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# Nanosized tubular clay minerals as inorganic nanoreactors for energy and environmental applications: A review to fill current knowledge gaps

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## Abstract

Modern society pays further and further attention to environmental protection and the promotion of sustainable energy solutions. Heterogeneous photocatalysis is widely recognized as one of the most economically viable and ecologically sound technologies to combat environmental pollution and the global energy crisis. One challenge is finding a suitable photocatalytic material for an efficient process. Inorganic nanotubes have garnered attention as potential candidates due to their optoelectronic properties, which differ from their bulk equivalents. Among them, clay nanotubes (halloysite, imogolite, and chrysotile) are attracting renewed interest for photocatalysis applications thanks to their low production costs, their unique physical and chemical properties, and the possibility to functionalize or dope their structure to enhance charge-carriers separation into their structure. In this review, we provide new insights into the potential of these inorganic nanotubes in photocatalysis. We first discuss the structural and morphological features of clay nanotubes. Applications of photocatalysts based on clay nanotubes across a range of photocatalytic reactions, including the decomposition of organic pollutants, elimination of NO<sub>x</sub>, production of hydrogen, and disinfection of bacteria, are discussed. Finally, we highlight the obstacles and outline potential avenues for advancing the current photocatalytic system based on clay nanotubes. Our aim is that this review can offer researchers new opportunities to advance further research in the field of clay nanotubes-based photocatalysis with other vital applications in the future.

**Keywords:** Photocatalyst; clay nanotubes; imogolite; halloysite; chrysotile.

32

### 33 **Introduction**

34           The hasty growth of the global economy and industrialization over the past  
35 century has also led to severe problems worldwide. The world's reserve of natural  
36 energy is expected to be depleted within the next 50 years [1]. Experts consider  
37 global warming and climate change to be a direct consequence of the exponential  
38 increase in the consumption of fossil fuels. The increase in industrial pollutants is  
39 another consequence of the extensive use of these resources [2–4]. Requirement for  
40 developing environmentally friendly and energy-conserving solutions to address  
41 environmental remediation.

42           Solar energy represents a highly promising resource due to its unique  
43 advantages. It offers an abundant and inexhaustible source of power, surpassing  
44 global energy consumption by several times [5–7]. Furthermore, solar energy is  
45 environmentally friendly, emitting minimal greenhouse gases, thereby helping to  
46 mitigate climate change. According to United Nations Development Programme  
47 data, the annual solar energy potential ranges from 1575 to 49387 exajoules (EJ) [8],  
48 which greatly exceeds our global annual energy consumption of 559.8 EJ. This  
49 remarkable surplus makes solar energy a viable and sustainable solution for driving  
50 human development. Numerous fields use solar energy, such as photovoltaics,  
51 thermal energy, artificial photosynthesis, solar architecture, and photocatalysis [9–  
52 13]. Among them, photocatalysis emerges as a cutting-edge method for harnessing  
53 sunlight and expediting molecular conversions to generate solar-derived fuels,  
54 primarily hydrogen (H<sub>2</sub>), paving the way to a clean and renewable energy source  
55 [14,15].

56 In photocatalysis applications, the extensively used photocatalysts such as  
57 TiO<sub>2</sub> and ZnO face two primary challenges [16–19]. They have a limited spectral  
58 response interval, only capturing a minor portion of the solar spectrum (less than  
59 5%), confined to the UV region [4,20]. Additionally, their high charge carrier  
60 recombination leads to poor quantum yield [21–25]. As a result, researchers are  
61 exploring alternative materials to overcome these limitations. Recent focus has been  
62 on 1D nanostructures, whose unique properties hold promise for enhancing  
63 photocatalytic activity and expanding its applications.

64 Since the emergence of carbon (C) nanotubes (NTs) at the beginning of the  
65 '90s [26], a considerable part of the literature has focused on applying one-  
66 dimensional (1D) tubular nanomaterials in numerous fields, including photocatalysis  
67 [27–29]. Carbon nanotubes and their inorganic (oxides, sulfides...) analogs have  
68 distinctive electronic characteristics such as exceptional electron mobility, the  
69 quantum confinement effect, and an extraordinarily large specific surface area [30–  
70 32]. The reverse movement of holes and electrons can be promoted by the existence  
71 of polarization within the photocatalytic material [33–35]. Numerous studies have  
72 reported that the tubular structure led to improved properties. Among them, titania  
73 nanotubes exhibited enhanced photocatalytic activity compared to other titania  
74 structures [36,37]. Thus, targeting photocatalysts with tubular structures should  
75 result in enhanced photocatalytic performance.

76 Although carbon is probably the most studied nanotube material [38–40],  
77 various nanotube materials, such as natural clays, have garnered significant interest  
78 because of their intriguing characteristics and attributes [41–44]. When referring to  
79 clay minerals (or phyllosilicate), we mostly talk about low-dimensional 2D  
80 nanostructures. However, clay minerals can adopt also 1D tubular structures. The

81 importance of tubular clay materials as a substituent for expensive CNTs and other  
82 nanomaterials is universally recognized [45,46]. Hydrosilicates are considered the  
83 most promising nanotube clays minerals due to their ability to scroll spontaneously:  
84 chrysotile ( $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ) [47], halloysite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) [48–50] and imogolite  
85 ( $\text{Al}_2\text{SiO}_3(\text{OH})_4$ ) [51–54]. The crystal structures of imogolite and halloysite combine an  
86 aluminum-oxygen dioctahedral sheet covalently bonded to a silicon-oxygen  
87 tetrahedra layer for halloysite or to isolated silicon-oxygen tetrahedral in the case of  
88 imogolite. For chrysotile, the sheet is classified as trioctahedral as it is mainly  
89 composed of magnesium [55]. The differences in the size of sheets and structure led  
90 to a bending momentum, transforming the layers into single-walled or multi-walled  
91 tubular [56–58]. Additionally, it's worth noting that the unique bending energy of  
92 these nanotubes is a key factor in their remarkable stability and mechanical  
93 properties, with a Young modulus around approximately 150 GPa for chrysotile [59],  
94 140 GPa for halloysite [60], and between 200-600 GPa for imogolite [61]. Recent  
95 research on imogolite nanotubes and hydroxyl vacancies in aluminosilicate and  
96 aluminogermanate nanotubes has further highlighted the significance of bending  
97 energy in influencing their overall mechanical behavior [57,58]. Understanding the  
98 bending energy of these nanotubes opens up exciting possibilities for tailored  
99 applications in various scientific and engineering fields.

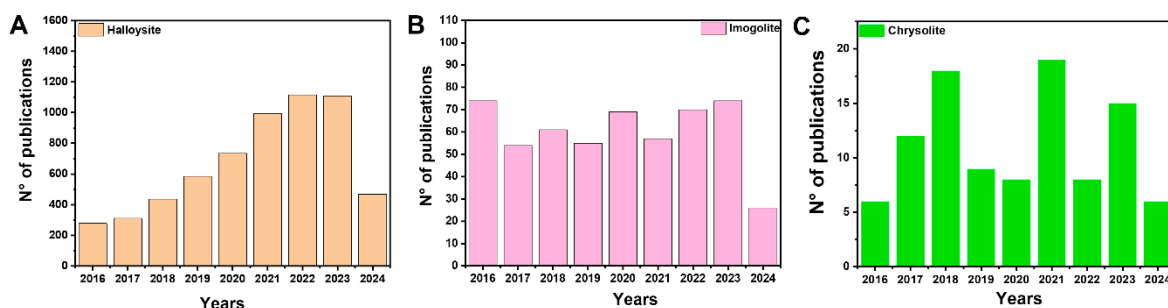
100         Due to their unique properties (e.g., improved light scattering and harvesting,  
101 shorter distances for charge transfer, and direct charge separation), materials with a  
102 tubular structure have recently found potential in the photocatalysis field [62].  
103 Consequently, tubular clay minerals such as imogolite, chrysotile, and halloysite hold  
104 the potential to be used, in principle, for such applications. The energy gaps of these  
105 nanotubes vary between 4.2 eV to 5.2 eV [63,64], which refers to the minimum

106 energy to excite and separate an electron ( $e^-$ ) and a hole ( $h^+$ ) toward the conduction  
107 and valence bands, respectively. Additionally, the 1D structure facilitated the  
108 effective diffusion of photogenerated electrons and holes [65]. For imogolite  
109 nanotubes, recent theoretical investigations have revealed that the curvature of the  
110 nanotube wall generates an electronic density distribution and increases the internal  
111 electric field, which causes a static force and facilitates the separation of electron-  
112 hole pairs [65,66]. Thus, the synergy between polarization and the one-dimensional  
113 structure of these photocatalysts is beneficial, as it can enhance the spatial  
114 separation of the charge carriers.

115         These clay materials (imogolite, chrysotile, and halloysite) can also be applied  
116 as support materials or in conjunction with other photocatalysts to improve the  
117 performance of the hybrid structures in degrading numerous pollutants [47,67,68].  
118 The improved photocatalytic efficiency results from the synergistic interaction of the  
119 unique characteristics of these clay materials, such as their exceptional light  
120 absorption, large specific surface area, and visible light absorption ability. It was  
121 noted that the halloysite was used in broader applications than the chrysolite and  
122 imogolite. This is due to the advantageous attributes of halloysite, such as its  
123 affordability and low toxicity, which surpass those of chrysolite [69]. While imogolite  
124 is not produced in large quantities yet their efficiency is greater than halloysite. The  
125 increasing fascination with halloysite is evident in the rising count of scientific  
126 publications and patents over the past decade (**Fig.1**).

127         As far as we know, this review is the first attempt to thoroughly examine  
128 recent advances in synthesizing and applying nanosized tubular clay, specifically  
129 halloysites, chrysolite and imogolites, as true photocatalysts, or in combination with  
130 other semiconductors for heterogeneous photocatalysis, with a particular focus on

131 their properties for energy and environmental applications. After a brief preamble on  
 132 the principles of photocatalysis, we focus on analyzing the synthesis, structural,  
 133 physiochemical properties, and photocatalytic activity of clay nanotubes (imogolite  
 134 nanotubes (INTs), halloysite nanotubes (HNTs) and chrysolite (CINTs)). We  
 135 introduce the significance of using nanotube architectures in photocatalysis and  
 136 discuss the polarization effect's role. This review subsequently addresses the  
 137 processes that improve photocatalyst performance when combined with tubular clay.  
 138 Lastly, research opportunities for tubular clay photocatalyst material are proposed.



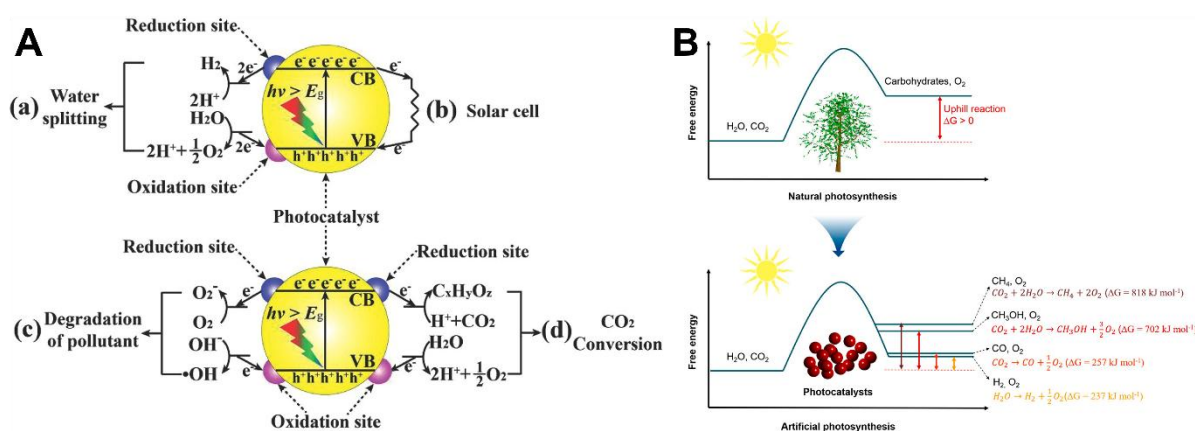
139  
 140 **Fig.1.** Yearly scientific publications and patents on **A)** halloysite, **B)** imogolite and **C)**  
 141 chrysolite nanotubes. The data displays the last decade (Data from the “Web of  
 142 Science”).

## 143 2. Semiconductor photocatalysis: General principles and mechanism

144 Photocatalytic reactions are regarded as one of the most effective methods for  
 145 harnessing solar power. In addition to the established techniques of generating solar fuels  
 146 by splitting water and reducing carbon dioxide, photocatalysis has found applications  
 147 across a wide range of fields [27,67,70–73], varying from pollutant degradation to fine  
 148 chemical production (**Fig.2A**) [74].

149 Generally, the photocatalysis downhill thermodynamics (Gibbs free energy change  
 150  $\Delta G < 0$ ) is purely enhanced by the induced reactive oxygen species (ROS) from the  
 151 photocatalysts' excitation under light irradiation (**Fig.2B**) [75]. However, the unfavorable

152 photosynthesis reaction ( $\Delta G > 0$ ), an uphill reaction, is primarily determined by  
 153 photogenerated holes and electrons characterized by high redox potentials (**Fig.2B**) that  
 154 need to be assured by the correct positioning of the conduction and valence bands [76].  
 155 From a thermodynamic point of view, photocatalytic degradation is much more feasible  
 156 than the challenging artificial photosynthesis processes, such as photocatalytic hydrogen  
 157 ( $H_2$ ) evolution and the production of hydrocarbon fuels from carbon dioxide ( $CO_2$ )  
 158 reduction.



159

160 **Fig. 2. A)** Water splitting, solar cell, pollutants photocatalytic degradation, and  
 161 photocatalytic reduction of  $CO_2$  mechanisms. Adapted with permission from [74],  
 162 Copyright (2014), Wiley. **B)** Schematic illustration of natural and artificial  
 163 photosynthetic systems [77], Copyright (2019), American Chemical Society.

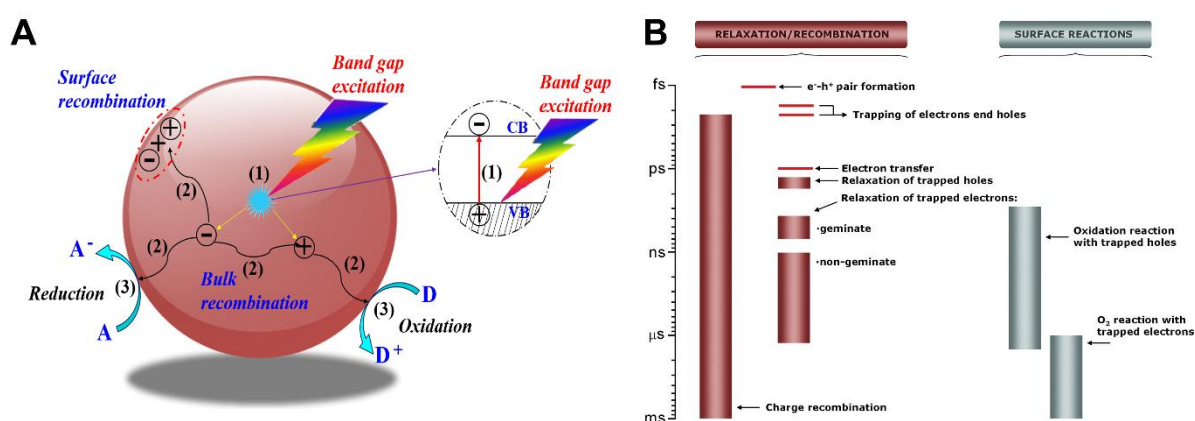
164

165 **Fig.3A** displays the redox mechanism for semiconductors (SCs) used as  
 166 photocatalysts. The mechanism involves three successive steps [78,79]. Initially, the  
 167 SC photocatalyst absorbs photons, and this causes electrons ( $e^-$ ) in the valence  
 168 band (VB) to jump to the conduction band (CB) when the photon energy ( $h\nu$ )  
 169 exceeds the bandgap energy ( $E_g$ ) of the semiconductor. Consequently, holes ( $h^+$ )  
 170 are left behind in the VB. These electrons and holes are crucial in driving reduction  
 171 and oxidation reactions to yield the desired product [79]. The subsequent step  
 172 involves separating and transferring photogenerated electron-hole pairs, directing  
 173 them toward the semiconductor's surface, although some of these pairs may



174 recombine within the bulk of the photocatalyst [80]. The last step comprises surface-  
 175 based reduction and oxidation reactions. The photogenerated charges located on  
 176 the surface of the semiconductor engage with chemical species, thus initiating the  
 177 desired chemical reactions. However, on the surface, certain photogenerated  
 178 electrons ( $e^-$ ) and holes ( $h^+$ ) may recombine without actively engaging in chemical  
 179 reactions. **Fig.3B** displays a schematic representation of the time scale  
 180 characteristics associated with the various phenomena related to charge carriers that  
 181 were previously discussed [81].

