

1 **A Facile Synthesis of Montmorillonite Supported CdAl<sub>2</sub>O<sub>4</sub> Nanocomposites**  
2 **with Photocatalytic and Hydrophobic Properties**

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19 Nanocomposites with Photocatalytic and Hydrophobic Properties. **Substantia**. *Just Accepted*.

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21 **Abstract**

22 The hydrothermal co-precipitation method was successfully employed to synthesize  
23 CdAl<sub>2</sub>O<sub>4</sub> supported by natural clay, montmorillonite to reduce the toxicity of solid and liquid  
24 wastes that cause serious harm to livestock and humans due to the discharge of dye wastes into  
25 water bodies. Characterization of the montmorillonite/CdAl<sub>2</sub>O<sub>4</sub> (MMT/CdAl<sub>2</sub>O<sub>4</sub>) composite was  
26 carried out using various techniques, including X-ray powder diffraction (XRD), scanning electron

27 microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM),  
28 photoluminescence spectroscopy (PL), diffuse reflectance spectroscopy (DRS), and BET surface  
29 area analysis. Experimental results indicate that CdAl<sub>2</sub>O<sub>4</sub> supported by montmorillonite at a 9%  
30 wt concentration exhibited superior photocatalytic activity compared to undoped CdAl<sub>2</sub>O<sub>4</sub> in the  
31 removal of the azo dye rhodamine-B (rh-B) under solar light irradiation. The FE-SEM images  
32 clearly reveal the formation of nanoclusters and nanoflakes interconnected via edge-to-flat-surface  
33 conjunction. Furthermore, BET analysis demonstrated that the surface area of MMT/CdAl<sub>2</sub>O<sub>4</sub>  
34 surpasses that of undoped CdAl<sub>2</sub>O<sub>4</sub>. Remarkably, montmorillonite-supported CdAl<sub>2</sub>O<sub>4</sub> exhibited  
35 excellent photocatalytic activity for up to four consecutive uses. A notable feature of  
36 montmorillonite/ CdAl<sub>2</sub>O<sub>4</sub> is its high hydrophobicity, as evidenced by a contact angle of 113.8°.  
37 This hydrophobic nature is particularly advantageous in the production of self-cleaning materials.

38 **Keywords:**

39 Montmorillonite clay; CdAl<sub>2</sub>O<sub>4</sub> nanoflakes; Rhodamine-B; Photodegradation; Contact angle

40

41 **1 Introduction**

42 In recent decades, heterogeneous photocatalysis has gained recognition as an eco-friendly  
43 method for energy conversion. Semiconductor photocatalysts, in particular, have shown great  
44 promise for environmentally cleaning by facilitating the degradation of organic contaminants [1-  
45 3]. Semiconductor-mediated photocatalysis is one of the most successful methods available for  
46 cleaning and dye purification procedures. Metal oxide coupling has been proven to be an effective  
47 method to improve the photocatalytic activities of nanomaterials, which can reduce the  
48 recombination of the photogenerated electron/hole pairs and lengthen their lifetime [4,5]. A

49 number of surface active materials such as activated carbon, zeolites, graphene and clay materials  
50 have been used as photocatalyst supports [6-8].

51 Natural clay materials, such as coal fly ash, bentonite, kaolinite, sepiolite, and  
52 montmorillonite, have demonstrated excellent support for semiconductor oxide materials in  
53 various photocatalytic studies [9-14]. Due its softness, plasticity, porosity, tangibility, pliability,  
54 and climatic adaptability, all at affordable cost, were viable characteristics to recognize its  
55 usefulness, and introduced several products. Among the many kinds of clay minerals,  
56 montmorillonite has been recognized as an effective adsorbent due to its high surface area,  
57 expandability, and swellability, montmorillonite within the smectite group has been found to be  
58 an effective adsorbent for the removal of dyes and cations. The structure and cation exchange  
59 capacity (CEC) of montmorillonite are linked to its adsorption capability. Because of its structure,  
60 montmorillonite clay interacts with cations and accommodates them in the voids between layers,  
61 giving it the properties of a molecular sieve. In general, the mineral's net negative charge  
62 determines Montmorillonite's adsorption capacity. MMT can also be used as a coagulant in ponds  
63 when it is finely powdered. When added to water, it causes the water to become "clouded," draws  
64 in tiny particles, and eventually sinks to the bottom. Although MMT effectively absorbs heavy  
65 metals, its impact on human health is still unknown [16-20].

66 Spinel oxides, denoted by the formula  $AB_2O_4$  with trivalent (B) and divalent (A) cations  
67 occupy octahedral and tetrahedral positions, while oxygen ions create a cubic unit cell. These  
68 materials are known for their chemical and thermal stability, finding applications in various fields  
69 like humidity sensors, ceramic catalysis, and magnetic materials [21]. Spinel compounds (general  
70 formula  $AB_2O_4$ ) are part of a large family of inorganic materials and have become the subject of  
71 extensive research in numerous industrial processes, as well as in the realm of nanoscience and

72 technology [22]. Their unique properties, such as high electrical resistivity, high coercivity, and  
73 moderate saturation magnetization, make them promising candidates for advanced applications in  
74 drug delivery systems, power electronics, sensors, catalysts, and spintronics [23-25]. Furthermore,  
75 aluminum spinel can be used as a suitable charge carrier and photocatalyst for a range of  
76 applications due to its exceptional optical, thermal, electrical, and magnetic properties. Cadmium  
77 aluminate ( $\text{CdAl}_2\text{O}_4$ ) is a significant spinel material and it has crucial applications in microwave  
78 devices, sensors, light helmets, light-emitting diodes, luminescence, pigment, gas sensors, and  
79 photocatalysts [26-29].

80 Rafiq et al. in their review assessed that, the ability of several nanomaterials to clean up  
81 dye-contaminated aquatic systems by focussing on essential parameters that affect the  
82 photocatalytic decolorisation of dyes. Numerous semiconductor nanocatalysts have demonstrated  
83 the ability to function as photocatalysts in the treatment of wastewater that contains textile colours.  
84 Operational characteristics are significantly impacted by photocatalyst efficiency. The nature of  
85 the sample to be degraded must be investigated because the impact of different parameters has  
86 occasionally proven contentious. Higher pH causes some reactive dyes to deteriorate, while lower  
87 pH causes others to do so. For photocatalytic dye degradation in wastewater, the reaction should  
88 therefore be conducted at the proper pH. The photocatalytic decolorisation of any dye is discovered  
89 to be influenced by a variety of factors, including reaction temperature, photocatalyst  
90 concentration, light intensity and irradiation duration, and dopant impact [30].

91 The co-precipitation technique has been widely used to prepare nanoparticles. It entails the  
92 simultaneous precipitation of multiple substances from a solution. With the help of a base and a  
93 solvent, metal hydroxides precipitate from salt precursors in an eco-friendly and economical  
94 manner. Co-precipitation is an easy method with controlled size distribution, high yield, and

95 solvents that are safe for the environment for creating inorganic and metal-based nanoparticles.  
96 Given these advantages, we utilized co-precipitation techniques to prepare CdAl<sub>2</sub>O<sub>4</sub>. Herein, we  
97 successfully synthesized montmorillonite-supported CdAl<sub>2</sub>O<sub>4</sub> and assessed its photocatalytic  
98 ability through the removal of rhodamine-B by solar-light radiation. Additionally, we investigated  
99 the hydrophobic nature of montmorillonite/CdAl<sub>2</sub>O<sub>4</sub>.

