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1 **Zn-Al layered double hydroxide-based nanocomposite functionalized with an**  
2 **octahedral molybdenum cluster exhibiting prominent photoactive and oxidation**  
3 **properties**

4  
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29

30 **Abstract**

31 A new layered double hydroxide (LDH)-based nanocomposite functionalized with an  
32 octahedral molybdenum atom cluster (MC) exhibiting prominent photoactive and  
33 oxidation properties was synthesized. Zn-Al LDH and Zn-Al LDH intercalated dodecyl  
34 sulfate compounds (abbreviated as LDH-1 and LDH-2 respectively) were prepared by  
35 the co-precipitation method in an aqueous solution. The MCs were simply introduced  
36 into the LDH-2 by an anion exchangeable method in dimethylformamide under ambient  
37 conditions. The extension of the basal spacing of the LDH-1 from 0.9 nm to about 5 nm  
38 by intercalating dodecyl sulfate and Mo<sub>6</sub> cluster was confirmed by several  
39 complementary technics. The octahedral structure of the Mo<sub>6</sub> cluster was retained after  
40 the modification process in an organic dispersing medium that was confirmed by  
41 ultraviolet-visible absorption and photoluminescence experiments. The possible  
42 chemical bonding between the  $[\text{Mo}_6\text{Cl}_8\text{Cl}_{6-x-y}(\text{H}_2\text{O})_x(\text{OH})_y]^{x-2}$  ( $x = 0, 1$  or  $2$  and  $y = 0,$   
43  $1, 2, 3$  ;  $x + y = 3$ ) clusters and LDH-2 was suggested on the basis of by X-ray  
44 photoelectron spectroscopy. The excellent photoactive and oxidation performance of the  
45 Mo<sub>6</sub> cluster on the methylene blue degradation in an aqueous solution was determined  
46 in the dark, under UV light ( $\lambda = 370$  nm) or with the existence of H<sub>2</sub>O<sub>2</sub>. The combination  
47 of the LDH-2 with a high absorbability and recyclability and the Mo<sub>6</sub> cluster will be a

48 promising candidate as a heterogenized homogeneous catalyst for removing organic  
49 pollutants.

50 **KEYWORDS:** molybdenum, octahedral cluster, outer surface functionalization, layered  
51 double hydroxide, photochemistry, pollutant degradation

52

## 53 **1. INTRODUCTION**

54 Among the various wastewater treatment techniques, the adsorption has been proposed  
55 as one of the best methods due to its inexpensiveness, universal nature, and ease of  
56 operation. Many studies have paid attention to determining new functional and large-  
57 scale productive materials for removing organic pollutants by adsorption combined with  
58 photocatalytic degradation [1]. This approach becomes an important pathway for  
59 pharmaceutical contaminant removal that attracts huge interests of the studies based on  
60 TiO<sub>2</sub>, ZnO, or graphene-functionalized materials [2, 3]. Besides, layered double  
61 hydroxides (LDH) are well known as important compounds due to their interlayer anion  
62 exchangeability and potential material for industrial-scale applications such that their  
63 fundamental understanding in heterogeneous catalysis, water treatment, and drug  
64 delivery is developed [4-5]. LDH with the general formula of  $[M^{2+}_x M^{3+}_x(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot mH_2O$  (x as the molar ratio  $M^{2+}/(M^{2+} + M^{3+})$  in the range 0.2–  
65 0.33) is composed of the divalent and trivalent metals occupying at the octahedral center  
66 [6]. The positive charges on the metal hydroxide layers are generated by the exchange  
67 of the divalent metals (Cu, Zn, Co, Mg, Cr...) by the trivalent metals (Al, Fe, Tb...) and  
68 it is neutralized by negatively exchangeable organic or inorganic ions (A = NO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>,  
69 SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>, Cl<sup>-</sup> or alkyl anions...) accompanied by the absorption of the interlayer water

71 molecules [7-12]. The remarkable advantages of the LDH are made of relatively  
72 inexpensive and safe elements, highly adjustable, and easily synthesized that becomes  
73 good advantages for industrial-scale applications. The physicochemical characteristics  
74 could be controlled by the flexible exchange of the chemical components of the metal  
75 hydroxide-based layer or the functionalization of the exchangeable interlayer ions.  
76 Based on the host lamellar structure and ionic exchangeable possibility, LDH has been  
77 widely studied in applicable fields such as absorbents [12], prominent photoactive  
78 catalysts [13, 14], energy conversion and storage [15], and drug delivery systems [16-  
79 18], as a result of the modification of the trivalent metal. Moreover, the efficiency of the  
80 catalytic characteristics of the LDH has been highlighted to study the organic reactions  
81 such as aldol condensation [19], ethanol electro-oxidation [20], and dinitrogen fixation  
82 [21]. Most of the cases depend on the catalytic possibility of the functional groups  
83 existing between the ionic metal hydroxide layers. Particularly, single-atom Au-  
84 intercalated NiFe LDH, Ce-doped MgAl LDH functionalized Au nanoparticles, or  
85 polyoxometalate-intercalated LDH have revealed the optimal achievements for catalytic  
86 applications [22-24].  
87 The improvement of the typical physicochemical characteristics or enhancement of the  
88 active sites by adjusting the interlayer trivalent or divalent metals of the LDH as well as  
89 exchanging a functionalized interlayer component was widely investigated. However,  
90 the challenge to figure out a suitable synthesis depends on the intrinsic property and size  
91 of the functional-controlling substances. In this study, the  $\text{Cs}_2\text{Mo}_6\text{Cl}_{14}$  (CMC) clusters  
92 compound, with excellent redox and optical properties, has been selected as a catalytic  
93 functionalized group to combine with the LDH. As is known, the basic concept of metal  
94 atom cluster (MC) was first introduced by F. A. Cotton in 1964 to define a finite group

95 of the metal atoms (two or more) that are held together by metal-metal bonds and  
96 surrounded by other nonmetal ligands [25]. Typically, the octahedral MC ( $M_6$ )  
97 composed of the  $\{M_6L_8^i\}^{4+}$  ( $M = Mo, W, Re$ ) metallic cores ( $L^i =$  inner ligand)  
98 coordinating with apical ligands ( $L^a = Cl, Br, I$  or  $OCOC_nF_{2n+1}$ ) exhibits strong  
99 absorption in both the ultraviolet (UV) and visible light ranges, resulting in a prominent  
100 luminescent emission within the deep red/near-infrared (NIR) region [26-29]. In the  
101 reduced form, the valence electron concentration (VEC) is equal to 24 electrons per the  
102  $[M_6L_8^iL_6^a]^{2-}$  cluster unit that visibly displays a redox characteristic for the catalyst  
103 application [30-32]. As previously reported, the excitation state of MC produces singlet  
104 oxygen ( $^1O_2$ ) with a strong catalytic activity for the photoreduction applications has  
105 been investigated [33]. However, the  $Mo_6$  cluster in the bulk powder state is limited in  
106 the applicability as well. Graphene oxide or h-BN are ones of the excellent candidates to  
107 enhance the photocatalytic applicability of the  $Mo_6$  cluster has a proven highly catalytic  
108 efficiency for the hydrogen production from water [34], water purification [35],  
109 synthesis of dimethyl carbonate from  $CO_2$  and methanol [36] or photoreduction of  
110 carbon dioxide into methanol [37]. A remarkable study has been progressing to  
111 simultaneously combine the gold nanoparticles and the  $Mo_6$  cluster on the graphene  
112 oxide resulting in an excellent photoactive possibility for the degradation of rhodamine  
113 B under visible light irradiation [38]. A few studies have continued to determine  
114 efficient supporting materials for the catalytic-characterized MC with the expectation to  
115 fabricate the heterogeneous nanostructured composite for photovoltaic,  
116 nanobiotechnology, or energy-saving fields [27, 28].  
117 The goal of this study is to focus on the photoactive and oxidation properties of the MC  
118 on dye degradation after combined with an LDH neutral supporting material with only

119 high absorbability and recyclability. Indeed, among LDH, Zn/Al LDH (abbreviated as  
120 LDH-1) exists a weak basic catalyst, and Zn also was the limiting species for the  
121 photocatalytic reaction [39]. It was almost used as an efficient absorbent and/or support  
122 for multifunctional catalysts. In this work, the new nanocomposite (abbreviated as  
123 Mo<sub>6</sub>@LDH-2) was prepared by the delamination of Zn<sub>2</sub>Al LDH co-intercalated dodecyl  
124 sulfate (abbreviated as LDH-2) in dimethylformamide and then introducing the as-  
125 synthesized [Mo<sub>6</sub>Cl<sup>i</sup><sub>8</sub>Cl<sup>a</sup><sub>6</sub>]<sup>2-</sup> cluster units. The initial octahedral structure of the Mo<sub>6</sub>  
126 cluster was not modified after incorporation into the LDH, as confirmed by the optical  
127 properties. The Mo-O-Al/Zn chemical bonding between the Mo atoms of the  
128 {Mo<sub>6</sub>Cl<sup>i</sup><sub>8</sub>}<sup>4+</sup> anion cluster core and the LDH was validated. The new Mo<sub>6</sub>@LDH-2  
129 nanocomposites were successfully fabricated by a quick, cheap, and reproducible  
130 method with high and stable efficiency of the Mo<sub>6</sub> cluster units. Moreover, we have  
131 demonstrated the catalytic activity of the Mo<sub>6</sub> cluster anion intercalated in the LDH on  
132 the methylene blue.

133

## 134 **2. MATERIALS AND METHODS**

### 135 *2.1 Materials*

136 The Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99%) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (98%, pH= 2~4) were supplied from  
137 Chameleon Reagent. Sodium n-dodecyl sulfate (CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OSO<sub>3</sub>Na) was  
138 purchased from the Kanto Chemical Company. The sodium hydroxide (NaOH, 5 mol/L)  
139 was purchased from Nacalai Tesque. All chemicals were used without purification. The  
140 deionized water with the conductance of 0.5·10<sup>-4</sup> S/m was obtained using Water  
141 Purifiers WG710 equipment at 25°C.

142

## 143 2.2 Methods

### 144 *Preparation of LDH-1 and LDH-2*

145 LDH-1 and LDH-2 were prepared by the co-precipitation method with the Zn and Al  
146 ratio of about 2 [7, 40]. Fixed amounts of the  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.02 mol) and  
147  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.01 mol) salts were simultaneously dissolved in 50 ml of deionized  
148 water and agitated by a magnetic stirrer for 1 h to obtain a homogeneous solution.  
149 Similarly, the transparent mixture solution containing the  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.02 mol),  
150  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.01 mol) and sodium dodecyl sulfate (SDS) (0.01 mol) in 50 ml of  
151 deionized water was used for the preparation of the LDH-2. The aqueous solution of  
152 NaOH (5 M) was then used to titrate the mixed salt solution until the pH value reached  
153 10. The solution was then agitated for 24 h at room temperature to increase the  
154 crystallinity of the LDH. The precipitated product was purified by deionized water  
155 several times until the pH was about 7. The collected solid powder was dried at 60°C for  
156 24 h for further use.