182 With the modern insight into the photocatalytic mechanisms, enhancing the  
 183 effectiveness of semiconductor photocatalysts involves expediting the production,  
 184 mobility, and reactivity of photo-induced charge carriers while minimizing electron-  
 185 hole recombination. Semiconductor materials with suitable bandgap structures for  
 186 solar light absorption, efficient conductivity for charge transport, minimal defects as  
 187 recombination sites, and rapid kinetics for surface reactions are highly favored  
 188 [82,83]. In general, for the reaction to proceed effectively, the reduction potential  
 189 should be lower than the bottom edge of the semiconductor's conduction band (CB),  
 190 enabling the transfer of electrons from the CB to the reactant. Furthermore, the  
 191 oxidation potential must exceed the VB of the catalyst to ensure the reactant can  
 192 readily accept holes.



193

194 **Fig. 3. A)** Schematic diagram illustrating principle of photocatalyst photocatalysis. **B)**  
195 Time intervals between "elementary steps" in a typical photocatalytic reaction.  
196 Adapted with permission from [81], Copyright (2012), American Chemical Society.

197

198 Adsorption plays a pivotal role in heterogeneous photocatalysis [84–86],  
199 particularly in the degradation and transformation of organic molecules or gases,  
200 where clay catalysts have emerged as significant contributors. Clay minerals, with  
201 their abundant surface area and reactive sites, offer a favorable environment for  
202 adsorption and catalytic processes [50,53,87]. Organic molecules or gas reactants  
203 adhere to the surface or interlayer spaces of clay catalysts through electrostatic  
204 interactions and other surface phenomena, initiating photocatalytic reactions. The  
205 subsequent generation of superoxide and hydroxyl radicals facilitates the breakdown  
206 of adsorbed molecules, leading to the desired transformations [88,89]. Despite the  
207 essential role of adsorption, competitive interactions among water molecules, other  
208 reactants, and target molecules may influence the photocatalytic efficiency,  
209 impacting active site availability and photogenerated species migration. While  
210 adsorption enhances catalytic efficiency by promoting reactant-catalyst interactions,  
211 excessive adsorption of certain compounds or intermediates can impede the process  
212 by acting as catalyst poisons [90]. Nonetheless, adsorption serves as the initial step  
213 in catalysis, concentrating reactants near active sites, and reducing the activation  
214 energy required for chemical transformations to occur. The versatility of clay  
215 catalysts allows for tailored surface properties and selective adsorption, enabling the  
216 direction of reactions toward desired pathways and improving overall process  
217 performance in terms of reaction rates, selectivity, and yield for various organic  
218 molecules or gas reactants [89].

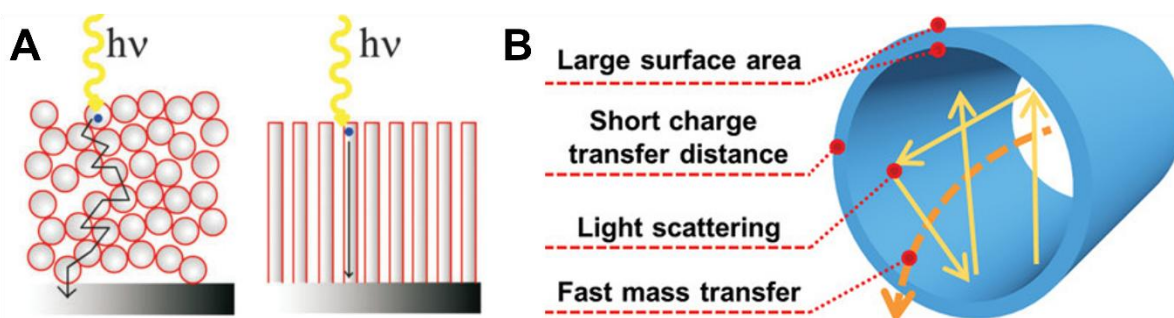
219 Recently, several studies demonstrated that tube morphology is one of the  
220 crucial parameters that can significantly influence the performance of the

221 photocatalyst [27,91,92]. In particular, there is compelling evidence that materials  
222 featuring nanotubes display improved photocatalytic activity compared to  
223 nanoparticles. Moreover, materials with tubular structures have been reported to  
224 exhibit much better photocatalytic performance than nanoparticulate systems. For  
225 instance, a study by Jiang et al [93] demonstrated that halloysite exhibits superior  
226 photocatalytic activity in photodegradation processes of different organic  
227 contaminants (rhodamine B, malachite green and ciprofloxacin) compared to their  
228 2D polymorph (kaolinite nanosheets). Their results highlight the enhancement of  
229 photocatalytic activity due to the tubular morphology of halloysite. The extended axis  
230 of nanotube photocatalysts provides a straight path for carrier transport [94], thus  
231 lowering photoinduced electron-hole pairs' trapping and recombination kinetics [95].  
232 This compares sharply with the transporting of the electron-hole pairs between  
233 nanoparticles. Moreover, nanotubes can provide a strong light-scattering effect,  
234 improving the light-harvesting properties [94]. Additionally, polarization can improve  
235 charge separation within a photocatalyst material by facilitating the movement of  
236 electrons and holes in opposite directions [96]. The nanotubes' geometry reduces  
237 the diffusion distance between the degrading compounds in the solution and the  
238 nanotubes' active surface area. Whereas the porous structure of nanoparticles  
239 imparts longer diffusion lengths [95]. These advantages can be applied to nanosized  
240 tubular clay minerals (halloysite, imogolite, and chrysotile). **Fig. 4A and Fig. 4B**  
241 outline the electron transport in two distinct architectures of the photocatalyst and  
242 schematic illustrations of some pros of nanotubular architecture for photocatalytic  
243 reaction, respectively.

244 We can summarize and highlight the action mechanism of clay nanotubes in  
245 altering photocatalytic properties as follows: The tubular architecture of these clay

246 variants provides a confined environment that boosts the efficiency of photocatalytic  
247 reactions by facilitating the adsorption of reactant molecules and promotes proximity  
248 to active sites and catalytic centers [93,97]. Additionally, the high surface area-to-  
249 volume ratio of clay nanotubes allows for increased contact between catalysts and  
250 reactants, enhancing reaction kinetics [93]. Moreover, their structural characteristics  
251 enable efficient light harvesting and photon utilization, while surface chemistry  
252 facilitates charge transfer processes crucial in photocatalytic reactions [98,99]. The  
253 polarization effect within tubular clay minerals further aligns molecules and charge  
254 carriers, streamlining charge transfer and reducing recombination rates, thus  
255 amplifying overall photocatalytic activity [100,101].

256



257

258 **Fig. 4. A)** A comparison of the electron pathways through nanoparticle and  
259 nanotubular structured TiO<sub>2</sub>. Reproduced with permission from [102], Copyright  
260 (2009). The Royal Society of Chemistry. **B)** Schematic illustration of some  
261 advantages of nanotubular architecture for photocatalytic reactions. Reproduced with  
262 permission from [103], Copyright (2019) Wiley.

263

### 264 3. Structural and physiochemical properties of the nanosized tubular 265 clay minerals.

266 Compared to other nanomaterials with spherical or platy shapes, nanotubes,  
267 such as chrysotile, halloysite, and imogolite, offer a larger surface area due to their  
268 unique hollow tubular structure [104]. In the following discussion, we will examine the  
269 detailed aspects of these nanosized tubular clay minerals, exploring their

270 composition, structure, and exceptional physiochemical properties that distinguish  
271 them in materials science.

272

273

### 274 **3.1. Structural and physiochemical properties of Halloysite**

275 Halloysite nanotubes (HNTs) represent an exciting source of 1D clay material  
276 that can be extracted in large quantities from deposits, making them economically  
277 viable. The most widely available halloysite supplies are from Dragon Mine (Utah-  
278 USA) and Northland (New Zealand) deposits [105,106]. Due to its distinctive tubular  
279 nanostructure, HNTs has garnered significant attention across various fields in  
280 recent years. Its applications range from controlled release of functional compounds,  
281 anticorrosion, adsorbents, catalysis supports and nanotemplate/nanoreactor  
282 [93,97,107–110].

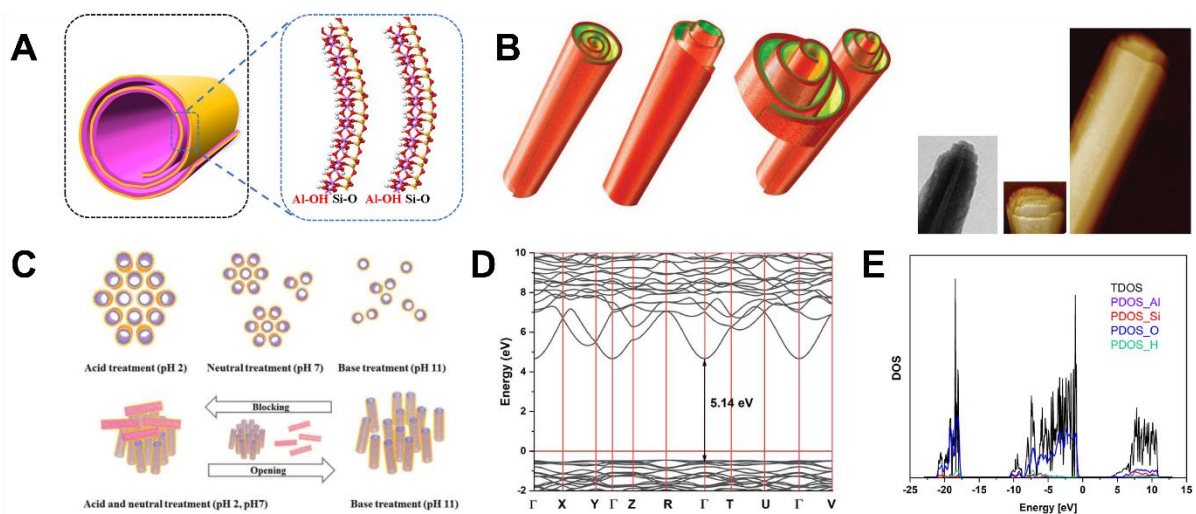
283 Halloysite is a dioctahedral 1:1 clay mineral with a chemical formula of  
284  $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , belonging to the kaolin group with a nanoscroll shape formed  
285 by rolling 5-20 aluminosilicate layers [111,112] (**Fig. 5A**). When  $n = 2$ , halloysite is  
286 referred to as halloysite-10 Å due to the average spacing of 10 Å between the unit  
287 layers. Water can be removed almost permanently by heating the halloysite samples  
288 at 120 °C, leading to halloysite-7 Å (with an interlayer spacing of 7Å) [87]. The  
289 structure of halloysite is known as monoclinic with unit cell parameters as follows:  $a$   
290 = 5.14,  $b = 8.9$ ,  $c = 17.7$  Å with angles  $\alpha$  ranging from 97 to 104 degrees,  $\beta$  from 90  
291 to 91.8 degrees, and  $\gamma$  fixed at 90 degrees. The halloysite is characterized by a  
292 hollow spiral structure [113] as illustrated by images using AFM and TEM techniques  
293 (**Fig. 5B**). The length of HNTs ranges typically within 0.5-1.5  $\mu\text{m}$  [111,112]. The outer

294 diameter ranges between 50 to 70 nm, while the inner cavity, also called lumen, has  
295 a 10 to 20 nm diameter. In addition, halloysite exhibits distinct internal and external  
296 chemistry. The inner lumen surface features an array of Al-OH groups resembling  
297 gibbsite and carries a positive charge, whereas the outer surface consists of  
298 Si-O-Si groups and bears a negative charge [41]. This characteristic of a different  
299 surface charge outside and inside the tube makes the incorporation of ligands and  
300 nanomaterials feasible in the desired location. Joo *et al.* [114] observed that  
301 changing the pH in a water suspension containing HNTs allowed the tailoring of the  
302 pore surface area, pore diameter, and pore volume of the recovered halloysite  
303 powder (**Fig. 5C**). Indeed, in an acidic solution, bundles of halloysite nanotubes are  
304 formed (blocking the halloysite nanotube inner pore). In contrast, HNTs are well  
305 dispersed in basic solution, and the end of each HNTs was separated from other  
306 HNTs. An important point it that the synthesis of halloysite remains an ongoing  
307 challenge due to the absence of well-established procedures. Research efforts in  
308 this area have been underway since the mid-20th century. However, to date,  
309 developing a reliable and efficient method for synthesizing halloysite in the laboratory  
310 continues to be an urgent and unresolved issue [115].

311 Continuing the research on the properties of the HNTs, Gianni et al [116].  
312 conducted a comprehensive theoretical study using DFT calculations to examine the  
313 electronic characteristics of halloysite nanotube models (**Fig. 5D**). Their study  
314 revealed that the pristine halloysite nanotube exhibits a band gap of 5.14 eV (**Fig.**  
315 **5E**). Through the analysis of the total density of states (TDOS) and projected density  
316 of states (PDOS) of halloysite, they highlighted that the lower and upper sections of  
317 the valence band consist primarily of oxygen 2s and oxygen 2p states, respectively.  
318 The oxygen atoms forming Al-O bonds significantly contribute to the valence band

319 compared to those involved in Si-O bonds [116,117]. The conduction band minimum  
 320 primarily comprises H 1s, Si 3s 3p, and partly O 2p, Al 3s 3p states. The same  
 321 calculations were confirmed by independent researchers [116,117].

322 The hollow structure of HNT acts as a nanoreactor, providing a confined  
 323 environment that enhances the effectiveness of catalysts. Recently, Jiang and  
 324 colleagues [93] investigated the use of natural HNT as a nanoreactor to improve  
 325 photochemical reactions. Their research demonstrated that introducing Fe doping  
 326 into the interior surface of HNT resulted in enhanced activity and adsorption  
 327 capabilities compared to the exterior surface. Notably, the unique photochemical  
 328 properties exhibited by the two surfaces of HNT led to spatial confinement effects,  
 329 resulting in superior photodegradation of organic species compared to kaolinite  
 330 nanosheets.



331

332 **Fig. 5.** **A)** Detailed structure of halloysite nanotubes. Reproduced with permission  
 333 [93]. Copyright (2021), American Chemical Society. **B)** Scheme of the rolling of  
 334 aluminosilicate sheets to create halloysite nanotubes, with alumina forming on the  
 335 interior (green), silica on the outside and representative TEM and AFM images of  
 336 HNTs. Reproduced with permission from [41]. Copyright (2015), Wiley. **C)** Schematic  
 337 representation of the inner space of halloysite nanotubes and the inter-space  
 338 between them following treatment with various pH solutions. Reproduced with  
 339 permission from [114], Copyright (2013), Royal Society of Chemistry. **D)** The  
 340 calculated band gaps for and **E):** The calculated TDOS and PDOS of respective

341 atoms for the the halloysite. Reproduced with permission from [116] Copyright  
342 (2023), Elsevier.

343

### 344 **3.2. Structural and physiochemical properties of imogolite**

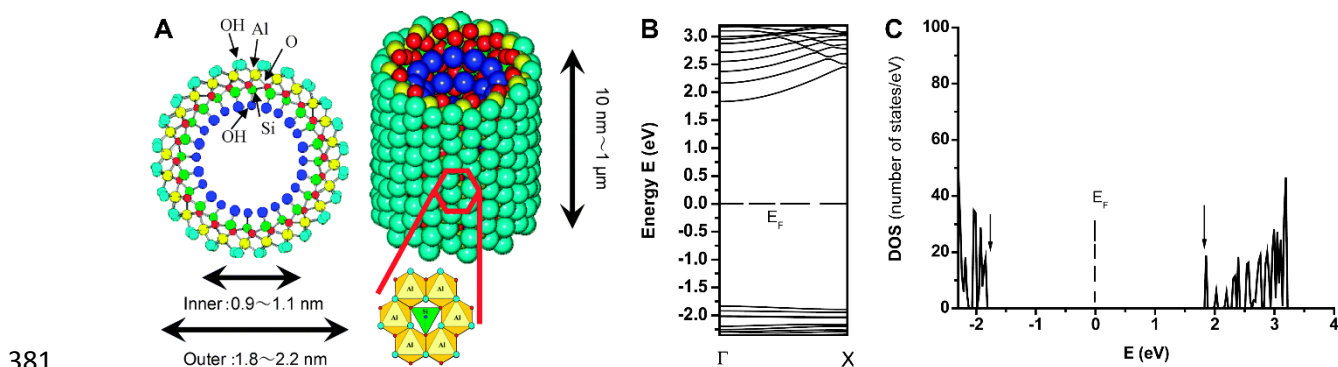
345 Yoshinaga and Aomine first discovered imogolite (INT) from volcanic ash in  
346 1962. INT is a naturally occurring aluminosilicate nanotube [118], characterized by  
347 the chemical formula  $(\text{OH})_3\text{Al}_2\text{O}_3\text{SiOH}$ , extending from the outer to the inner surface  
348 of these nanotubes [53,119]. This particular nanotube features an inner and outer  
349 diameter of about 1.0 nanometers and approximately 2 nanometers, respectively  
350 [54], while the length varies from hundreds of nanometres to the micrometer scale  
351 **(Fig. 6A)**. The interior of imogolite exhibits silanol (SiOH) groups, while the exterior  
352 showcases both Al–O–Al and Al–OH–Al groups, providing imogolite nanotubes with  
353 amphoteric properties [120]. The spontaneous rolling of an Al–O and Si–O bond into  
354 a single-walled nanotube is caused by the difference in bond length. More  
355 interestingly, these configurations exhibit a clearly defined minimum in strain energy  
356 [57,58,121], facilitating monodispersity in nanotube diameter and chirality [122]. It is  
357 worth highlighting that the structure of imogolite differs significantly from that of  
358 halloysite. In imogolite, the curved octahedral  $[\text{Al}(\text{OH})_3]$  layer shapes the inner  
359 surface of the nanotubes, whereas the outer surface is composed by Si–O–Si group  
360 [53]. These distinctions are at the core of the unique characteristics of imogolite  
361 nanotubes. Moreover, INTs are often regarded as the clay equivalent of carbon  
362 nanotubes, exhibiting remarkable resemblances in aspect ratios, rigidity, and  
363 dimensions [112].

