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Synthesis, structure and photocatalytic reactivity of layered CdS/$H_2La_2Ti_3O_{10}$ nanocomposites

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A fabrication process has been optimized to produce photocatalytic $H_2La_2Ti_3O_{10}$/CdS nanocomposites by a stepwise exchanging reaction of $H_2La_2Ti_3O_{10}$ with n-$C_3H_7NH_2$ (or n-$C_8H_{17}NH_2$), $Cd(CH_3COO)_2$ and H_2S gas, which was obtained by H^+-exchanging reaction of $K_2La_2Ti_3O_{10}$ with HCl other than the normally used HNO_3. XRD, TEM, FT-IR, TG, ICP and BET methods were used to investigate the pillaring-process. Results showed that the particle size of pillared cadnium sulphide was less than 1nm and the amount of intercalated CdS increased from 12.2 wt% to 16.5 wt% when n-$C_8H_{17}NH_2$ took the place of n-$C_3H_7NH_2$ to "pre-expand" the interlayer of $H_2La_2Ti_3O_{10}$. The possible reason of this success was mentioned. The photocatalytic properties of the resulting powders were evaluated by using photodecomposition of methyl orange as the model system. Compared with the unpillared $K_2La_2Ti_3O_{10}$, the pillaring of CdS gave rise to a remarkable enhancement of its photoactivity and the decomposition rate of methyl orange was improved from 50% to 95%.

1. Introduction

Among various methods for solar energy conversion, much attention has been paid to photocatalytic water splitting for its potential significance in obtaining directly clean and high energy containing H_2 from abundant H_2O. If successfully developed with an economic viability, this would be the ultimate technology that could solve both energy and environmental problems altogether in the future. It has been reported that some oxides, which are mainly Perovskite-type layered compounds, such as $K_2La_2Ti_3O_{10}$, $K_4Nb_6O_{17}$, $RbLnTa_2O_7$ (Ln=La, Pr, Nd, Sm) etc. show reasonable activities in photochemical reaction under UV irradiation [1–5]. Recently, intense research efforts have been devoted to the pillaring of nanoparticles into layered inorganic solids, which can provide a useful method not only for creating novel porous materials but also for improving the catalytic activity of the layered material. The pillared materials are usually prepared by intercalation of large alkylamine molecules followed by inorganic cations or metal alkoxides into layered hosts. Actually, it has been reported that the pillaring of semiconductor materials such as Fe_2O_3, TiO_2, CdS and CdS–ZnS mixture into layered host material give rise to remarkable enhancement of their photocatalytic activity compared with unsupported catalysts [6–10].

$K_2La_2Ti_3O_{10}$, a layered perovskite-type compound with a hydrated interlayer space is generally accepted as photocatalytic materials because of their high quantum yield and high photoactivities comparing with TiO_2 [11]. However, there are few reports about how to enhance its photoactivity by pillaring method because of its high interlayer charge distribution, even the strong organic bases can't be intercalated into the interlayer [12], which results in the failure of pillaring-process. So researches focused on $K_2La_2Ti_3O_{10}$ are mainly about how to exfoliate it into sheets conveniently and use these sheets to

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fabricate monolayer or multilayer thin films by self-assembly method [13, 14]. In this paper, the pillaring of CdS in the interlayer of $H_2La_2Ti_3O_{10}$ was successfully realized by modifying H^+-exchanging reaction, and HCl was used as the exchanging acid other than HNO_3 according to pervious reports [12–14]. The decomposition of methyl orange was used as the model system to evaluate the photocatalytic properties of $H_2La_2Ti_3O_{10}$/CdS, $H_2La_2Ti_3O_{10}$ and $K_2La_2Ti_3O_{10}$ and the optimal reaction condition was achieved. It was found that the photocatalytic activity of $H_2La_2Ti_3O_{10}$/CdS was greatly improved by the pillaring of CdS.

2. Experimental

2.1. Preparation of the samples

$K_2La_2Ti_3O_{10}$ was prepared by calcination a mixture of K_2CO_3, TiO_2 and $La(NO_3)_3$ at 1100°C for 11 h [11–14]. The protonated $K_2La_2Ti_3O_{10}$(denoted as H–La) was prepared by exchanging K^+ of $K_2La_2Ti_3O_{10}$(1 g) in 200 mL of 1 mol L^{-1} HCl at 60°C for 3 days. The acid solution was renewed every 24 h in order to remove K^+ completely from the compound. The product was washed with distilled water and dried in vacuum at 30°C and was designed as H–La–HCl. For comparing, H–La–HNO_3 was prepared according to Ref. 13.