157

### 158 *Synthesis of $\text{Mo}_6@$ LDH-1 and $\text{Mo}_6@$ LDH-2 nanocomposites*

159 The CMC cluster unit was prepared according to a procedure already reported that  
160 combined the use of solid-state and solution chemistries [41, 42]. LDH-1 or LDH-2 (0.3  
161 g) was dispersed in 140 ml of dimethylformamide (DMF) by ultrasonication for 1 h.  
162 The yellow CMC cluster powder (0.06 g) was similarly dissolved in 60 ml of DMF  
163 solution by ultrasonication. LDH-1 or LDH-2 and CMC cluster solutions were then  
164 mixed and continually agitated for 24 h to improve the intercalation. The yellow-  
165 colored product was separated and washed with DMF to eliminate the residual  $\text{Mo}_6$



166 cluster, then dried at 60°C for 24 h for further characterizations. The experimentally  
167 determined wt. % concentration of the CMC cluster powder in the Mo<sub>6</sub>@LDH-1 and  
168 Mo<sub>6</sub>@LDH-2 nanocomposite was about 16.7 wt.%.

169

### 170 *2.3 Catalytic test*

171 The catalytic activity of the LDH and Mo<sub>6</sub>@LDH samples was characterized by  
172 measuring the degradation possibility of methylene blue (MB) in an aqueous solution.  
173 The difference in the catalytic activity and adsorption-desorption isotherm was  
174 evaluated through the tests for LDH-2 and Mo<sub>6</sub>@LDH-2 (catalyst/MB = 20). The  
175 investigation was performed on the solution containing 20 mg of a catalyst in 10 ml of  
176 MB solution (20 mg/L) (catalyst/MB = 100) at room temperature without or with i) the  
177 addition of the H<sub>2</sub>O<sub>2</sub> solution (5% in ethanol, Sanwa Chemical Co., Ltd.), ii) irradiation  
178 of ultraviolet (UV) light ( $\lambda = 370$  nm) or iii) in the presence of both H<sub>2</sub>O<sub>2</sub>/UV system. A  
179 source of the UV light was generated by a 300 W Xenon lamp (MAX-303, Asahi  
180 Spectra Co., Ltd.). The MB degradable efficiency of the filtered catalyst-mixed MB  
181 solution was confirmed by the UV-Vis absorption spectroscopy (V-650, Jasco). The  
182 C/C<sub>0</sub> index was calculated based on the intensity ratio of the optical absorption peak at  
183 664 nm of MB with and without the existence of the catalyst. The catalytic reaction rate  
184 and the effect of H<sub>2</sub>O<sub>2</sub> concentration on the degradation reaction of MB with and  
185 without the UV light were investigated. For comparison, the catalytic test of the CMC  
186 cluster alone was also carried out at the same Mo<sub>6</sub> cluster concentration (16.7 wt%) in  
187 the Mo<sub>6</sub>@LDH-2 nanocomposite.

188

### 189 *2.4 Characterizations*

190 The average hydrodynamic diameters and distribution of the LDH-2 and Mo<sub>6</sub>@LDH-2  
191 powders in water were measured by an ultrafine particle analyzer (Nanotracs NPA151 -  
192 Nanotracs ULTRA, Microtracs Inc., USA) incorporated the controlled reference method  
193 (CRM) in a dynamic light scattering instrument. The crystalline layered structure of the  
194 samples was determined by powder X-ray diffraction (XRD) (SmartLab, RIGAKU, 40  
195 kV and 30 mA) in the 2 $\theta$  angle range from 1° to 50° for the bulk powder at the scan  
196 speed of 1/ min with the Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The optical absorbances of the  
197 powders were measured by UV-Vis-NIR spectroscopy (V570, Jasco Corp.) in the  
198 wavelength range of 220 to 2000 nm at the scan rate of 400 nm/min. Emission spectra  
199 of the powder were obtained by high-performance fluorescence spectroscopy (JASCO  
200 FP8500) connected to a Xenon lamp at the scan rate of 500 nm/min. The surface  
201 morphology and the elemental composition were analyzed by field emission scanning  
202 electron microscopy (FE-SEM, S4800, Hitachi High-Technologies Corp.) at 10 kV  
203 coupled with an energy-dispersive X-ray (EDX) analysis device. High-resolution  
204 observations of the powder were performed by a high-resolution transmission electron  
205 microscopy (HRTEM) (JEOL JEM 2100F) equipped with an EDX analysis device.  
206 Inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 720-ES)  
207 coupled with ion-chromatography (ThermoFisher Scientific ICS-1600) was used to  
208 verify the element concentration. The typical chemical vibrations of the samples were  
209 verified by Fourier transform infrared spectroscopy (FTIR) (Thermo scientific Nicolet  
210 4700) in the wavenumber range from 4000 to 400 cm<sup>-1</sup>. The nitrogen adsorption  
211 isotherm according to the BET model of the LDH-2 and Mo<sub>6</sub>@LDH-2 nanoparticles  
212 was performed in saturated vapor pressure of about 100 kPa at the temperature of 140°C  
213 for 2 days (BELSORP-max II, Microtracs BEL Corp.). Thermogravimetric analysis

214 (TGA) and differential thermal analysis (DTA) were carried out using a TG/DTA 6200  
215 apparatus (SII, EXSTAR 6000, Hitachi, Japan) operated in an N<sub>2</sub> atmosphere at the  
216 heating rate of 10/min. The electron binding energy spectra within the CMC and  
217 Mo<sub>6</sub>@LDH-Zn/Al were measured by X-ray photoelectron spectroscopy (XPS) (PHI  
218 Quantera SXM (ULVAC-PHI)) using Al K $\alpha$  radiation at 20 kV and 5 mA and taken off  
219 the angle of 45°. All binding energies were calibrated concerning the C 1s peak of the  
220 adventitious carbon at 285 eV.

221

### 222 3. RESULTS AND DISCUSSION

223 **Figure 1a** shows the powder XRD patterns of the as-synthesized LDH-1, Mo<sub>6</sub>@LDH-1,  
224 LDH-2, and Mo<sub>6</sub>@LDH-2 powders, and the characteristic peaks are observed. The  
225 LDH-1 exhibits the typical characteristic of the LDH phase assigned to structure I. The  
226 characteristic diffraction peaks (indexation in bracket) are located at 2 $\theta$  angles of 11.6°  
227 (003), 23.4° (006), 34.5° (009) and 39° (015), 46° (018) corresponding to the basal  
228 planes as claimed in previous reports [43]. Besides, the remarkable patterns of the ZnO  
229 phase formed on the brucite-like sheets were also verified with the peaks at the 2 $\theta$   
230 angles of 32°, 34°, and 36° in this study [43]. In the case of Mo<sub>6</sub>@LDH-1, it shows the  
231 same lamellar structure with LDH-1 without the change in the XRD peak positions. The  
232 basal plane spacing value of the 003 planes calculated by Bragg's law for LDH-1 is  
233 about 0.9 nm which is too narrow to intercalate the CMC clusters with a size of 1.2 nm  
234 [42]. For this reason, the dodecyl sulfate (DS) anion was selected to expand the space of  
235 the metal hydroxide layers in LDH-1 to form LDH-2. The XRD result of LDH-2  
236 illustrates that a new series of reflections of the (003), (006) and (009) planes of LDH-2  
237 simultaneously appear at the lower 2 $\theta$  angle assigned to structure II and the d<sub>003</sub> spacing

238 value increases from 0.9 to 2.7 nm. In addition, LDH-2 still retained the original layered  
239 structure as seen for structure I in LDH-1. This result confirmed the partial exchange of  
240  $\text{NO}_3^-$  anions by the 2 nm-sized dodecyl sulfate anions as seen in previous reports [43,  
241 44]. Very interestingly, the intercalation in the CMC cluster causes a significant  
242 reduction of peak intensity assigned to structure II of LDH-2 as seen in the XRD pattern  
243 of  $\text{Mo}_6@$ LDH-2. It could be suggested that a part of the DS intercalated LDH, which is  
244 mixed with the  $\text{Mo}_6$  cluster, becomes a poorly crystallized phase, or undergoes  
245 exfoliation. Good interaction between the DMF molecules and dodecyl sulfate anions is  
246 efficient to expand the basal space between the brucite-like layers of LDH-2 that assists  
247 in the movement and intercalation of the  $\text{Mo}_6$  cluster during the intercalation step. The  
248 average hydrodynamic diameters and distributions of LDH-2 and  $\text{Mo}_6@$ LDH-2 in water  
249 are displayed in **Figure S1**. The average hydrodynamic diameter of LDH-2 reduces  
250 from 0.5980  $\mu\text{m}$  to 0.2815  $\mu\text{m}$  for  $\text{Mo}_6@$ LDH-2 corresponding to the broader size  
251 distribution. This result is agreeable with the crystallinity reduction of the LDH phase as  
252 claimed in the XRD pattern, resulting in a partial exfoliation. The BET surface areas of  
253 LDH-2 of about 50.0  $\text{m}^2/\text{g}$  and  $\text{Mo}_6@$ LDH-2 of about 20.4  $\text{m}^2/\text{g}$  were evaluated by the  
254 nitrogen adsorption isotherm (**Fig. S2a**). The shape of the nitrogen adsorption isotherm  
255 curves of LDH-2 and  $\text{Mo}_6@$ LDH-2 is almost similar to the characteristic of the LDH.  
256 That proves the retention of the layered structure of the LDH in  $\text{Mo}_6@$ LDH-2 after the  
257 partial exfoliation as suggested in the XRD pattern. The decrease of the adsorbed  
258 volume agrees with the pore diameter distribution in **Figure S2b** which shows the  
259 significant reduction of the small pore size in the range below 20 nm. The schematic  
260 representation of the process to fabricate the LDH and the possible structure of its  
261 nanocomposite based on the XRD pattern are illustrated in **Figure 1b**.

262 The HRTEM image of Mo<sub>6</sub>@LDH-2 shows black areas assigned to the aggregated Mo<sub>6</sub>  
263 cluster anion (**Fig. 2a**). In the beginning, the CMC cluster dissociates in the solvent to  
264 form the Cs<sup>+</sup> cations and [Mo<sub>6</sub>Cl<sub>8</sub>Cl<sub>6</sub><sup>a</sup>]<sup>2-</sup> anions. Moreover, it is well known that the  
265 [Mo<sub>6</sub>Cl<sub>8</sub>Cl<sub>6</sub><sup>a</sup>]<sup>2-</sup> anion is able to quickly exchange apical Cl ligands by water molecules  
266 or hydroxyl anions to obtain [Mo<sub>6</sub>Cl<sub>8</sub>Cl<sub>6-(x+y)</sub><sup>a</sup>(H<sub>2</sub>O)<sub>x</sub>(OH)<sub>y</sub>]<sup>x-2</sup> (x + y ≤ 6) clusters [45].  
267 Indeed, the interlayer galleries of LDH are containing water molecules and hydroxyl for  
268 balancing the positively charged surface, which can react with the apical Cl ligands.  
269 Following a theoretical suggestion, we can assume that only the Mo<sub>6</sub> anion or neutral  
270 compound can adsorb or deposit on the positive metal hydroxide surface of the LDH, so  
271 in that case x = 0 or 1 and y = 0 to 5.

272 The layer structure of Mo<sub>6</sub>@LDH-2 is confirmed in the STEM image and the  
273 calculation of the basal spacing distance of about 5 nm as seen in Figures **2b** and **2c**.  
274 STEM-EDX mapping of the Mo<sub>6</sub>@LDH-2 nanocomposite confirms the existence of Mo  
275 and Cl atoms as presented in **Figure 2d**.