364 The major limitation of INTs, from an industrial point of view, is their inability to  
365 create extensive deposits [123]. However, its synthesis was established quite rapidly  
366 after its discovery. In 1977, for the first time, Farmer et al. [124] synthesized



367 imogolite nanotubes by coprecipitating silicon and aluminum in an aqueous solution.  
368 They established that the yield and rate of formation of imogolite nanotubes are  
369 optimal for (i) a pH of 4.5, (ii) low reactant concentrations, and (iii) a temperature  
370 between 90 and 100 °C [125].

371 The electronic characteristics of INTs depend on their diameter, chemical  
372 composition, and chirality. An indicator of a promising photocatalyst is its band gap.  
373 Bursill et al. [126] were the first to predict a relatively wide band gap for these  
374 nanotubes. Subsequent band gap values for imogolite nanotubes have been shown  
375 to range from 3.6 to 5.3 eV [57,58,64,127,128]. Moreover, Li and co-workers [127]  
376 demonstrated that the structure of the energy band and the electron density of states  
377 were near the Fermi level (set at  $E=0$ ) for a single-walled imogolite (**Fig. 6B**). Their  
378 findings indicated a direct band gap with an  $E_g$  of approximately 3.67 eV. Moreover,  
379 the energy gap shown in the DOS (**Fig. 6B**) corresponds to the energy band gap  
380 shown in **Fig. 6C**.



382 **Fig. 6. A)** Structural illustration of imogolite. Reproduced with permission from [129],  
383 Copyright (2014), Royal Society of Chemistry. **B)** The energy bands of the single-  
384 walled imogolite nanotube and **C)** the electron density of states. Reproduced with  
385 permission from [127]. Copyright (2008), IOP Publishing.

386

### 387 3.2.1. Synthesis and physiochemical properties of compounds

388 analogous to imogolites

389 Chemically tuning synthetic materials primarily aims to expand the range of  
390 potential industrial applications. Similarly, synthetic procedures often allow for better  
391 control over reproducibility, composition, purity, and specific desired characteristics,  
392 unlike natural clay specimens, which frequently contain impurities and can be less  
393 readily available. Notably, in the case of nanotubular structures, it is essential to  
394 establish practical approaches for controlling the functionality of both their inner and  
395 outer surfaces.

396 Wada and co-workers successfully substituted the silicon atoms with  
397 germanium in the imogolite structure by modifying the precursors of the synthesis  
398 [130]: By using electron microscopy and X-ray scattering analysis, they found that  
399 the diameter of imogolite nanotubes increases as the  $[\text{Ge}]/([\text{Ge}]+[\text{Si}])$  ratio increases.  
400 Conversely, they also observed a reduction in the length of the tubes with the  
401 increase in this substitution rate. It's worth mentioning that by replacing NaOH with  
402 urea in the synthesis procedure, some researchers substantially increased the length  
403 of Ge tubes [131,132]. However, Maillet et al. [133] observed in their study that the  
404 nanotube shape is regulated by the initial aluminum salt ( $C_{\text{Al}}$ ) concentration,  
405 generating either single-walled nanotubes (Ge-SWINT,  $C_{\text{Al}} > 0.75 \text{ mol L}^{-1}$ ) or double-  
406 walled (Ge-DWINT,  $C_{\text{Al}} < 0.4 \text{ mol L}^{-1}$ ) (**Fig. 7A**) [53]. These structures (Ge-SWINT  
407 and Ge-DWINT) have been thoroughly investigated through experimental and  
408 computational studies [65]. The results of this study proved that the Ge-DWINT  
409 structure exhibits more excellent stability compared to Ge-SWINT, possibly  
410 attributable to hydrogen bonding stabilization. It has also been deduced that while  
411 aluminosilicate nanotubes exhibit insulating properties, their dehydroxylation can  
412 alter them into semiconductor materials [133]. On the other hand, Alvarez-Ramirez

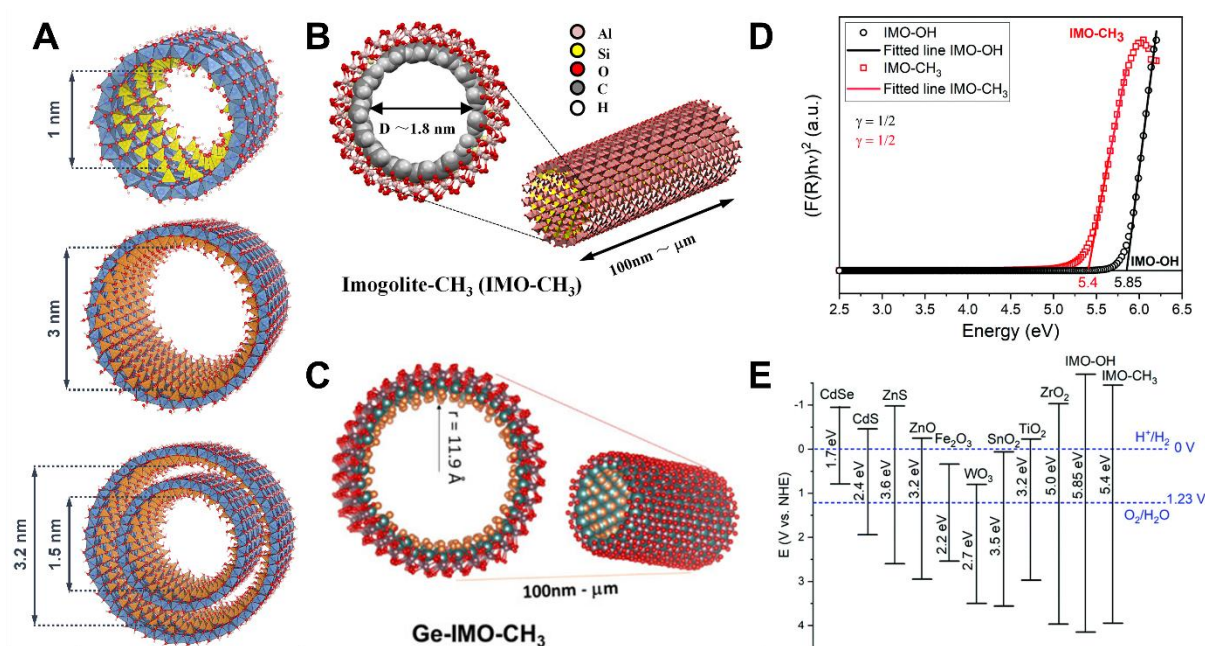
413 [128] performed ab initio simulations, from which they estimated a band gap range of  
414 4.3-4.8 eV for Ge-Imo.

415 Surface modification has also been applied to Imogolite nanotubes. Bottero et  
416 al. [134] were the first to report the synthesis of silicon-based imogolite with a fully  
417 methylated inner wall (**Fig. 7B**) [135]. A few years later, the technique was  
418 successfully transposed to germanium imogolite nanotubes (**Fig. 7C**) [136,137]. It  
419 was worth mentioning that the methylation of imogolite nanotubes was confirmed to  
420 induce a significant increase in their affinity with molecules such as CH<sub>4</sub>, CO<sub>2</sub>, or N<sub>2</sub>  
421 [138]. Curiously, Pignié et al. [100] recently reported that the imogolite IMO-CH<sub>3</sub> (5.4  
422 ± 0.2) has a smaller energy gap than the pure imogolite IMO-OH (5.85 ± 0.30) (**Fig.**  
423 **7D**). This value is similar to the band gap related to ZrO<sub>2</sub> (**Fig. 7E**), whose  
424 photocatalytic activity has been extensively studied. Given the similarity in band gaps  
425 and valence/conduction bands between ZnO<sub>2</sub> and imogolite variants (IMO-CH<sub>3</sub> and  
426 MO-OH) [100] and the successful use of ZnO<sub>2</sub> in harnessing solar energy [139–141],  
427 it suggests imogolite holds promise as a viable candidate for effective photocatalytic  
428 applications. Furthermore, the versatility of imogolite nanotube functionalization  
429 opens exciting opportunities in the field of photocatalysis.

430 Finally, focused on these encouraging findings, other isomorphous substitutions  
431 have been studied lately, especially regarding the partial replacement of Al<sup>3+</sup> with  
432 Fe<sup>3+</sup> in the outer wall [142–144]. Despite these enhancements, they do not  
433 substantially alter the nanotube diameter, with doping rates remaining below 1%  
434 [142]. Alvarez-Ramírez's work has shown that the incorporation of Fe alters the  
435 electronic characteristics of the nanotubes, consequently causing the band gap  
436 value to decrease. This decrease is observed from 4.7 eV to 2.0-1.4 eV for the Fe-  
437 silicon nanotubes and from 4.2 eV to 2.6-1.0 eV for the Fe-germanium imogolite-like

438 nanotube [63]. "In addition to iron substitution, other trivalent dopants or cation  
 439 vacancies have been theoretically contemplated, which have the potential to bring  
 440 about substantial alterations in the band structure of these nanotubes [145–148].  
 441 Therefore, these different perspectives on the optical and electronic properties of  
 442 modified imogolite nanotubes open the way to their practical use as a photochemical  
 443 nano-reactor.

444



445

446 **Fig. 7.** Inner diameter size for **A)** Si-SWINT, Ge-SWINT and Ge-DWINT.  
 447 Reproduced with permission from [53], Copyright (2018) MDPI. **B)** Methylated  
 448 imogolite (IMO-CH<sub>3</sub>). Reproduced with permission from [137], Copyright (2017)  
 449 Elsevier. **C)** SW Ge-IMO-CH<sub>3</sub>. Reproduced with permission from [135], Copyright  
 450 (2019) American Chemical Society. **D)** Band gap energy of IMO-OH and IMO-CH<sub>3</sub>  
 451 and **E)** Comparison of the gap band of the imogolite with other selected compounds.  
 452 Reproduced with permission from [100], Copyright (2021) Royal Society of  
 453 Chemistry.

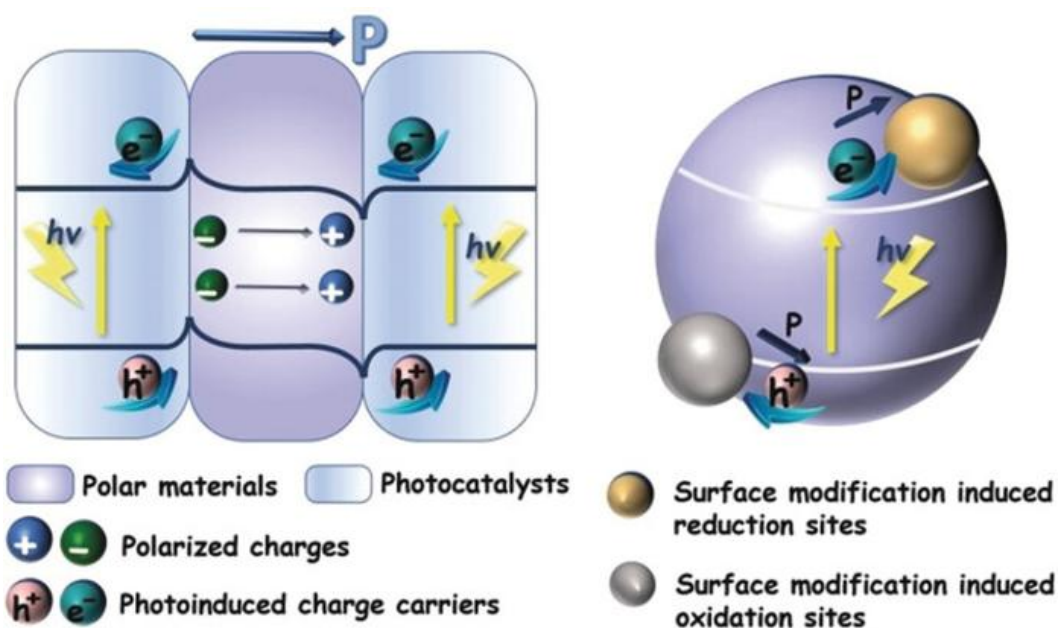
454

### 455 3.2.2. The role of polarization of imogolite in photocatalysis

456 As mentioned, a fundamental challenge in photocatalysis lies in rapidly  
 457 recombining electron-hole pairs within photocatalysts. While the charge migration

458 requires hundreds of ps, bulk charge recombination occurs much faster, taking only  
459 a few ps. which is considerably swifter than charge transport [149]. For that reason,  
460 Therefore, suppressing the process of electron-hole pairs recombining ( $e^-/h^+$ ) stands  
461 as a crucial factor in improving the performance of photocatalysts. The electric field  
462 inside the substance induces a static force on the charges in the opposite direction,  
463 which makes it possible to increase their lifetime by limiting their recombination  
464 [101]. This electric field also promotes their transport to the interfaces where the  
465 chemical reactions of interest occur (**Fig. 8**). Discussions regarding the potential role  
466 of persistent polarizations in facilitating efficient separation of electrons ( $e^-$ ) and holes  
467 ( $h^+$ ) have started to appear in the literature [150–152].

468         However, it is essential to note that in the case of imogolite, the nanotube  
469 serves a unique dual role, acting as both a polar material and a photocatalyst,  
470 distinguishing it from the scenario presented here [53,65,100,119]. The inherent  
471 polarization of imogolite nanotubes, coupled with their photocatalytic activity, creates  
472 a synergetic effect that significantly enhances their performance in light-driven  
473 catalytic reactions. This dual functionality showcases how imogolite seamlessly  
474 integrates both the roles of a polar medium and a photocatalyst, offering a unique  
475 and promising platform for efficient photoinduced catalysis, where the material's  
476 polar nature finely tunes charge separation and transport.



477

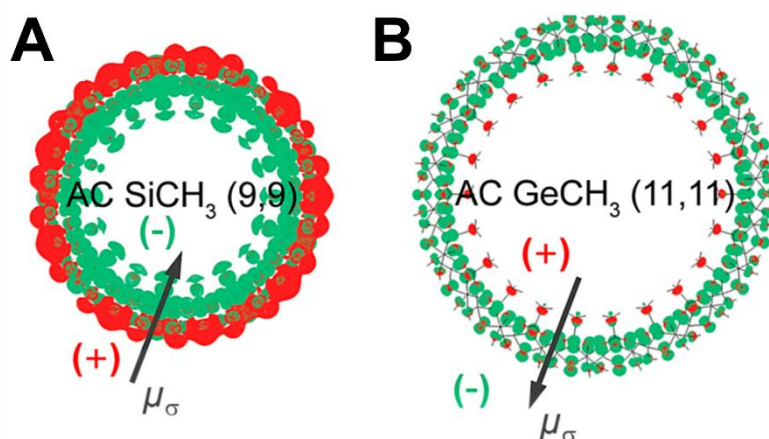
478 **Fig. 8.** The scheme for polarization promoted surface charge separation.  
 479 Reproduced with permission from [101] .Copyright (2019), Wiley.

480

481 In this context, Gustafsson and co-workers first discussed the intrinsic  
 482 polarization in natural imogolite in 2001 [153]. They explained that the pKa of the  
 483 hydroxyl functions that compose the inner and outer surfaces could not justify the  
 484 evolution of the charge of the outer surface of INTs as a function of pH. In general, in  
 485 aluminum oxides, the aluminol functions, similar to imogolite, remain uncharged over  
 486 a broad pH range, from 0 to 11.9 [153]. Moreover, surface complexation of ions by  
 487 these groups is not considered possible. Consequently, they assumed that the outer  
 488 tube walls are unreactive toward ions. The authors, therefore, proposed a model in  
 489 which negative and positive charges accumulate on the internal and external  
 490 surfaces of the nanotube, respectively. These charges are not dependent on the pH.  
 491 They thus defended the existence of polarization through the wall.

