

1 **Polymer and graphitic carbon nitride based nanohybrids for the photocatalytic**  
2 **degradation of pharmaceuticals in wastewater treatment – a review**

3

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## 20 ABSTRACT

21 Pharmaceuticals, including antibiotics and anti-inflammatory drugs, have been frequently  
22 detected in water reservoirs, in concentrations ranging from ng/L to µg/L, owing to their wide  
23 use in treatment of human and animal disease. Their uncontrolled use results in their in-  
24 creased release into the environment which is harmful for humans, animals, aquatic life and  
25 aquatic system. To remove these pollutants from water bodies, various processes including  
26 adsorption, membrane and bioreactors have been employed. Among them photocatalysis is  
27 one of the most advantageous treatment. Application of advanced chemical treatment, includ-  
28 ing advanced oxidation or reduction processes (AOPs or ARPs) based on organic-inorganic  
29 nanohybrids (OINHs) as photocatalysts revealed high effectiveness. OINHs are combination  
30 of two or more components which are organic and inorganic in nature. These materials have  
31 been synthesized by various methods and offers novel features owing to synergistic effect of  
32 their component. These materials are synthesized through sol-gel, surface functionalization,  
33 one pot synthesis, wrapping, and electrospinning methods. Organic components are essential  
34 in enhancing photocatalytic activity through increasing stability, surface area, functionality  
35 and light responsiveness of nanohybrid. Reports suggest >99% degradation of studied phar-  
36 maceuticals by these type of photocatalysts in time range of 30-60 minutes. High effective-  
37 ness was reported for carbamazepine, ciprofloxacin, diclofenac, ibuprofen, naproxen, parace-  
38 tamol, sulfamethoxazole and tetracycline. This review summarizes recent literature on appli-  
39 cation of OINHs i.e. graphene oxide, g-C<sub>3</sub>N<sub>4</sub>, and polymer based nanohybrids, in photocata-  
40 lytic removal of pharmaceuticals from wastewater via AOPs while elaborating on toxicity of  
41 pharmaceuticals, synthesis of OINHs and degradation mechanism of pharmaceutical drugs.  
42 Current challenges faced in this field as well as future recommendations are also discussed.

43



44 **Keywords:** Organic-inorganic Nanohybrids; Z-scheme Heterojunction; Photocatalytic Deg-  
45 radation; Water Treatment; Electrospinning; Environmental Pollutants; Emerging Organic  
46 Contaminants EOCs; Radicals; Metal Oxides; TiO<sub>2</sub>.

47

## 48 **1. Introduction**

49 Pharmaceuticals are defined in broad term as therapeutic drugs that are used to cure and/or  
50 prevent diseases in human beings; antibiotics, nonsteroidal anti-inflammatory drugs  
51 (NSAIDs), anticonvulsants, analgesics, chemotherapeutics, and  $\beta$ -blockers are common clas-  
52 ses of pharmaceutical products that are used commonly [1, 2]. Uncontrolled and excessive  
53 use of pharmaceuticals results in their untreated release into the environment. Main sources  
54 of pharmaceuticals release into aquatic systems are untreated effluents from hospitals, munic-  
55 ipal plants, landfill leachate, surface run off, and illegal disposal[3-6]. Recent studies report  
56 release of 30-90% active and non-metabolized antibiotics into environment through urine and  
57 feces[7, 8]. This emerging class of water pollutants negatively affect human life and aquatic  
58 environment. For instance, excess of acetaminophen results in deadly liver damage as well as  
59 skin problem [9, 10]. Presence of antibiotics such as amoxicillin, tetracycline, and ampicillin  
60 in aquatic system results in generation of antibiotics resistance strains of bacteria [11-17].  
61 Conclusively pharmaceuticals in water bodies are highly hazardous for human and aquatic  
62 life as well. These pollutants accumulate in ecosystem owing to their persistent nature and  
63 slow degradation rate. Their removal is further necessitated by their recalcitrant chemical  
64 and physical properties and accumulation in environmental food chain [18, 19]. To protect  
65 human and animal in particular and ecosystem in general, elimination of such persistent and  
66 eco-toxic pharmaceutically active compounds from water bodies is a crucial step that needs  
67 immediate attention. Typically, pharmaceuticals are present in treated water bodies in the  
68 range of ng/L to  $\mu\text{g/L}$  [20, 21]. Owing to their physiochemical properties, such as high vola-  
69 tility, polarity, lipophilicity, and persistence, and quantity in water, conventional treatments  
70 are not suitable for their removal[22].