276 In order to confirm the stability of the octahedral structure of the Mo<sub>6</sub> cluster in  
277 Mo<sub>6</sub>@LDH-2, the optical properties of the reflectance and the photoluminescence were  
278 evaluated. It could be seen that LDH-1 and LDH-2 show a high optical absorption  
279 below 400 nm while Mo<sub>6</sub>@LDH-2 is composed of the adsorbing part of the Mo<sub>6</sub> cluster  
280 below 400 nm and the LDH below 370 nm (**Fig. 3a**). This result confirms the retention  
281 of the octahedral Mo<sub>6</sub> structure on the LDH. In **Figure 3b**, LDH-1 and LDH-2 normally  
282 possess no photoluminescence in the NIR range while the Mo<sub>6</sub> cluster shows a strong  
283 emission at 700 nm in the deep red/NIR region. However, the photoluminescent  
284 intensity of the Mo<sub>6</sub> cluster is not strong in the spectrum of Mo<sub>6</sub>@LDH-2, this is due to  
285 the significant change in the apical halogen ligand of the CMC cluster. As known, the

286 photoluminescent property of the Mo<sub>6</sub> cluster is decreased when the apical halogen  
287 ligands are replaced by H<sub>2</sub>O molecules or hydroxyl anion [32, 41, 45].

288 The chemical bonding of the prepared compounds was verified by FT-IR spectroscopy  
289 presented in **Figure 4**. In the FT-IR spectrum of LDH-1 appears a strong peak at 1385  
290 cm<sup>-1</sup> that indicates for the NO<sub>3</sub><sup>-</sup> linking existing in the basal spacing of the LDH. In  
291 addition, the vibrational bands for Zn-O at 427 cm<sup>-1</sup>, Zn-OH at 608 cm<sup>-1</sup> of the brucite-  
292 like layers, O-H bending at 1650 cm<sup>-1</sup> and O-H stretching at the broadband of 3450 cm<sup>-1</sup>  
293 of the free inter-lamellar water molecules are observed. The FT-IR spectrum of LDH-2  
294 shows the vibrational bands assigned to the dodecyl sulfate: i) C-H stretching  
295 vibrational band of CH<sub>2</sub> at 2928 cm<sup>-1</sup> and CH<sub>3</sub> at 2854 cm<sup>-1</sup> from the alkyl chain and ii)  
296 asymmetric stretching vibrational band at 1220 cm<sup>-1</sup> and symmetric stretching  
297 vibrational band at 1059 cm<sup>-1</sup> originating from the OSO<sub>3</sub><sup>-</sup> group [43]. The vibrational  
298 signal of NO<sub>3</sub><sup>-</sup> at 1385 cm<sup>-1</sup> in LDH-2 decreases after exchanged by DS anions. The FT-  
299 IR spectrum of Mo<sub>6</sub>@LDH-2 would be composed of the vibrational band of the LDH-2  
300 and Mo<sub>6</sub> clusters. Following the typical band intensity for DS, the concentration of DS  
301 is obviously reduced by an exchange of the Mo<sub>6</sub> cluster. It should be noted that new  
302 peaks appear at 1654 cm<sup>-1</sup> that were properly related to the O-H bending vibrational  
303 band of the H<sub>2</sub>O free molecules with strong hydrogen bonding [46] as recognized in the  
304 report of the [Mo<sub>6</sub>Br<sub>8</sub>Br<sub>6</sub>]<sup>2-</sup> cluster [47]. From this result, the hydrogen bonding could  
305 be created between apical groups of the [Mo<sub>6</sub>Cl<sub>8</sub>Cl<sub>6-(x+y)</sub>(H<sub>2</sub>O)<sub>x</sub>(OH)<sub>y</sub>]<sup>x-2</sup> clusters and  
306 the free interlayer-adsorbed water molecules in the LDH.

307 **Figure 5** shows the TG, DTG, and DTA results of the LDH-1, LDH-2, and Mo<sub>6</sub>@LDH-  
308 2. The total mass loss was respectively, figured to be about 40 wt. %, 50 wt. % and 46  
309 wt. % for LDH-1, LDH-2, and Mo<sub>6</sub>@LDH-2 after heating to 800°C. The

310 thermogravimetric behavior (DTG) shows the mass loss with four steps in the  
311 temperature range of 50-200 °C, 200-300 °C, 300-500 °C and 500-800°C for LDH-1, 50-  
312 150, 150-250, 250-400 and 400-800°C for LDH-2, and 50-150, 150-320, 320-600 and  
313 600-800°C for Mo<sub>6</sub>@LDH-2. The weight loss in the first step indicates the release of the  
314 interlayer water molecules adsorbed on the surface of the Zn<sup>2+</sup>/Al<sup>3+</sup> ionic brucite-like  
315 layers. Dehydroxylation and thermal degradation of the counter anion is realized at the  
316 second decomposing step and, simultaneously, metal oxidation occurs with the  
317 dehydroxylation of the brucite-like layers. The complete dehydroxylation occurs in the  
318 temperature range of 500-800°C that destroys the brucite-like structure of the LDH. In  
319 the last step, all the counter anions, which are strongly adsorbed on the metal oxide  
320 crystallites, would be removed.

321 The DTA curves of LDH-2 almost display only an exothermic event because of the  
322 quick decomposition of the dodecyl sulfate during the beginning steps. In contrast, the  
323 DTA results of LDH-1 and Mo<sub>6</sub>@LDH-2 show a similar endothermic event in the  
324 second thermal decomposing step. In this step, the phase transformation starts to occur  
325 and accelerates the melting process to destroy the crystallinity of the brucite-like layers  
326 in the third decomposition step. In Mo<sub>6</sub>@LDH-2, the surfactant concentration was  
327 significantly reduced that did not affect the decomposition as seen in LDH-2. In the  
328 third and fourth degradation steps, the performance of the metal oxide from the  
329 dihydroxylation of the brucite-like layers also enhances the enthalpy of the thermal  
330 event that linearly increases the endothermic value [43]. Interestingly, in the third  
331 degradation step of the DTA curve of Mo<sub>6</sub>@LDH-2, a clearly enhanced endothermic  
332 peak appears at 450 °C due to the formation of molybdenum oxide caused by the  
333 destruction of the Mo<sub>6</sub> octahedral structure.

334 **Figure 6a** summarizes the XPS spectra of the CMC and Mo<sub>6</sub>@LDH-2. All the binding  
335 energies were calibrated concerning the C1s peak of the adventitious carbon at 285 eV.  
336 The binding energies of the Zn, Al, C, O, Cs, Mo, Cl, and S elements in the CMC and  
337 Mo<sub>6</sub>@LDH-2 powders are listed in **Table S1**. Interestingly, the Cs element was not  
338 found in Mo<sub>6</sub>@LDH-2, as presented in **Figure 6a**. As already explained, in the solvent,  
339 the CMC cluster dissociated to 2 Cs<sup>+</sup> and 1 [Mo<sub>6</sub>Cl<sub>8</sub>Cl<sub>6</sub>]<sup>2-</sup> ions and the Cs<sup>+</sup> cation can  
340 be kept by the exchangeable anion adsorbed on the LDH or Cl<sup>-</sup> from CMC, which was  
341 removed through the washing step. The binding energies of Zn 2p and Al 2p are  
342 respectively assigned by the two peaks at 1022.3 eV (2p<sub>3/2</sub>) and 1045.4 eV (2p<sub>1/2</sub>) and a  
343 peak of 74.7 eV that agrees with a previous study [48]. The dodecyl sulfate component  
344 is confirmed by the appearance of the binding energy of the S2p at the peak of 169.1 eV.  
345 It is important to verify the difference in the binding energy of the Mo and Cl  
346 components in the Mo<sub>6</sub> cluster after intercalated into the LDH.

347 In **Figure 6b**, the Mo3d XPS spectrum of the CMC cluster shows peaks at 229.7 eV  
348 (3d<sub>5/2</sub>) and 232.8 eV (3d<sub>3/2</sub>) assigned to the Mo<sup>2+</sup> cation from the [Mo<sub>6</sub>Cl<sub>14</sub>]<sup>2-</sup> cluster [36].  
349 In the XPS spectrum of Mo<sub>6</sub>@LDH-2, the Mo3d binding energy is recognized by the  
350 peaks at 229.7 eV (3d<sub>5/2</sub>) and 232.6 eV (3d<sub>3/2</sub>) related to the Mo<sub>6</sub><sup>-</sup> cluster [49, 50, 51].  
351 Interestingly, one new peak at 234 eV (3d<sub>3/2</sub>) indicating Mo-O appears in the  
352 Mo<sub>6</sub>@LDH-2 compound. It could be proof for the interaction between the Mo atom  
353 from the Mo<sub>6</sub> cluster and O atom from the hydroxalate layers of the LDH to form the  
354 Mo-O-Zn or Mo-O-Al bonding. This behavior has been also claimed by Haiping Li et al.  
355 for the Zn(Al)-O-Bi(Mo) bonds between the Bi<sub>2</sub>MoO<sub>6</sub> groups and Zn/Al-LDH [52].  
356 Moreover, the O1s XPS spectrum of Mo<sub>6</sub>@LDH-2 shows a peak at 530.9 eV indicating  
357 O-Mo bonding that was not confirmed in the XPS spectrum of the CMC cluster as



358 expected (**Tab. S1**). In addition, the binding energy assigned to the O1s of CMC with a  
359 peak at 532.6 eV that is verified for the freely absorbed water molecules (**Tab. S1**)  
360 while the binding energy of O1s of Mo<sub>6</sub>@LDH-2 is also characterized by a peak at  
361 530.9 eV which indicates the O-Zn, O-Al, or O-Mo bonding.