492 Teobaldi's group conducted density functional theory (DFT) calculations  
 493 concerning INTs, focusing on various physico-chemical structures [57,154]. These  
 494 simulations have shown that INTs exhibit a persistent polarization corresponding to a

495 spatial separation of the VB and CB in real space (**Fig. 9**) [57,154]. This separation  
496 enhances the separation of holes ( $h^+$ ) and electrons ( $e^-$ ) through optical charge-  
497 transfer excitations inside the walls of the nanotubes.



498

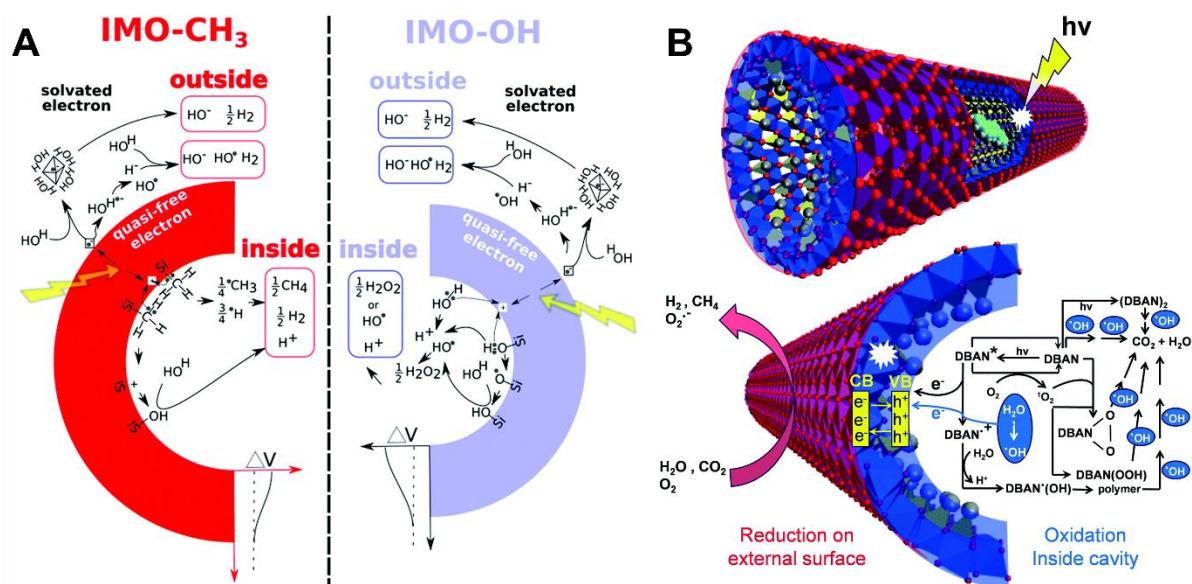
499 **Fig. 9.** Front image of armchair methylated INTs  $(OH)_3Al_2O_3Y(CH_3)$  showing the real-  
500 space separation between the boundaries of the conduction band (red) and valence  
501 band (green).  $Y = Si$  in (A) and  $Ge$  in (B). The direction of the permanent dipole  
502 surface density  $\mu_\sigma$  of the nanotube wall is indicated by the black arrow. Reproduced  
503 with permission from [122], Copyright (2018) Nature.

504

505 Furthermore, the excellent chemical separation characteristics of hybrid  
506 hydrophobic/hydrophilic Imo NTs, along with their ease of modification  
507 [136,138,155,156] could be very favorable for the effective separation of photo-  
508 oxidized and photo-reduced reactants and products (**Fig. 10A** and **Fig. 10B**). Articles  
509 discussing the potential beneficial impact of permanent polarizations on the effective  
510 separation of holes ( $h^+$ ) and electrons ( $e^-$ ) have started to appear in the literature  
511 [65,100,154,157], prompting increasing interest in this field.

512 Although INTs have been utilized as catalyst supports (as discussed in  
513 section 4) and initial findings have been reported regarding their efficacy in the  
514 photocatalytic decomposition of organic dyes [40,97,98], this subject is yet to be  
515 explored.





516

517 **Fig. 10. A)** Schematic of the reaction mechanisms at play in two types of  
 518 imogolites (IMO-CH<sub>3</sub> and IMO-OH). For clarity, water radiolysis was left out. The  
 519 intra-wall electric field ( $\Delta V$ ), which drives charge separation, is schematically  
 520 represented. Reproduced with permission from [66], Copyright (2021) The Royal  
 521 Society of Chemistry. **B)** Illustration of potential key photodegradation pathways for  
 522 DBAN enclosed in Imo-CH<sub>3</sub> nanotubes in an aqueous medium. Reproduced with  
 523 permission from [96], Copyright (2021) The Royal Society of Chemistry.

524

525

### 526 3.3. Structural and physiochemical properties of chrysotile

527 Chrysolite is a hydrated magnesium silicate with a stoichiometric composition  
 528 of Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>. Natural chrysotile, commonly known as white asbestos [158,159],  
 529 is part of the serpentine group of minerals. It has found extensive applications across  
 530 diverse industries thanks to its remarkable properties, including high tensile strength,  
 531 flexibility, and excellent resistance to heat and chemicals. However, despite its  
 532 extensive use, there are growing concerns about the potential health risks of  
 533 exposure to chrysotile fibers. Inhalation of these tiny fibers can result in severe  
 534 respiratory problems, including lung diseases like asbestosis and mesothelioma,  
 535 which is a rare and aggressive form of cancer [159–161].



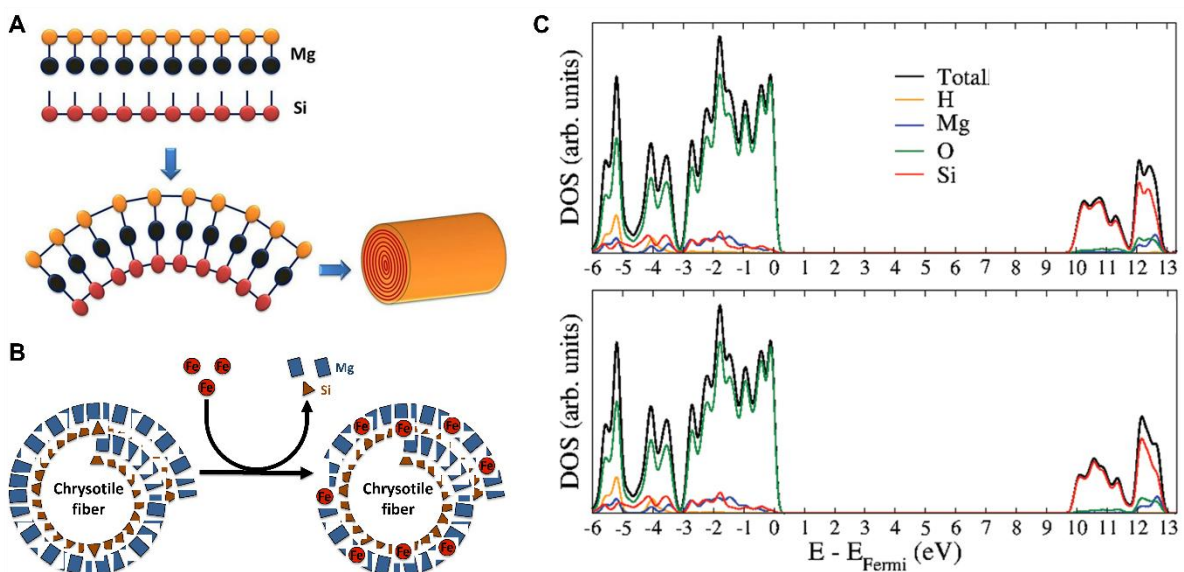
536 Chrysotile consists of a silicate sheet  $(\text{Si}_2\text{O}_5)_n^{2n-}$ , where the neighboring  
537 tetrahedra share the oxygen atoms present in the tetrahedron, and a non-silicate  
538 sheet  $[\text{Mg}_3\text{O}_2(\text{OH})_4]_n^{2n+}$  [162]. The curvature of the sheets spreads along a favored  
539 axis, giving rise to the tubular chrysotile structure similar to that seen for halloysite  
540 **(Fig. 11A)**. The concentric sheets developing the fibers exhibit a curvature radius  
541 ranging from 2.5 to 3.0 nanometers for the inner layers, expanding to approximately  
542 25 nanometers for the outer layers. As a result, unit fibers (fibrils) have external  
543 diameters that vary between 20 and 50 nanometers [163]. Researchers have tried to  
544 refine chrysotile's structure through the Rietveld method. In a study conducted by  
545 Falini et al. [164], they refined nano-chrysotile within the monoclinic Cc space group,  
546 determining lattice constants  $a=5.340(1)$ ,  $b=9.241(1)$ ,  $c=14.689(2)$  Å, and  $\beta=93.66$   
547  $(3)^\circ$  [165]. The chemical composition of chrysotile differs depending on the mineral  
548 deposit. In fact, the substitution of silicon and magnesium can occur in chrysotile. In  
549 the brucite layer, it is possible to substitute magnesium with  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ , or  $\text{Ni}^{2+}$  [166].  
550 Conversely, in the silicate layer, silicon can be replaced by  $\text{Al}^{3+}$  or rarely  $\text{Fe}^{3+}$  [167]  
551 **(Fig. 11B)**.

552 Chrysotile exhibits chemical stability, incombustibility, and exceptional thermal  
553 insulation properties [168]. Additionally, its fibrils are known for their strength and  
554 remarkable flexibility. These fibers exhibit low thermal conductivity (0.3-0.4 W/(m K)),  
555 exceptional ability to withstand high temperatures, and a high melting point  
556 (approximately 1500 °C). They possess greater rigidity compared to steel, are  
557 impressive, resistant to corrosion, and not expensive compared to synthetic fibers  
558 [169].

559 The investigation conducted by Lourenço et al [171]. on the electronic  
560 properties of Single-Walled Chrysotile Nanotubes (NTs) using the self-consistent

561 charge density-functional tight-binding method (SCC-DFTB) sheds light on the  
 562 intricate electronic structure of chrysotile. Their findings reveal intriguing insights into  
 563 the total (DOS) and partial density of states (PDOS) of zigzag (40,0) and armchair  
 564 (25,25) chrysotile NTs (**Fig. 11C**). Surprisingly, they discovered that the chirality and  
 565 size of the NTs do not significantly alter their electronic structure, as evidenced by  
 566 the similarity in DOS and PDOS profiles (Figure 5). Specifically, in the valence band,  
 567 the predominant states are attributed to oxygen atoms, while in the conduction band,  
 568 electronic states of silicon atoms play a pivotal role in shaping the total DOS.  
 569 Interestingly, the contribution of magnesium and hydrogen atoms to the total DOS is  
 570 comparatively smaller than that of silicon and oxygen in both valence and conduction  
 571 bands.

572



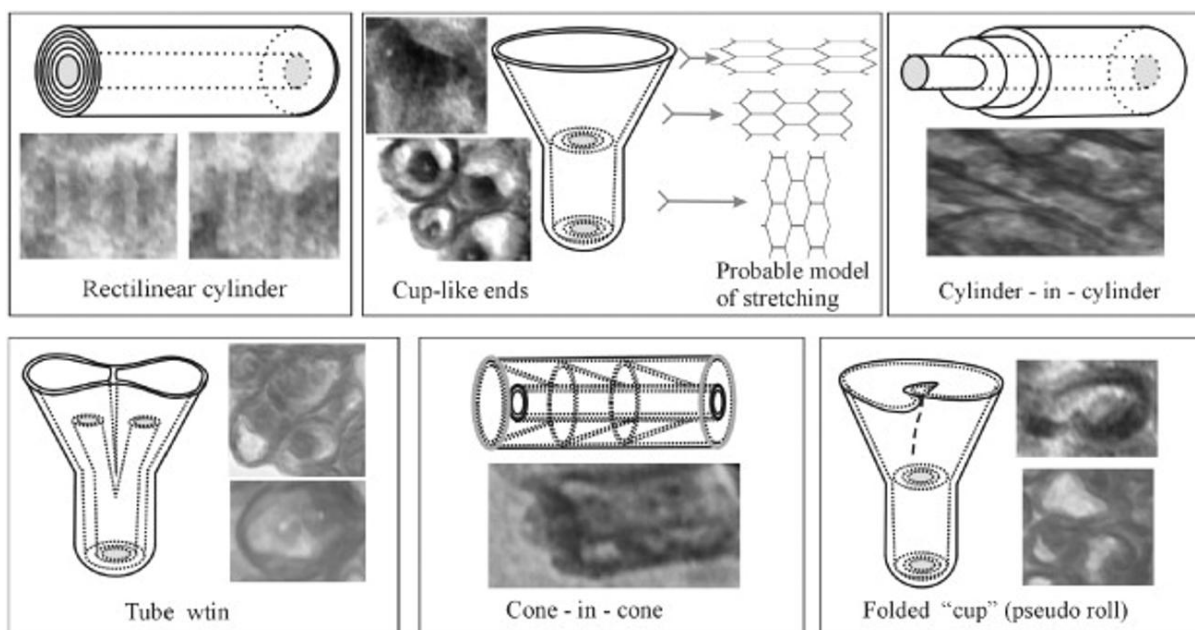
573

574 **Fig. 11. A)** structure of chrysotile. Reproduced with permission from [170], Copyright  
 575 (2013) Scientific research. **B)** Depiction of magnesium and silicon substitution by iron  
 576 in the chrysotile fiber structure. Reproduced with permission from [167], Copyright  
 577 (2020) MDPI. **C)** Total and partial density of states (PDOS) of the (a) zigzag (40,0)  
 578 and (b) armchair (25,25) chrysotile nanotubes. Reproduced with permission from  
 579 [171], Copyright (2012), American Chemical Society.

580

581 An electron-microscopic study of chrysotile by Voitylov et al. showed diverse  
582 morphologies of nanotubes: cones, cylinders, and socket tubes (**Fig. 12**). Conical  
583 nanotubes exhibit external diameters between 20 and 50 nm, while cylindrical  
584 nanotubes have external diameters between 20 and 70 nm. The inner diameter of  
585 cylindrical nanotubes is 35 nm. Notably, various other forms of chrysotile can also be  
586 found in nature (e.g., cylinder-in-cylinder, tube twins, rectilinear cylinders, cone-in-  
587 cone tubes, and cylinders with cup-like ends) [169]. It was revealed that synthesis  
588 conditions, including factors like temperature, hydrothermal treatment duration, and  
589 the composition of the precursor solution, influence specific morphological  
590 characteristics of the nanotubes [172].

591 Chrysotile has attracted significant attention due to its catalytic activity. The  
592 abundance of active sites and its high surface area make chrysotile-based catalysts  
593 highly promising for various chemical reactions [173]. These catalysts have  
594 demonstrated remarkable efficiency in numerous processes, such as polymerization,  
595 hydrolysis, reduction, and oxidation [174–177], making them versatile tools for  
596 organic synthesis and industrial applications. The distinctive fibrous morphology of  
597 chrysotile nanotubes creates an environment conducive to catalytic reactions,  
598 leading to improved selectivity and reaction kinetics.



599

600 **Fig. 12.** The hypothetical models of the chrysotile nanotubes. Reproduced  
 601 with permission from [169], Copyright (2011) Elsevier.

602

#### 603 **4. Applications in photocatalysis**

604 In the realm of photocatalysis, the interface interaction between tubular clay  
 605 carriers and active components emerges as a pivotal determinant of performance  
 606 and efficacy. Photocatalysis relies on the intricate interplay between light-absorbing  
 607 materials and catalytic species to drive chemical transformations for environmental  
 608 remediation and energy conversion [178,179]. Within this context, the interface  
 609 interaction orchestrates the spatial arrangement, charge transfer dynamics, and  
 610 surface chemistry crucial for photogenerated charge carrier migration and surface  
 611 redox reactions [178–180]. Physical adsorption of photocatalytic species onto the  
 612 tubular clay surfaces establishes localized reaction sites, amplifying photon capture  
 613 efficiency and catalytic activity [180–184]. Chemical bonding between the active  
 614 components and the clay matrices bolsters stability, mitigates photocorrosion, and  
 615 prolongs catalyst lifespan under harsh irradiation conditions. Electrostatic

616 interactions, in turn, regulate the distribution and orientation of photoactive species,  
617 optimizing interfacial charge transfer processes and redox kinetics [180–185].  
618 Surface coordination phenomena further fine-tune the electronic structure and  
619 surface reactivity of the catalyst, tailoring its performance to specific photocatalytic  
620 applications [181–185].

621         Due to clay's excellent structural properties and surface areas, nanotubes  
622 (chrysotile, halloysite, and imogolite) can be used as a catalyst or co-catalyst in  
623 photocatalytic systems. This section summarizes the application of clay nanotubes in  
624 photocatalysis from four aspects: Pollutant degradation in the water and air,  
625 photocatalytic hydrogen evolution reactions, disinfection of bacteria, and  
626 photocatalytic nitrogen fixation.