100

## 101 **2 Materials and methods**

### 102 **2.1 Chemicals and Reagents**

103 Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, NaOH, EtOH and Montmorillonite clay (Na,Ca)<sub>0.3</sub>  
104 (Al,Mg)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·nH<sub>2</sub>O) were supplied by Himedia chemicals, Rhodamine-B (Rh-  
105 B;C<sub>28</sub>H<sub>31</sub>ClN<sub>2</sub>O<sub>3</sub>; M.W- 479.01-CAS 81-88-9)) dye was supplied by CDH (P) Limited. The purity  
106 of all the purchased chemicals were AR grade (99 % purity). Distilled water was used over the  
107 experiments.

### 108 **2.2 Characterization Techniques**

109 X-Ray diffraction (XRD) pattern of catalysts were obtained using a Siemens D5005  
110 diffractometer with Cu K $\alpha$  ( $\lambda = 0.151418$  nm) radiation. The diffractograms were recorded in 2 $\theta$   
111 range between 10 and 80° in steps of 0.02° with count time of 20s at each point. The morphology  
112 of catalyst was examined using Model ULTRA-55 field emission scanning electron microscope  
113 (FE-SEM). Samples were mounted on a gold platform placed in the scanning electron microscope  
114 for taking images at various magnifications. HR-TEM images were taken using the 200kV Ultra  
115 High Resolution Transmission Electron Microscope  
116 JEOL-2010, having high resolution Optical microscope and Leica microscope. A small quantity  
117 of catalyst suspension was dropped onto copper grids with holey carbon film. The grids were dried

118 under natural conditions and examined. The diffuse reflectance spectra of all the catalysts were  
119 recorded in Shimadzu UV 2450 model equipped with an integrating sphere and using powdered  
120 BaSO<sub>4</sub> as a reference. The photoluminescence (PL) spectrum at room temperature was recorded  
121 using a Perkin-Elmer LS 55 fluorescence spectrometer. The specific surface areas of the catalysts  
122 were determined using a Micromeritics ASAP 2020 sorption analyzer. The samples were degassed  
123 at 423K for 12 hours and analysis was performed at 77K with N<sub>2</sub> gas as the adsorbate. The  
124 Brunauer-Emmett-Teller (BET) multipoint method least-square fit provided the specific surface  
125 area. The hydrophobicity of catalyst coating was obtained from the water contact angle. A drop  
126 shape analyser (DSA) (Kruss GmbH Germany) was used to record the contact angle.

## 127 **2.2 Synthesis of montmorillonite supported CdAl<sub>2</sub>O<sub>4</sub>**

128 The synthesis of both pure *CdAl<sub>2</sub>O<sub>4</sub>* and *MMT* supported *CdAl<sub>2</sub>O<sub>4</sub>* samples were carried  
129 out through a co-precipitation method. Initially, 50mL of 0.5M Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O and 50mL of 0.3M  
130 Cd(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O were separately dissolved in 50mL of distilled water. After that, the  
131 Cd(CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O solution was slowly added to Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O solution with vigorous stirring.  
132 Subsequently, 0.500g (9% wt) of MMT powder, mixed with 10mL of ethanol, was introduced to  
133 the previous solutions with constant stirring. Following this, 0.2M of NaOH was dissolved in  
134 30mL of distilled water followed by slowly adding to the combined aqueous solutions. The  
135 resulting solution was stirred at 80°C for 5 hours. The resulting product was collected by washing  
136 with ethanol and distilled water, and dried at 100°C for 5 hours. Finally, the *MMT* supported  
137 *CdAl<sub>2</sub>O<sub>4</sub>* nanoparticles were calcinated for 6 hours at 700°C, denoted as 9% wt *MMT/CdAl<sub>2</sub>O<sub>4</sub>* for  
138 easy understanding. The pure *CdAl<sub>2</sub>O<sub>4</sub>* nanoparticles and 5% wt *MMT* supported *CdAl<sub>2</sub>O<sub>4</sub>* were  
139 synthesized by the similar process for comparison.

## 140 **2.3 Photocatalytic degradation**

141 Photocatalytic degradation experiments were performed in summer days from 11 am to 2 pm  
142 under a direct sunlight illumination (Tiruvannamalai, Tamilnadu, India). A transparent borosilicate  
143 glass tube with 40 cm in height and 20 mm in diameter was employed as reaction vessel. After 30  
144 minutes of magnetic stirring in the dark, the dye and *MMT/CdAl<sub>2</sub>O<sub>4</sub>* solutions reached equilibrium  
145 of adsorption and desorption. The photodegradation process was carried out outdoors. To ensure  
146 thorough mixing of the reaction solution and to introduce oxygen, a pump was used to  
147 continuously aerate a 50 mL dye solution containing *MMT/CdAl<sub>2</sub>O<sub>4</sub>*. There was no significant  
148 solvent evaporation during the lighting period. The first sample was collected during the  
149 adsorption phase while it was still dark. A two-milliliter sample was retained, and at predetermined  
150 intervals, it was centrifuged and diluted to ten milliliters. The solar light intensity, evaluated with  
151 the LT Lutron LX-10/A Digital Lux meter, was  $I_{\text{solar}} = 1250 \times 100 \text{ Lux} \pm 10$ .

## 152 **2.4 Contact angle measurements**

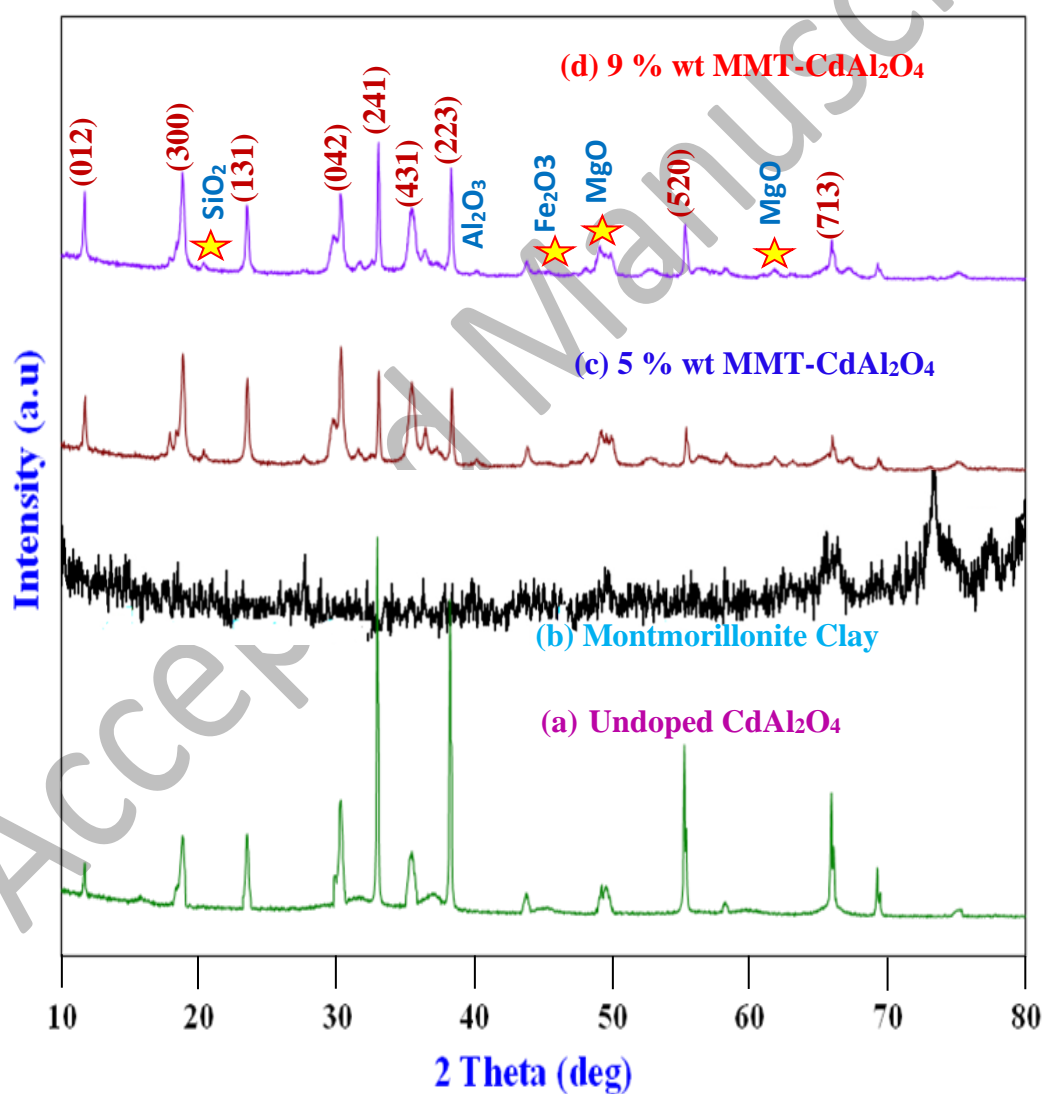
153 Water contact angles were measured on a Drop Shape Analyzer (DSA) from Kruss GmbH  
154 in Germany. The volume of the water droplet was about 4  $\mu\text{L}$  based on at least four measurements.  
155 The average of these values represented the substrate's water contact angle (WCA). Spin coating  
156 was successfully applied to glass substrates to produce *MMT/CdAl<sub>2</sub>O<sub>4</sub>*-modified silane coatings at  
157 room temperature. *MMT/CdAl<sub>2</sub>O<sub>4</sub>* photocatalyst-coated substrates were heated at 125 °C for 2  
158 hours in a controlled furnace to confirm the densification of the gel network.