362 Similarly, the XPS spectrum of the CMC cluster for the Cl2p including three clear peaks  
363 at 198.3 eV (2p<sub>3/2</sub>), 200.4 (2p<sub>3/2</sub>), and 200.2 (2p<sub>1/2</sub>) while only one broad peak was  
364 observed for the Cl2p for Mo<sub>6</sub>@LDH-2 (**Fig. 6c**). To distinguish the inner and apical Cl  
365 ligands, the spectrum deconvolution of the Cl2p region was performed for the XPS  
366 spectra of the Cl2p of CMC cluster and Mo<sub>6</sub>@LDH-2, as listed in Table 2. The  
367 deconvolution spectrum of the Cl 2p region of the CMC cluster shows four peaks at  
368 198.25, 199.85, 200.39 and 201.99 eV that indicate Cl<sup>(a)</sup>2p<sub>3/2</sub>, Cl<sup>(a)</sup>2p<sub>1/2</sub>, Cl<sup>(i)</sup>2p<sub>3/2</sub> and  
369 Cl<sup>(i)</sup>2p<sub>1/2</sub>, respectively (**Fig. 6d and Tab. 1**) [53]. For Mo<sub>6</sub>@LDH-2, the XPS  
370 deconvolution of the Cl2p shows the same peaks at 198.25 eV (Cl<sup>(a)</sup>2p<sub>3/2</sub>), 199.85 eV  
371 (Cl<sup>(a)</sup>2p<sub>1/2</sub>), 201.35 (Cl<sup>(i)</sup>2p<sub>3/2</sub>), and 201.95 eV (Cl<sup>(i)</sup>2p<sub>1/2</sub>) which are properly related to  
372 Mo-Cl of the [Mo<sub>6</sub>Cl<sup>i</sup><sub>8</sub>Cl<sup>a</sup><sub>6</sub>]<sup>2-</sup> anion (**Fig. 6e**). The ratio Cl<sup>(a)</sup>2p/ Cl<sup>(i)</sup>2p was  
373 experimentally calculated to be 5.8/8 for the [Mo<sub>6</sub>Cl<sup>i</sup><sub>8</sub>Cl<sup>a</sup><sub>6</sub>]<sup>2-</sup> anion in the CMC cluster  
374 and 3.6/8 for the [Mo<sub>6</sub>Cl<sup>i</sup><sub>8</sub>Cl<sup>a</sup><sub>6-(x+y)</sub>(H<sub>2</sub>O)<sup>a</sup><sub>x</sub>(OH)<sup>a</sup><sub>y</sub>]<sup>x-2</sup> anion in Mo<sub>6</sub>@LDH-2. This  
375 deconvolution agrees with an analysis of the XPS spectra as mentioned in Table 1,  
376 following the average loss of at least three apical Cl ligands on the Mo<sub>6</sub> anion in  
377 Mo<sub>6</sub>@LDH-2. All these results support for the possible chemical bonding between the  
378 [Mo<sub>6</sub>Cl<sup>i</sup><sub>8</sub>Cl<sup>a</sup><sub>3</sub>(OH)<sup>a</sup><sub>3</sub>]<sup>2-</sup> or [Mo<sub>6</sub>Cl<sup>i</sup><sub>8</sub>Cl<sup>a</sup><sub>3</sub>(H<sub>2</sub>O)<sup>a</sup><sub>3</sub>(OH)<sup>a</sup><sub>2</sub>]<sup>1-</sup> anionic clusters or  
379 [Mo<sub>6</sub>Cl<sup>i</sup><sub>8</sub>Cl<sup>a</sup><sub>3</sub>(H<sub>2</sub>O)<sup>a</sup><sub>2</sub>(OH)<sup>a</sup><sub>1</sub>] neutral cluster and the hydroxide of ZnAL LDH. Very  
380 interestingly, new peaks of the Cl2p were noted in the deconvolution spectrum at 198.9  
381 eV (2p<sub>3/2</sub>) and 200.5 eV (2p<sub>1/2</sub>) that suggested the energy bonding of Cl with another

382 metal (Zn or Al) [48]. It could be explained that the apical  $\text{Cl}^-$  anions separated from the  
383  $\text{Mo}_6$  cluster by exchange with the interlayer water molecules will directly adsorb on the  
384 positively charged hydrotalcite surface of the LDH. Aiming to clarify the quantitative  
385 analysis of the element components of  $\text{Mo}_6@$ LDH-2, an ICP-OES analysis was  
386 performed that indicated the ratio of Zn, Al, and Mo atoms of about 1.96, 1.00, and 0.38.  
387 The Mo element definitely existed in the  $\text{Mo}_6@$ LDH-2 at a significant concentration as  
388 well as confirmed in the STEM-EDX mapping image. The ratio between the Cl and Mo  
389 atoms in  $\text{Mo}_6@$ LDH-2 indicated by ICP-OES analysis was 2.23 (the theoretical ratio is  
390 2.33) which means almost all the original Cl (from ligands) still exist in the  
391 nanocomposite after treatment. This result suggests too that a part of the  $\text{Cl}^-$  could be  
392 directly adsorbed on the LDH.

393 As known, the  $\text{H}_2\text{O}_2/\text{UV}$  or  $\text{H}_2\text{O}_2/\text{catalyst}$  systems are widely used in advanced  
394 oxidation technology, one of the most environmentally friendly techniques to degrade  
395 pollutants [54]. In this study, the efficiency of the MB degradation caused by the  $\text{Mo}_6$   
396 cluster deposited on LDH with and without UV and  $\text{H}_2\text{O}_2$  or both as a radical generating  
397 source. **Table S2** and **Figure 7** present the change in the  $C/C_0$  value that was calculated  
398 from the optical absorbance (664 nm) of the samples and blank illustrated in **Figure S3**.  
399 First, the evaluation of the MB adsorbing possibility of LDH-2 and  $\text{Mo}_6@$ LDH-2 was  
400 performed by stirring with MB aqueous solution (catalyst/MB = 20/1) for 72h in the  
401 dark (**Fig. S3a**). The intensity of the adsorbing peak at 664 nm assigned to MB  
402 significantly decreased by about 80 wt% caused by  $\text{Mo}_6@$ LDH-2, meanwhile, it is 66  
403 wt% for LDH-2. Considering the BET surface area of LDH-2 of about  $50.0 \text{ g/m}^2$  and  
404  $\text{Mo}_6@$ LDH-2 of about  $20.4 \text{ g/m}^2$  (**Fig. S2**), the adsorbing possibility of the  $\text{Mo}_6@$ LDH-  
405 2 should be lower than that of LDH-2. That means a part of the degraded MB is caused

406 by the oxidation reaction of the Mo<sub>6</sub> cluster. To clarify this phenomenon, the Mo<sub>6</sub> cluster,  
407 LDH-2, Mo<sub>6</sub>@LDH-2 powders were dispersed in the MB solution (catalyst/MB = 20/1)  
408 in the dark, with UV or H<sub>2</sub>O<sub>2</sub> or both of them for 2 h (**Fig. S3b and c**). The calculated  
409 C/Co value of all samples was presented in **Figure 7a** and **Table S2**.

410 In **Figure 7a**, the decrease in the degraded MB concentration caused by the CMC  
411 cluster was recorded at 57% in the dark, at 98% with UV or H<sub>2</sub>O<sub>2</sub> that proved strong  
412 oxidation and photoactive properties of the Mo<sub>6</sub> cluster [30, 31]. As a result,  
413 Mo<sub>6</sub>@LDH-2 also displays the MB degrading efficiency that is 71 wt% in dark and  
414 96% with H<sub>2</sub>O<sub>2</sub>. Their MB degrading possibility slightly reduce in the irradiation of the  
415 UV light for the same catalyst. This result is proof for the advantage of the intercalation  
416 of the Mo<sub>6</sub> cluster on the LDH in comparison with LDH that shows the degraded MB  
417 concentration at 54% in the dark and 65% with H<sub>2</sub>O<sub>2</sub>. Barras et al. reported the  
418 photocatalytic degradation of rhodamine B over [Mo<sub>6</sub>Br<sub>8</sub>(N<sub>3</sub>)<sub>6</sub>]<sup>2-</sup> cluster units under  
419 sunlight irradiation with catalyst/rhB ratio of 1/1 for 2 h [38]. Besides, Ivanova et al.  
420 also claimed the efficient photocatalyst of the hexamolybdenum cluster supported on  
421 exfoliated hexagonal boron nitride (h-BN) nanosheet with the catalyst/rhB ratio of  
422 100/1 [35]. In comparison, the H<sub>2</sub>O<sub>2</sub>/Mo<sub>6</sub>@LDH system also shows a catalytic  
423 efficiency with the catalyst/MB ratio of 100/1 even in the dark.

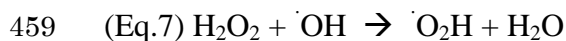
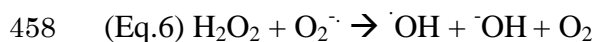
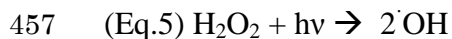
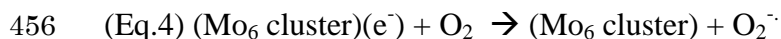
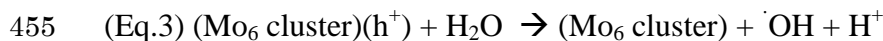
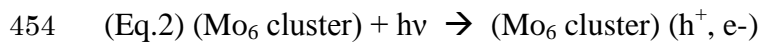
424 For the first time, the combination of the Mo<sub>6</sub> cluster and H<sub>2</sub>O<sub>2</sub> was performed to test  
425 the oxidation reaction on dye degradation and it shows excellent results. Only H<sub>2</sub>O<sub>2</sub> is  
426 unable to degrade the MB cations. H<sub>2</sub>O<sub>2</sub> is suggested as an effective agent accelerating  
427 for the Mo<sub>6</sub> cluster in the initial step of the MB degradation process.

428 **Figure 7b and 7c** illustrate the degradation rate and effect of the H<sub>2</sub>O<sub>2</sub> concentration on  
429 the catalytic activity of the H<sub>2</sub>O<sub>2</sub>/Mo<sub>6</sub>@LDH-2 with and without UV ( $\lambda=370$  nm) light

430 illumination as well as the change in the solution color as seen in **Figure S4**. The tested  
431 suspensions were collected every 30 minutes from the original suspension for 210  
432 minutes. The catalytic activity for the MB degradation decreases when the H<sub>2</sub>O<sub>2</sub>  
433 concentration is increased. For this result, a suitable amount of H<sub>2</sub>O<sub>2</sub> for the 20 mg  
434 catalyst to obtain the optimal catalytic activity is recorded at 0.3 mM in both cases with  
435 and without UV light illumination. The rate of the MB degradation by the H<sub>2</sub>O<sub>2</sub>/  
436 Mo<sub>6</sub>@LDH-2 is also confirmed with the strong reduction of the MB concentration for  
437 the first 30 min that includes the absorption of MB on the surface of the LDH. The pH  
438 increases, which is recorded during light irradiation, suggests the appearance of  
439 hydroxyl anions during the initial and propagating reactions. Moreover, the chemically  
440 component modification of the Mo<sub>6</sub>@LDH-2 nanocomposite after the reaction with MB  
441 in the presence of the H<sub>2</sub>O<sub>2</sub> solution was measured by FTIR spectroscopy as seen in  
442 **Figure S5**. The vibrational band assigned to the NO<sub>3</sub><sup>-</sup> group was significantly decreased  
443 accompanying a decrease in the O-H vibrational band assigned to the free H<sub>2</sub>O  
444 molecules that prove the use of interlayer-absorbed H<sub>2</sub>O<sub>2</sub> molecules for the degradation  
445 reaction of MB. Nevertheless, the XRD patterns of the Mo<sub>6</sub>@LDH-2 before and after  
446 the test with the MB degradation show no change as seen in **Figure S6**. That means the  
447 layered structure of LDH is not modified and the degradation of the MB almost occurs  
448 mostly on the outside surface of the Mo<sub>6</sub>@LDH-2 nanosheets. In addition, the MB  
449 degradable possibility by Mo<sub>6</sub>@LDH-2 was observed for the concentration reduction of  
450 about 66% for the second recycling run.

451 In summary, the non-photochemical reactions for the degradation of MB based on the  
452 Mo<sub>6</sub>@LDH-2 nanocomposite is suggested by the following equations [36, 37, 38, 55].

453 (Eq.1) H<sub>2</sub>O<sub>2</sub> + (Mo<sub>6</sub> cluster) → (Mo<sub>6</sub> cluster) (h<sup>+</sup>) + ·OH + OH<sup>-</sup>



460 The  $\text{Mo}_6$  cluster plays an important role as an electron supplying source for the initial  
461 reaction with the strong support of  $\text{H}_2\text{O}_2$  to generate free radicals as seen in Eq. 1. The  
462 radical generating process is less efficient when the  $\text{Mo}_6$  cluster is excited by UV light  
463 because of taking two steps as depicted by Eq. 2 and Eq. 3 to form hydroxyl radicals  
464 ( $\cdot\text{OH}$ ), and Eq. 4 to form superoxide radical ( $\text{O}_2^{\cdot-}$ ). For this reason,  $\text{Mo}_6@LDH-2$  with  
465  $\text{H}_2\text{O}_2$  presents a higher catalytic activity than  $\text{Mo}_6@LDH-2$  with UV light. During the  
466 initiating process by  $\text{Mo}_6@LDH-2$  with  $\text{H}_2\text{O}_2$  and UV light, the Eq. 5 and Eq. 6 site  
467 reactions could significantly occur to reduce the  $\text{H}_2\text{O}_2$ . The degradation rates of the  
468 pollutants will decrease with the increase in the  $\text{H}_2\text{O}_2$  concentration despite Eq. 7. The  
469 generated hydroxyl radical can randomly attack the MB organic compound by hydrogen  
470 abstraction, electron transfer, and radical combination to form the oxidation products  
471 [56].

