Supporting Information

Formation mechanism and photocatalytic activity of hierarchical NiAl-LDH films on Al substrate prepared under acidic conditions

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1. Materials

All of the reagents used in this work were of analytical grade and used without further purification. The aluminum substrate (purity: 99.99%; thickness: 0.1 mm) was purchased from Xinjiang Joinworld Co., Ltd., China. $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Ethanol, HNO_3 and $NH_3 \cdot H_2O$ were purchased from Laiyang Fine Chemical Factory (China). NaOH and methyl orange (MO) were purchased from Tianjin Bodi Chemical Co., Ltd., China.

Rhodamine B (Rh B) was obtained from Aladdin Reagent Co., Ltd., Shanghai, China. Deionized water was used in all the experimental processes.

2. Preparation of NiAl-LDH/Al films

The NiAl-LDH film was prepared by a simplified *in situ* growth technique. The aluminum sheet (2×3 cm) was cleaned with ethanol, 1 M NaOH solution and deionized water in sequence before use. The 0.1 M Ni^{2+}-containing solution was obtained by dissolution of $Ni(NO_3)_2 \cdot 6H_2O$ in deionized water, and the pH value was adjusted to 1, 2, 3, 4, 5 and 6 respectively, by addition of $NH_3 \cdot H_2O$ or HNO_3. Each resulting solution was transferred to a glass tube, and the as-prepared Al substrate was placed vertically in the solution. The tube was sealed by cling film and heated to 80 ^oC in water bath for different times. The pH values of the solutions were detected at regular time intervals at room temperature. The resulting films were rinsed with deionized water and dried under ambient conditions. The precipitate in bulk solution was filtrated, washed with deionized water and dried under ambient conditions. The white film coating on Al substrate is denoted as NiAlp*x*t*y*, and the precipitate formed in bulk solution is denoted as NiAlp*x*t*y*-p (*x* means the initial pH value of the Ni^{2+}-containing solution and *y* means the immersion time (hour) of the Al substrate in solution).

Solutions containing Zn^{2+}, Co^{2+} and Mg^{2+} respectively were prepared to fabricate MAlp2t24 (M=Zn, Co, Mg) samples, using the same *in situ* growth method as

NiAlp2t24.

3. Sample Characterization

The powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer (Cu Kα radiation, λ = 1.5406 Å) at 35 kV, 30 mA, with a scan step of 0.02 ^{o} and a 2θ angle ranging from 5 ^{o} to 70 ^{o}. Fourier transform infrared (FT-IR) spectra of samples were collected in KBr pellets on a Nicolet 5700 Fourier transformation infrared spectroscope (Thermo Electron Co., USA), at the range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1}. The morphology of the samples was investigated using a field emission scanning electron microscope (FESEM, FEI Sirion 200, Netherlands) with an energy-dispersed X-ray (EDX) unit (INCA Oxford). The accelerating voltage applied was 10 kV. All samples were sputtered with platinum. To investigate the surface nature of samples, X-ray photoelectron spectroscopy (XPS) spectra were recorded on an ESCALAB 250Xi X-ray photoelectron spectrometer using Al Kα radiation with constant pass energy of 20 eV.

The photocatalytic activity of the film samples was evaluated by photocatalytic degradation of MO and Rh B in aqueous solution. In the case of MO degradation, a 50 mL of 20 mg L^{-1} MO was placed in a photocatalytic reactor, to which a film catalyst (2×3 cm) was added lying on the bottom of the reactor. Then the solution was irradiated immediately with ultraviolet light from a high-pressure mercury lamp (125 W, GGZ-125, Shanghai Yaming Fiya Lighting Appliance Co., Ltd., E_{max} = 365 nm)

under stirring condition without preadsorption of MO on catalyst. Although the LDH film covers both side of the Al substrate, only one side of the film sample was exposed to the mercury lamp which was located above the reactor. As for Degussa P25 TiO_2, 1.0 mg TiO_2 was added into the MO solution for the photodegradation reaction. The weight of the TiO_2 was equal to the weight of LDH powder scraped from two sides of one Al substrate (NiAlp2t24 sample). The temperature of the solution was controlled at room temperature by circulating water. During irradiation, at given time intervals, the concentration of MO was monitored by colorimetry using a UV/VIS spectrophotometer (UV-1801, Beijing Beifen-Ruili Analytical Instrument (Group) Co., Ltd.). Centrifugation was performed to separate the TiO_2 powder from the solution to determine the concentration of MO when P25 TiO_2 was used as photocatalyst. Blank dye degradation was also carried out under similar condition without the catalyst. MO adsorption experiments on NiAlp*x*t24 (x = 1-6) were performed under stirring condition in the dark. In the case of photodegradation of Rh B, a 50 mL of 50 mg L^{-1} Rh B solution was used for NiAlp2t24 and P25 TiO_2 photocatalysts.