## 159 **3 Results and Discussion**

### 160 **3.1 Characterization of nanocomposite**

161 X-ray diffraction (XRD) measurement was conducted to assess the crystallinity of the  
162 synthesized photocatalysts. Figure 1a-c present the XRD patterns for undoped *CdAl<sub>2</sub>O<sub>4</sub>*, 5% wt  
163 *MMT/CdAl<sub>2</sub>O<sub>4</sub>*, and 9% wt *MMT/CdAl<sub>2</sub>O<sub>4</sub>* photocatalysts. In Figure 1a, the undoped *CdAl<sub>2</sub>O<sub>4</sub>*

164 photocatalyst displays the diffraction peaks at  $13.75^\circ$ ,  $19.25^\circ$ ,  $26.37^\circ$ ,  $31.02^\circ$ ,  $33.56^\circ$ ,  $37.50^\circ$ ,  
165  $38.85^\circ$ ,  $55.18^\circ$ , and  $67.60^\circ$ , which were corresponding to the (012), (300), (131), (042), (241),  
166 (431), (223), (520), and (713) planes of monoclinic primitive  $CdAl_2O_4$  (JCPDS No. 34-0071). [31,  
167 32]. Fig. 1b represents the diffraction peaks of montmorillonite clay alone. Meanwhile, in Figure  
168 1c and 1d, newly formed peaks indicated by star symbols corresponded well with raw MMT for  
169  $SiO_2$ ,  $Fe_2O_3$ ,  $MgO$  and  $Al_2O_3$ , confirming the presence of MMT clay in the  $MMT/CdAl_2O_4$   
170 photocatalysts [33].



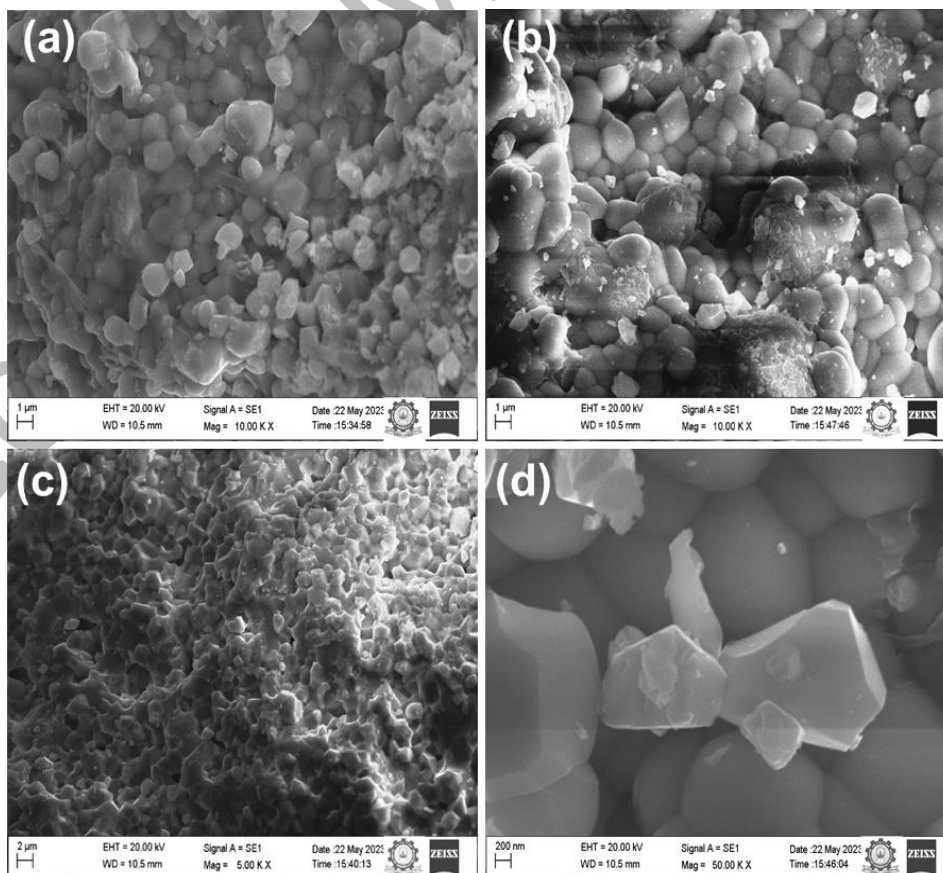


187 **Fig. 1** XRD patterns of the (a) undoped CdAl<sub>2</sub>O<sub>4</sub> (b) Montmorillonite clay (c) 5% wt  
188 *MMT/CdAl<sub>2</sub>O<sub>4</sub>* and (d) 9% wt *MMT/CdAl<sub>2</sub>O<sub>4</sub>* photocatalysts

189 A typical diffraction peak of montmorillonite clay is observed around 7.25° corresponding  
190 to basal spacing of 13.46Å (Fig. SI 1). And after intercalation of CdAl<sub>2</sub>O<sub>4</sub> this peak disappears.  
191 Importantly, no crystalline impurities or typical diffraction peaks were observed, indicating the  
192 good purity of the synthesized photocatalysts. Furthermore, the Scherrer equation was utilized to  
193 calculate the crystallite sizes of CdAl<sub>2</sub>O<sub>4</sub>.

$$194 \quad \Phi = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

195 In this equation,  $\Phi$ ,  $\lambda$ ,  $K$ ,  $\beta$  and  $\theta$  represents the crystalline size, the wavelength of the X-  
196 ray used, the shape factor, the full line width at the half-maximum height of the peak, and the  
197 Bragg angle, respectively. Using this equation, the average crystallite size of hexagonal CdAl<sub>2</sub>O<sub>4</sub>  
198 was determined to be 36.8 nm.