CdS was incorporated by modifying the procedures used in the preparation of a CdS-pillared titanates reported by Sato, T. et al. [15–16]. H–La–HCl was converted to $(C_3H_7NH_3)_2La_2Ti_3O_{10}$ by stirring H–La–HCl powders (ca. 1 g) in 20 vol% of n-propylamine($C_3H_7NH_2$) aqueous solutions (50 ml) at 60°C for 3days. The solid material was separated by centrifugation and further dried in vacuum at 30°C. CdS particles was pillared into the interlayer of H–La–HCl by reacting H_2S gas with Cd^{2+} exchanged compound, which were obtained by the ion exchange reaction in 0.4 mol L^{-1} $Cd(CH_3COO)_2$ solution at 50°C for 3 days using $(C_3H_7NH_3)_2La_2Ti_3O_{10}$ as the precursor. The obtained sample was designated as $H_2La_2Ti_3O_{10}$/CdS(C_3).

$H_2La_2Ti_3O_{10}$/CdS(C_8) was fabricated by the same method mentioned above, the difference was that $(C_8H_{17}NH_3)_2La_2Ti_3O_{10}$ was used as the starting material which was obtained by stirring H–La–HCl (1 g) in 50 vol% of $C_8H_{17}NH_2$/ethanol solutions(50 ml) at 60°C for 3 days.

The photocatalytic activities of the samples were evaluated by methyl orange decomposition under UV irradiation using revolving reaction system. A 300 W high-pressure mercury lamp provided the irradiation with a wavelength centered at 365 nm. The initial concentration of methyl orange in a quartz reaction vessel was fixed at approximately 20 mg L^{-1} with as-prepared catalysts loading of 1.0 g L^{-1}. The reaction cell (50 ml) was bubbled with air at a flow rate of 10 mL min^{-1}. The extent of methyl orange decomposition was determined by measuring the absorbance value at 465 nm using UV-1100 spectrometer [17].

2.2. Characterization of the samples

The crystalline phase of the products were identified by X-ray diffraction (XRD) analysis (Bruker D8 ADVANCE) using Cu kα ($\lambda = 0.15405$ nm) irradiation. The preparative process was monitored by FT–IR spectroscopy with a Bluker Vector22 spectrometer. Transmission electron microscopy (TEM) was performed on an H-800 TEM using 175 kV acceleration voltage. The water content in the interlayer was deduced by measuring the weight lost at 800°C using thermo-gravimetric (TG) analysis[18], which was carried out with a Shimadzu TGA-50 thermogravimetric at a heating rate of 20°C min^{-1} under air atmosphere. The BET specific surface area of samples was obtained by nitrogen adsorption/desorption isotherms at liquid nitrogen temperature (77 K) using a Coulter SA 3100 instrument. The approximate content of pillared CdS was determined by Inductively Coupled Plasma (ICP) spectroscopy (Perkin-Elmer Optima-2000 DV).

3. Results and discussion

3.1. Intercalation of CdS into the interlayer of $H_2La_2Ti_3O_{10}$

Fig. 1 shows the XRD patterns of $K_2La_2Ti_3O_{10}$ before and after H^+-exchanging reaction. It can be seen that the XRD patterns of H–La (Fig. 1 (b)(c)) exchanged by both HCl and HNO_3 are in accordance with the standard results well (JPCDS 480943), which indicates the result product is certain to $H_2La_2Ti_3O_{10} \cdot xH_2O$. But there still exists some difference between them, the interlayer distance of H–La–HNO_3 is larger than that of H–La–HCl, which implies that the interlayer structure of the H^+-exchanged products is influenced by the kind of exchanging acid. TG analysis results of H–La are shown in Fig. 2. According to our knowledge [18, 19], the weight loss below 60°C represents the release of physical adsorbed water. The mass loss between 80–250°C is attributed to the decomposition of the interlayer water molecules and the last weight loss represents the release of water in