4. Characterization and Results

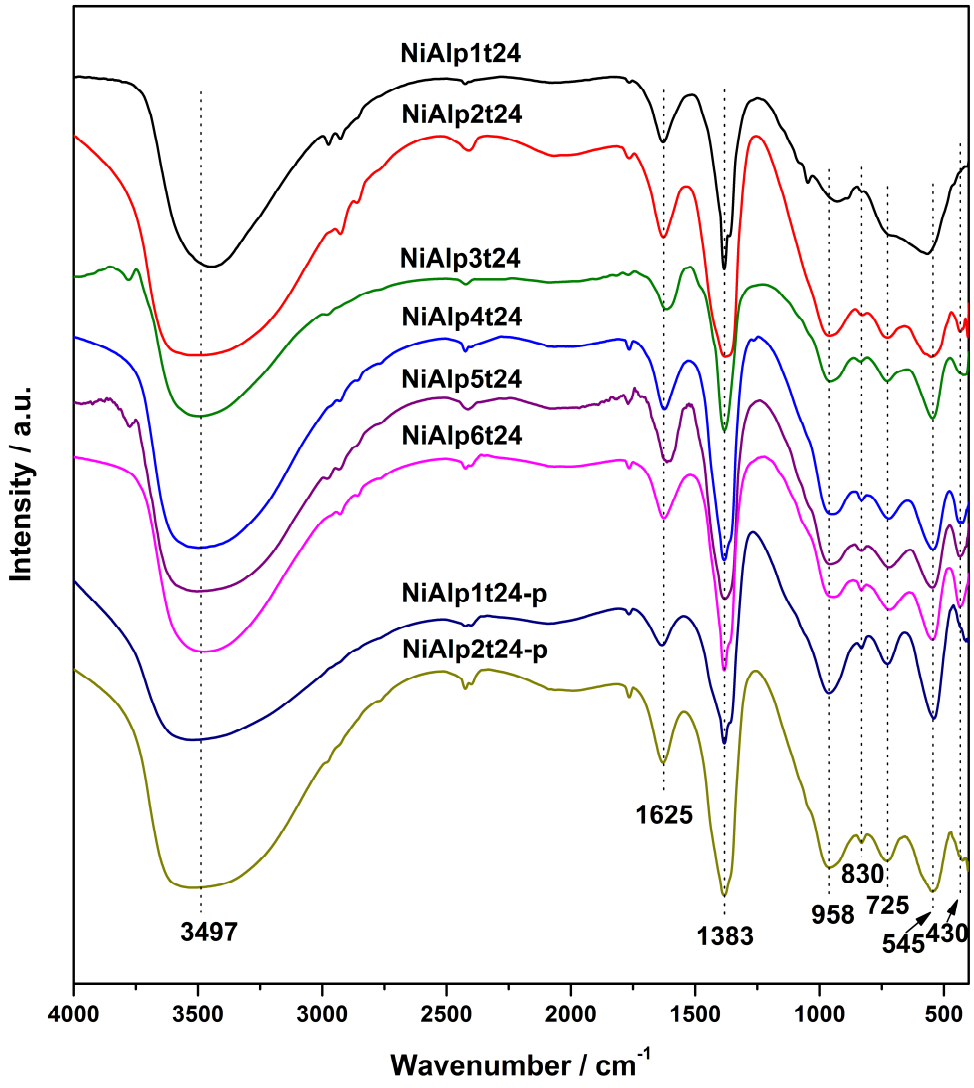
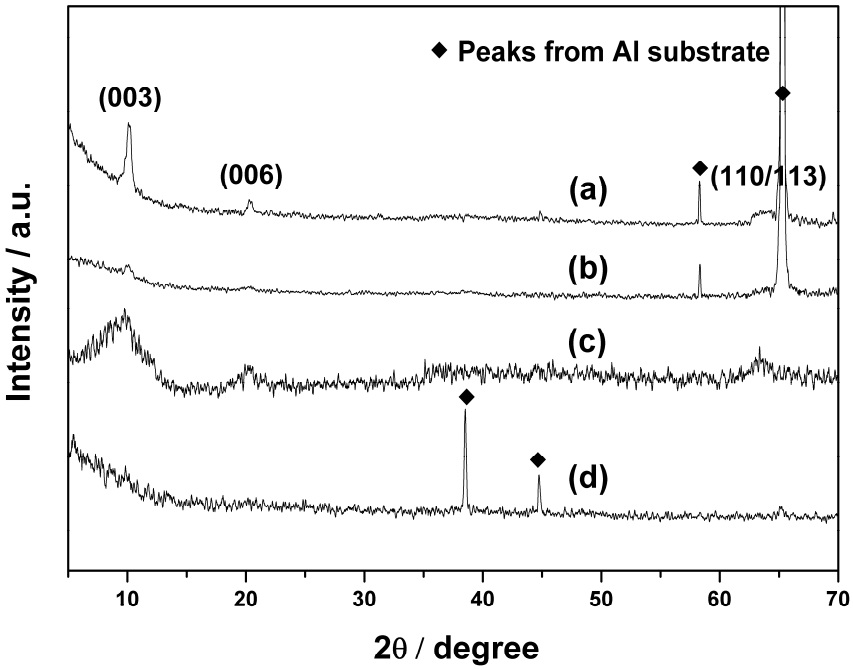


Fig. S1 FT-IR spectra of scraped powder of NiAlp*x*t24 (*x* = 1-6) and NiAlp*x*t24-p (*x* = 1, 2).

The broad and intense band centered around 3497 cm^{-1} is due to the OH stretching mode of layer hydroxyl groups and of interlayer water molecules.[1-3] All samples have a weak peak centered at 1625 cm^{-1}. This peak is associated with the bending mode of water.[1-3] The intense band at 1383 cm^{-1} and weak band at 830 cm^{-1} are ascribable to

the stretching and the bending mode of the nitrate anions respectively [2,3], suggesting that NO_3^- is the intercalated anion of NiAl-LDH in NiAlp*x*t24 (*x* = 2-6) and NiAlp*x*t24-p (*x* = 1, 2). The bands around 725 and 545 cm^{-1} can assigned to translation modes of the hydroxyl groups influenced by Al^{3+}.[1,4] The corresponding deformation mode is observed at around 958 cm^{-1}.[1,4] According to the literatures, the band centered at 430 cm^{-1} can be ascribed to M-O-M bonds [3] or translation modes of the hydroxyl groups influenced by Al^{3+}.[1] The FT-IR spectra of NiAlp*x*t24 (*x* = 2-6) and NiAlp*x*t24-p (*x* = 1, 2) are very similar to each other due to the same LDH structure. The spectrum of NiAlp1t24, however, is quite similar to the spectrum of amorphous aluminum hydroxide reported in ref. 5, showing different features from those of NiAlp*x*t24 (*x* = 2-6) in the wavelength range of 1000-400 cm^{-1}.