211

212 **Fig. 2** FE-SEM images of the 9% wt  $MMT/CdAl_2O_4$  photocatalyst at various  
213 magnifications: (a, b) 1  $\mu m$  (c) 2  $\mu m$  and (d) 200 nm

214 The surface structure and particle sizes of the synthesized samples were investigated using  
215 scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-  
216 TEM) techniques. SEM images of the 9% wt  $MMT/CdAl_2O_4$  photocatalyst are presented in Figure  
217 2a-d, revealing a flake-like morphology with intermittent nanosponge like particle. The presence  
218 of MMT particles is likely responsible for the observed surface morphologies. The elements  
219 present in the montmorillonite clay were confirmed by EDAX image (Fig. SI 3). The  
220 microstructures exhibit a nanosponge-like structure with high porosity. Micro-size hierarchical  
221 shape composed of nanosized building blocks offer several advantages, including numerous  
222 mesopores that enhance the transfer of organic materials.

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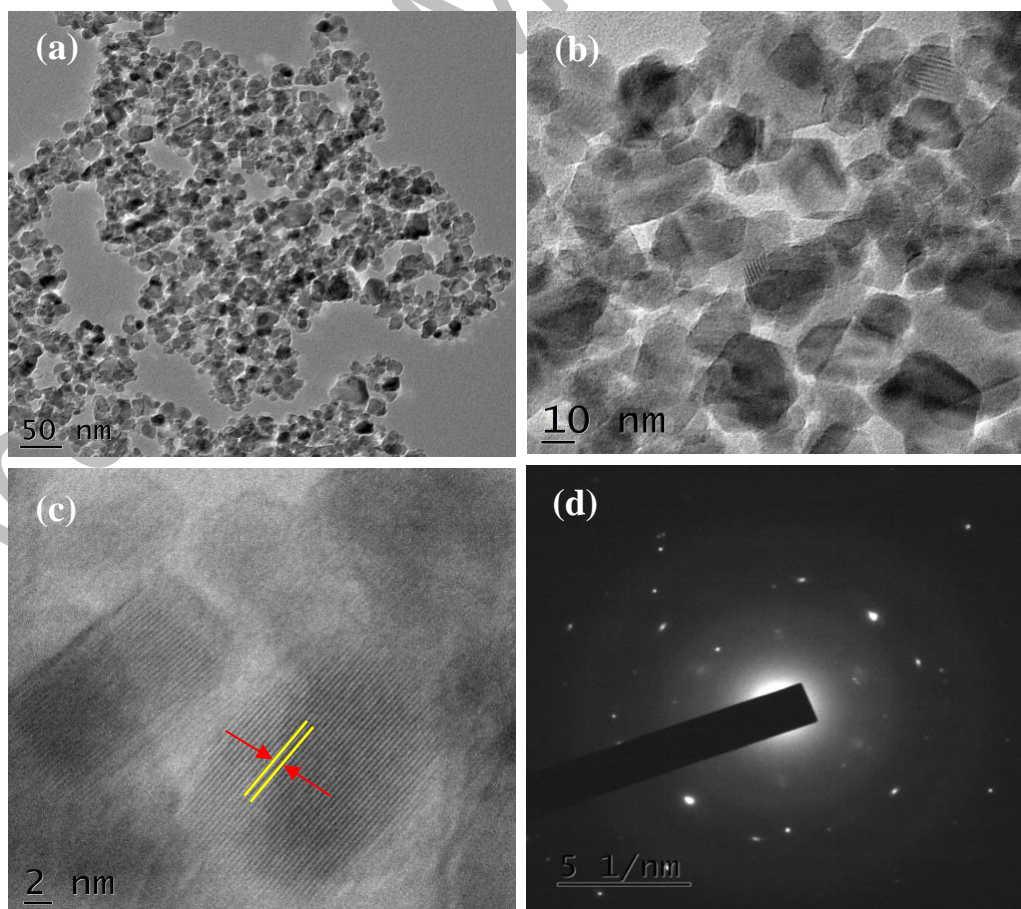
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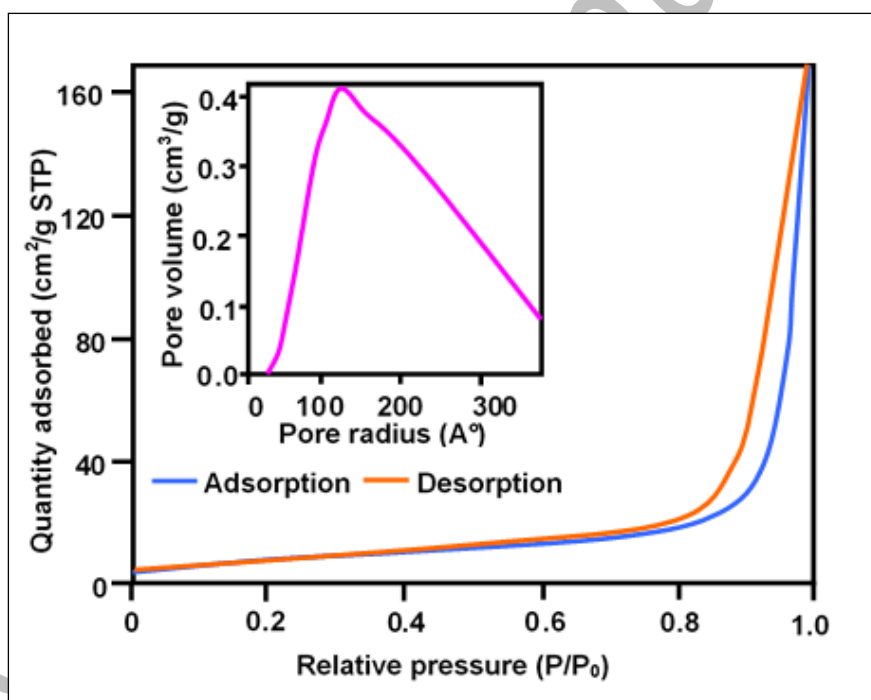


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240 **Fig. 3** HR- TEM images of the 9% wt  $MMT/CdAl_2O_4$  photocatalyst at (a) 50 nm, (b) 10 nm and  
241 (c) Lattice fringes at 2 nm and (d) SAED pattern on 5 1/nm

242 Moreover, Figure 3a-d displays HR-TEM images of 9% wt  $MMT/CdAl_2O_4$  photocatalyst,  
243 showing spherical and hexagonal particle shapes with uniform element distribution. The dark areas  
244 in the images indicate the presence of MMT clay on the surface of  $CdAl_2O_4$ . From the lattice  
245 fringes (Figure 3c), the d spacing value calculated as 0.214 nm. The selected area electron  
246 diffraction (SAED) image in (Figure 3d) confirms the occurrence of (131) plane of  $CdAl_2O_4$   
247 structure.