472 The representation of the structure and activity mechanism of  $\text{Mo}_6@LDH-2$  for the  
473 degradation of MB is illustrated in **Figure 8**. The efficiency of the catalytic activity  
474 depends on the generation of highly reactive radicals and the stability of the radicals.  
475 Without the light irradiation,  $\text{ZnAl-LDH}$  acts as a weak basic catalyst with the

476 hydroxide group the surface. ZnAl-LDH did not show the photocatalytic possibility due  
477 to the weak performance of the Zn metal in the photocatalytic reaction [39]. In addition,  
478 dye degradation was caused by the photocatalytic and oxidizing reactions. As a result,  
479 the catalytic property of the Mo<sub>6</sub>@LDH-2 was mostly originated from the photoactive  
480 and oxidizing Mo metal cluster and the absorption caused by LDH. In the reduced form,  
481 the valence electron concentration (VEC) occupying in the d orbitals of the six Mo  
482 atoms, is equal to 24 electrons per Mo<sub>6</sub> cluster unit and it is reduced by a strong  
483 oxidizing agent [31]. Moreover, a chemically and an electrochemically reversible  
484 system has been reported. The Mo<sub>6</sub> cluster unit also provides one electron when excited  
485 by the light and transfer to O<sub>2</sub> to form singlet oxygen (<sup>1</sup>O<sub>1</sub>) thus exhibiting a powerful  
486 oxidant property [30, 32]. It could be summarized in this study that i) the reducing form  
487 of the Mo<sub>6</sub> cluster can oxidize the MB molecules, ii) the Mo<sub>6</sub> cluster can combine with  
488 H<sub>2</sub>O<sub>2</sub> to create powerful, oxidizing hydroxides (OH<sup>•</sup>), ii) the Mo<sub>6</sub> cluster can be excited  
489 by the UV light to form the hole and electron pair on the photoexcited cluster which  
490 reacts with H<sub>2</sub>O molecules to create the OH<sup>•</sup> radicals, and superoxide radical (O<sub>2</sub><sup>•-</sup>),  
491 particularly, singlet oxygen (<sup>1</sup>O<sub>1</sub>) as a powerful oxidant caused by photoluminescence  
492 [36,37,38]. The oxygen-based radicals will first attack the C=S+-C linking of the MB  
493 molecule existing on the surface of the LDH. A degradation mechanism of MB caused  
494 by the oxygen-based radical is reported to form hydroxylation and oxidation products in  
495 a previous study [57]. To understand the impact of the UV light on the catalytic reaction,  
496 we consider some possible reasons. The UV light at 370 nm was used with the purpose  
497 to optimally create the <sup>1</sup>O<sub>1</sub>, O<sub>2</sub><sup>•-</sup> and OH<sup>•</sup> oxygen-based radicals on the Mo<sub>6</sub> cluster which  
498 directly react with MB. Unfortunately, from Figure 3, the UV light at 370 nm is partially  
499 absorbed by the Zn-Al hydroxide layers that cause the decrease of the excitation photon

500 used for the Mo<sub>6</sub> cluster. In addition, the hole in the photoexcited Mo<sub>6</sub> cluster also reacts  
501 with water to form protons which reduce the concentration of the OH<sup>•</sup> radicals. In the  
502 catalyst with the H<sub>2</sub>O<sub>2</sub>/UV system, the H<sub>2</sub>O<sub>2</sub> molecules could be degraded by the UV  
503 energy. For this reason, the UV light will negatively affect the MB reducing the  
504 efficiency of the Mo<sub>6</sub> cluster when UV light and H<sub>2</sub>O<sub>2</sub> are used at the same time. In  
505 summary, the prominent catalytic activity of the Mo<sub>6</sub> cluster stabilized on ZnAl-LDH  
506 has been confirmed. The combination of the LDH with high absorbability and the  
507 recyclability and the chemically reserving Mo<sub>6</sub> cluster will be a promising candidate as  
508 a homogeneous catalyst for gas reactions with a strong selection based on the layer  
509 structure.

510

#### 511 **4. CONCLUSIONS**

512 A heterogeneous nanocomposite of ZnAl-LDH functionalized with the molybdenum  
513 octahedral cluster (~ 16.7 wt. %) was successfully synthesized by the precipitation and  
514 anion exchanging method under ambient conditions. The partially exfoliated ZnAl-  
515 LDH functionalized with the Mo<sub>6</sub> cluster was carried out. The interaction between the  
516 Mo<sub>6</sub> clusters and ZnAl-LDH is suggested to be via hydrogen bonding and/or new Mo-  
517 O-Al/Zn covalent linkage. The photoactive and oxidation of the Mo<sub>6</sub> cluster in the  
518 Mo<sub>6</sub>@LDH nanocomposite present the important role to degrade methylene blue (MB).  
519 This point was investigated under UV ( $\lambda = 370$  nm), in the presence of H<sub>2</sub>O<sub>2</sub>, or both of  
520 UV and H<sub>2</sub>O<sub>2</sub> as radical initial agents. The efficiency of the degradation of MB using  
521 the Mo<sub>6</sub>@LDH-2 nanocomposite is evaluated at more than about 90 wt% after 2 h with  
522 H<sub>2</sub>O<sub>2</sub> as optimal co-agent. These results proved that the octahedral Mo<sub>6</sub> clusters are  
523 efficiently retained on the brucite-like layers that provide new heterogeneous catalytic

524 materials' family for gas reactions in the future.

525

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533 XPS measurements.

534

## 535 APPENDIX A. SUPPLEMENTARY MATERIAL

536 Supplementary data to this article can be found online at

537

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724

## 725 **FIGURE CAPTIONS**

726 **Figure 1.** A) Powder-XRD patterns of LDH-1,  $\text{Mo}_6\text{@LDH-1}$ , LDH-2,  $\text{Mo}_6\text{@LDH-2}$   
727 with the indications of the planes of 003 (■), 006 (●), 009 (▲) and the lozenge symbol  
728 (◆) assigned for the ZnO phase. B) The schematic representation of the process to  
729 fabricate the LDH and designed structure of its nanocomposite.

730 **Figure 2.** A) The HR-TEM, B) STEM images of the layered structure, and C) profile of  
731 spacing distance between the layers, and D) STEM-EDX mapping of the  $\text{Mo}_6\text{@LDH-2}$   
732 nanocomposite.

733 **Figure 3.** A) UV-Vis absorbance spectra and B) room temperature photoluminescence  
734 spectra excited by 325 nm (He-Cd) laser of CMC cluster, LDH-1, LDH-2, and  
735  $\text{Mo}_6\text{@LDH-2}$ .

736 **Figure 4.** FTIR spectra of CMC cluster and  $\text{Mo}_6\text{@LDH}$  nanocomposites.

737 **Figure 5.** Thermal analysis of LDH-1, LDH-2, and  $\text{Mo}_6\text{@LDH-2}$

738 **Figure 6.** (A) XPS binding energy (eV) spectrum of the CMC powder and the



739 Mo<sub>6</sub>@LDH-2 nanocomposite, XPS spectra of (B) Mo 3d, (C) Cl 2p region.

740 Deconvolution spectra of Cl 2p region of (D) the CMC and (E) Mo<sub>6</sub>@LDH-2.

741 **Figure 7.** A) The MB-degradable possibility caused by (1) Mo<sub>6</sub> cluster, (2) Mo<sub>6</sub>@LDH-

742 2, and (3) LDH-2 without and with H<sub>2</sub>O<sub>2</sub> during stirring for 2 h, B) the degradation rate

743 and C) the effect of H<sub>2</sub>O<sub>2</sub> concentrations on MB-degradable possibility by Mo<sub>6</sub>@LDH-2

744 for 210 minutes with and without UV light ( $\lambda=370$  nm) illumination.

745 **Figure 8.** Schematic representation of the heterogeneous activation mechanism of

746 Mo<sub>6</sub>@LDH-2 initialed by UV ( $\lambda=370$  nm) and H<sub>2</sub>O<sub>2</sub> oxidation agents.

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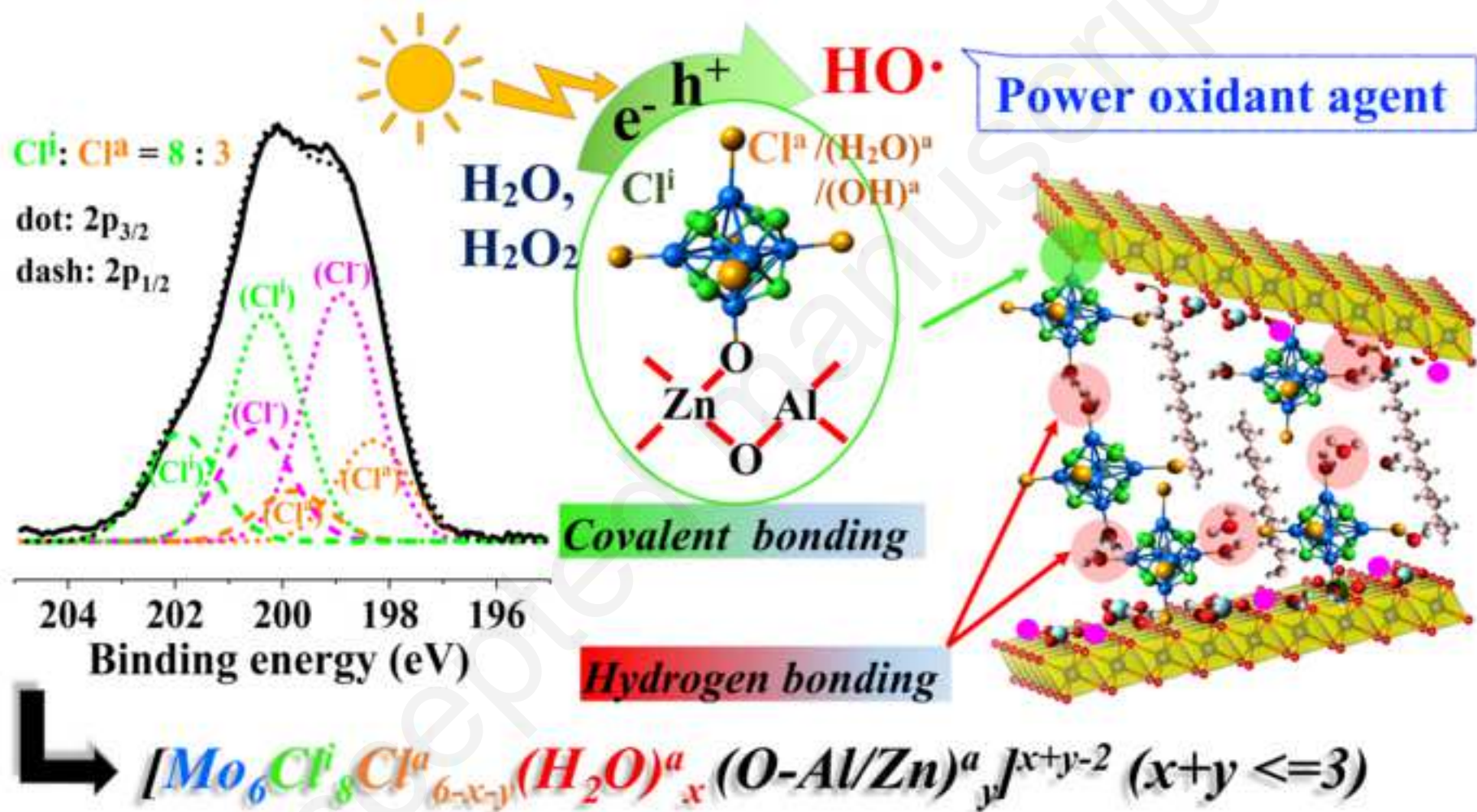
#### 749 TABLES

750 Table 1. XPS binding energy (eV) of deconvolution spectra of Cl 2p region of the

751 [Mo<sub>6</sub>Cl<sup>i</sup><sub>8</sub>Cl<sup>a</sup><sub>6</sub>]<sup>2-</sup> anions of CMC cluster and Mo<sub>6</sub>@LDH-2.