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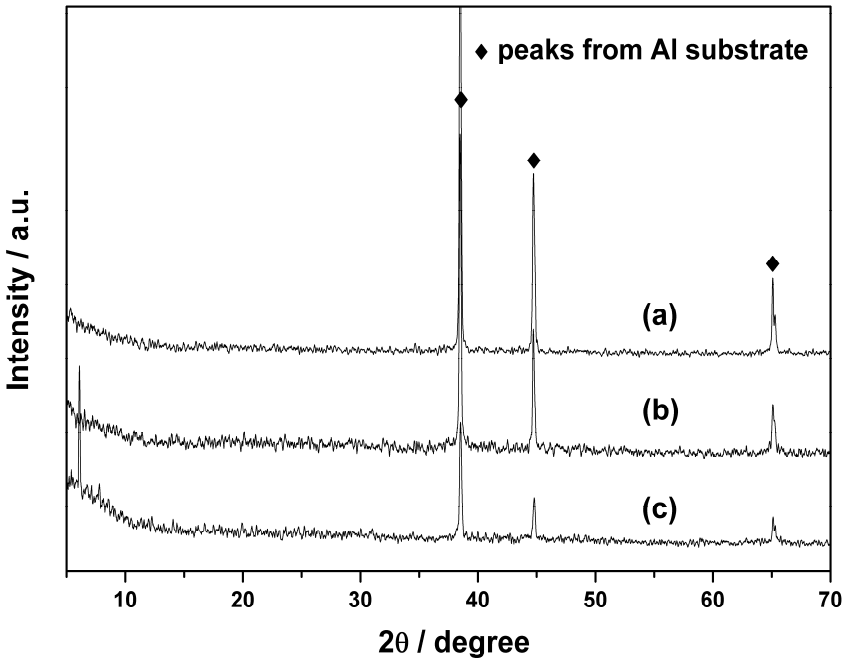
2 Fig. S2 XRD patterns of (a) NiAlp2t72 film, (b) NiAlp2t24 film, (c) NiAlp2t12-p and

3 (d) scraped powder of NiAlp2t12 film.



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2 Fig. S3 XRD patterns of scraped powders of (a) ZnAlp2t24, (b) CoAlp2t24 and (c)

3 MgAlp2t24. Diffraction peaks of LDHs were not detected in the XRD patterns of the

4 three samples.

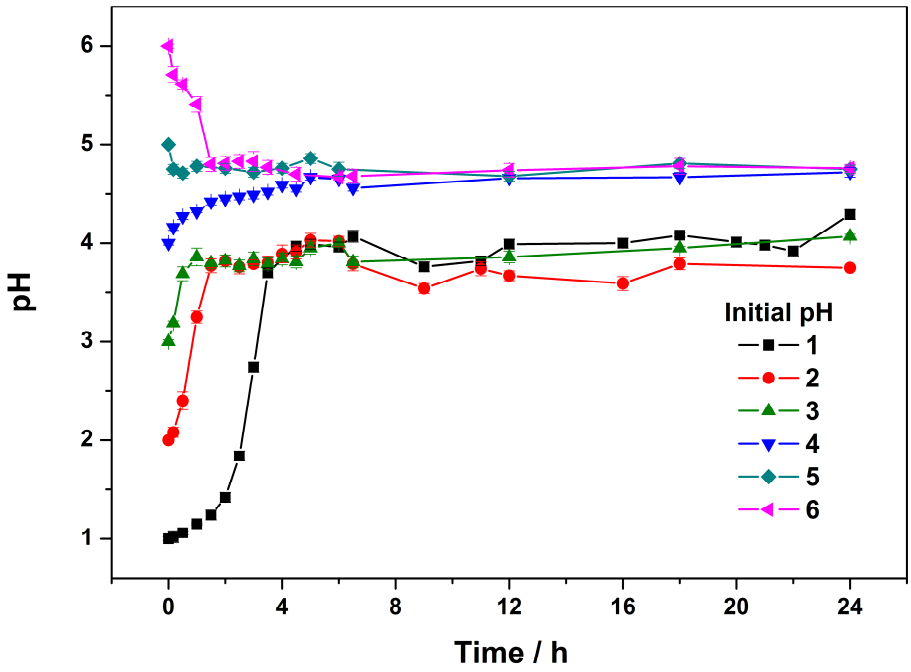


Fig. S4 Variations of pH value of Ni^{2+}-containing solution during the immersion of Al substrates in it.

Figure S4 plots pH curves of Ni^{2+}-containing solutions against reaction time. According to the final pH value, these curves can be roughly divided into two groups: solutions with initial pH 1-3 experienced increase of pH value to 3.7-4.3, and solutions with initial pH 4-6 experienced increase or decrease of pH value to 4.7-4.8. The increase of the solution pH value can be attributed to the consumption of H^+ by reacting with aluminium, providing Al^{3+}. At the same time, tiny bubbles were observed forming on the surface of Al substrate during the reaction. The lower the initial pH value, the higher the concentration of Al^{3+} in solution. The high concentration of Al^{3+} is supposed to be responsible for the formation of LDH precipitation in bulk solutions with initial pH 1 and 2.

In addition, it has been reported that aluminium can dissolve at the interface by reacting with OH^- to form $Al(OH)_3$ or $Al(OH)_4^-$ species in alkaline condition (at pH 7-8).[6] In this work, although the reaction was carried out in acidic condition, the rapid decrease of the pH value of solutions with initial pH 5 and 6 suggests that similar reactions may occur, i.e., aluminium hydr(ous) oxide species began to form soon after the Al substrates were immersed into the corresponding solutions.