71 In recent decades, advanced treatment processes for water treatment have gained increasing  
72 interest among researchers and these include electrochemical reduction[23], membrane filtra-  
73 tion [24, 25], precipitation [26], electrodialysis [27], photocatalysis [28, 29], cavitation[30,  
74 31], percarbonate-[32] and persulfate-based processes[33], and electrodeionization [34].  
75 Photocatalysis is one of the advanced oxidation processes (AOPs) that has been regarded as a  
76 promising technology due to its high efficiency[29, 35, 36]. In photocatalysis, pharmaceuti-  
77 cals are degraded into simple molecules through their reaction with photogenerated reactive  
78 chemical species on the surface of photocatalyst. Photocatalyst is a substance or material that  
79 determines the rate of photocatalytic reaction, thus, its design and fabrication are crucial steps  
80 and have been considered a challenge that is being faced with deep interest by the research  
81 community [37-39].

82 There is a lot of research on synthesis of photocatalysts and their application in removal of  
83 pharmaceuticals from water through advanced oxidation processes and these photocatalysts  
84 include  $\text{TiO}_2$ ,  $\text{ZnS}$ ,  $\text{NiS}$ ,  $\text{CuS}$ ,  $\text{HgO}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{BiOBr}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{BiVO}_2$ ,  $\text{BiS}$ ,  $\text{ZnO}$  and organic-  
85 inorganic nanohybrids (OINHS) [39-45]. Among all these photocatalysts, OINHS are unique  
86 a class of materials with efficient catalytic activity due to certain features that result from  
87 combination of their organic and inorganic components. Organic component provide en-  
88 larged surface area of OINHS which increases photoactive sites and promote charge carrier  
89 production. Organic components are high light absorbing materials and this property is en-  
90 hanced by inorganic component. Structural stability is one of prerequisite of photocatalysis,  
91 OINHS offer high structural stability owing to its highly stable organic component. Last but  
92 not least, structural tunability is crucial for optimizing performance of photocatalysts aimed  
93 at introducing such properties that can be instrumental for industrial scale applications, long  
94 term stability, good adsorption, and large surface area[46-48]. These features make them  
95 highly suitable candidates for industrial scale removal of pharmaceuticals from wastewater



96 through AOPs. Since these materials are combination of two or more components into single  
97 domain while reflecting the properties of each material, they are named as hybrid materials  
98 [49]. In specific terms, hybrid materials are made up of at least two molecularly dispersed  
99 components and these component are essentially organic and inorganic in nature [50]. OINHs  
100 have been synthesized by sol-gel method, surface functionalization, one pot synthesis, wrap-  
101 ping method, and electrospinning of nanohybrids [51].

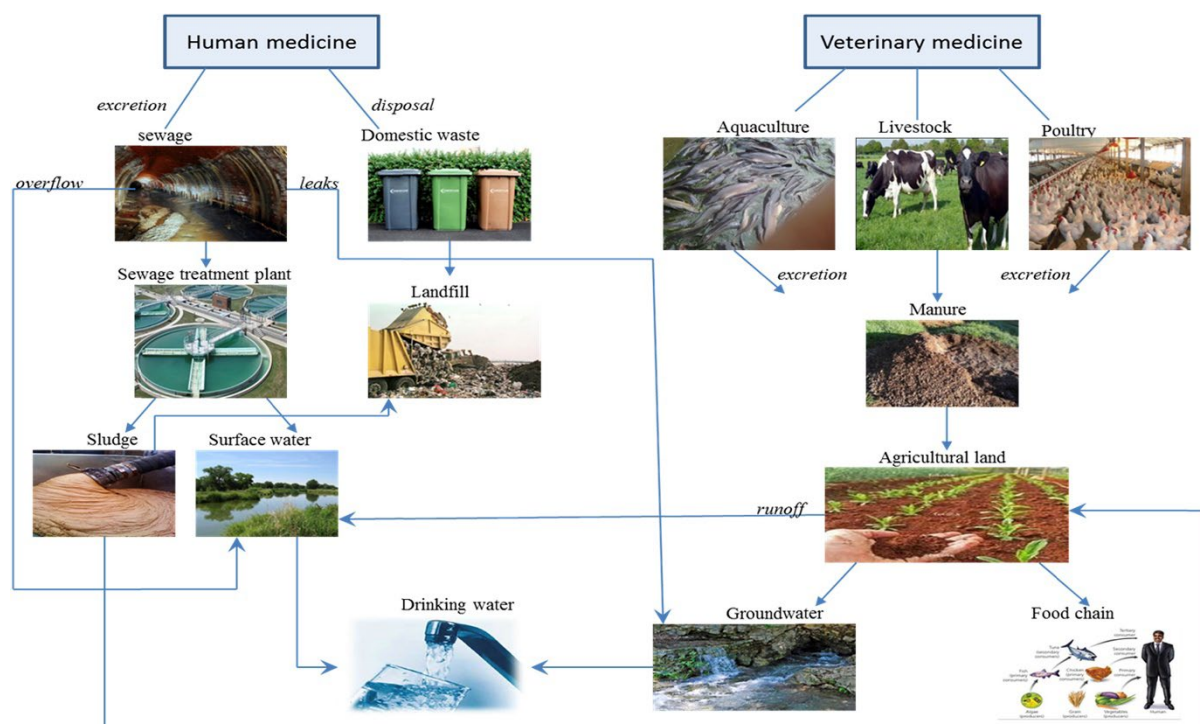
102 There is absence of elaborative studies that can summarize recent developments in the field  
103 of OINHs for photocatalytic degradation of pharmaceuticals in wastewater. This paper at-  
104 tempts to fill this gap by providing vital information of toxicity, sources, chemical nature of  
105 pharmaceuticals. It also introduces OINHs, elaborates their synthesis and application in re-  
106 moval of pharmaceuticals from wastewater while providing to the reader with their novel  
107 features and tunability for optimization of these materials aimed at their application at indus-  
108 trial scale. A necessary information of mechanisms of degradation assisted by these function-  
109 al materials is also provided. Besides, current challenges faced by these materials and future  
110 possibilities are also recommended in last.