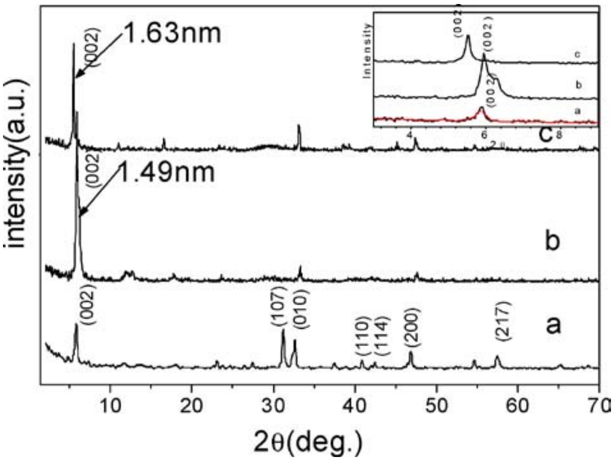
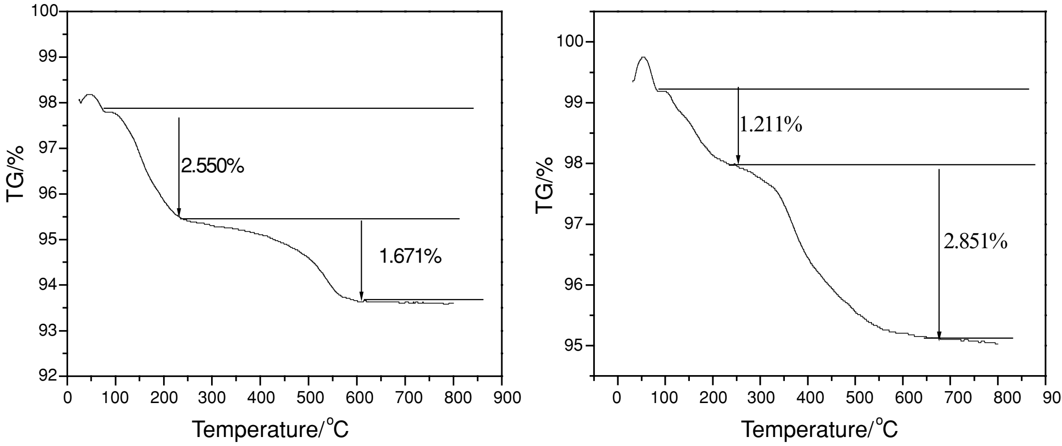


Figure 1 XRD patterns of (a) $K_2La_2Ti_3O_{10}$, (b) H–La–HCl, (c) H–La–HNO_3.



(a) (b)

Figure 2 TG curves of (a) H–La–HNO_3 and (b) H–La–HCl.

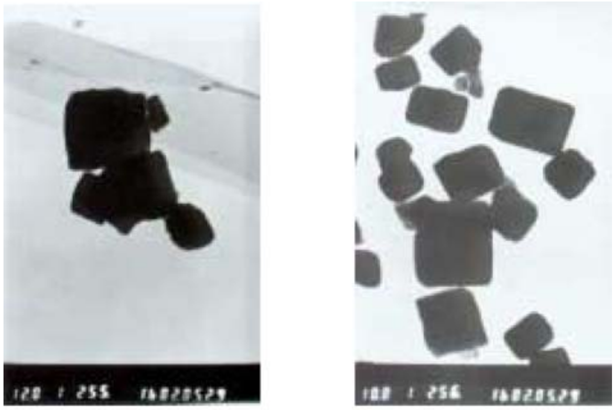
the anionic sheets, which were signed as m and n respectively. So the calculated numbers of interlayer water molecules of H–La–HCl and H–La–HNO_3 are approximately 0.4 and 0.8 respectively, which imply that more water molecules were intercalated into the interlayer of H–La–HNO_3 (See Table I). This may account for the different d(002) values in the XRD profiles [20] and the difference in the alkylamine "pre-expand" section [21]. But the total amount of water molecules ($m + n$) both in H–La–HCl and H–La–HNO_3 are quite similar, indicating that the molecular formula of H^+-exchanging product is uniform and is signed as $H_2La_2Ti_3O_{10} \cdot 0.3H_2O$. In order to be brief, the $H_2La_2Ti_3O_{10}$ used in the latter section were all referred to H–La–HCl without special identification.