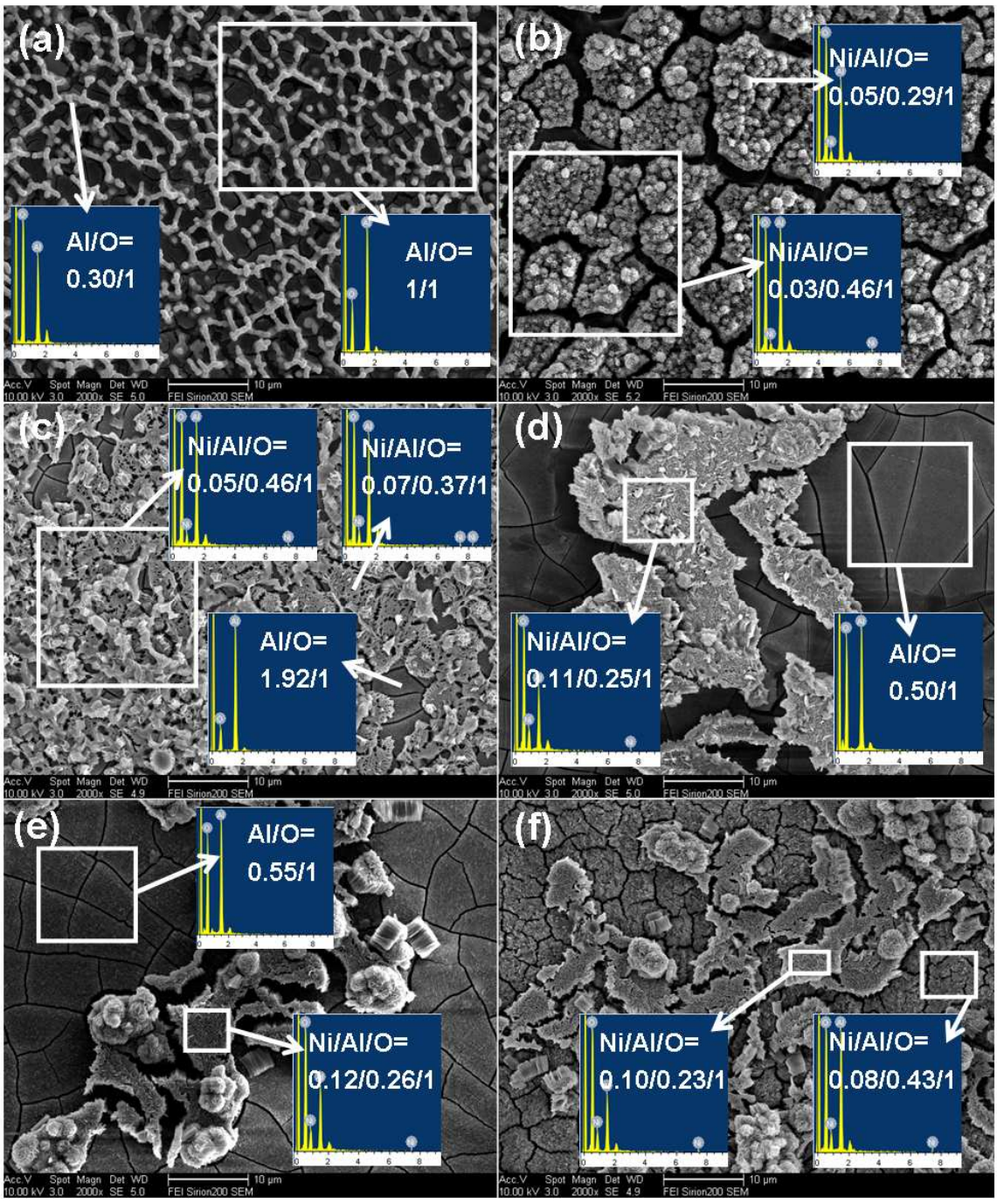
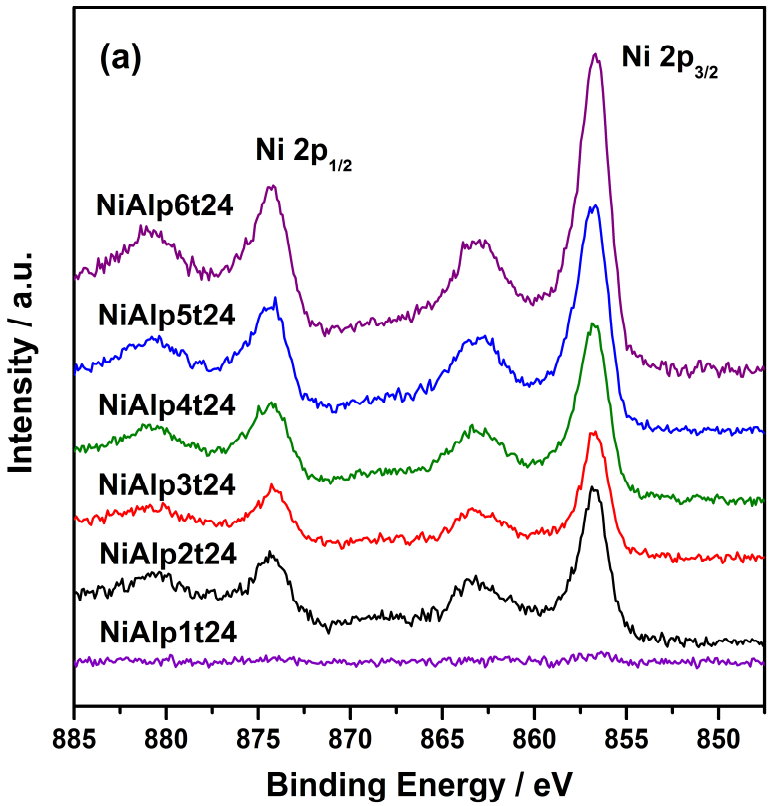


Fig. S5 SEM images of NiAlp*x*t24, *x* = (a) 1, (b) 2, (c) 3, (d) 4, (e) 5 and (f) 6. Insets are the EDX results of corresponding areas and spots.

According to Fig. S5, signal of Ni has not been detected on NiAlp1t24 and those pillar-like protrusions should be amorphous aluminium hydroxide which is consistent with the FT-IR result (Fig. S1) and the XRD result (Fig. 1). As the initial pH value of

Ni^{2+}-containing solution increasing from 2 to 6, the Ni/Al ratio of NiAlp*x*t24 (*x* = 2, 3, 4, 5, 6) LDH film increased simultaneously. At the same time, an interlayer of aluminium hydr(ous) oxide can be observed between the LDH film and Al substrate on NiAlp*x*t24 (*x* = 3, 4, 5) with the peeling of LDH film. And a new layer of microcrystal began to form on the exposed interlayer on NiAlp6t24.