752 Table 2. The concentration of the component elements in the CMC powder and the

753 Mo<sub>6</sub>@LDH-2 nanocomposite by the peak analysis of the XPS measurements.



## Highlights

ZnAl-LDHs were successfully functionalized with the hexamolybdenum cluster by covalent linkage.

A Mo<sub>6</sub>@LDHs nanocomposite retains the photoactive and oxidation properties of the Mo<sub>6</sub> cluster

Three nanomaterial phases were found in the lamellar structure of the Mo<sub>6</sub>@LDHs

H<sub>2</sub>O<sub>2</sub>/Mo<sub>6</sub>@LDHs efficiently accelerated the degradation reaction of methylene blue with and without UV light illumination

## TABLES

Table 1. XPS binding energy (eV) of deconvolution spectra of Cl 2p region of the  $[\text{Mo}_6\text{Cl}_8\text{Cl}_6^{\text{a}}]^2$  anions of  $\text{Cs}_2\text{Mo}_6\text{Cl}_{14}$  cluster and  $\text{Mo}_6@LDH-2$ .

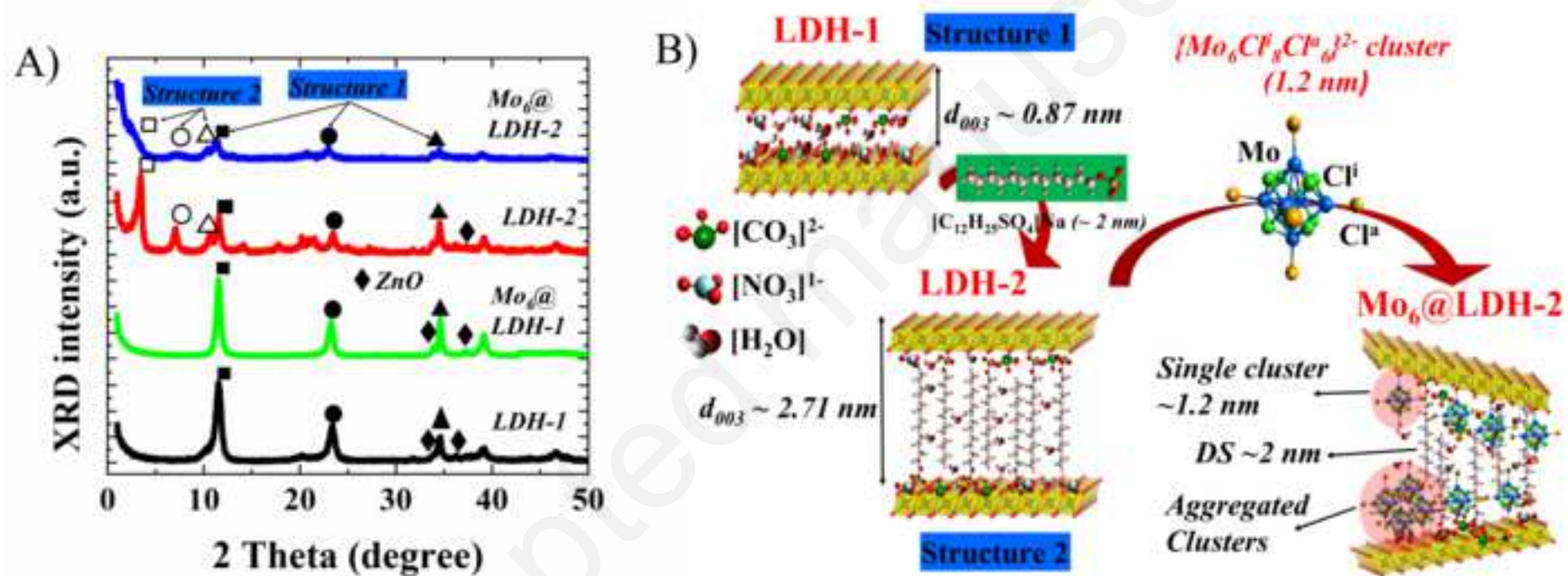
Sample	B.E	FWHM	Height	% area	Peak	$\text{Cl}^{\text{i}}/\text{Cl}^{\text{a}}/\text{Cl}^{\text{new}}$
$\text{Cs}_2\text{Mo}_6\text{Cl}_8\text{Cl}_6^{\text{a}}$	198.25	1.15	15637	27.88	Cl 2p <sub>3/2</sub> (a)	8/5.8/0
	199.85	1.15	7895	14.08	Cl 2p <sub>1/2</sub> (a)	
	200.39	1.16	21005	37.78	Cl 2p <sub>3/2</sub> (i)	
	201.99	1.16	11265	20.26	Cl 2p <sub>1/2</sub> (i)	
$\text{Mo}_6@LDH-2$	198.25	1.6	977	11.90	Cl 2p <sub>3/2</sub> (a)	8/3.6/8.6
	198.90	1.6	2403	28.28	Cl 2p <sub>3/2</sub>	
	199.85	1.6	488	5.95	Cl 2p <sub>1/2</sub> (a)	
	200.35	1.6	2207	26.89	Cl 2p <sub>3/2</sub> (i)	
	200.50	1.6	1081	13.17	Cl 2p <sub>1/2</sub>	
	201.95	1.6	1051	12.81	Cl 2p <sub>1/2</sub> (i)	

Table 2. The concentration of the component elements in the  $\text{Cs}_2[\text{Mo}_6\text{Cl}_{14}]$  powder and the  $\text{Mo}_6@LDH-2$  nanocomposite by the peak analysis of the XPS measurements.

Element component (% at.)	$\text{Cs}_2\text{Mo}_6\text{Cl}_{14}$	$\text{Mo}_6@LDH-2$
Al	0	3.8
Zn	0	12.4
S	0	1.5
C	28.5	29.1
O	5.2	47.3
Cl	42	3.8
Mo	17.7	2.1

Cs	6.6	0
Cs/ Mo/Cl	2.2/6.0/14.2	0/6.0/10.7

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Figure

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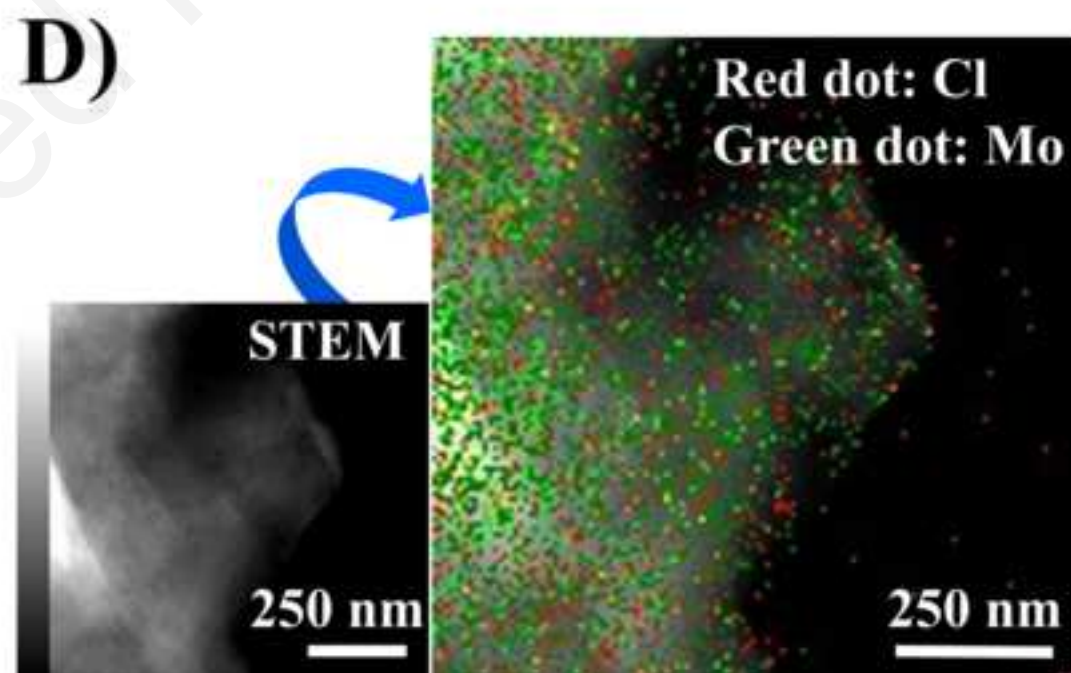
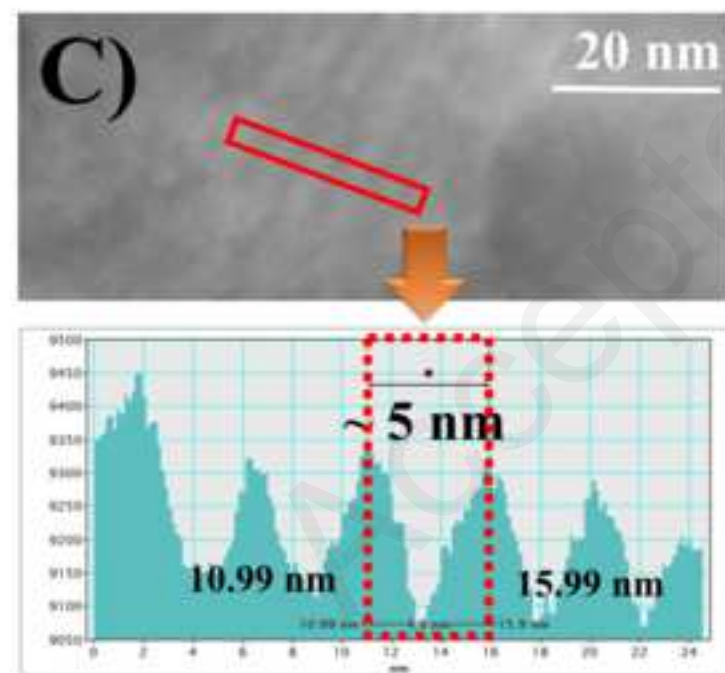
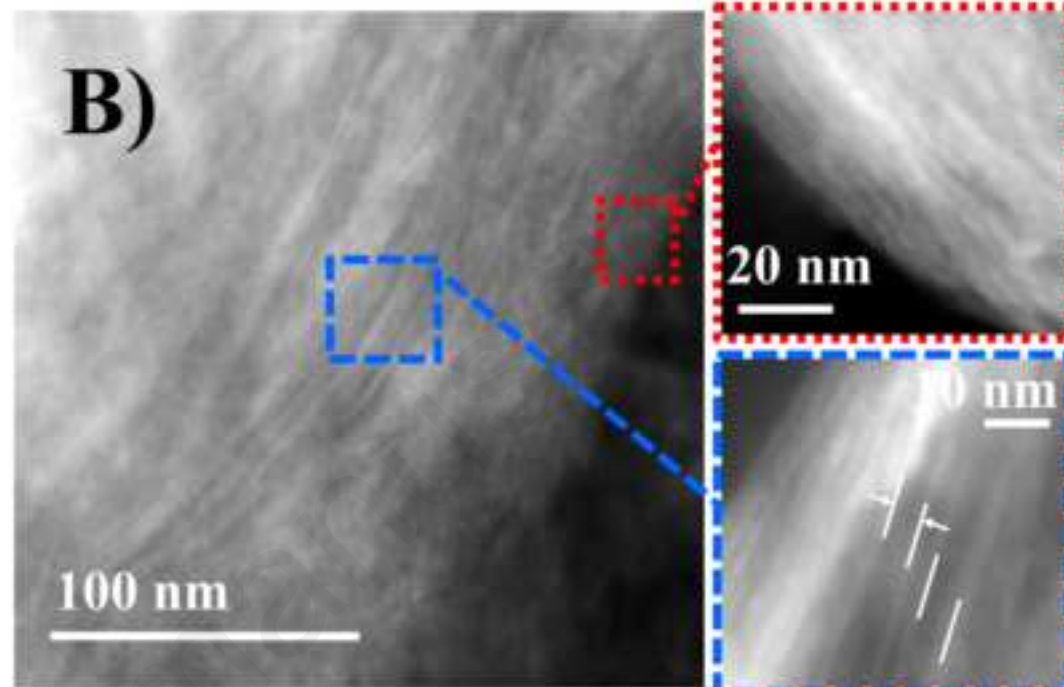
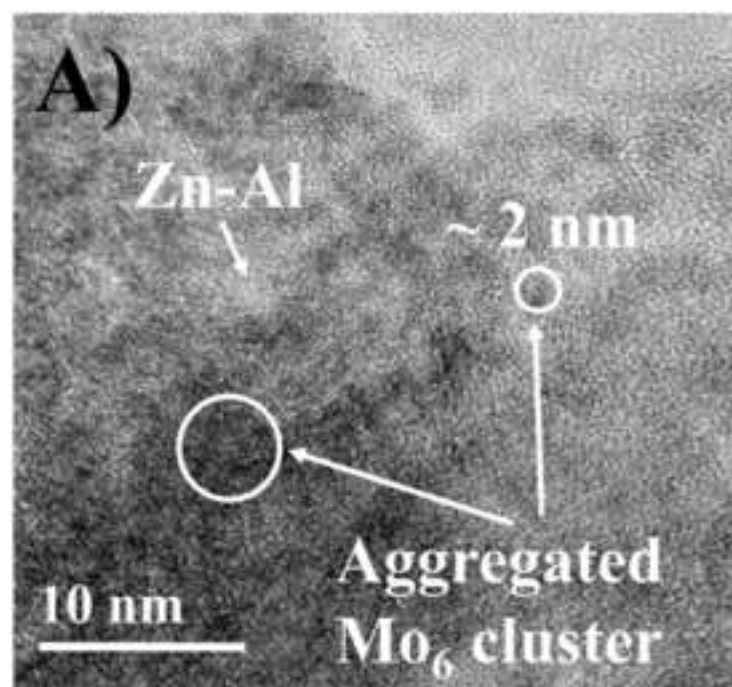