## 111 **2. Sources and health risks of pharmaceuticals**

112 Pharmaceuticals and their metabolites or residues enter into environment from various  
113 sources including pharmaceutical industry, hospital and municipal wastewater, and illegal  
114 disposal, as presented in Figure 1[11]. These micropollutants cannot be degraded by conven-  
115 tional water treatment plants, therefore, they are released continuously into the water bodies  
116 [52]. One of the major pathways for pharmaceuticals to enter into the environment is from  
117 human and animal excretion that is released into sewage system. Reports suggest that about  
118 70% of pharmaceutical active ingredients and their metabolites enter into the environment  
119 from feces and elevate their level in wastewater[53]. Conventional wastewater treatment



120 plants cannot remove these pollutants and as a result these pollutants enter into freshwater  
121 streams[54, 55].



122  
123 Figure 1: Sources of pharmaceutical pollutants and their pathway into environment. Repro-  
124 duced from [11]. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).  
125

126 Pharmaceutical micropollutants are hardly biodegradable, highly toxic, and persistent at low  
127 levels and as a result, they cause serious environmental concern for aquatic and human  
128 life[56]. Reportedly, the main sink of these pollutants in the environment includes effluents  
129 from wastewater treatment plants, sewage water, and ground water supply, causing feminiza-  
130 tion of male fish, and human health, by creating antibiotic resistant bacteria[1, 57, 58].

131 Although, non-steroidal anti-inflammatory drugs (NSAIDs) are present in the range of ng/L  
132 to µg/L, they pose various health threats including DNA damage, oxidative stress, behavioral  
133 changes, and bioaccumulation tissues in aquatic algae, fish and mollusks [52, 59, 60]. Dico-  
134 fenac (DCF) is one of the commonly used NSAIDs, its continuous intake leads to several

135 adverse effects on fish including cytotoxicity of gills and in human it can cause liver prob-  
136 lems[61]. Risk of continuous use of DCF can be estimated from its classification by the Unit-  
137 ed States Food and Drug Administration (US-FDA) as pregnancy risk class C [53, 62-65].  
138 Another NSAID, ibuprofen, is one of the commonly used drugs for relieving pain in humans  
139 since 1960s and it is an emerging pollutant due to its refractory and persistent nature. Reports  
140 suggest its concentration around 20 ng/L in surface water and 3.8 $\mu$ g/L in sewage water. Its  
141 prolonged exposure for humans is cytotoxic, genotoxic and it can cause oxidative stress [39,  
142 52]. Salicylic acid is one of the intermediates of ibuprofen and it is highly toxic, even it can  
143 delay postembryonic development among amphibians [39, 66]. Paracetamol overdose causes  
144 covalent modification in thiol group of proteins and ultimately death through nucleic acids  
145 damage, cell necrosis, and lipid oxidation [52]. Antibiotics presence in the environment caus-  
146 es generation of antibiotic resistant bacteria [67]. Many concerns relates also to tetracycline  
147 antibiotics [45]. Similarly there are other pharmaceuticals, such as norfloxacin (NOR) and  
148 carbamazepine (CBZ), highly hazardous for human health and disrupting embryonic devel-  
149 opment of aquatic organisms [68-70]. Fish grown in pharmaceutical-contaminated water may  
150 pose a serious health threat if they are consumed by humans. Unmetabolized or active ingre-  
151 dients of pharmaceuticals accumulate in fish that are not only harmful for themselves but also  
152 for human beings. Excellent reviews are referenced here for detailed information on sources,  
153 chemical nature, toxicity and potential risk of pharmaceuticals in water bodies [11, 67, 71-  
154 74]. To protect ecosystem from this existential threat, there is immediate need to remove or  
155 degrade these pollutants for water bodies.