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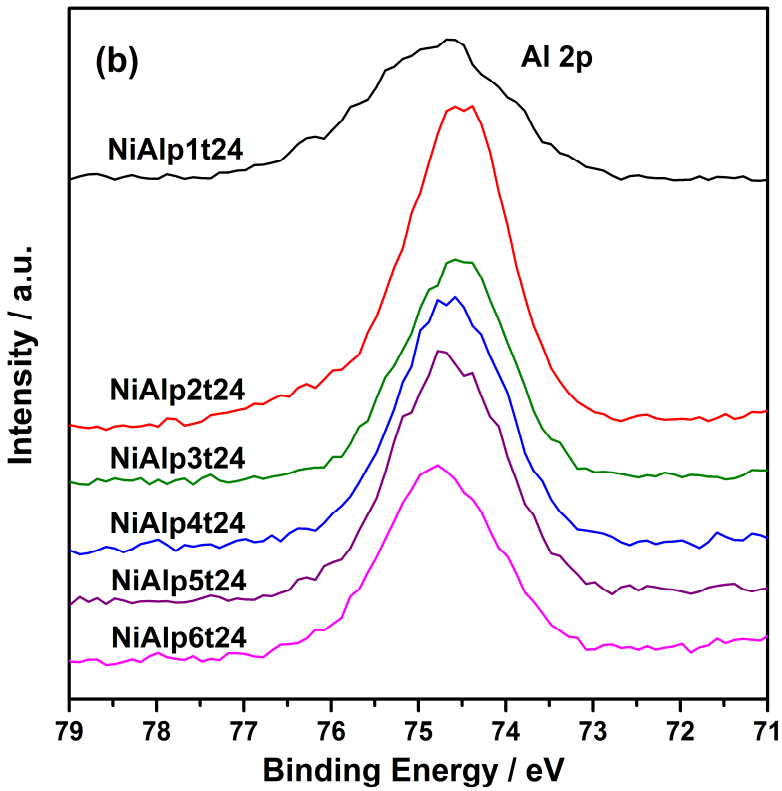

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3 Fig. S6 XPS spectra of NiAlp*x*t24 (*x* = 1-6) films, (a) Ni 2p and (b) Al 2p.

From Fig. S6 (a), it can be seen that the binding energy (BE) values of the main Ni $2p_{3/2}$ peak are approximately in the same region (around 856.7 eV), suggesting that the electronic state of Ni in NiAlp*x*t24 (*x* = 2-6) are similar. Signal of Ni was not detected in NiAlp1t24, which is consistent with the EDX result presented in Fig. S5.

The Al 2p BE values of NiAlp*x*t24 are in the range of 74.29 eV ～ 74.79 eV, implying the difference of chemical environment of Al. The broad Al 2p peak of NiAlp1t24 centred at 74.68 eV is assigned to the Al^{3+} in aluminium hydr(ous) oxide. When the NiAl-LDH phase was formed, the Al 2p peak (NiAlp2t24) shifted to a lower value by 0.4 eV (around 74.29 eV). Similar variation of Al 2p BE value during the formation of the LDH phase was also reported by Y. Yang et al.[5] and Y. F. Gao et al..[7] Consulting the references, we suggest that formation of the Al-O-Ni bond in NiAl-LDH leads to increase in charge density of outer orbital of Al and decrease in binding energy compared to the Al-O-Al bond in aluminium hydr(ous) oxide. With the increase of the initial pH value (pH = 3-6), the peeling of the LDH film became severer. The BE value of Al 2p shifted back to higher value due to the exposure of aluminium hydr(ous) oxide interlayer on NiAlp*x*t24 (*x* = 3-6).

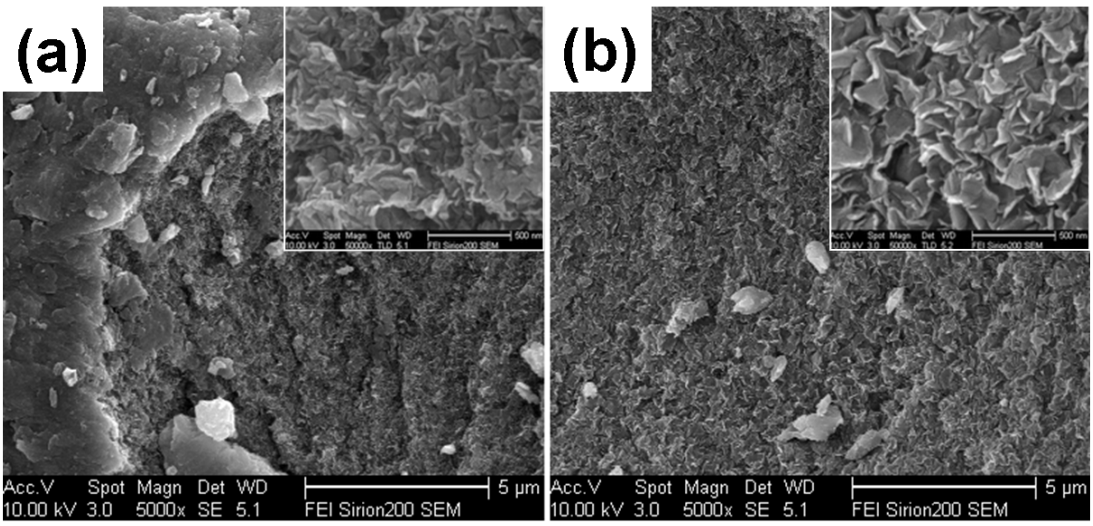
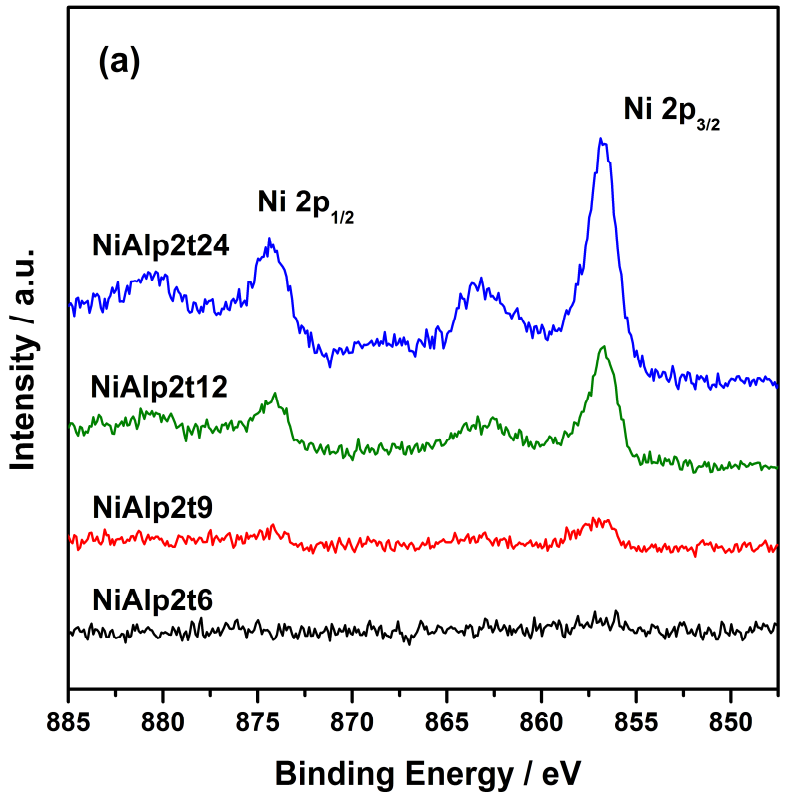


