, A., Dilla, M. & Strunk, J. Identification and exclusion of intermediates of photocatalytic CO_2 reduction on TiO_2 under conditions of highest purity. *Phys. Chem. Chem. Phys.* **18**, 10809–10817 (2016).
9. Bai, S., Zhang, N., Gao, C. & Xiong, Y. Defect engineering in photocatalytic materials. *Nano Energy* **53**, 296–336 (2018).
10. Chang, P. *et al.* Ca-rich Ca-Al-oxide, high-temperature-stable sorbents prepared from hydrotalcite precursors: synthesis, characterization, and CO_2 capture capacity. *ChemSusChem* **4**, 1844–1851 (2011).
11. Iguchi, S. *et al.* Photocatalytic conversion of CO_2 in an aqueous solution using various kinds of layered double hydroxides. *Catal. Today* **251**, 140–144 (2015).
12. Zhao, H. *et al.* CO_2 photoreduction with water vapor by Ti-embedded MgAl layered double hydroxides. *J. CO_2 Utilization* **15**, 15–23 (2016).
13. Kong, T. T. *et al.* Preparation of hydrotalcite-like Ti/Li/Al-LDHs and its performance in CO_2 adsorption. *J. Fuel Chem. Technol.* **44**, 1017–1024 (2016).
14. Azzouz, A. *et al.* Polyol-modified layered double hydroxides with attenuated basicity for a truly reversible capture of CO_2 . *Adsorption* **19**, 909–918 (2013).
15. Shao, M. *et al.* The synthesis of hierarchical Zn-Ti layered double hydroxide for efficient visible-light photocatalysis. *Chem. Eng. J.* **168**, 519–524 (2011).
16. Teruel, L., Bouizi, Y. & Atienzar, P. Hydrotalcites of zinc and titanium as precursors of finely dispersed mixed oxide semiconductors for dye-sensitized solar cells. *Energy Environ. Sci.* **3**, 154–159 (2010).
17. Hu, X. M. *et al.* Hybrid photoanodes based on nanoporous lithium titanate nanostructures in dye-sensitized solar cells. *J. Inorg. Mater.* **30**, 1037–1042 (2015).
18. Mayra, G. *et al.* Role of the synthesis route on the properties of hybrid LDH-graphene as basic catalysts. *Appl. Surf. Sci.* **396**, 821–831 (2017).
19. Ding, X. *et al.* Hydrothermal synthesis, structural analysis and performance of regular Mn-Zn-Mg-Al- CO_3 quaternary layered double hydroxides(LDHs). *Chin. J. Inorg. Chem.* **28**, 331–341 (2012).
20. Xue, X. Y., Zhang, S. H. & Zhang, H. M. Structures of LDHs intercalated with ammonia and the thermal stability for ploy(vinylchloride). *Am. J. Anal. Chem.* **6**, 334–341 (2015).
21. Zhang, Y. *et al.* A facile approach to superhydrophobic LiAl-layered double hydroxide film on Al-Li alloy substrate. *J. Coat. Technol. Res.* **12**, 595–601 (2015).
22. Xi, Y. Z. & Davis, R. J. Influence of water on the activity and stability of activated Mg-Al hydrotalcites for the transesterification of tributyrin with methanol. *J. Catal.* **254**, 190–197 (2008).
23. Zhang, Z. *et al.* The influence of synthesis method on the CO_2 adsorption capacity of $\text{Mg}_3\text{Al-CO}_3$ hydrotalcite-derived adsorbents. *Sci. Adv. Mater.* **6**, 1154–1159 (2014).
24. Shen, S., Guo, P., Zhao, L., Du, Y. & Guo, L. Insights into photoluminescence property and photocatalytic activity of cubic and rhombohedral ZnIn_2S_4 . *J. Solid State Chem.* **184**, 2250–2256 (2011).
25. Li, J. & Yang, Y. J. New type ternary NiAlCe layered double hydroxide photocatalyst for efficient visible-light photoreduction of CO_2 into CH_4 . *Mater. Res. Exp.* **5**, 026204 (2018).

26. Silva, C. G., Bouizi, Y., Fornés, V. & García, H. Layered double hydroxides as highly efficient photocatalysts for visible light oxygen generation from water. *J. Am. Chem. Soc.* **131**, 13833–13839 (2009).
27. Sahu, R. K., Mohanta, B. S. & Das, N. N. Synthesis, characterization and photocatalytic activity of mixed oxides derived from ZnAlTi ternary layered double hydroxides. *J. Phys. Chem. Solids* **74**, 1263–1270 (2013).
28. Shen, S. *et al.* Titanium dioxide nanostructures for photoelectrochemical applications. *Prog. Mater. Sci.* **98**, 299–385 (2018).
29. Sakr, A. A. E. *et al.* Synthesis of Zn-Al LDHs intercalated with urea derived anions for capturing carbon dioxide from natural gas. *J. Taiwan Inst. Chem. Eng.* **44**, 957–962 (2013).
30. Kong, T. T. *et al.* Preparation of Cu/Fe/Al-LDHs and photocatalytic reduction of CO₂ prepare CH₄. *J. Xi'an Univ. Sci. Technol.* **36**, 86–91 (2016).
31. Segall, M. D. *et al.* First-principles simulation: ideas, illustrations and the CASTEP code. *J. Phys.-Condens. Matter* **14**, 2717–2744 (2002).
32. Centi, G. & Perathoner, S. Opportunities and prospects in the chemical recycling of carbon dioxide to fuels. *Catal. Today* **148**, 191–205 (2009).
33. Xiang, G. *et al.* Large-scale synthesis of metastable TiO₂(B) nanosheets with atomic thickness and their photocatalytic properties. *Chem. Commun.* **46**, 6801–6803 (2010).

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Author Contributions

T.T.K. and Y.Z. conceived the experiment and wrote the manuscript, T.T.K. and J.H. conducted the experiments, T.T.K., X.G.J. and W.Z.W. analysed the results. All authors reviewed the manuscript.

Additional Information

Competing Interests: The authors declare no competing interests.

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