### 156 **3. Organic-inorganic nanohybrids (OINHs)**

157 The term “hybrid” is defined as combination of two or more different components into a sin-  
158 gle material, while properties of both materials are reflected in that single material [49]. Or-



159 ganic-inorganic nanohybrids can be defined in more specific terms as combination of two  
160 components, organic and inorganic, to form a molecularly dispersed single material [50]. In  
161 terms of type, OINs are classified into homogenous and heterogeneous materials. In ho-  
162 mogenous nanohybrid, miscible organic and inorganic components are combined. While, in  
163 case of heterogeneous, these components are not miscible. Inorganic components are com-  
164 monly a nanomaterials that have size dimension in the range of 1-100 nm [75]. In OINs, the  
165 core material is of prime importance for its photocatalytic properties, particularly the band  
166 gap is a determining factor for performance. It is essential to critically analyze changes in  
167 band gap induced by doping with various materials. Typically, doping introduces an intra-  
168 band electronic energy level which reduces energy dissipation and is instrumental in enhanc-  
169 ing separation of charges, i.e. an essential phenomenon for reaction initiation for the degrada-  
170 tion of pharmaceuticals[76]. Secondly, g-C<sub>3</sub>N<sub>4</sub> which is a metal-free polymeric system has  
171 been discussed. It has a band gap of 2.7 eV with a slight response to visible light. Another  
172 strategy to adjust band gap is formation of Z-scheme heterojunction where different energy  
173 levels are introduced leading to narrowing of band gap. Z-scheme heterostructures impart  
174 photocatalytic materials with higher separation efficiency of electrons-holes, wide range of  
175 light response, and strong redox ability[77]. For instance, Prabhavathi *et al.* synthesized Z-  
176 scheme heterostructures based on CoWO<sub>4</sub>/ g-C<sub>3</sub>N<sub>4</sub> and investigated its effectiveness against  
177 photocatalytic degradation of norfloxacin. Formation of Z-scheme heterostructures was in-  
178 strumental in narrowing band gap from 2.7 to 1.90 eV leading to higher photocatalytic activi-  
179 ty[68]. A similar phenomenon was observed in Z-scheme heterostructure of rGO/BSO/g-  
180 C<sub>3</sub>N<sub>4</sub> where band gap was reduced from 2.7 to 2.34 eV [78]. There are several other reports,  
181 where Z-scheme heterostructures were synthesized aimed at narrowing band gap and enhanc-  
182 ing catalytic performance [78-83]. Table 1 demonstrates the band gap of pristine core materi-  
183 al in the range of 1-1.7 eV and 1.0-2.7 eV for rGO and g-C<sub>3</sub>N<sub>4</sub>, respectively. Compared to



184 pristine core material, band gap of synthesized material may decrease [79, 84, 85] or in-  
185 crease[86-88] depending on several factors including synthesis, doping, and morphological  
186 features. Conventionally, decrease in band gap of material is desired for their efficient appli-  
187 cation in the degradation of pharmaceuticals. Although an increase in band gap was observed  
188 in some cases, this was not high enough to alter the photocatalytic properties of materials  
189 and, hence, reduce the photocatalytic activity for different pharmaceuticals degradation which  
190 remained high (88-97%). To make the material responsive in visible light range, a doping and  
191 heterostructure formation was found to be a successful strategy. Various studies reports  
192 changes in the band gap of these materials[89, 90]. More detailed information is discussed in  
193 another excellent review [91].