At the same time, the diffraction profiles of protonated $K_2La_2Ti_3O_{10}$ are much stronger and larger than that of $K_2La_2Ti_3O_{10}$, indicating the crystallinity of $H_2La_2Ti_3O_{10}$ is better [22] and this suspect agreed the TEM results as well. The morphologies of the $K_2La_2Ti_3O_{10}$ and $H_2La_2Ti_3O_{10}$ were shown in Fig. 3. It can be seen that the products are square-like and agreed with Ref. 13, 14 as well, but $H_2La_2Ti_3O_{10}$ shows higher dispersibility and more regular morphology implying the integrity of $H_2La_2Ti_3O_{10}$ is better preserved.

The pillaring process of $H_2La_2Ti_3O_{10}$ was identified also by XRD experiments (see Fig. 4 and Table II). After intercalation, the main peak corresponding to (002) of $H_2La_2Ti_3O_{10}$ still exists indicating that the layer structure was maintained and the (002) peak significantly shifted to a lower 2θ angles for samples (b), (c) and (d), suggesting the expansion of the interlayer by incorporation of $C_3H_7NH_3^+$, $C_8H_{17}NH_3^+$ and CdS [15, 16]. The gallery height of $(C_3H_7NH_3)_2La_2Ti_3O_{10}$, determined by subtracting the $La_2Ti_3O_{10}{}^{2-}$ layer thickness of 0.86 nm, was 1.33 nm. Since the length of n-$C_3H_7NH_3^+$ is ca. 0.5 nm, it is suspected that two molecules of n-$C_3H_7NH_3^+$

TABLE I. Calculated numbers of H_2O molecules in $H_2La_2Ti_3O_{10} \cdot xH_2O$ determined from TG results

Sample	m (interlayer)	n (layer)	$m + n$
H–La–HNO_3	0.83	0.54	1.37
H–La–HCl	0.39	0.92	1.31



(a) (b)

Figure 3 TEM image of samples: (a) $K_2La_2Ti_3O_{10}$, (b) $H_2La_2Ti_3O_{10}$..

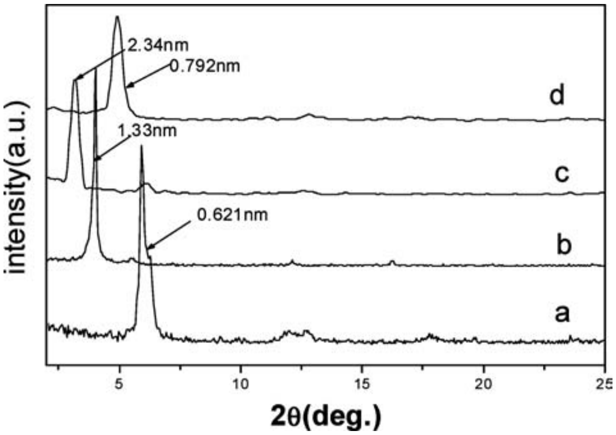


Figure 4 XRD patters of $H_2La_2Ti_3O_{10}$ before and after CdS pillaring (a) $H_2La_2Ti_3O_{10}$; (b) $(C_3H_7NH_3)_2La_2Ti_3O_{10}$; (c) $(C_8H_{17}NH_3)_2La_2Ti_3O_{10}$ (d) $H_2La_2Ti_3O_{10}$/CdS(C_3).

TABLE II. Interlayer distance, amount of CdS and specific surface area of the products

Sample	Interlayer height (nm)	Content of CdS (wt%)*	Specific surface Area (m^2g^{-1})
$K_2La_2Ti_3O_{10}$	0.635	0	1.52
$H_2La_2Ti_3O_{10}$	0.621	0	33.1
$(C_3H_7NH_3)_2La_2Ti_3O_{10}$	1.330	0	/
$H_2La_2Ti_3O_{10}$/CdS(C_3)	0.792	12.2	22.5
$(C_8H_{17}NH_3)_2La_2Ti_3O_{10}$	2.340	0	/
$H_2La_2Ti_3O_{10}$/CdS(C_8)	0.821	16.5	25.7

*The amount of CdS was estimated by ICP. Approximate amount of $H_2La_2Ti_3O_{10}$/CdS was dissolved in a mixed solution of H_2SO_4/H_2O_2 (3:1) and the solution was diluted to the concentration of La^{3+} is about 50 ppm.