#### 627         **4.1. Degradation of organic pollutants by photocatalysis**

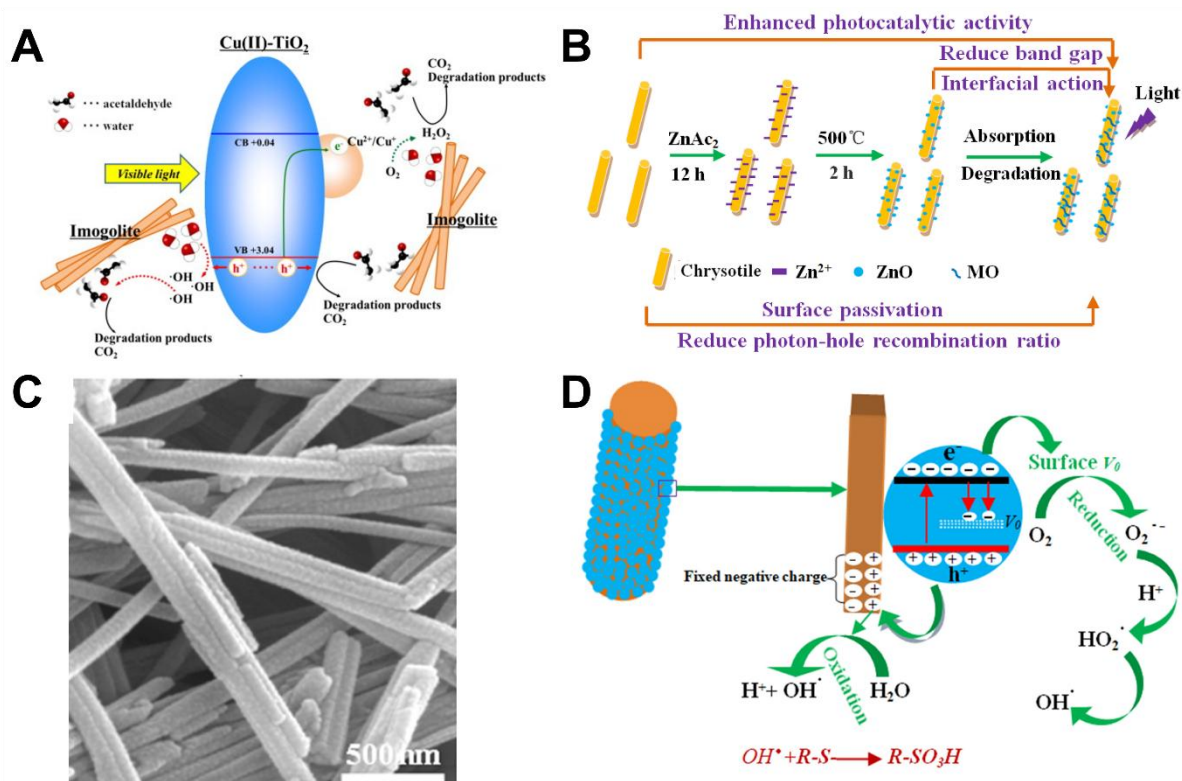
628         With the development of modern industry, a wide range of toxic pollutants,  
629 including synthetic dyes, phenol, and pharmaceutical substances, have been  
630 discharged into the air, water, and soil, resulting in substantial harm to the  
631 environment and living organisms. Thus, various approaches, including chemical  
632 degradation, physical adsorption, and biodegradation methods, have been employed  
633 for environmental restoration [186–193]. However, many traditional approaches to  
634 environmental remediation were deemed ineffective and had the potential to result in  
635 secondary pollution. In recent years, solar-driven photocatalysis technology has  
636 emerged as an environmentally friendly, efficient, and cost-effective solution for  
637 addressing environmental pollution removal. Due to their excellent structural  
638 properties and surface areas, clay nanotubes have been attractive candidates for  
639 utilizing eco-friendly waste treatment in air and water environments.

640 For instance, Katsumata et al [67]. successfully crafted a nanotubular  
641 imogolite structure through a hydrothermal process, subsequently employing it to  
642 fabricate composites of imogolite/TiO<sub>2</sub> and imogolite/Cu(II)-grafted TiO<sub>2</sub> (**Fig, 13A**).  
643 The authors reported that, under visible light illumination, the composite  
644 imogolite/Cu(II)-grafted TiO<sub>2</sub> demonstrated a notable improvement in its efficiency for  
645 the photodegradation of acetaldehyde when compared to both TiO<sub>2</sub> and Cu(II)-  
646 grafted TiO<sub>2</sub>. Furthermore, this enhanced activity appeared less influenced by the  
647 relative humidity. This result suggests a unique role of imogolite in effectively  
648 adsorbing acetaldehyde. The researchers found that imogolite adsorbs acetaldehyde  
649 and captures intermediates, including CH<sub>3</sub>COOH, during the acetaldehyde  
650 decomposition process. These intermediates are subsequently degraded to CO<sub>2</sub>  
651 through the action of radical species generated on the catalyst surface. The authors  
652 suggested the imogolite-containing composite as a highly efficient photocatalyst and  
653 could utterly eliminate the VOCs [67].

654 Similarly, Liu et al. [45] created a novel chrysotile@ZnO nanocomposite by  
655 coating ZnO on the surface of chrysotile, as illustrated in (**Fig 13B**). The  
656 photocatalytic performance of the chrysotile@ZnO nanocomposite was evaluated  
657 under UV light irradiation (365 nm), focusing on its capability for the photocatalytic  
658 decomposition of methylene blue (MB) dye. It has been stated that ZnO  
659 nanoparticles are homogeneously distributed across the chrysotile surface (**Fig,**  
660 **13C**). The team achieved up to 99.5% MB dye degradation after 60 min illumination  
661 compared with only 76% obtained with the ZnO, showing that the composite  
662 displayed improved light absorption and charge transport. Furthermore, it showcased  
663 a capacity for efficient recycling, retaining effectiveness even during the third cycle.  
664 The bandgap and photon-hole recombination rate of ZnO nanoparticles are lowered

665 by the combined effects of surface passivation and chrysotile's interfacial action. This  
 666 improvement results in enhanced photodegradation of organic pollutants, introducing  
 667 a new level of performance to chrysotile (**Fig, 13D**).

668



669

670 **Fig. 13. A)** Cu(II)-grafted TiO<sub>2</sub>-imogolite composite: Potential photodegradation  
 671 mechanisms of acetaldehyde under visible light irradiation. Reproduced with  
 672 permission from [67]. Copyright (2013) Elsevier. **B).** Graph illustrating the  
 673 chrysotile@ZnO nanocomposites' formation process. **C)** SEM images of  
 674 chrysotile@ZnO nanocomposites. **D)** Diagrammatic representation of MB's  
 675 photocatalytic degradation process over chrysotile@ZnO nanocomposites in the  
 676 presence of UV light. Reproduced with permission from [45], Copyright (2020)  
 677 Elsevier.

678

679 In a captivating study conducted by Wu and his colleagues [194], they  
 680 explored the potential of novel hetero-structural g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>/commercial halloysite  
 681 composites in the elimination of ciprofloxacin from wastewater (**Fig, 14A**). Their  
 682 findings reveal that the introduction of halloysite nanotubes (HNTs) and the g-C<sub>3</sub>N<sub>4</sub>-  
 683 TiO<sub>2</sub> heterojunction significantly augmented the efficiency of charge transfer and

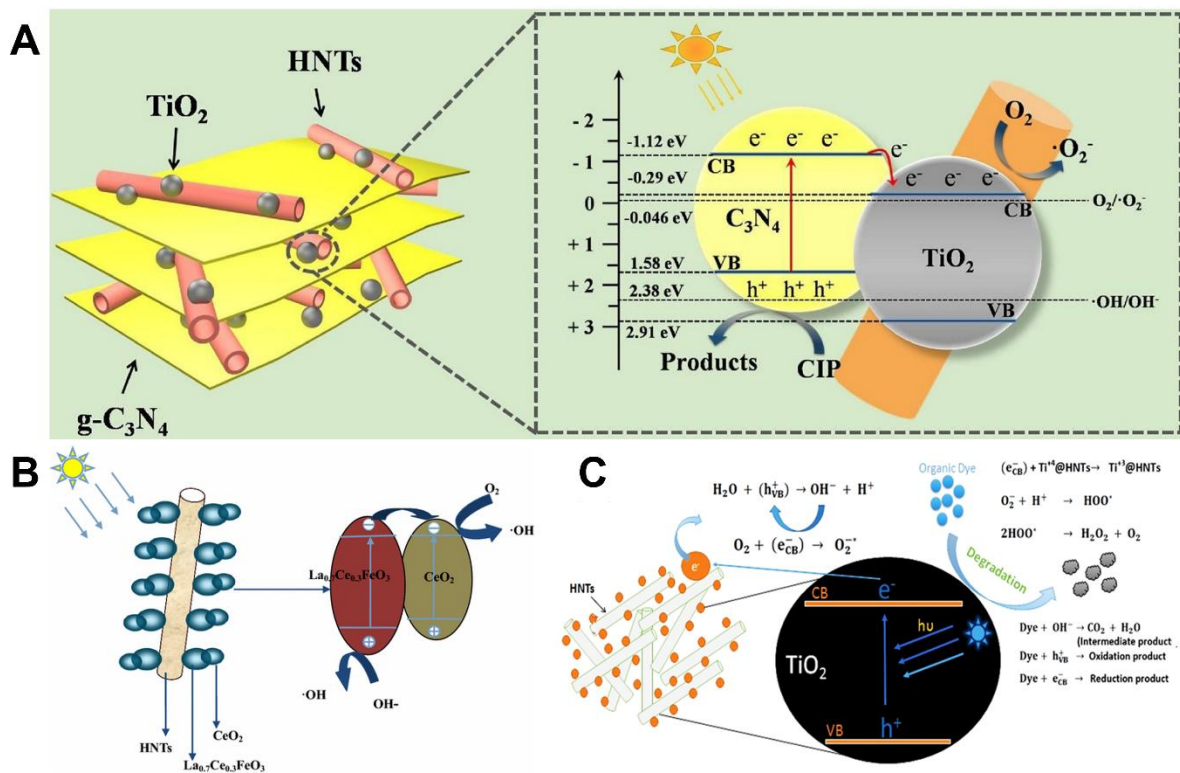
684 separation among photogenerated electron-hole pairs. This enhancement endowed  
685 the  $g\text{-C}_3\text{N}_4/\text{TiO}_2/\text{HNTs}$  hybrid material with remarkable photoelectric performance  
686 and stability. Notably, the composite achieved an impressive 87% degradation of  
687 ciprofloxacin within 60 minutes, owing its rapid photoelectron-hole pair transfer and  
688 separation capabilities. The most significant result was the remarkable reusability of  
689 the  $\text{C}_3\text{N}_4/\text{TiO}_2/\text{HNTs}$  nanocomposites even after 4 cycles.

690 In a related investigation, Li et al. [195] investigated the photocatalytic  
691 degradation of chlortetracycline, a common antibiotic, under visible light irradiation.  
692 They achieved this by immobilizing  $\text{LaFeO}_3$ , one of the most important perovskite-  
693 type semiconductor, onto the surface of halloysite nanotubes (HNTs) through a  
694 simple sol-gel method (**Fig, 14B**). Their findings indicated that untreated halloysite  
695 lacked photocatalytic activity. However, when chlortetracycline was exposed to pure  
696  $\text{LaFeO}_3$ , 74% of the drug degraded within a 90 min. Notably, the degradation rate  
697 increased to 87% with the use of  $\text{LaFeO}_3/\text{HNTs}$  as catalyst, underscoring the  
698 enhanced performance facilitated by this composite. The improved efficacy was  
699 attributed to the adsorptive capacity of HNTs and the augmented electron transfer  
700 capacity of  $\text{LaFeO}_3$ , providing insights into the synergistic mechanisms underlying  
701 the composite's photocatalytic behavior.

702 In the other study, Mishra et al [99]. developed a  $\text{TiO}_2@\text{HNT}$  photocatalyst  
703 through a combination of sol-gel and phase inversion methods, yielding a stable and  
704 highly efficient photocatalyst (**Fig, 14C**). This composite exhibited enhanced  
705 photocatalytic activity attributed to the electrostatic interaction between  $\text{TiO}_2$  and the  
706 HNT surface. Under UV light, the nanocomposite effectively degraded 87.47% and  
707 96.87% of methylene blue and rhodamine B, respectively. The strong electrostatic  
708 interaction between  $\text{TiO}_2$  and HNTs facilitated the generation of more electron-hole



709 pairs, thereby increasing photocatalytic activity. Particularly for methylene blue and  
 710 rhodamine B dyes, which carry positive charges, HNTs improved the stability and  
 711 supply of photo-generated charges, enhancing dye molecule absorption on the  
 712 photocatalyst. This effect stemmed from electrostatic attractive and repulsive forces  
 713 originating from the negatively charged HNTs surface. Crucially, the TiO<sub>2</sub>@HNTs  
 714 photocatalyst demonstrated non-photo-corrosive behavior during three consecutive  
 715 cycles of photocatalytic degradation, highlighting its suitability for practical  
 716 applications.



717

718 **Fig. 14. A)** Schematic of possible mechanism for photodegradation of CIP  
 719 over g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>/HNTs heterojunction composites. Reproduced with permission  
 720 from [194]. Copyright (2018) Elsevier. **B).** Schematic illustration of photocatalysis  
 721 mechanism for La<sub>0.7</sub>Ce<sub>0.3</sub>FeO<sub>3</sub>/HNTs. Reproduced with permission from [195].  
 722 Copyright (2016) Springer. **C).** Schematic representation of the photocatalytic activity  
 723 of TiO<sub>2</sub>@HNTs photocatalyst. Reproduced with permission from [99]. Copyright  
 724 (2019) Springer.

725

726           Jatav et al. [196] recently conducted a hydrothermal growth of  $\text{In}_2\text{S}_3$  on  
727 aluminogermanate double-walled imogolite nanotubes. Their investigation involved  
728 using methyl orange (MO) as the target pollutant for assessing photocatalytic  
729 performance. The findings demonstrated that the presence of INT facilitated the  
730 growth of  $\text{In}_2\text{S}_3$  on its surface, while the morphology of  $\text{In}_2\text{S}_3$  was significantly  
731 affected by the reaction time. When the reaction time extended to three and five  
732 hours, the tubular morphology of INT transformed into elongated sheets.  
733 Remarkably, the photocatalytic study revealed that the  $\text{In}_2\text{S}_3$ -decorated INT showed  
734 an improvement in the rate of MO photocatalytic degradation of about 400% when  
735 compared to pristine  $\text{In}_2\text{S}_3$ , despite the composite showing a 14% increase in  
736 bandgap. This improvement in photocatalytic performance was ascribed to the  
737 exceptional mobility of photogenerated holes, which sped up MO's oxidative  
738 processes directly.