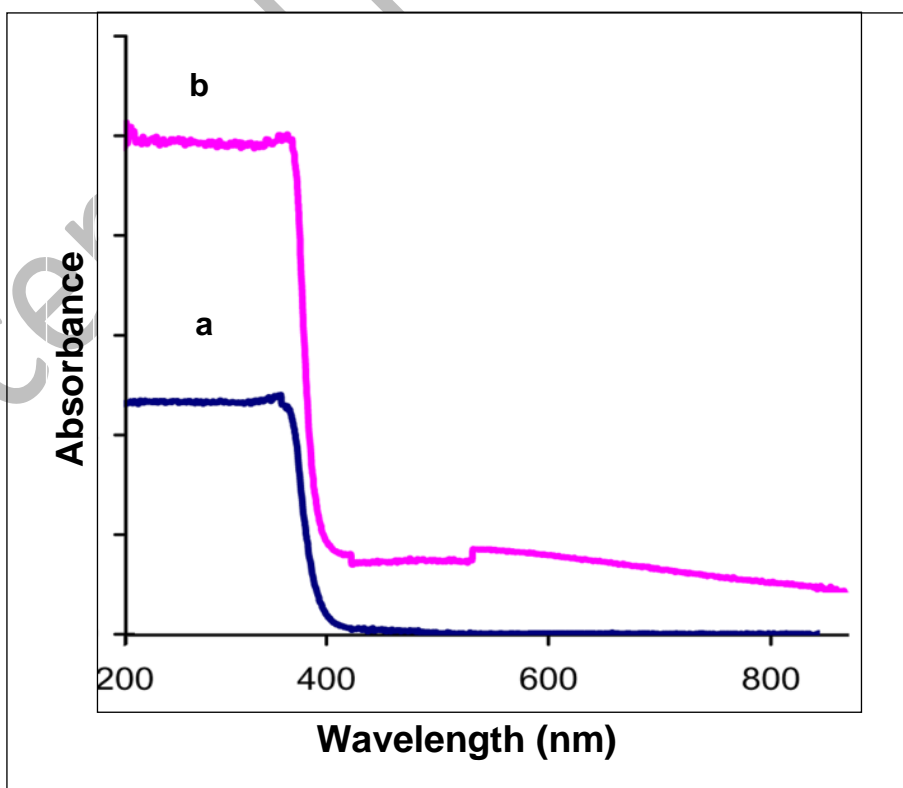
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249 **Fig. 4** BET adsorption–desorption isotherms and pore size distribution plots of the 9% wt  
250  $MMT/CdAl_2O_4$  photocatalyst

251 The pore structure and surface area of 9% wt  $MMT/CdAl_2O_4$  photocatalyst were examined  
252 using nitrogen adsorption–desorption isotherms. The Barrett–Joyner–Halenda (BJH) technique  
253 was employed to analyze the pore size distribution. Notably, as shown in Figure 4, a significant

254 enhancement in the adsorption volume of  $N_2$  in the  $P/P_0$  range of 0.65 to 0.90, indicating good  
255 homogeneity and macroporous size in the catalyst. In addition, the average pore radius, as  
256 indicated by the pore size distribution plot presented in the insert of Figure 4, is  $125.7\text{\AA}$  for the 9%  
257 wt  $MMT/CdAl_2O_4$  and bare  $CdAl_2O_4$  has pore radius of  $90.23\text{\AA}$ . The resultant 9% wt  
258  $MMT/CdAl_2O_4$  photocatalyst exhibits a large specific surface area of  $42.15\text{m}^2\text{g}^{-1}$ , compared to  
259 undoped  $CdAl_2O_4$  ( $20.4\text{m}^2\text{g}^{-1}$ ) contributing to its improved photocatalytic activity.

260 To gain further insight into the photocatalytic mechanism, various factors, including optical  
261 absorption, emission properties, and specific area, were considered. An efficient material requires  
262 an appropriate band-gap to absorb light efficiently, generating charge carriers that catalyze the  
263 breakdown of dye molecules. In addition, the diffuse reflectance spectra of undoped  $CdAl_2O_4$  and  
264 9% wt  $MMT/CdAl_2O_4$  photocatalysts are shown in Figure 5a and 5b, respectively.

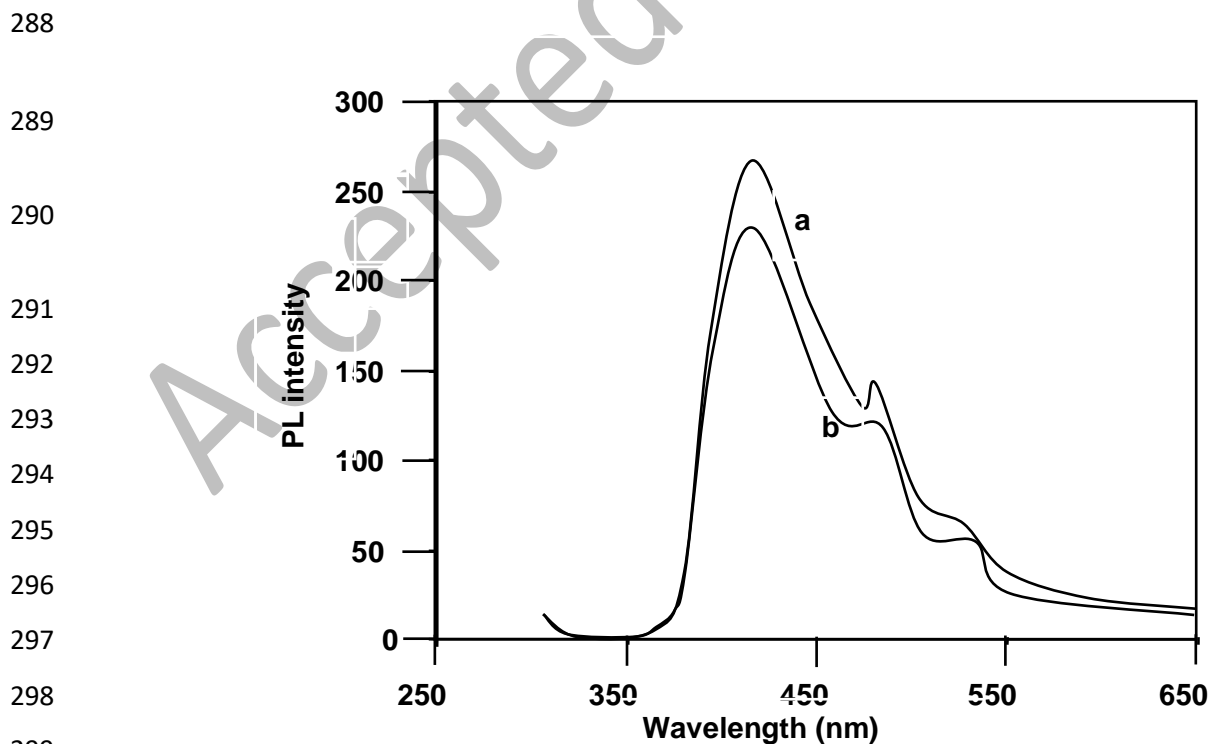


276 **Fig. 5:** Diffuse reflectance spectra of the (a) undoped CdAl<sub>2</sub>O<sub>4</sub> and (b) 9 % wt  
277 *MMT/CdAl<sub>2</sub>O<sub>4</sub>* photocatalysts

278 In the UV region, 9% wt *MMT/CdAl<sub>2</sub>O<sub>4</sub>* photocatalyst exhibits double the intensity of UV  
279 absorption compared to undoped CdAl<sub>2</sub>O<sub>4</sub>. The addition of 9% wt MMT results in a significant  
280 rise in the resultant peak intensities and a little decrease in E<sub>g</sub> values. The energy gap of  
281 *MMT/CdAl<sub>2</sub>O<sub>4</sub>* nanoparticles is computed using the Tauc plot, which is afforded in the following  
282 equation

$$283 \quad \alpha = A(h\nu - E_g)^{1/2} / h\nu$$

284 Where E<sub>g</sub>,  $\alpha$ , A and h $\nu$  signify energy gap, photon energy, absorption coefficient, and the  
285 proportionality constant, The E<sub>g</sub> of all synthesized materials were computed by linear fitting (ah $\nu$ )<sup>2</sup>  
286 versus photon (h $\nu$ ) energy as 3.35 [30, 32] and 2.81eV for undoped CdAl<sub>2</sub>O<sub>4</sub> and *MMT/CdAl<sub>2</sub>O<sub>4</sub>*  
287 nanoparticles respectively as displayed in Fig. SI.2