Fig. S7 SEM images of (a) NiAlp1t24-p and (b) NiAlp2t24-p. Insets are images at high magnification.



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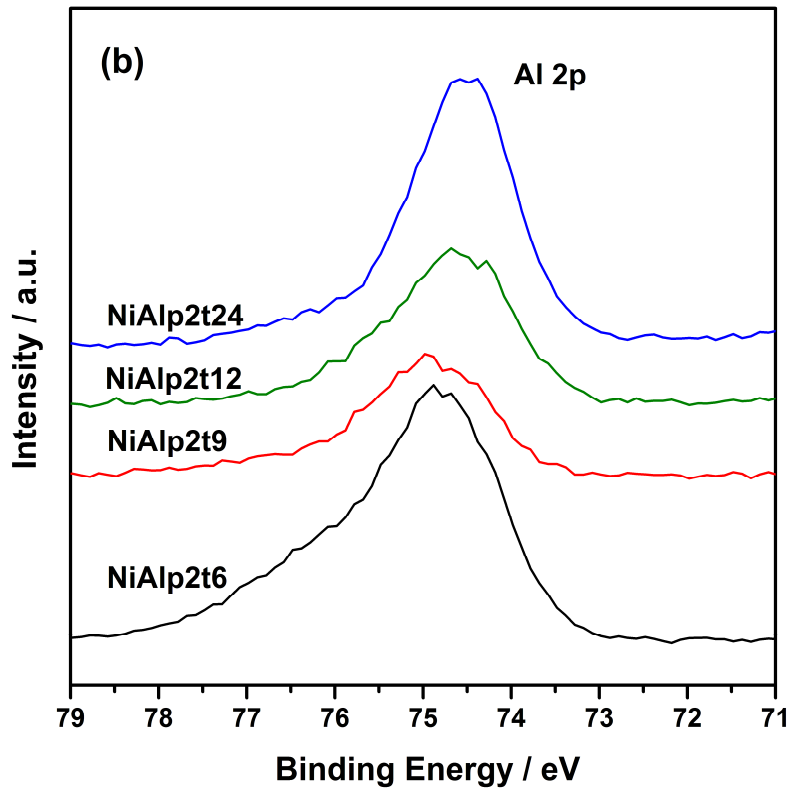

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3 Fig. S8 XPS spectra of NiAlp2t*y* films (*y* = 6, 9, 12, 24), (a) Ni 2p and (b) Al 2p.

XPS measurements have been performed to investigate the surface nature of NiAlp2t*y*. From the spectra of Ni 2p presented in Fig. S8(a), it can be seen that the BE value of Ni $2p_{3/2}$ (NiAlp2t*y*, y = 9, 12, 24) are approximately in the same region (around 856.8 eV) except for NiAlp2t6, suggesting that the electronic states of Ni are similar. This result implies that the Ni^{2+} was not involved in the NiAl-LDH formation reaction until 9 h later.

According to the XPS spectra of Al 2p shown in Fig. S8(b), the shift of the Al 2p BE to lower values with increasing reaction time from 6 to 24 h is obvious. This result indicates that the electronic atmosphere of Al atom was changed. The formation of Al-O-Ni bond in NiAl-LDH on aluminium hydr(ous) oxide interlayer must be responsible for the negative shift in Al 2p BE value.[2]