are vertically arranged in the interlayer of $H_2La_2Ti_3O_{10}$. The layer distance of $(C_8H_{17}NH_3)_2La_2Ti_3O_{10}$ is 2.34 nm. Since the length of n-$C_8H_{17}NH_2$ is 1.30 nm [23], it is estimated that two molecules of n-$C_8H_{17}NH_3^+$ are arranged in the interlayer with a bending about 25.84°from gallery orientation [bending angle was derived by a calculation of $\cos^{-1}\{$interlayer distance/(2 × the length of $C_8H_{17}NH_2$)$\}$] [22, 23]. And the distance of $H_2La_2Ti_3O_{10}$/CdS was 1.65 nm; taking into account of the layer thickness of $La_2Ti_3O_{10}{}^{2-}$, the particle size of CdS incorporated was estimated as less than 0.79 nm. These results are quite similar to other alkylamine and CdS pillared tetratitanate [15, 16], illustrating that the CdS particles do be pillared into the interlayer of $H_2La_2Ti_3O_{10}$ for the first time, which can also be confirmed by the FT-IR results.

From Fig. 5 (b), we can see the characteristic absorption bands of $-NH_3^+$ (1470 and 1573 cm^{-1}) and $-CH_2-$ (2900 cm^{-1}). According to XRD patterns, this result implied that n-$C_3H_7NH_2$ was intercalated into the interlayer of $H_2La_2Ti_3O_{10}$ After CdS pillaring, the characteristic absorption bands of $-NH_3^+$ and $-CH_2-$ decreased, indicating that the interlayer n-$C_3H_7NH_2$ was completely exchanged by the Cd^{2+}. The absorption bands between 1000 and 400 cm^{-1} have little changes implied that the layered structure was maintained during the pillaring process.

According to Ref. 20, the interlayer width of layered compounds increased with the increasing of the length of incorporated n-alkylamine (n-$C_nH_{2n+1}NH_2$). So if long-sized alkylamine such as $C_8H_{17}NH_2$ is used, the gallery height of the $(C_8H_{17}NH_3)_2La_2Ti_3O_{10}$ will be larger, and the content of CdS incorporated in the interlayer will be more. The experimental results as expected are listed in Table II. With the help of n-propylamine to "pre-expand", the amount of incorporated CdS is 12.2 wt%, but when n-$C_8H_{17}NH_2$ was used to "pre-expand", the amount of CdS in the interlayer increased to 16.5 wt%. This result is very helpful to enhance its photocatalytic reactivity.

Concerning the mentioned analysis, it came to the conclusion that by using HCl as the exchanging acid, $H_2La_2Ti_3O_{10}$/CdS nanocomposite was synthesized successfully. The reason is that during acid-exchanging reaction, more water molecules were intercalated into the interlayer of H–La–HNO_3 than that of H–La–HCl, this may result in the handicap of alkylamine intercalation during the "pre-expand" stage [21]; On the other hand, the dissolution of La_2O_3 in anion sheets in HNO_3 may lead to the instability of the layer structure. Concerning these two aspects, using HNO_3 in acid-exchanging reaction according the previous reports leads to the failure of pillaring process.

3.2. Photocatalytic activity measurement

Fig. 6 shows the photocatalytic reaction goes with irradiation time. Most important of all, it was found that the photo-degraded amounts of methyl orange decreased in the sequence of $H_2La_2Ti_3O_{10}$/CdS > $H_2La_2Ti_3O_{10}$ > $K_2La_2Ti_3O_{10}$ and the decomposition rate was about 95%, 62% and 50% respectively in 70 min. In general, the excellent photoactivity of the $H_2La_2Ti_3O_{10}$/CdS nanocomposite might be attributing to the extremely

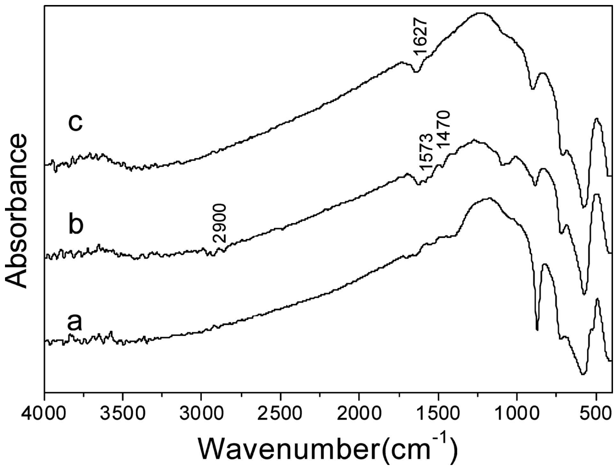


Figure 5 FT-IR spectra of (a) $H_2La_2Ti_3O_{10}$ (b) $H_2La_2Ti_3O_{10}$-pro (c) $H_2La_2Ti_3O_{10}$/CdS.