300 **Fig. 6** Photoluminescence spectra of the (a) undoped  $\text{CdAl}_2\text{O}_4$  and (b) 9% wt  $\text{MMT}/\text{CdAl}_2\text{O}_4$   
301 photocatalysts

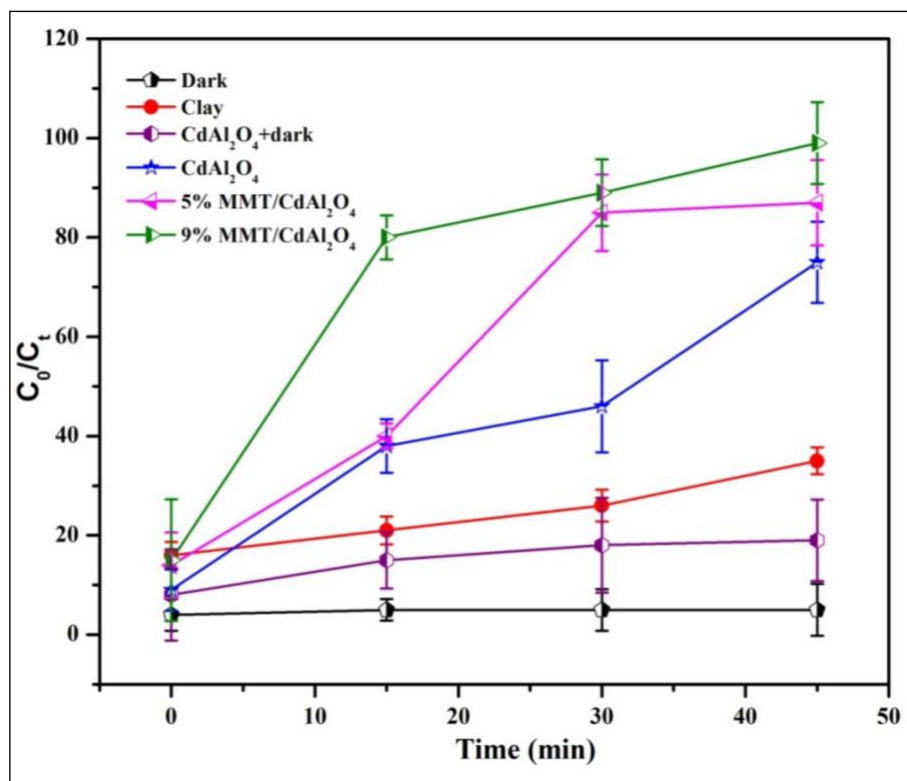
302 In addition, Figure 6a and 6b display the photoluminescence spectra of undoped  $\text{CdAl}_2\text{O}_4$   
303 and 9% wt  $\text{MMT}/\text{CdAl}_2\text{O}_4$  photocatalysts, respectively. The photoluminescence intensity of 9 %  
304 wt  $\text{MMT}/\text{CdAl}_2\text{O}_4$  photocatalyst is lower than that of undoped  $\text{CdAl}_2\text{O}_4$ , indicating reduced  
305 electron-hole pair recombination due to the presence of loaded MMT on  $\text{CdAl}_2\text{O}_4$ . This reduction  
306 in fluorescence intensity contributes to enhanced photocatalytic activity and reduced electron-hole  
307 pair recombination.

### 308 **3.2. Photocatalytic Study**

309 Figure 7 illustrates the photocatalytic activity of the synthesized undoped  $\text{CdAl}_2\text{O}_4$ ,  
310 5% wt  $\text{MMT}/\text{CdAl}_2\text{O}_4$  and 9% wt  $\text{MMT}/\text{CdAl}_2\text{O}_4$  towards the removal of rh-B dye by direct solar-  
311 light radiation. The dye is resistant to self photolysis and for the same experiment with  
312  $\text{MMT}/\text{CdAl}_2\text{O}_4$  in the dark, a decrease (10%) in dye concentration was observed due to the  
313 adsorption of dye on the catalyst. The degradation outcomes display there is no significant changes  
314 in dye concentration under the absence of light and catalyst. With 9% wt  $\text{MMT}/\text{CdAl}_2\text{O}_4$   
315 photocatalyst, rh-B dye almost completely degrades within 45 minutes. However, under the same  
316 conditions, undoped  $\text{CdAl}_2\text{O}_4$  and 5%  $\text{MMT}/\text{CdAl}_2\text{O}_4$  achieved 68% and 78.5% degradation of rh-  
317 B dye, respectively. The montmorillonite clay shows nearly 35% of adsorption. These results  
318 indicate that the prepared 5%  $\text{MMT}/\text{CdAl}_2\text{O}_4$  photocatalyst is more effective than other catalysts in  
319 degrading rh-B when exposed to direct solar-light. This underscores higher photocatalytic activity  
320 of  $\text{MMT}/\text{CdAl}_2\text{O}_4$  photocatalyst, attributed to the loaded MMT clay. Under UV light irradiation  
321  $\text{MMT}/\text{CdAl}_2\text{O}_4$  produce maximum dye degradation percentage compare other pure MMT clay and  
322 undoped  $\text{CdAl}_2\text{O}_4$  (Fig. SI.4).

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338 **Fig. 7** Photodegradation of rh-B dye with different catalysts: dye concentration =  $3 \times 10^{-4}$  M,  
339 catalyst suspended =  $3 \text{ g L}^{-1}$ , pH = 7, airflow rate =  $8.1 \text{ mL s}^{-1}$ ,  $I_{\text{solar}} = 1250 \times 100 \text{ Lux} \pm 10$ .  
340 Irradiation time = 45 min)

341 Under visible irradiation, the  $e^-$  on MMT doped  $\text{CdAl}_2\text{O}_4$  sample are photoexcited into their  
342 particular (CB), leaving  $h^+$  on the valence band (VB), thereby making photoexcited charge carriers.  
343 The photoexcited  $e^-$  on the CB of MMT doped  $\text{CdAl}_2\text{O}_4$  rapidly transformed into that of trapping  
344 level of MMT/ $\text{CdAl}_2\text{O}_4$ , while the photoexcited  $h^+$  on the VB of MMT/ $\text{CdAl}_2\text{O}_4$  reacts with the  
345 water molecules to produce the  $\text{OH}^\bullet$  radicals and generated  $e^-$  near to CB of the trap state can  
346 interact with the dissolved  $\text{O}_2$  to produce  $\text{O}_2^{\bullet-}$  (superoxide radicals). Finally, these two radicals  
347  $\text{O}_2^{\bullet-}$  and  $\text{OH}^\bullet$  react with the dye molecule and convert the dye into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Further, the  
348 increased degradation efficiency can be attributed to two primary factors such as (i) MMT's ability



349 to absorb UV light, doubling the absorption compared to undoped  $\text{CdAl}_2\text{O}_4$  and (ii) the larger  
350 surface area of  $\text{MMT}/\text{CdAl}_2\text{O}_4$  photocatalyst compared to undoped  $\text{CdAl}_2\text{O}_4$  photocatalyst. In fact,  
351 MMT is an electron acceptor due to the presence of Lewis acids. The electrons from these  
352 aluminum sites are then transferred to the  $\text{O}_2$  molecules in the  $\text{CdAl}_2\text{O}_4$  solution, which result in  
353 delay in the recombination reaction. Additionally, the presence of metal oxides in loaded MMT  
354 contributes to this electron transfer and may lead to the formation of sporadic energy levels,  
355 reducing the band gap energy and preventing electron-hole recombination [34]. A proposed  
356 mechanism in Figure 8 views MMT as an impurity in the attached with  $\text{CdAl}_2\text{O}_4$  photocatalyst.