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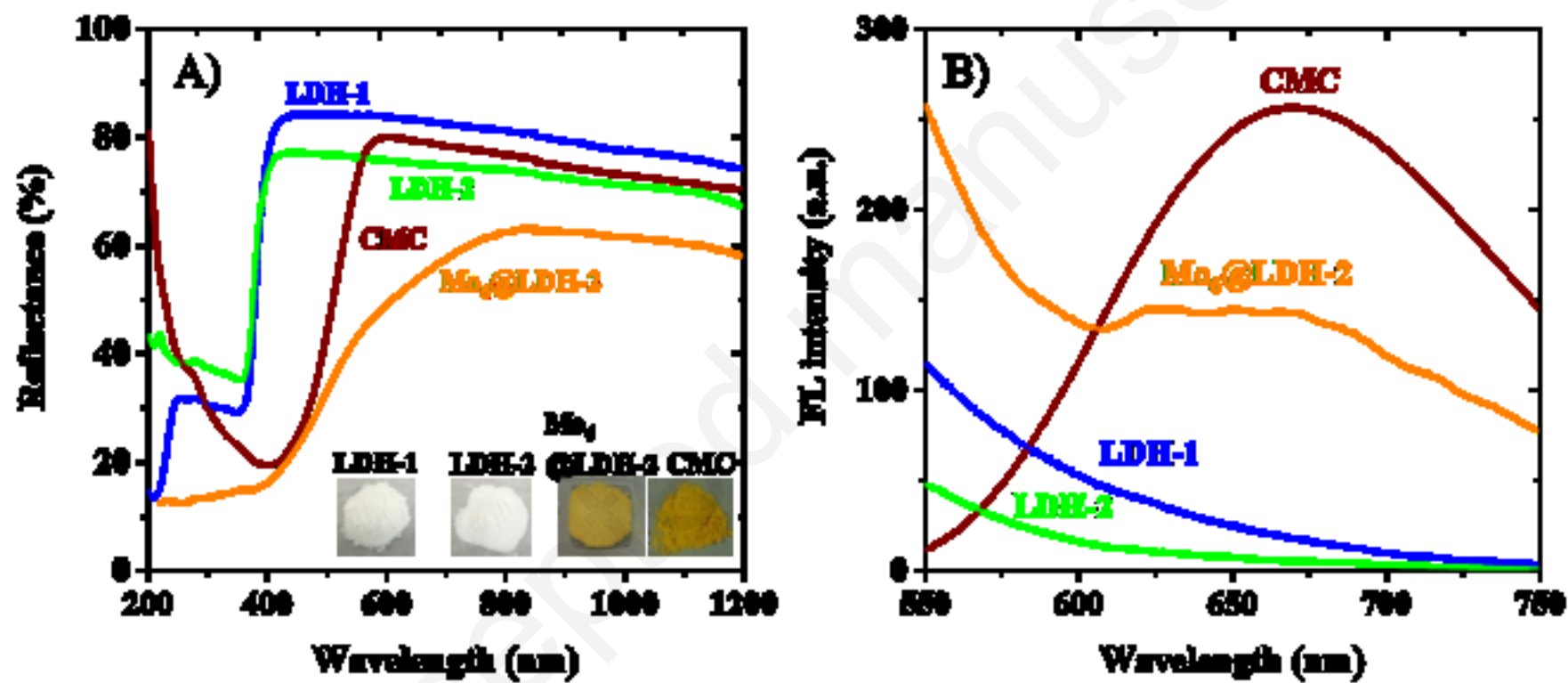