194

195 Table 1: Comparison of band gap values of core material before and after formation of  
 196 OINHs.

OINHs material	Band Gap (eV)		Reference
	Pristine	Doped	
rGO/BSO/g-C <sub>3</sub> N <sub>4</sub>	2.7	2.34	[78]
CoWO <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	2.7	1.92	[68]
SmVO <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	2.7 [91]	2.41	[85]
rGO/ Fe <sub>2</sub> O <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	2.7	1.82	[92]
Fe <sub>3</sub> O <sub>4</sub> /CeO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	2.7	1.50	[93]
g-C <sub>3</sub> N <sub>4</sub> @ZnO	2.7	2.27	[94]
g-C <sub>3</sub> N <sub>4</sub> /NiO/ZnO/ Fe <sub>3</sub> O <sub>4</sub>	2.7	2.8	[86]

197 In history of nanohybrids, clay-based nanohybrids were first materials of this class to be re-  
 198 ported[95]. In OINHs, commonly employed inorganic components are metals, metal oxides,  
 199 ceramics, layered double hydroxides, and magnetite whereas common organic components  
 200 are polymers, and micelles [96, 97]. This unique class of materials is developed by self-  
 201 assembly or grafting connection of inorganic clusters and organic components [98]. Some-  
 202 times, fragments of inorganic and organometallic complexes are used to construct OINHs  
 203 [99]. In OINHs, beneficial properties of organic and inorganic materials are combined by  
 204 discretely joining them into single domain [94]. In addition to beneficial properties of indi-  
 205 vidual components, synergistic effect between the two components is also induced which  
 206 results in excellent magnetic, electrical, and optical properties. Synergistically-induced optoe-  
 207 lectrical properties widen the scope of these materials in various fields including photocataly-  
 208 sis [96, 100]. In OINHs, organic and inorganic components are joined through diverse inter-



209 faces and on that basis OINHs are divided into two classes. Class I include OINHs in which  
210 components are joined by weak interfaces such as hydrogen, electrostatic bonds, or Van de  
211 Waals forces. Unlike class I, in class II nanohybrids organic and inorganic components are  
212 joined by strong covalent or ionic-covalent bonds. Much of OINHs contain both type of inter-  
213 faces but strong bonds dominate in determining the properties of class II materials[101]. Oth-  
214 er than synthetic OINHs, nature is full of these materials, in fascinating forms, including  
215 shells, ivory, bones, ferritin, magnetotactic bacteria, and chitons. Nanohybrids biopolymers  
216 such as collagen and chitin are combined with inorganic materials including iron oxides, sili-  
217 ca calcium compounds, and other composites through a variety of interfacial bonding [95].  
218 Owing to unique and novel features of OINHs, they are used in biomedical application such  
219 as gene delivery, drug delivery, antimicrobial and imaging, while photocatalysis is an im-  
220 portant application for environmental remediation[94, 102-104]. Owing to large surface area,  
221 structural stability and tunability, and excellent charge transfer properties, these are promis-  
222 ing materials for photocatalytic removal of pharmaceuticals from wastewater through ad-  
223 vanced oxidation process. For the systematic study of OINHs, we divided them into two clas-  
224 ses on the basis of organic components, which are elaborated on following pages.

### 225 **3.1 g-C<sub>3</sub>N<sub>4</sub> based OINHs**

226 Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is a fascinating carbon-base conjugated polymer. Morpho-  
227 logically and structurally, it is a sheet like material with regular pattern of triazine units. Ow-  
228 ing to its metal-free and highly light responsive nature, it has been under intensive attention  
229 of material scientists to harness its intrinsic properties for the development of novel materials  
230 for a variety of applications [105-107]. Particularly, its metal-free semiconductor nature and  
231 tri-s-triazine units are a game changers for photocatalytic applications, while it has a moder-  
232 ate band gap of 2.70 eV and responds in visible region up to 460 nm [108]. There are various  
233 studies that report on development of visible light responsive OINHs photocatalysts based on