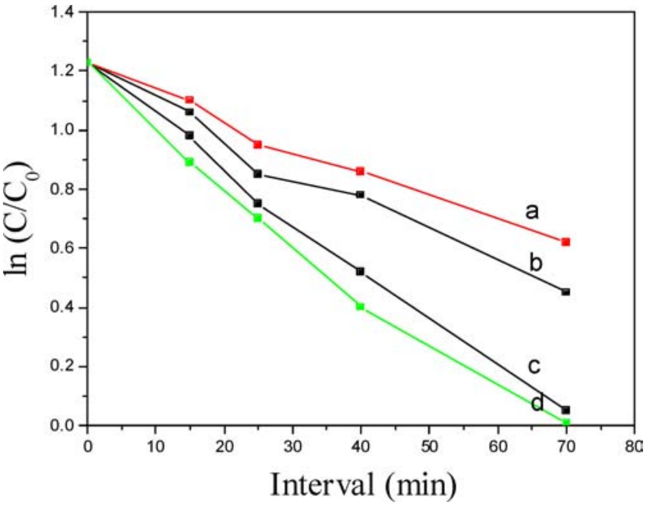


Figure 6 Absorption spectra of methyl orange solution (20 mg L-1) photocatalyzed by (a) $K_2La_2Ti_3O_{10}$; (b) $H_2La_2Ti_3O_{10}$; (c) $H_2La_2Ti_3O_{10}$/CdS (C3); (d) $H_2La_2Ti_3O_{10}$/CdS (C_8) with different intervals.

small particle size of incorporated CdS and good contact between CdS and $La_2Ti_3O_{10}{}^{2-}$ layers [16]. On the other hand, the coupling of two semiconductor particles with different energy level is useful to achieve effective charge separation. In $H_2La_2Ti_3O_{10}$/CdS, a photo-generated electron can transfer from CdS to the $La_2Ti_3O_{10}{}^{2-}$ layer, while the holes remain in the CdS particles. This helps to diffuse the electrons and holes before reaching the interface, and the holes and electrons can be effectively captured by the electrolyte in the solution [1, 14–16]. At the same time, $H_2La_2Ti_3O_{10}$/CdS (C_8) showed a little higher photoactivity than $H_2La_2Ti_3O_{10}$/CdS (C_3) because it contained more CdS in the interlayer. This result suggests that using long sized alkylamine to pre-expand the interlayer helps to obtain higher amount of pillaring particles and higher photoactivity.

On the other hand, both $K_2La_2Ti_3O_{10}$ and $H_2La_2Ti_3O_{10}$ are efficient photocatalyst because of their unique layered structure and active semiconductor $La_2Ti_3O_{10}{}^{2-}$ layer. But $H_2La_2Ti_3O_{10}$ showed higher photoreactivity because of its more crystallization rate (see Fig. 3) and higher BET surface area (see Table II). So the well-crystallized catalyst with higher surface area of $H_2La_2Ti_3O_{10}$ shows higher photo-activity than that of $K_2La_2Ti_3O_{10}$ [1].

4. Conclusion

The pillaring of CdS in layered $H_2La_2Ti_3O_{10}$ has been fabricated using the conventional intercalating reaction for the first time by modifying the acid-exchanging action; HCl took the place of HNO_3 during the H^+-exchanging reaction, which had less effect on the layer structure. The fabricating process was identified by XRD, TEM, ICP and FT–IR methods. The gallery height of $H_2La_2Ti_3O_{10}$/CdS is less than 1nm and the amount of incorporated CdS increased from 12.2 wt% to 16.5 wt% when n-$C_8H_{17}NH_2$ was used to "pre-expand" the interlayer of $H_2La_2Ti_3O_{10}$ instead of n-$C_3H_7NH_2$. The optimal reaction condition was studied and the photo-activities of $H_2La_2Ti_3O_{10}$/CdS, $H_2La_2Ti_3O_{10}$ and $K_2La_2Ti_3O_{10}$ were compared. It was found that incorporation CdS into the layer of $H_2La_2Ti_3O_{10}$ could enhance its photoactivity obviously and improve the amount of pillared CdS helps to achieve better photoreactivity.

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