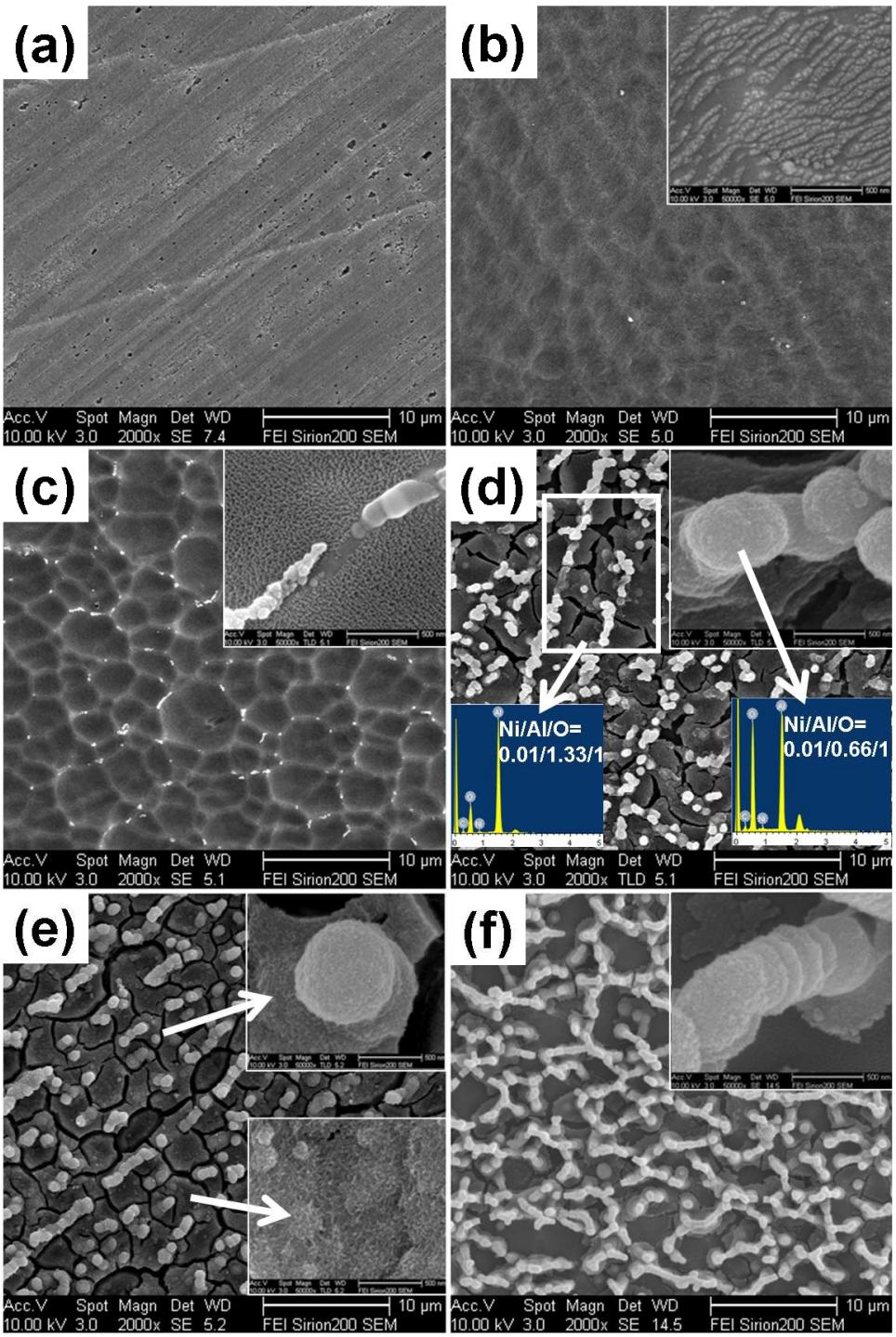


Fig. S9 SEM images of surface morphology of Al substrate immersed in Ni^{2+}-containing solution with initial pH 1 for (a) 0 h, (b) 6 h, (c) 12 h, (d) 16 h, (e) 20 h and (f) 24 h at low magnification. Insets are images at high magnification and the EDX results of corresponding area and spot.

Although the evolution of solution's pH value of NiAlp1t24 exhibits a similar trend with that of NiAlp2t24, the SEM images of NiAlp1t24 shown in Fig. S9 are not just replications of NiAlp2t24 at similar pH values. After 6 h reaction, the Al substrate was covered with shallow pits, 2-4 μm in diameter, as a result of the corrosion by acid. Stripes formed by tiny spots can be observed in the inset (Fig. S9(b)). The pits became deeper with white protrusions formed on the edges after 12 h (Fig. S9(c)). When the reaction time increased to 16 h, numerous white pillar-like protrusions were formed on the network-like cracked substrate. The composition of the protrusions by EDX is Ni/Al/O=0.01/0.66/1. This result suggests that alumina has been formed on the substrate, which is different from the AlOOH on NiAlp2t6 (Al/O=0.51/1, Fig. 3). After a prolonged reaction time of 20 h, a layer of microcrystal began to form, which can be observed in Fig. S9(e). However, LDH platelets were not observed in Fig. S9(f). Formation of $Al(OH)_3$ on NiAlp1t24 was confirmed by EDX (Fig. S5) and FT-IR (Fig. S1) results, which indicates that these microcrystals (Fig. S9(e)) are not nuclei of LDH crystallite. In fact, the Al_2O_3 on NiAlp1t16 converted to $Al(OH)_3$ (Fig. S5(a)) when the immersion time extended to 24 h. Based on the above observation, we conclude that LDH could not be formed on the phase boundary of Al_2O_3 at present condition. The formation of aluminium hydr(ous) oxide interlayer may be the main factor which resulting in the formation of LDH crystallites on NiAlp*x*t24 (x = 2-6).