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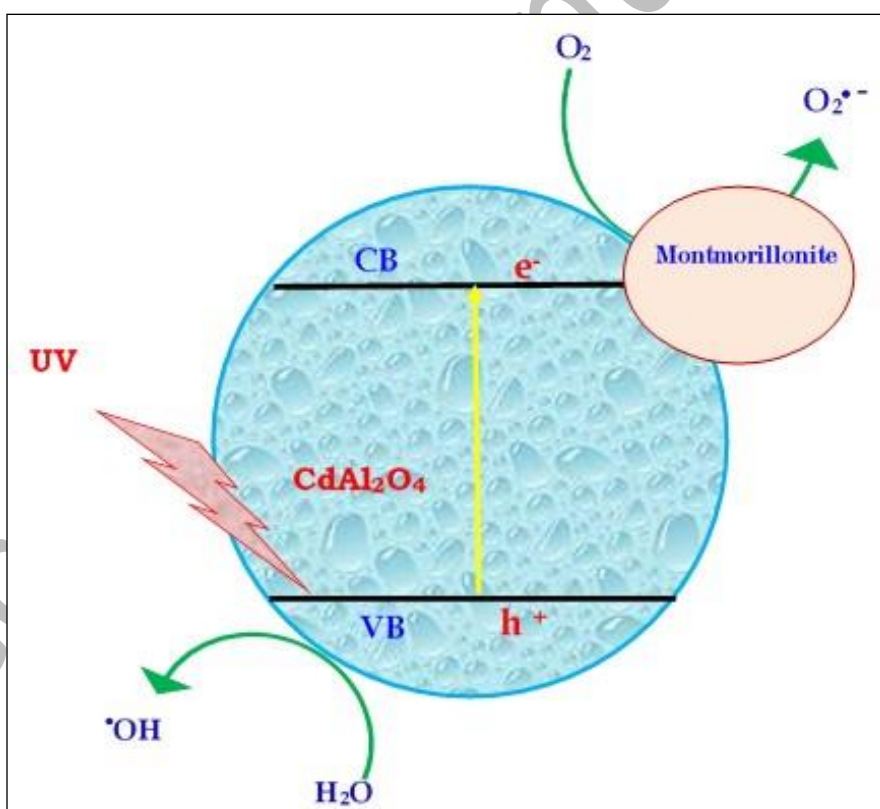
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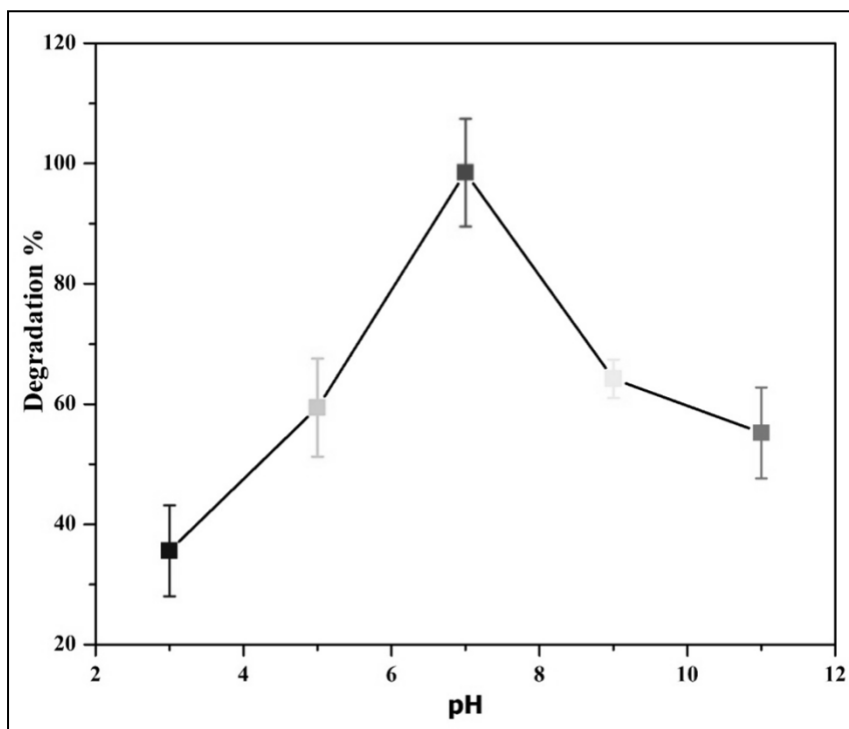
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**Fig. 8** A possible photodegradation mechanism of the  $\text{MMT}/\text{CdAl}_2\text{O}_4$  photocatalyst





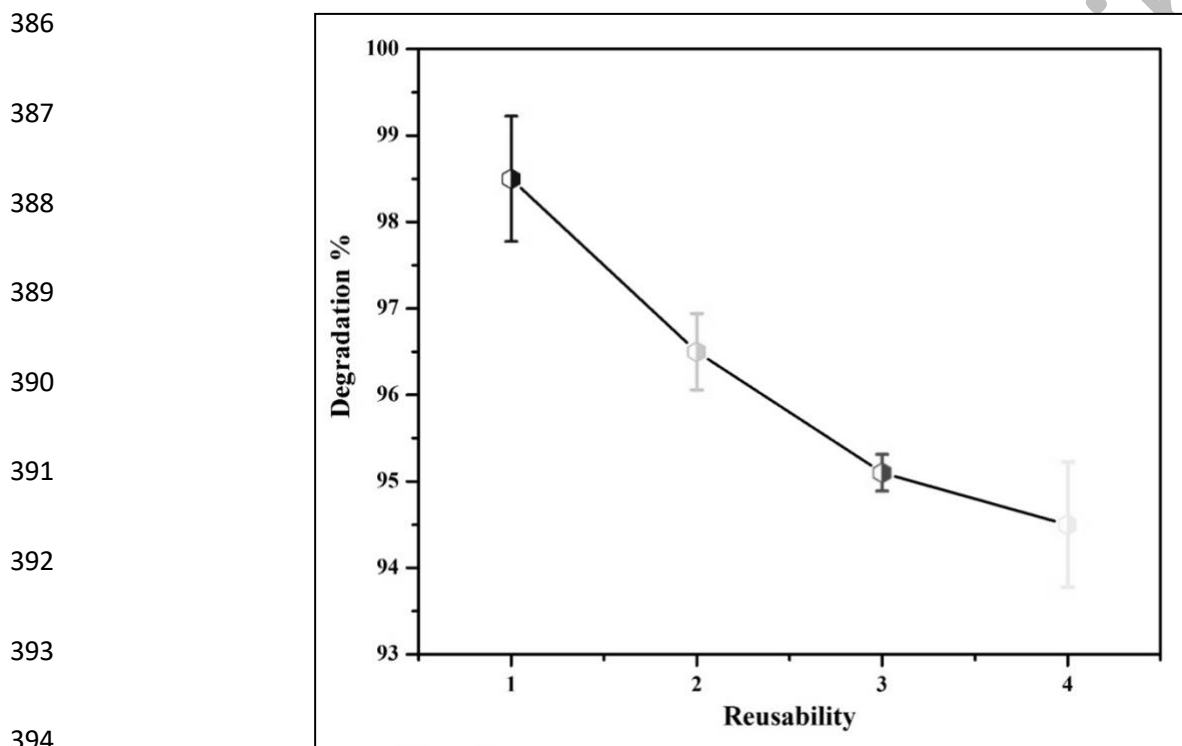
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370 **Fig. 9** Effect of solution pH on rh-B degradation using 9% wt  $MMT/CdAl_2O_4$  photocatalyst (dye  
 371 concentration =  $3 \times 10^{-4} M$ , catalyst suspended =  $3 g L^{-1}$ , airflow rate =  $8.1 mL s^{-1}$ ,  $I_{solar} = 1250$   
 372  $\times 100 \text{ Lux} \pm 10$ , irradiation time = 45 min)

373 The pH of the solution significantly affects photocatalytic degradation. Figure 9 illustrates  
 374 the impact of pH on the photocatalytic removal of rh-B within the pH range of 3–11. The results  
 375 indicate that increasing the pH from 3 to 7 enhances rh-B removal ability, with a neutral pH of 7  
 376 being the optimal condition for effective rh-B removal using the 9% wt  $MMT/CdAl_2O_4$   
 377 photocatalyst.