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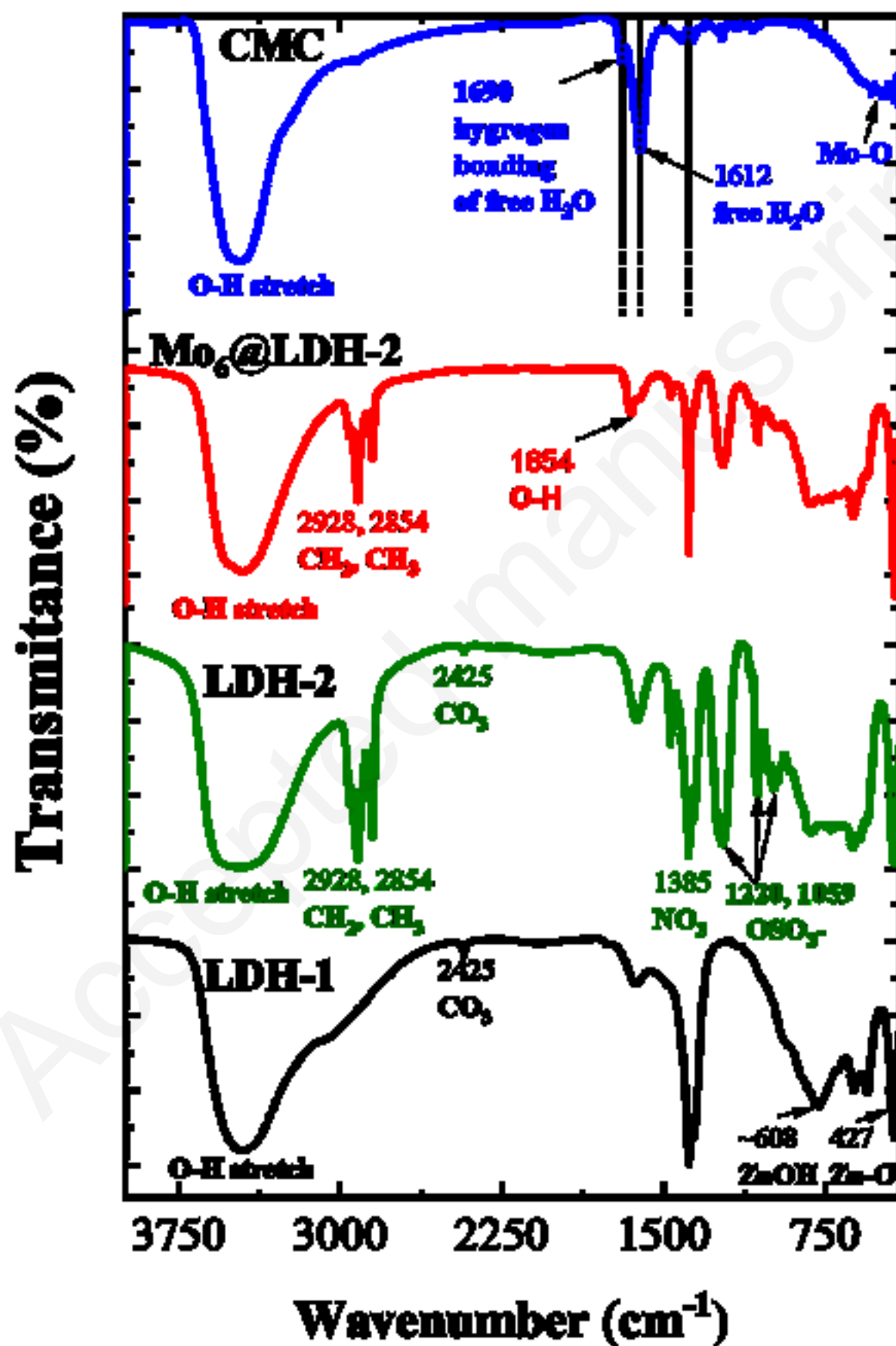
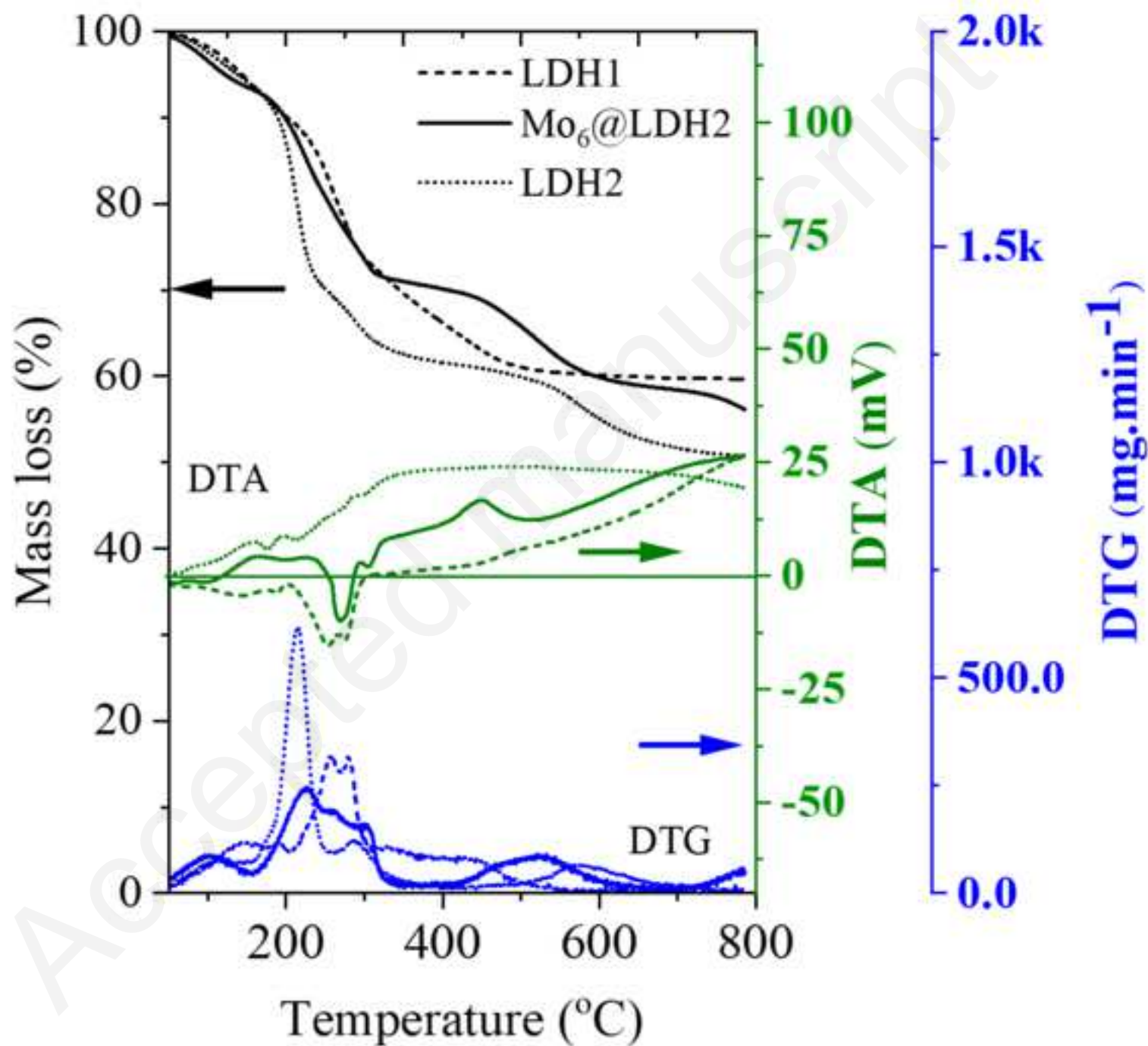
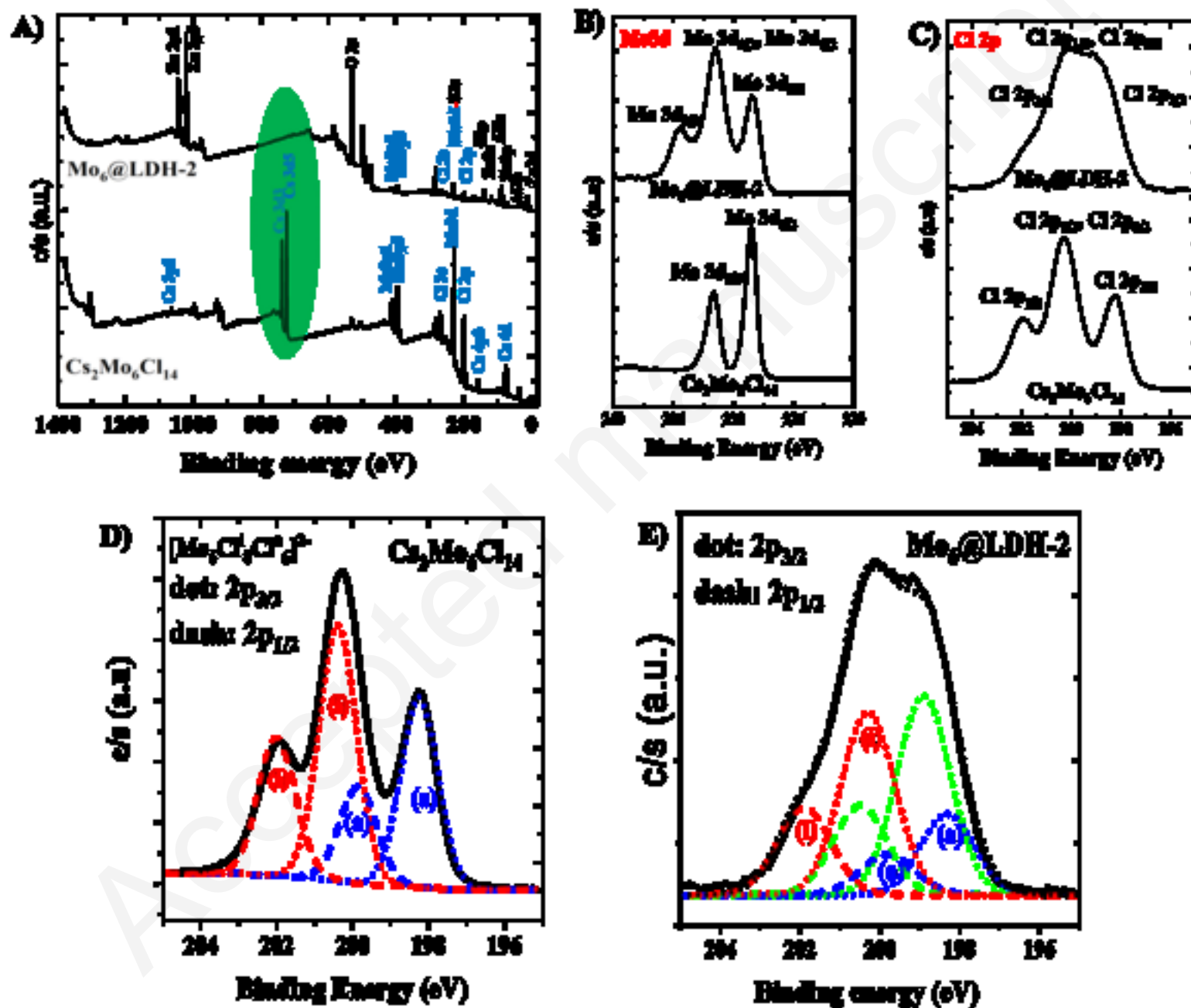


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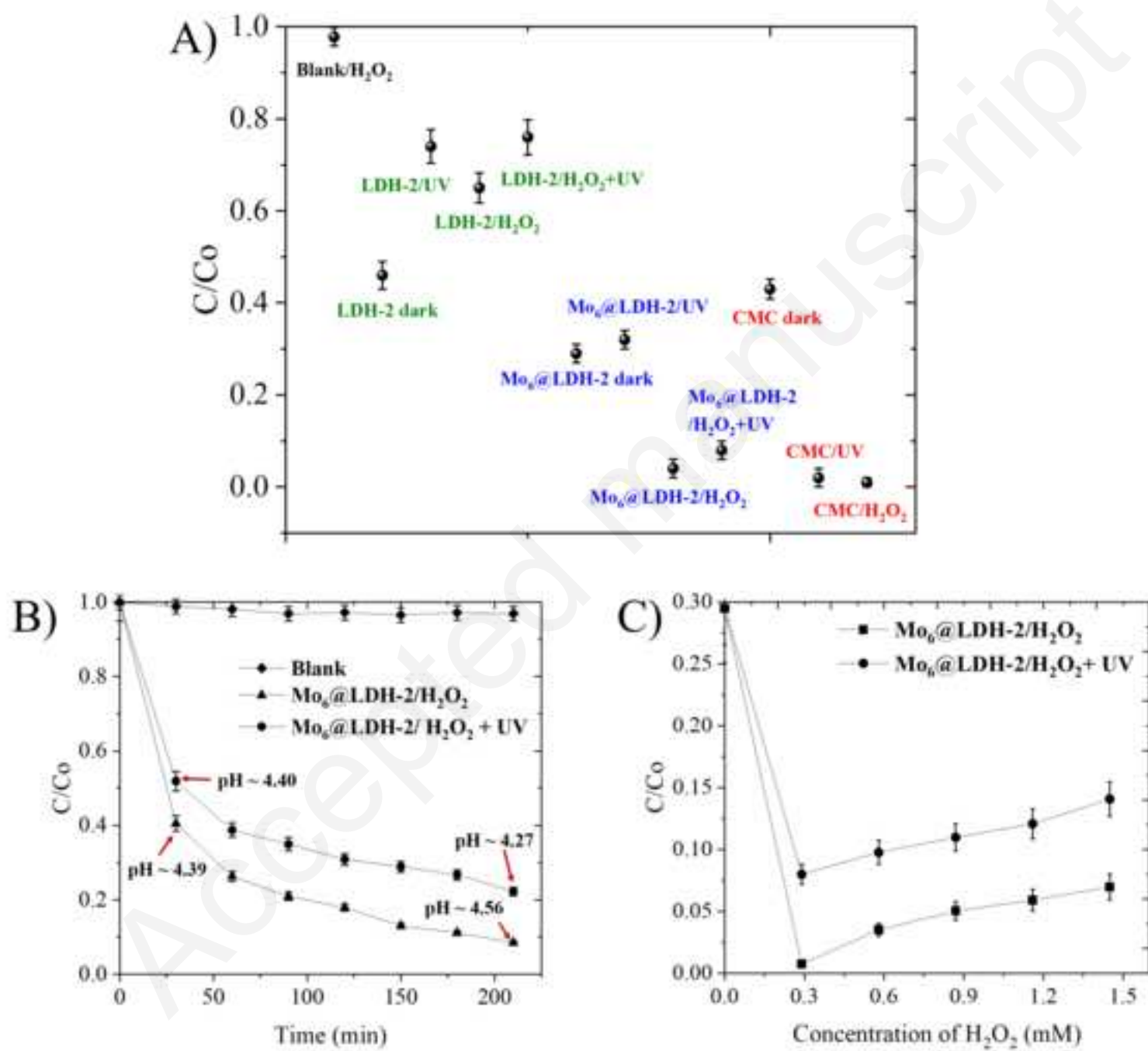


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