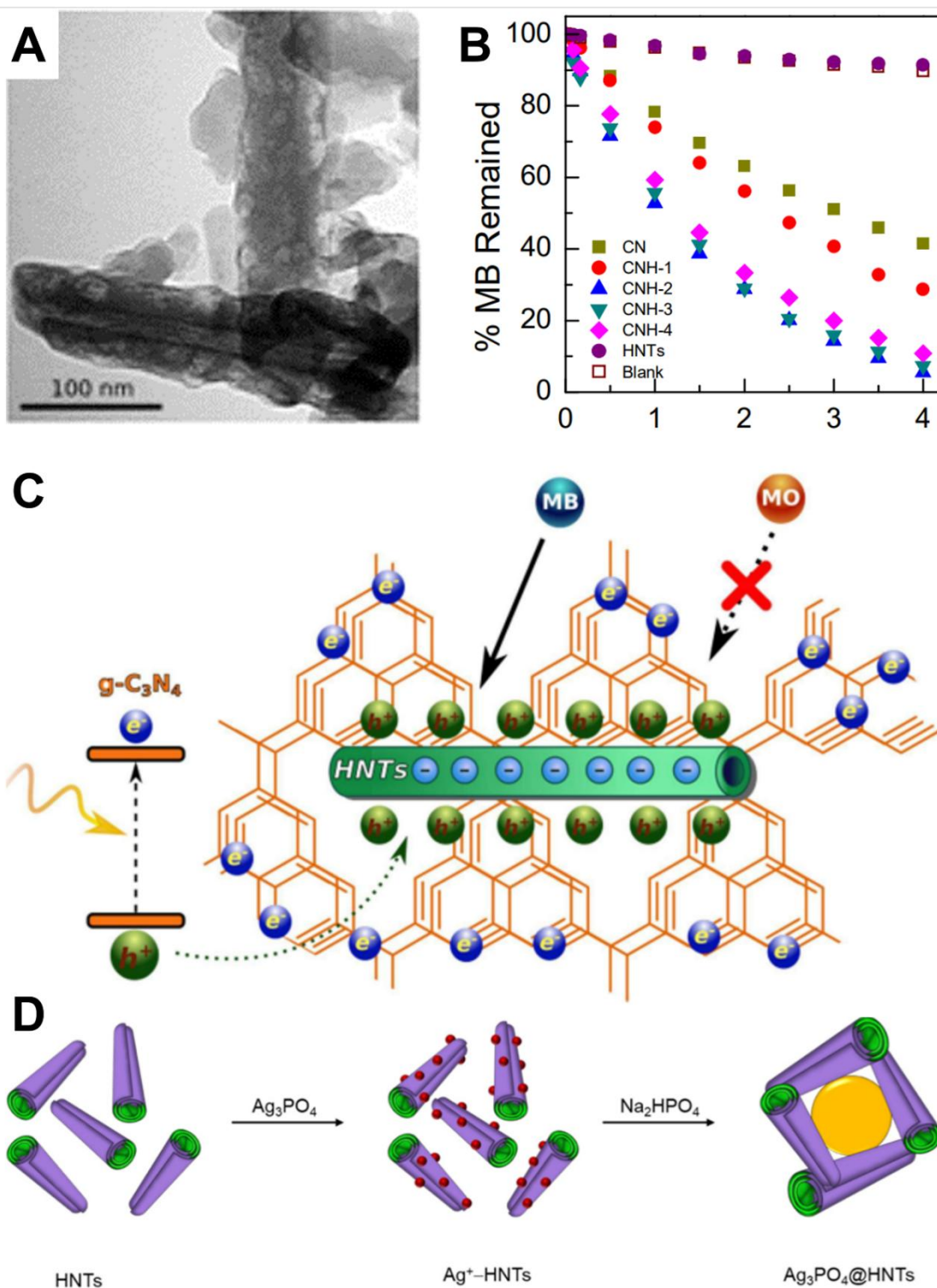
739           A literature survey reveals that using tubular clay minerals increases the  
740 photocatalytic activity of several photocatalyst materials [47,197–200]. Among these  
741 tubular clay materials, Halloysite stands out as one of the most widely used for  
742 photocatalytic applications. Due to its tubular structure and large specific surface  
743 area, it is used as a stabilizer to inhibit nanoparticle aggregation. Christoforidis et al.  
744 [200] exploited the self-assembly method to generate a hetero-architecture of  
745 Halloysite-graphitic carbon nitride ( $\text{gC}_3\text{N}_4$ ) with different mass ratios 2, 4, 6, and 10  
746 wt.% of Halloysite (denoted by CNH-x). Utilizing both pure visible light and solar light  
747 simulation, the composites were then tested for the photodegradation of neutral,  
748 positively, and negatively charged pollutants, including methyl orange (MO), phenol,  
749 and MB. TEM images (**Fig, 15A**) proved that the deposition of small-sized  $\text{gC}_3\text{N}_4$   
750 sheets onto the halloysite surface showed no apparent aggregation. It has been

751 experimentally provided that various compositions of Hall@gC<sub>3</sub>N<sub>4</sub> composites  
752 exhibited photocatalytic activities greater than bare Halloysite and gC<sub>3</sub>N<sub>4</sub>. The best  
753 composite, CNH-2 catalyst (the one containing 4 wt% of HNTs), was able to degrade  
754 MB dye within 4h under solar light (**Fig, 15B**). Moreover, after four cycles of MB  
755 degradation under solar-like light irradiation, the CNH-2 composite displayed no  
756 noticeable decline in photocatalytic activity, signifying its remarkable photostability.  
757 Moreover, adding HNTs into gC<sub>3</sub>N<sub>4</sub> led to an improvement in photocatalytic activity  
758 compared to gC<sub>3</sub>N<sub>4</sub> alone for the degradation of neutral and positively charged  
759 pollutants. This enhancement was attributed to the electrostatic interaction between  
760 the negatively charged Halloysite surface and the photogenerated e<sup>-</sup>/h<sup>+</sup> in gC<sub>3</sub>N<sub>4</sub>,  
761 which reduced charge carrier recombination rate (**Fig, 15C**). The negatively charged  
762 surface of Hal served two purposes in the case of the positively charged pollutant,  
763 such as MB: it enhanced MB adsorption and moved it close to graphitic carbon  
764 nitride. Conversely, the photocatalytic degradation of the negatively charged  
765 substrate, like MO, was similar to that of g-C<sub>3</sub>N<sub>4</sub>. In this case, while the repulsion  
766 between the negatively charged Halloysite and the negatively charged substrate  
767 (MO) had an adverse impact, it actually led to improved charge separation,  
768 consequently boosting the overall activity. Overall, Halloysite nanotubes (HNTs) had  
769 demonstrated to have a double function: (a) improving the abundance and stability of  
770 the photogenerated charges; (b) enhancing the adsorption of MB dye on the  
771 nanocomposite. These two functions are induced by electrostatic forces, combining  
772 attraction and repulsion, stemming from the negatively charged surface of HNTs.

773         Likewise, the negatively charged halloysite nanotube surface combined with  
774 the electrostatic interactions of Ag cations served as a starting point to synthesize a  
775 core-shell structured photocatalyst based on halloysite [199]. Subsequently, the

776 nucleation and growth of  $\text{Ag}_3\text{PO}_4$  led to the formation of  $\text{Ag}_3\text{PO}_4$ @halloysite  
777 nanotubes ( $\text{Ag}_3\text{PO}_4$ @HNTs) nanocomposite (**Fig, 15D**). The nanocomposites  
778 exhibited remarkable photocatalytic effectiveness in decomposing RhB dye under  
779 ultraviolet illumination. The outstanding photocatalytic capabilities of these  
780 photocatalysts were attributed to both halloysite and  $\text{Ag}_3\text{PO}_4$ ; mainly, halloysite  
781 shells' presence guarantees rapid dye adsorption onto the catalyst surface and  
782 concurrently reduces the band gap of  $\text{Ag}_3\text{PO}_4$ , as well as minimizing the  
783 recombination rate. The decrease in recombination was attributed to the lowered  
784 interface defect density and the field-effect passivation produced by the negative  
785 fixed charge within the halloysite shell.

786 Many works have been conducted on the photocatalytic activities of clays  
787 nanotube photocatalysts to remove different types of organic pollutants, as  
788 summarised in Table 1.



789

790 **Fig. 15. A)** TEM images of Halloysite nanotubes@ $\text{g-C}_3\text{N}_4$ , **B)** Photocatalytic  
 791 degradation of MB dye over Halloysite nanotubes@ $\text{g-C}_3\text{N}_4$  under solar light  
 792 irradiation. **C)** Proposed mechanism of the enhanced charge carries separation in  
 793 the Halloysite nanotubes@ $\text{g-C}_3\text{N}_4$  nanocomposites. Reproduced with permission  
 794 from [200], Copyright (2016) Royal Society of Chemistry. **D)** Schematic Illustration of  
 795 core-shell structured  $\text{Ag}_3\text{PO}_4\text{@Hal}$  nanocomposites formation process  $\text{Ag}_3\text{PO}_4\text{@Hal}$   
 796 nanocomposites. Reproduced with permission from [199], Copyright (2017) Elsevier.

797

**Table. 1.** Studies of clay nanotubes photocatalysts for various pollutants

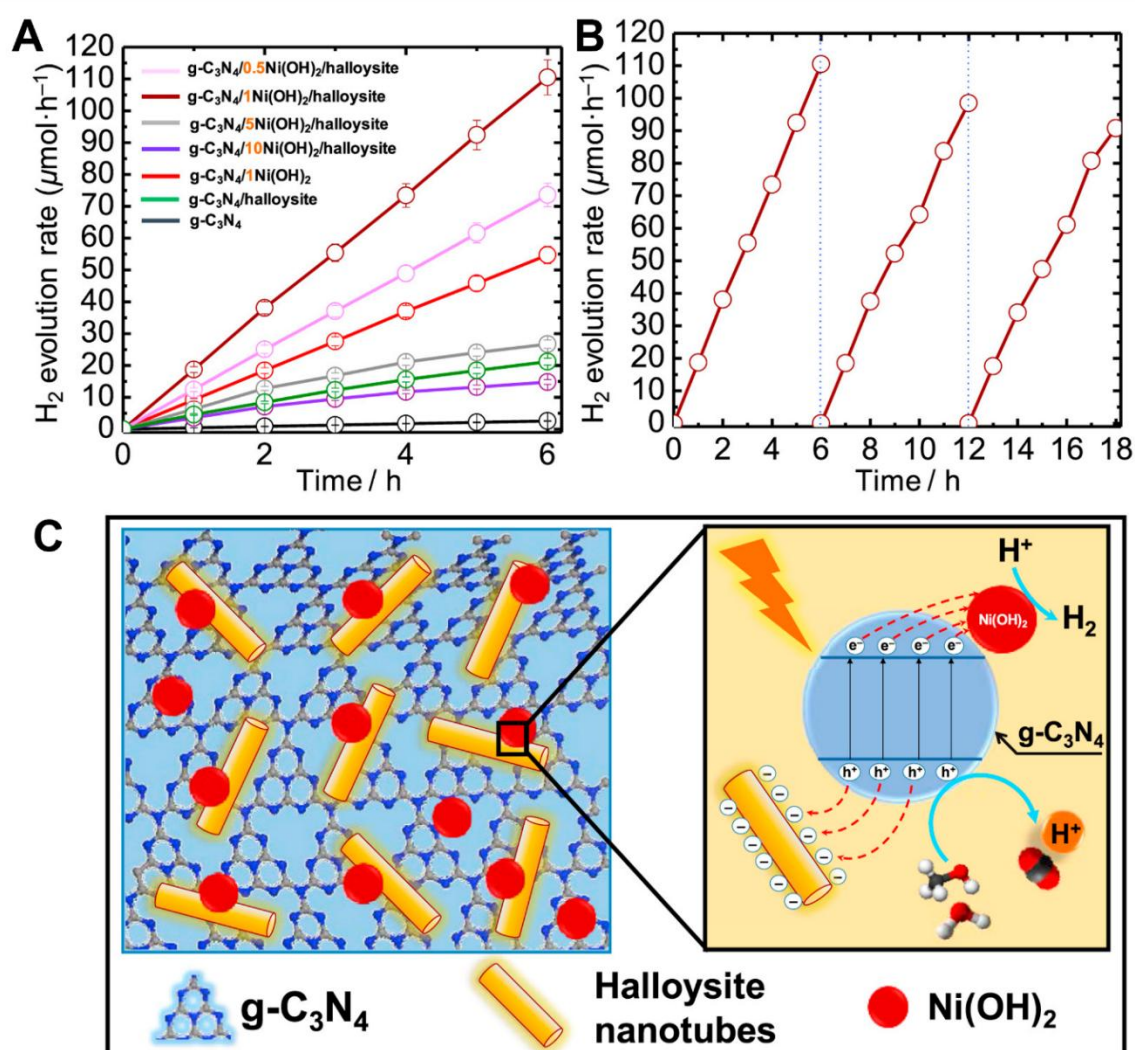
Clay nanotube	Photocatalyst	light source	Pollutants	Photocatalytic degradation activity	Ref
Chrysotile	Chrysotile@SnO <sub>2</sub>	Hg lamp (centered at 450 nm, 250 W)	MB dye	99% (90 min)	[47]
	Chrysotile@ZnO	250 W high-voltage Hg lamp (365 nm)	MB dye	99.5% (60 min)	[45]
	Chrysotile@ZnO	365 nm UV light	4-nitrophenol	39% (300 min)	[98]
	Chrysotile@TiO <sub>2</sub>	Xe light source	CV dye	~66% (240 min)	[201]
Imogolite	Fe-0.050-MeIMO	8 W mercury vapor lamp emitting at 254 nm	TRZ dye	100% (300min)	[202]
	Me-IMO	8 W mercury vapor lamp emitting at 254 nm	TRZ dye	80% (300min)	[202]
	INT-In <sub>2</sub> S <sub>3</sub>	300 W Xe lamp	MO dye	90% (120min)	[196]
	TiO <sub>2</sub> -IMO	UV light lamp (1.0 mW/cm <sup>2</sup> )	CH <sub>3</sub> CH <sub>2</sub>	90% (60min)	[67]
Halloysite	Halloysite@Fe <sub>2</sub> O <sub>3</sub>	UV low pressure Hg immersion lamp TNN 15/32	2,6-dichloroaniline (26DCA)	84.6% (300 min)	[203]
	Halloysite@TiO <sub>2</sub>	UV low pressure Hg immersion lamp TNN 15/32	2-chloroaniline (2CA)	84.9% (300 min)	[203]
	Ag <sub>3</sub> PO <sub>4</sub> -25 wt% HNTs	26 W Sylvania visible lamp.	naproxen sodium	~80% (10 min)	[204]
	La <sub>2</sub> O <sub>3</sub> /CeVO <sub>4</sub> @halloysite	300 W Xenon lamp ( $\lambda \geq 420$ nm)	TC dye	87.1% (60 min)	[205]
	N-TiO <sub>2</sub> / Halloysite	xenon lamp, PLS-SXE300, 300W	phenol	70% (150 min)	[206]
	Ag <sub>2</sub> CO <sub>3</sub> -75 wt.% Halloysite	26 W Sylvania visible lamp	RhB dye	97 % (40 min)	[207]
	CdS@Halloysite	xenon lamp, 500W	TC dye	93% (60 min)	[208]
	Ag@ Halloysite	500 W mercury lamp	TC dye	95.81% (80 min)	[209]
	Ag/AgBr/ Halloysite	200 W xenon lamp with a UV cutoff filter	RhB dye	98%% (30 min)	[210]
	AgNPs@N-Halloysite	500 W xenon lamp	MB dye	90% (60 min)	[211]
	Co <sub>3</sub> O <sub>4</sub> @ Halloysite	60 W high-pressure mercury lamp	MB dye	97 % (120 min)	[197]
	Halloysite@W18O49	300 W Mercury lamp	MO dye	99 % (120 min)	[198]
	Bi <sup>3+</sup> - CdS/Halloysite	500 W xenon lamp	TC dye	90% (30 min)	[212]
	Ce-TiO <sub>2</sub> /HNT	300 W Xe lamp ( $\lambda > 420$ )	Tetracycline	78% (60 min)	[213]
	Carbon-TiO <sub>2</sub> -HNT (8%)	50 W UV lamps ( $\lambda < 420$ nm)	MB dye	81% (90 min)	[214]
	Pani-TiO <sub>2</sub> -HNT (0.5 g/L)	XPA-7 photochemical system (800 W Xe lamp)	RhB dye	76.49 % (360 min)	[215]
Amylose-HNT-TiO <sub>2</sub>	12 W UV lamp ( $\lambda = 253$ nm)	4-nitrophenol	90% (240 min)	[216]	

## 801 4.2. Photocatalytic water splitting

802 Photocatalytic water splitting has been widely explored as a vital clean energy  
803 source. Photogenerated electrons and holes are simultaneously generated when  
804 exposed to light in the general mechanism of photocatalytic water splitting for  
805 hydrogen production. Following this, electrons and holes migrate to the  
806 photocatalyst's surface to participate in the reaction. The photocatalyst's potential  
807 and valence band level should be positioned at a lower energy level than  $H^+/H_2$  and  
808 higher than  $OH^-/O_2$  potential [9,15,217]. To ensure a successful  $H_2$  evolution  
809 reaction, the photocatalyst's conduction band (CB) energy level must be below 0 V  
810 versus the normal hydrogen electrode (NHE) at pH 7. Similarly, for effective  $H_2O$   
811 oxidation, the valence band (VB) energy level should be above 1.23 V versus NHE.  
812 Therefore, theoretically, for water splitting, the lowest bandgap is 1.23 eV. These  
813 energy level requirements are vital to promote favorable redox processes during  
814 photocatalysis. Recently, it was proven that using clay nanotubes could improve  
815 photocatalytic activity and facilitate separation and recycling [205,208].  
816 Hojamberdiev and co-workers [218] stated that the synthesis of a novel  $Ni(OH)_2@g-$   
817  $C_3N_4$ /halloysite composite photocatalyst by mixing an easily prepared  $gC_3N_4$  with  
818 low-cost  $Ni(OH)_2$  nanoplatelets, inexpensive and earth-abundant halloysite  
819 nanotubes. The obtained composite was used as an efficient photocatalyst for  
820 hydrogen evolution. As-prepared photocatalysts' hydrogen evolution reaction activity  
821 was assessed using an aqueous solution with 10 vol% methanol as a sacrificial  
822 agent. The investigation of the  $Ni(OH)_2$  loading effect showed that the 1 wt%  
823  $Ni(OH)_2@g-C_3N_4$ /halloysite photocatalyst exhibited the maximum photocatalytic  
824 hydrogen evolution rate ( $18.42 \mu\text{mol}\cdot\text{h}^{-1}$ ) compared to  $Ni(OH)_2@g-C_3N_4$  ( $9.12$   
825  $\mu\text{mol}\cdot\text{h}^{-1}$ ) and was 40 times higher than  $g-C_3N_4$  alone ( $0.43 \mu\text{mol}\cdot\text{h}^{-1}$ ) (**Fig. 16A**).  
826 Furthermore, 1 wt%  $Ni(OH)_2@g-C_3N_4$ /halloysite photocatalyst showed negligible



827 decrease in  $\text{H}_2$  evolution activity after three cycles (**Fig. 16B**). The halloysite's  
 828 negatively charged surface, which effectively traps photogenerated holes, lowers the  
 829 rate of electron-hole recombination, and lengthens the electron lifespan, provided an  
 830 explanation for these results (**Fig. 16C**). Moreover, a computational model was  
 831 employed to assess the adsorption properties of  $\text{H}_2\text{O}$  and  $\text{MeOH}$  molecules on the  
 832 catalyst surface. The findings indicated that the presence of halloysite,  $\text{g-C}_3\text{N}_4$  and  
 833  $\text{Ni(OH)}_2$  enhanced the adsorption of water and methanol on the co-catalyst surface.