378 To evaluate the reusability of the 9% wt  $MMT/CdAl_2O_4$  photocatalyst for photoreactions,  
 379 the catalyst was removed and cleaned with methanol following the complete dye degradation. The  
 380 recovered catalyst, after drying for 90 minutes at  $100^\circ C$ , was utilized in the subsequent cycle. Five

381 consecutive cycles of rh-B degradation under solar light demonstrated the photocatalyst's good  
382 stability and reusability (Figure 10). Until the fourth cycle, there is a slight decrease in degradation;  
383 after that, no further change is observed. In the fourth run, at 45 minutes of radiation, a degradation  
384 efficiency of 95.5% was achieved. These findings demonstrate that 9% wt  $MMT/CdAl_2O_4$   
385 photocatalyst exhibits excellent stability and reusability.

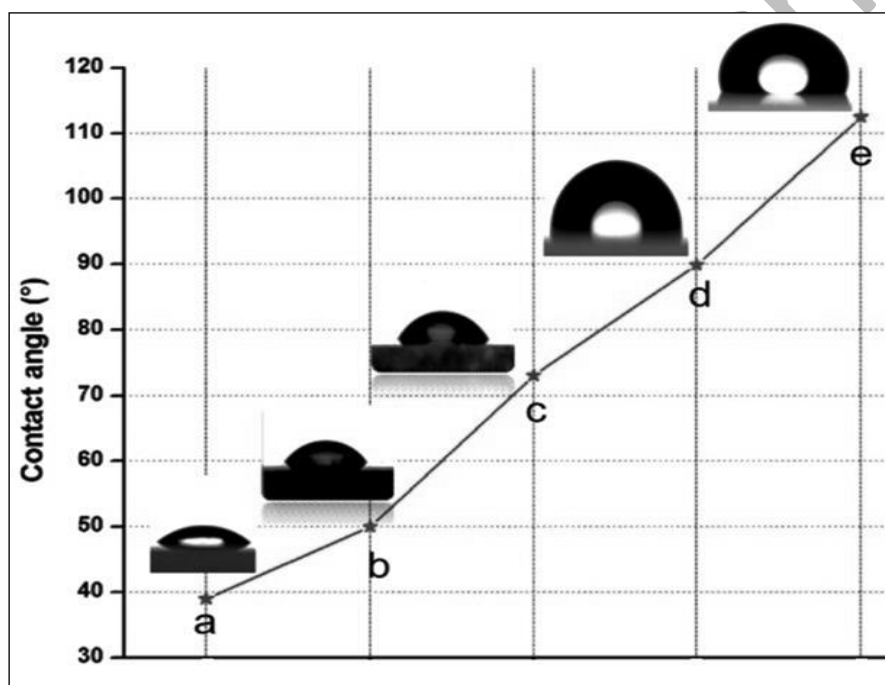


395 **Fig. 10** Reusability of 9 % wt  $MMT/CdAl_2O_4$  photocatalyst on rh-B degradation (dye  
396 concentration =  $3 \times 10^{-4}$  M, pH = 7, catalyst suspended =  $3 \text{ g L}^{-1}$ , airflow rate =  $8.1 \text{ mL s}^{-1}$ ,  $I_{\text{solar}} = 1250$   
397  $\times 100 \text{ Lux} \pm 10$ , irradiation time = 45 min)

### 398 3.3 Hydrophobicity property

399 Water-repellent materials find a wide range of applications, and this property was studied  
400 using water contact angle assessments (Figure 11). The contact angle of an uncoated glass slide is  
401  $37.2^\circ$  (Figure 11a), which increases progressively with increasing TEOS values ( $58.4^\circ$ , Figure  
402 11b), TEOS +  $CdAl_2O_4$  ( $80.5^\circ$ , Figure 11c), TEOS + 5% wt  $MMT/CdAl_2O_4$  ( $100.2^\circ$ , Figure 11d),

403 and TEOS + 9% wt  $MMT/CdAl_2O_4$  ( $113.8^\circ$ , Figure 11e). The extreme hydrophobicity properties  
404 of TEOS (Tetraethyl orthosilicate)-containing  $MMT/CdAl_2O_4$  is evident, with the O-Si-O groups  
405 being altered and the surface becoming rougher due to the presence of 9% wt MMT with  $CdAl_2O_4$ .  
406 In general, the catalyst's hydrophobic nature results in water contact angle of  $90^\circ$  [35]. This  
407 hydrophobic nature results in a water contact angle of  $113.8^\circ$ , further demonstrating its extreme  
408 hydrophobicity property.



419  
420 **Fig. 11** Water contact angle assessments (a) uncoated glass slide, (b) TEOS coated glass slide,  
421 (c) TEOS+CdAl<sub>2</sub>O<sub>4</sub> and (d) TEOS+5% wt  $MMT/CdAl_2O_4$  and (e) TEOS/9% wt  $MMT/CdAl_2O_4$

#### 423 4 Conclusions

424 In summary, a facile hydrothermal co-precipitation technique was employed to produce  
425 montmorillonite-supported  $CdAl_2O_4$  ( $MMT/CdAl_2O_4$ ) without using any surfactants or organic  
426 solvents. The FE-SEM results showed that the as synthesized photocatalyst consists of microflakes

427 and nanoclusters structures. The HR-TEM results confirmed the homogeneous spreading of  
428 elements, indicating the strongly attached within oxides, where particles take on hexagonal and  
429 spherical structures. Photodegradation results reveal that 9% MMT-supported  $CdAl_2O_4$  is much  
430 effective at degrading rh-B dye than both raw and undoped  $CdAl_2O_4$ , particularly at neutral pH 7.  
431 Reduced fluorescence intensity in  $MMT/CdAl_2O_4$  leads to decreased electron-hole pair  
432 recombination and improved photocatalytic activity. Moreover, the montmorillonite/ $CdAl_2O_4$   
433 showed a water contact angle of  $113.8^\circ$ , showing its extreme hydrophobicity nature. This study  
434 introduces a novel application for montmorillonite, naturally occurring clay, in semiconductor  
435 oxide materials for energy and environmental applications.

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#### 440 **Supplementary Information**

441 To learn more about the characterization data of montmorillonite supported  $CdAl_2O_4$   
442 nanocomposites, refer to the supplemental information file, which contains XRD pattern of 9% wt  
443 Montmorillonite clay supported  $CdAl_2O_4$ , Tauc energy plot, EDAX image of Montmorillonite  
444 clay and Photodegradability of Rh-B dye with different catalysts.

#### 445 **DECLARATIONS**

#### 446 **Ethical Approval**

447 Not applicable

#### 448 **Competing interests**

449 There was no indication of potential conflicts of interest by the authors.

#### 450 **Authors' contributions**

451 The data was collected by K. Kalpana

452 The data analysis was done by Dr. K. Rajathi.

### 453 **Funding**

454 Not applicable

### 455 **Availability of data and materials**

456 The writers are unwilling to share the data they used.

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