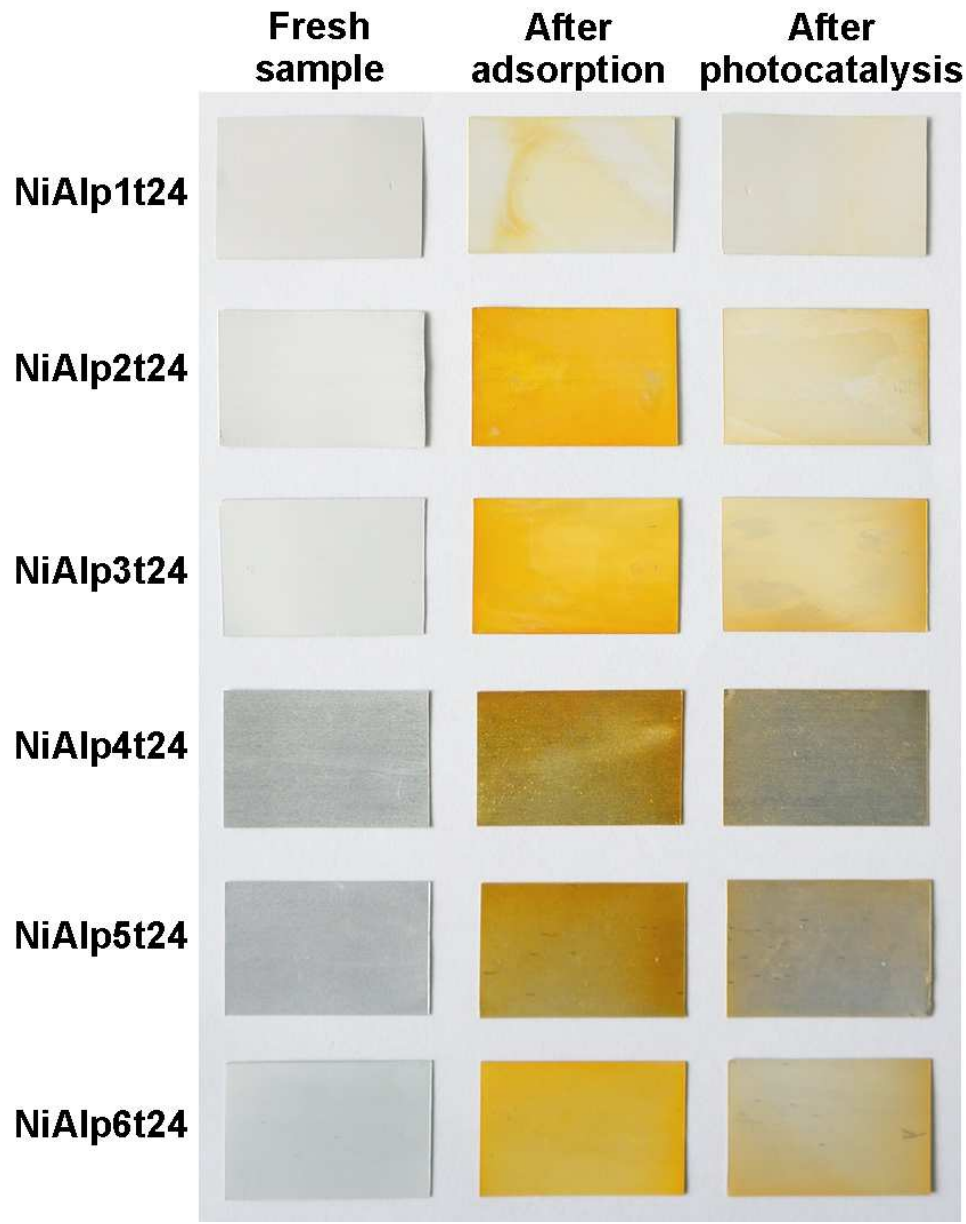
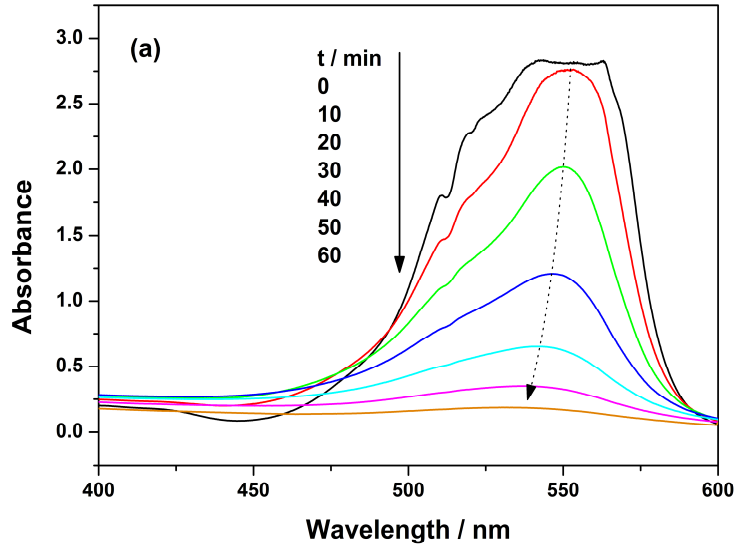


Fig. S10 Digital photograph of fresh NiAlp*x*t24 samples, samples after MO adsorption experiments and samples after MO photocatalysis experiments.

From Fig. S10, it is clear to see that compared to fresh samples, NiAlp*x*t24 turned yellow after the adsorption experiments, suggesting the adsorption of MO on the sample surface. Meanwhile, the colors of samples after photocatalysis experiments are much lighter than those after adsorption experiments, although experimental

conditions are identical except for the UV irradiation in the photocatalysis experiments. This distinct difference in color indicates that MO adsorption on NiAlp*x*t24 has little effect on the MO concentration during the photocatalytic reaction. The decrease of the MO concentration should be mainly ascribed to photocatalysis of NiAlp*x*t24 other than MO adsorption on NiAlp*x*t24 under UV irradiation.



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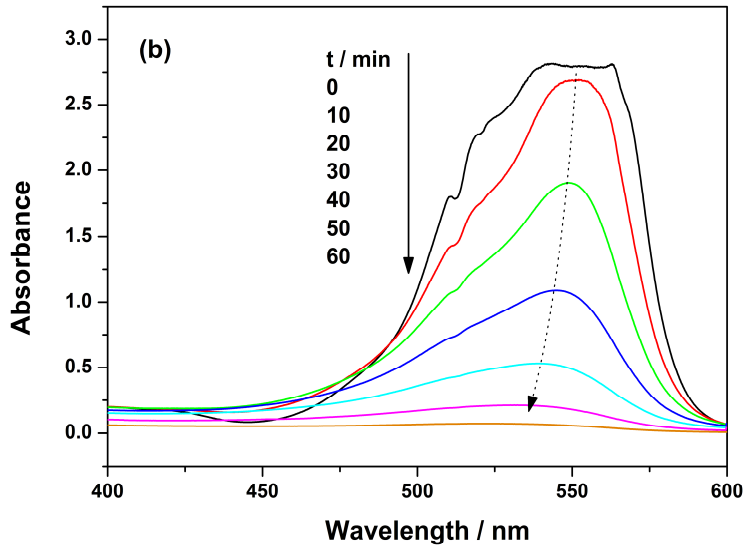

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3 Fig. S11 Spectral changes of Rh B (initial concentration 50 mg L^{-1}) over the catalysts,

4 (a) NiAlp2t24 and (b) P25 TiO_2.

5 As shown in Fig. S11, the absorption maximum of the Rh B solution steadily

6 decreases with increasing irradiation time, indicating gradual degradation of the Rh B.

7 The photocatalytic performance of NiAlp2t24 LDH film is similar to that of P25 TiO_2

8 powder in photodegradation of Rh B.

References:

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