834

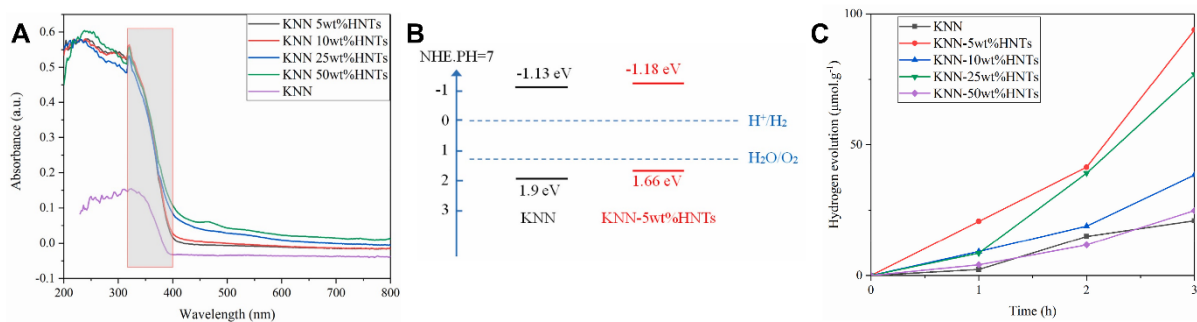
835 **Fig. 16. A)**  $\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4/\text{halloysite}$  nanocomposites: reaction time courses of  
 836 visible light-driven hydrogen evolution. **B)** Reaction time courses of visible-light-  
 837 driven hydrogen evolution on  $1.0\text{Ni(OH)}_2/\text{g-C}_3\text{N}_4/\text{halloysite}$  nanocomposite for three  
 838 successive runs. **C)** Graphical representation of the evolution of photocatalytic  
 839 hydrogen evolution over developed nanocomposites, showing the separation and



840 transfer of photogenerated charge carriers. Reproduced with permission from [218],  
841 Copyright (2019) Elsevier.

842

843 Recently, Lu et al. [219] successfully synthesized several  
844  $K_{0.5}Na_{0.5}NbO_3$ /halloysite nanocomposites by changing the halloysite concentration  
845 from 0 to 25 wt.% via a solid phase reaction process. These hybrid samples were  
846 then used to analyze the photocatalytic hydrogen evolution performance under UV  
847 light illumination (Xenon arc lamp). The authors demonstrated that by incorporating  
848 halloysite (HNTs), the absorption spectrum of  $K_{0.5}Na_{0.5}NbO_3$  (KNN) exhibited a  
849 substantial enhancement in the UV region, with the absorption intensity in the 200-  
850 300 nm range increasing approximately two-fold (**Fig. 17A**). Introducing HNTs into  
851 KNN reduced the band gaps from 3.03 eV to 2.64 eV (**Fig. 17B**). Moreover, the  
852 authors demonstrated that the conduction band ( $E_{CB}$ ) of KNN-5wt%HNTs  
853 nanocomposite was changed to a lesser value from -1.13 eV to -1.18 eV compared  
854 with the pure  $K_{0.5}Na_{0.5}NbO_3$ , providing more straightforward water reduction to  
855 hydrogen. Notably, the composite material KNN-5wt%HNTs demonstrated an  
856 excellent hydrogen production performance ( $31.28 \mu\text{mol}\cdot\text{g}^{-1} \text{h}^{-1}$ ) under UV light  
857 irradiation, producing 4.48 times as much  $H_2$  as  $K_{0.5}Na_{0.5}NbO_3$ . (**Fig. 17C**). The  
858 findings of this study confirm that the judicious incorporation of halloysite can  
859 improve  $H_2$  production efficiency.



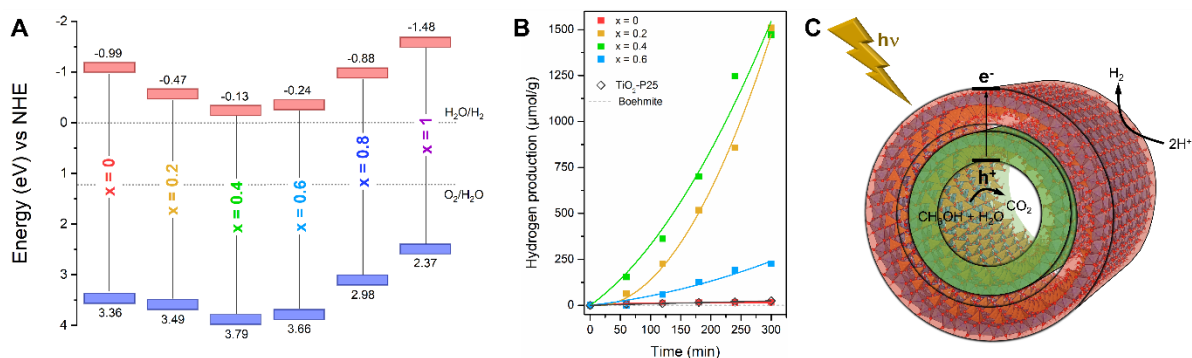
860

861 **Fig. 17.**  $K_{0.5}Na_{0.5}NbO_3$ -halloysite nanotubes composites. **A)** Spectra of optical  
862 absorption, **B)** illustrative sketch of the energy band structures and **C)** hydrogen

863 evolution reaction for different composites. Reproduced with permission from [219],  
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865

866 In a recent research conducted by our research group [220], we achieved a  
867 milestone in literature by modifying double-walled aluminogermanate INTs through  
868 the incorporation of titanium into the NT walls. The precursor ratio, denoted as  $x =$   
869  $[Ti]/([Ge]+[Ti])$ , was varied between 0 and 1. The optical properties of the catalysts  
870 we prepared revealed a significant reduction in the band gap ( $E_g$ ) energy from 4.35  
871 eV (for pristine Ge-DWINT) to 3.96 eV ( $x = 0.2$ ) and further to 3.92 eV ( $x = 0.4$ ).  
872 Increasing the Ti/Ge ratio consistently decreased the  $E_g$  to 3.85 eV. Additionally, Ti-  
873 doping initially caused a downward shift of the VB edge (0.13 and 0.43 eV for ratios  
874 of 0.2 and 0.4, respectively), followed by an upward shift with further increases in the  
875 Ti/Ge ratio. A similar trend was observed for the CB edge, which shifted down to -  
876 0.13 eV (for a ratio of 0.4) and up to -1.43 eV (**Fig. 18A**). Interestingly, this evolution,  
877 with an optimum around  $x = 0.4$ , coincided with the disappearance of nanotubes in  
878 favor of boehmite and anatase phases. We examined the photocatalytic properties of  
879 the prepared photocatalysts for  $H_2$  production under artificial solar-light irradiation to  
880 assess the impact of Ti-doping. Optimal ratios were determined at  $x = 0.2$  and  $x =$   
881 0.4, yielding  $H_2$  production rates of 1509 and 1472  $\mu\text{mol g}^{-1}$ , respectively (**Fig. 18B**).  
882 These rates surpassed those of the composites, bare reference, and  $TiO_2$  P25  
883 benchmark NP SC. The enhanced photoactivity stemmed from the narrowed band  
884 gap and downward shifts of the CB edges in both composites. As illustrated in **Fig.**  
885 **18C**, photogenerated charges ( $e^-/h^+$ ) trigger dissociative adsorption of sacrificial  
886 electron donors (SED) and hole scavenging, leading to the release of hydrogen ions  
887 ( $H^+$ ) within the nanotube's internal cavity. Reduction, resulting in  $H_2$  formation,  
888 predominantly occurs on the outer surface of the nanotubes, while oxidation  
889 predominantly occurs within the nanotubes.



890

891 **Fig. 18. A)** energy diagram scheme of the Ti/Ge samples as a function of the  
 892 substitution ratio. **B)** Hydrogen evolution reaction under solar-light irradiation for a)  
 893 Ge-DWINT and Ti/Ge samples with different ratios. **C)** Schematic illustration of the  
 894 proposed H<sub>2</sub> production mechanism. Reproduced with permission from [220],  
 895 Copyright (2023) wiley.

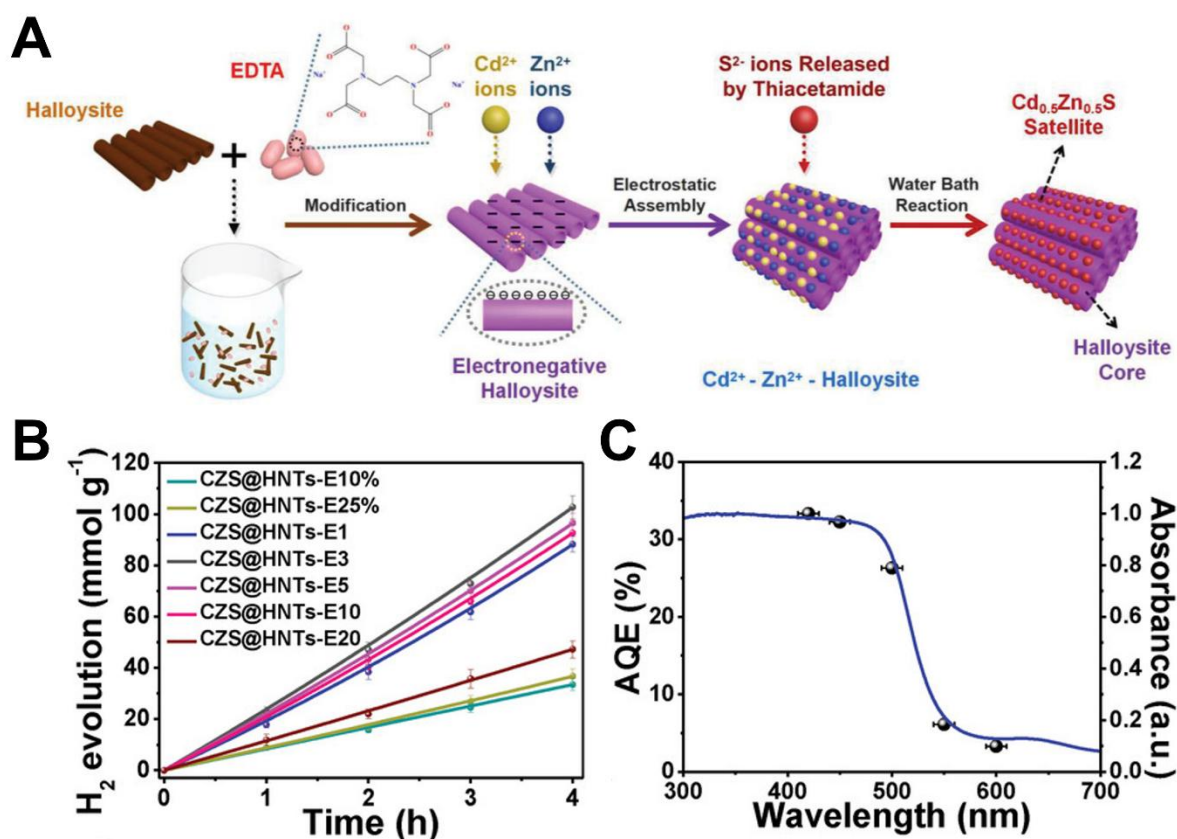
896

897 In an intriguing study conducted by Zhang et al. [221], they fabricated a  
 898 satellite-core structured Cd<sub>0.5</sub>Zn<sub>0.5</sub>S@halloysite hollow nanotubes with a 0D-1D  
 899 configuration, modified by EDTA with varying amounts, denoted as CZS@HNTs-EX.  
 900 This was achieved through a facile in-situ assembly approach for photocatalytic H<sub>2</sub>  
 901 evolution. As depicted in **Fig. 19A**, the organic solvent EDTA was initially employed  
 902 to modify the halloysite, rendering its surface negatively charged. Then, because of  
 903 the electrostatic attraction Cd<sup>2+</sup> and Zn<sup>2+</sup> cations were added and adsorbed onto the  
 904 halloysite. The addition of thioacetamide finally caused the Cd<sub>0.5</sub>Zn<sub>0.5</sub>S nanospheres  
 905 to grow in situ on the surface of the halloysite that had been modified by EDTA. It  
 906 was highlighted in this work that the CZS@HNTs-E3% composite exhibited an  
 907 appealing photocatalytic H<sub>2</sub> evolution after 4 hours of illumination with a yield of  
 908 102.67 mmol g<sup>-1</sup> (**Fig. 19B**) and high apparent quantum efficiency (AQE) of 32.29%  
 909 at λ = 420 nm, higher than majorities of H<sub>2</sub> evolution photocatalysts (**Fig. 19C**). Only  
 910 a slight decrease in H<sub>2</sub> production was observed after five cycles, while maintaining  
 911 the crystallinity and morphology of the CZS@HNTs-E3% hollow nanotubes. This  
 912 highlights the potential of recyclable catalysts for industrial applications.

913 Furthermore, the authors demonstrated that the enhancement of the photocatalytic  
914 of CZS@HNTs-EX was attributed to the succeeding factors: I) the hollow  
915 architecture of halloysites caused by several reflections and scattering of light within  
916 the cavity, extending the optical transmission path and enhancing the light utilization.  
917 II) Halloysites allow an excellent dispersion of  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ , promoting the diffusion of  
918 charge carriers to the catalyst-solution interface. III) EDTA embedded on halloysites  
919 draws and uses considerable photogenerated  $\text{h}^+$ , promoting the charge separation of  
920  $\text{e}^-$  and  $\text{h}^+$ , permitting more  $\text{e}^-$  to migrate to the surface of  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$  for participation  
921 in the reductive reaction. IV) Owing to the  $\text{h}^+$  capture, the  $\text{h}^+$ -dominated photo-  
922 oxidation of  $\text{S}^{2-}$  in  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$  is hindered, causing excellent photochemical stability  
923 in CZS@HNTs-E3.

924 As far as we are aware, no research has been conducted on the utilization of  
925 imogolite or chrysotile for photocatalytic water splitting. It is, therefore, important to  
926 pursue efforts in this direction. Given the success of halloysite-based composites in  
927 promoting photocatalytic hydrogen evolution, it is reasonable to believe that  
928 imogolite and chrysotile might exhibit similar or superior effects.

929



930

931 **Fig. 19. A)** Schematic representation of the EDTA-mediated CZS@HNT synthesis  
 932 process. **B)** Hydrogen evolution time courses for CZS@HNTs-EX samples with  
 933 varying EDTA to halloysite mass ratios. **C)** Photocatalytic performance of  
 934 CZS@HNTs-E3 under monochromatic light irradiation: UV-vis spectrum and  
 935 wavelength dependence. Reproduced with permission from [221], Copyright (2019)  
 936 WILEY.

937

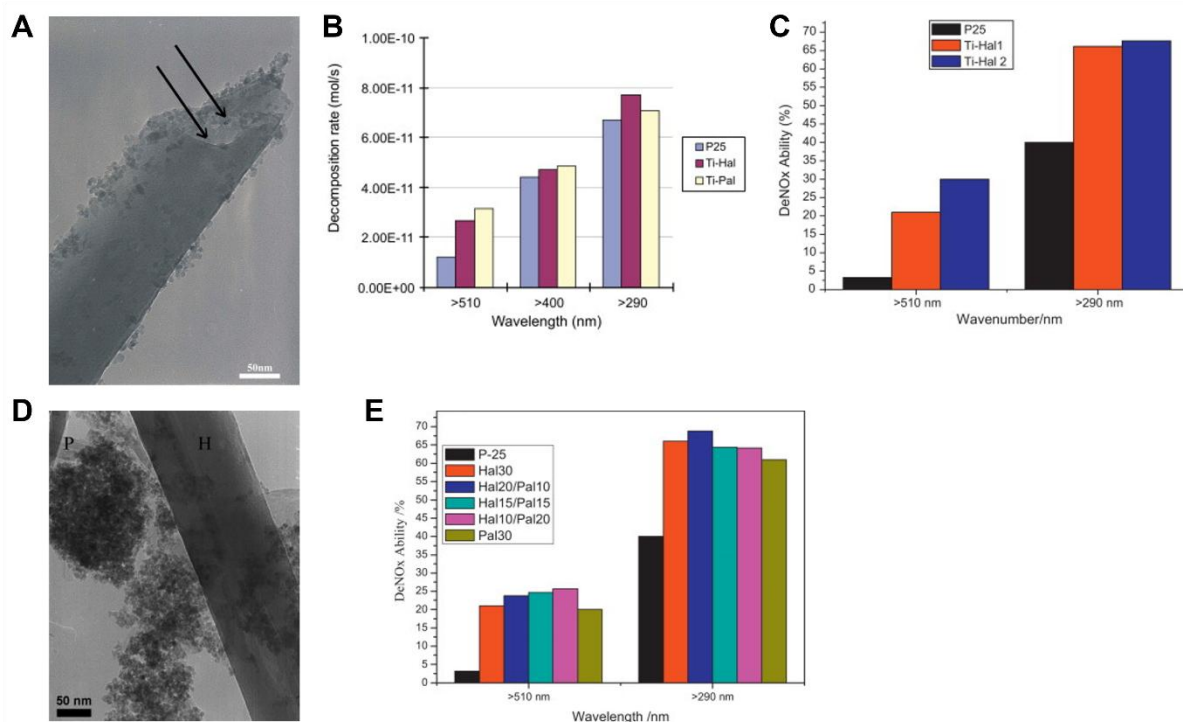
### 938 4.3. Photocatalytic removal of NO<sub>x</sub>

939 Nitric oxide (NO<sub>x</sub>) emission into the atmosphere is causing increasing concern.  
 940 This pollutant is produced through fossil fuel utilization and combustion of industrial  
 941 burners. The NO<sub>x</sub> emitted into the atmosphere causes acid rain [221–224], climate  
 942 changes, and ozone layer destruction [222,223]. Thus, its quantitative removal or  
 943 reduction is highly desired. In fact, numerous catalytic processes for the conversion  
 944 of nitrogen gases (e.g., NO and NO<sub>2</sub>) into oxygen (O<sub>2</sub>), nitrogen (N<sub>2</sub>), or nitrate (NO<sub>3</sub><sup>-</sup>  
 945 ) have been developed, including adsorption, selective catalytic reduction,  
 946 nonselective catalytic reduction, wet scrubbing, and biofiltration. However, these

947 techniques can only be used to treat NO<sub>x</sub> in extreme concentrations; their efficiency  
948 and economic benefits are reduced at lower NO<sub>x</sub> concentrations. Currently, for low-  
949 concentration NO<sub>x</sub> in the air at room temperature, the photocatalytic removal of NO<sub>x</sub>  
950 is regarded as a green and low-cost technology and has attracted much attention.  
951 Indeed, some studies have removed or reduced the NO<sub>x</sub> through clay nanotube  
952 systems. For instance, to remove NO<sub>x</sub> in the presence of UV and Visible light  
953 irradiation, Papoulis et al. [224] reported a sol-gel approach for forming  
954 TiO<sub>2</sub>@halloysite nanocomposites. This was performed under hydrothermal  
955 conditions with a halloysite sample from Limnos Island in Greece. The TEM results  
956 of the as-prepared nanocomposite exhibited an excellent distribution of TiO<sub>2</sub> on the  
957 external surfaces of the halloysite nanotube (**Fig. 20A**). The halloysite acts as a clay  
958 stabilizer, preventing the aggregation of nanoparticles because of its substantial  
959 specific surface area and its tubular surface [197,198]. The photocatalytic results  
960 clearly show that the as-prepared TiO<sub>2</sub>@halloysite nanocomposite has significantly  
961 better photocatalytic efficiency in decomposing NO<sub>x</sub> gas when exposed to UV ( $\lambda =$   
962 290 nm) and visible light ( $\lambda = 510$  nm) illumination: these are, respectively, 2.61 and  
963 1.15 times higher than pristine commercial TiO<sub>2</sub> (P25), (**Fig. 20B**). The well-  
964 dispersed TiO<sub>2</sub> has explained this higher activity on the halloysite surface. The same  
965 research group used the same method to synthesize two TiO<sub>2</sub>@halloysite  
966 nanocomposites, utilizing halloysite from two distinct geographical regions: Greece  
967 and the USA [68]. The two clays showed a good dispersion of TiO<sub>2</sub> NPs in their  
968 respective nanocomposites, and both had interparticle mesopores measuring  
969 approximately 5.7 nm. It was observed that both nanocomposites demonstrated  
970 promising photocatalytic performance for the NO<sub>x</sub> gas decomposition under visible  
971 light ( $\lambda = 510$  nm) and UV light irradiation ( $\lambda = 290$  nm) (**Fig. 20C**). The

972 TiO<sub>2</sub>@halloysite nanocomposite with halloysite from the USA demonstrated higher  
973 photocatalytic performance, likely due to its larger specific surface area. (187 m<sup>2</sup>/g).

974 Furthermore, it also revealed considerably improved photocatalytic activity for  
975 NO<sub>x</sub> gas decomposition under visible light ( $\lambda = 510$  nm) and UV light irradiation ( $\lambda =$   
976 290 nm), which are, respectively, 9.38 and 1.69 times higher than pristine  
977 commercial TiO<sub>2</sub> (P25) (**Fig. 20C**). In another study by the same research group  
978 [225], a three-phase nanocomposite was prepared using two distinct nanoclay  
979 minerals, halloysite, and palygorskite, in combination with TiO<sub>2</sub> (denoted by Hal:  
980 PAL-TiO<sub>2</sub>) (**Fig. 20D**). The authors demonstrated that the Hal:PAL-TiO<sub>2</sub>  
981 nanocomposite exhibited a grey color with enhanced absorption in the visible light  
982 region compared to titania P25, which showed no absorption in the same region. The  
983 photocatalytic activity of these systems was further evaluated in this system by  
984 decomposing the NO<sub>x</sub> gas as a function of irradiation time. The results  
985 demonstrated that the Hal:PAL-TiO<sub>2</sub> nanocomposite displayed significantly higher  
986 activity than the commercial TiO<sub>2</sub> P25 under both UV and visible light irradiation, with  
987 up to 8 times higher efficiency under UV light and 1.72 times higher efficiency under  
988 visible light (**Fig. 20E**).



989

990 **Fig. 20. A)** TEM images showing TiO<sub>2</sub> grains of about 3–15 nm on halloysite tubes  
 991 **B)** Photocatalytic activities in decomposing NO<sub>x</sub> gas by commercial titania P25,  
 992 TiO<sub>2</sub>-treated halloysite (Ti-Hal) and TiO<sub>2</sub>-treated palygorskite. Reproduced with  
 993 permission from [224], Copyright (2010) Elsevier. **C)** Photocatalytic activities in  
 994 decomposing NO<sub>x</sub> gas by commercial titania P25, TiO<sub>2</sub>-treated halloysite (from  
 995 Greece) and TiO<sub>2</sub>-treated halloysite (from USA). Reproduced with permission from  
 996 [68], Copyright (2013) Elsevier. **D)** TEM micrographs showing the three-phase  
 997 nanocomposites Hal10:Pal20-TiO<sub>2</sub>. **E)** Photocatalytic activity for NO<sub>x</sub> gas  
 998 decomposition by commercial titania (P25), single clay-TiO<sub>2</sub>, and three-phase  
 999 nanocomposites. Reproduced with permission from [225], Copyright (2014) Elsevier.

1000

#### 1001 4.4. Photocatalytic disinfection of bacteria

1002 Disinfection of bacteria is of particular importance. Numerous efforts have been  
 1003 dedicated to developing environmentally friendly technologies for disinfecting  
 1004 microorganisms in water [226–228]. However, despite traditional water disinfection  
 1005 technologies such as ozone, chlorination, and ultraviolet methods, they have many  
 1006 disadvantages. For example, they may be chemically or energy-demanding and  
 1007 produce toxic by-products. Photocatalytic disinfection of bacteria, on the other hand,  
 1008 is a non-toxic and eco-friendly process that does not create any harmful by-products.

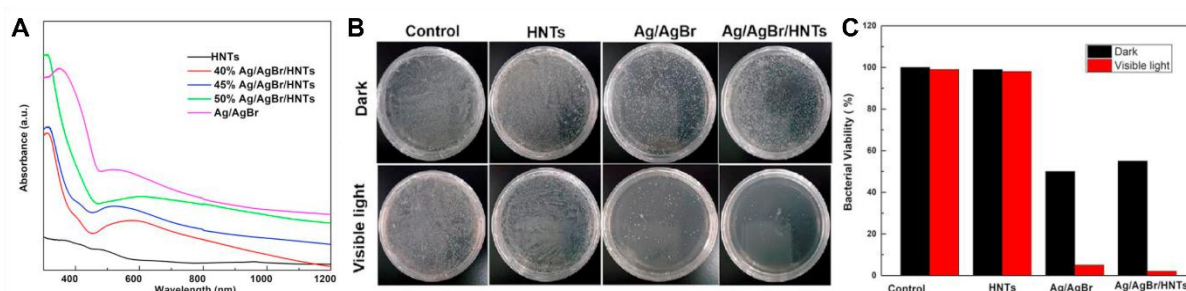


1009 Escherichia coli is a reliable indicator of water quality concerns within the diverse  
1010 spectrum of bacteria, often signaling potential fecal contamination due to its  
1011 presence [226]. The performance of nanotube clay photocatalysts in such  
1012 applications has been recently investigated. For instance, Xu et al. [210] successfully  
1013 synthesized a novel composite consisting of Ag/AgBr/halloysite nanotube via a facile  
1014 sol-gel method and used it to kill gram-negative bacterium *E. Coli* when exposed to  
1015 visible light. This study's findings revealed that all Ag/AgBr/halloysite  
1016 nanocomposites exhibited strong absorption in the range of 300 to 1000 nm (**Fig.**  
1017 **21A**). Furthermore, according to the PL spectrum, the Ag/AgBr/halloysite nanotube  
1018 emitted relatively weak light compared to Ag/AgBr alone, signifying higher separation  
1019 of the photoexcited electron-hole pairs in the composites and indicating enhanced  
1020 photocatalytic activity. According to the findings of this study, it was found that when  
1021 the bacteria was treated with 45% Ag/AgBr/halloysite nanotube composite under  
1022 irradiation, up to 98% of *E. Coli* was killed, surpassing the efficacy of Ag/AgBr alone  
1023 under the same conditions (**Fig. 21B and 21C**). Based on this study's experimental  
1024 observation and characterization results, the formation of the composite is the key  
1025 factor behind the increased photocatalytic disinfection of bacteria.

1026 In the presence of the Ag/AgBr/halloysite nanotube composite, the photocatalytic  
1027 mechanisms are as follows: first, the halloysite nanotube serves as the supporting  
1028 structure in the composite, preventing the decomposition of Ag/AgBr particles; then,  
1029 the charged surface of the halloysite efficiently improves the separation of electron-  
1030 hole pairs and promotes the adsorption of *E. Coli*.

1031 The earlier studies show that halloysite has received considerable attention as a  
1032 photocatalyst. However, it is essential to highlight that research concerning the use  
1033 of imogolite or chrysotile for photocatalytic bacterial disinfection has been scarcely

1034 explored. This is not so surprising in the case of chrysotile since these nanotubes  
1035 are known to be toxic, limiting their use. For imogolite nanotubes, some research  
1036 groups have explored their potential for treating pathogenic bacteria without  
1037 employing photocatalysis techniques [229,230]. While these investigations represent  
1038 a valuable exploration of imogolite's antimicrobial properties, they also emphasize  
1039 the need for additional research to unlock its full potential for combating bacterial  
1040 contamination.



1041 **Fig. 21. A)** UV-Vis absorption spectra of Ag/AgBr/Halloysite nanotube  
1042 nanocomposite. **B)** Photographs of colonies of *E. coli* treated with HNTs, Ag/AgBr,  
1043 and 45%Ag/AgBr/HNTs without and with visible light irradiation, respectively; **C)**  
1044 Histograms of *E. coli* viability. Reproduced with permission from [210], Copyright  
1045 (2021) Elsevier.

## 1047 5. Conclusion and future perspectives

1049 Nanosized tubular clay materials have garnered significant interest due to  
1050 their distinctive physicochemical characteristics. The most representative examples  
1051 of tubular clay materials are imogolite, halloysite, and chrysotile. Although these  
1052 clays have similar morphology, their chemical structure and properties differ.

1053 Considering that these nanotubular clay materials have a high surface area  
1054 arising from their nanotubular structure, large pore volumes, higher adsorption  
1055 capacity, and good mechanical properties, they could offer a wide range of promising  
1056 applications in photocatalysis. Moreover, these tubular clays also serve as easily

1057 obtainable and low-cost supports to prevent the aggregation of semiconductor  
1058 materials. However, the only drawback of using these materials as photocatalysts is  
1059 their wide band gap, which limits their potential in photocatalytic reactions.

1060 Thus, the primary aim of this review has been to compile an extensive  
1061 overview over several decades, including the recent trends in the development of  
1062 imogolite, halloysite, and chrysotile, as well as their main physicochemical  
1063 properties. Furthermore, we have systemically provided an overview of current  
1064 research progress on these materials for photocatalytic applications, mainly focusing  
1065 on their intrinsic merits and the challenging aspects of photocatalysis. This review  
1066 has also elucidated their versatile photocatalytic applications, including the  
1067 decomposition of organic dye contaminants, selective organic transformation via  
1068 photocatalysis, hydrogen generation, bacterium disinfection, and reducing nitrogen  
1069 oxide (NO<sub>x</sub>) pollution.

1070 Although research has been done on using clay nanotubes as photocatalysts,  
1071 substrates, or in combination with other photocatalysts in heterogeneous  
1072 photocatalysis, most investigations in this domain remain in their early stages.  
1073 Therefore, based on this review, future research should prioritize the following  
1074 aspects:

1075 (i) Most current research combines imogolite, halloysite, and chrysotile with  
1076 traditional semiconductors (such as TiO<sub>2</sub> and ZnO). Future research should  
1077 attempt to combine these clays with new semiconductors. For example, it is  
1078 possible to develop a co-catalyst without precious metals that can be added to  
1079 these clay nanotube-based photocatalysts. In addition, the cost should be  
1080 carefully considered for industrial applications.

- 1081 (ii) Although numerous studies have examined the photocatalytic capabilities of  
1082 clay nanotube-based nanocomposites in degrading dye pollutants, most of  
1083 these works have focused solely on MB, RhB, TC, and MO dyes. Therefore, it  
1084 is imperative to extend the range of organic pollutants like antibiotics, drug  
1085 components, and pesticides to assess the photocatalytic degradation potential  
1086 of such materials comprehensively.
- 1087 (iii) This review also recommends using actual polluted water instead of  
1088 simulated wastewater and emphasizes the importance of measuring  
1089 degradation efficiency through parameters such as TOC removal  
1090 percentage. Standardization of measurements is also desirable in order to  
1091 compare the different systems, particularly in terms of stability.
- 1092 (iv) Undoubtedly, there is a substantial need for in-depth research to elucidate  
1093 the detailed photocatalytic mechanism of clay nanotubes. This requires the  
1094 utilization of innovative characterization and computational methods,  
1095 including but not limited to density functional theory (DFT). Such  
1096 investigations are crucial for enhancing our understanding of these materials  
1097 and their photocatalytic processes. There are many more photocatalytic  
1098 experiments in reducing CO<sub>2</sub> in the presence of imogolite, halloysite, and  
1099 chrysotile that can be done. This research field seems promising and, to our  
1100 knowledge, has not yet been investigated by any researcher, nor has there  
1101 been any published data.
- 1102 (vi) Future experimental research will be motivated by imogolite's potential to  
1103 improve polarization in photocatalytic applications, given its natural  
1104 polarizability and ease of manufacture. This implies that imogolite will soon be  
1105 used for energy conversion, adding a new substance to the vast field of  
1106 photocatalysis.

1107 (vii) The current research on imogolite, halloysite, and chrysotile photocatalysts  
1108 predominantly centers around small-scale laboratory investigations. The focus  
1109 should shift towards creating environmentally friendly large-scale preparation  
1110 methods in the future.

1111 Compared to similar nanotube materials, like CNTs, the current study of clay  
1112 nanotube photocatalysts still needs to be improved. From the number of applications  
1113 reported in our review article, we conclude that halloysite, chrysotile, and imogolite  
1114 are versatile materials that can provide new opportunities and directions in the field  
1115 of photocatalysis.

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1119

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