234 g-C<sub>3</sub>N<sub>4</sub> and other inorganic components. For instance, Hu *et al.* fabricated a binary OINH of  
235 TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> for the degradation of DCF and carbamazepine (CBZ) in wastewater. The syn-  
236 thesized photocatalyst was ecofriendly in nature and capable of degrading 98.9 % and 99.8%  
237 of DCF and CBZ within 90 min, respectively [70, 109]. Recovery of photocatalyst has been a  
238 challenging task in photocatalytic degradation of pharmaceutical pollutants in wastewater; to  
239 this end, Kumar *et al.* synthesized C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> OINH having the feature of high-  
240 er photoactivity with Z-scheme heterojunction system and magnetic recovery. The synthe-  
241 sized photocatalyst was employed for the degradation of ibuprofen (IBP) and the catalyst was  
242 able to remove 98% of ibuprofen (IBP) in 15 min under irradiation of visible  
243 light. Photocatalyst was recovered and reused revealing only 11% loss of photoactivity after  
244 three cycles, which indicates its stability and possibility of reuse [83]. For practical applica-  
245 tions, structural stability is of prime importance. Liu *et al.* combined graphitic carbon nitride  
246 and graphene oxide in a ternary OINH g-C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub>/rGO and employed it for the photo-  
247 catalytic degradation of IBP. An ecofriendly microwave assisted method was used to synthe-  
248 size the photocatalyst. The as-synthesized photocatalyst led to 93% degradation of IBP. Crys-  
249 tal and morphological structure was observed after three cycles and photocatalyst showed no  
250 change of properties. To evaluate the activity of photocatalyst in real matrices, river water  
251 containing IBP was used for photocatalytic activity testing under sunlight and the result was  
252 promising for practical applications[110]. A comprehensive comparison of g-C<sub>3</sub>N<sub>4</sub> based  
253 OINHS for the photocatalytic removal of pharmaceuticals from wastewater, alongside their  
254 synthesis strategy are presented in this review. Conclusively, g-C<sub>3</sub>N<sub>4</sub> based photocatalysts  
255 offer highly suitable band gap, high chemical stability, and good electron carriers capability  
256 with cost effective and ecofriendly synthetic methods; these aspects present g-C<sub>3</sub>N<sub>4</sub> based  
257 OINHS photocatalysts highly suitable for photocatalytic degradation of pharmaceutical in  
258 wastewater.



### 259 3.2 Polymer based OINHs

260 Polymers are large structural entities joined by same linkage between similar units. These are  
261 different form  $g\text{-C}_3\text{N}_4$  in terms of offer better processibility, dispersibility and fine tuning for  
262 electron transfer process. In polymer based OINHs, polymer matrices with different size and  
263 shape are coupled with a variety of organic and inorganic materials. Such nanohybrids offer  
264 distinctive chemical and physical properties owed to synergistic effects between the two  
265 components[111]. Polymer based nanohybrids are excellent photocatalytic materials when  
266 coupled with nanomaterial semiconductors and one of the main advantages they offer is large  
267 surface area to volume ratio [112]. There are several polymers which have been employed to  
268 develop OINHs for photocatalytic applications including polyaniline[113], polypyrrole[114],  
269 polythiophene[115], and polyfuran [116]. Among these polymers, polyaniline attracted inten-  
270 sive attention from researchers owing to its higher stability, redox properties, tunable electri-  
271 cal conductivity, and low cost and easy synthesis [117]. To study the synergistic effect of  
272 polyaniline on photocatalytic properties, Kumar *et al.* fabricated magnetic ternary  
273 PANI/LaFeO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub> (PLC) nanohybrid through in situ polymerization of aniline and em-  
274 ployed it for the photocatalytic degradation of pharmaceutical pollutant clozapine (CZP).  
275 Polymer based composites degraded 94.2 % of pharmaceutical pollutant in 120 min. The  
276 photocatalytic activity of the polymer based OINHs was far greater than its individual com-  
277 ponents [82]. Polypyrrole is another polymer which has been employed for the preparation of  
278 core-shell nanohybrid with ZnO and employed for the degradation of DCF. Ppy-ZnO degrad-  
279 ed 81% of DCF under sunlight irradiation which was higher than individual polypyrrole and  
280 ZnO. Higher photocatalytic activity was attributed to large surface area, mesoporous structure  
281 and narrow band gap of nanocomposite [19]. For the degradation of ibuprofen (IBP), poly (o-  
282 phenylenediamine)/antimony oxide nanohybrid was fabricated. POPD/Sb<sub>2</sub>O<sub>3</sub> nanohybrid  
283 degraded 92% of pharmaceutical pollutant in 60 min under sunlight irradiation. Polymer na-



284 nohybrid lost only 5.3% of its initial photocatalytic activity, which indicates that it is highly  
285 stable and can be employed for practical applications [118]. Summarized data elaborated fur-  
286 ther on polymer based OINs for photocatalytic removal of pharmaceuticals from  
287 wastewater. In summary, polymer based OINs offer large surface area, higher stability, nar-  
288 row band gap, and cost effectiveness.

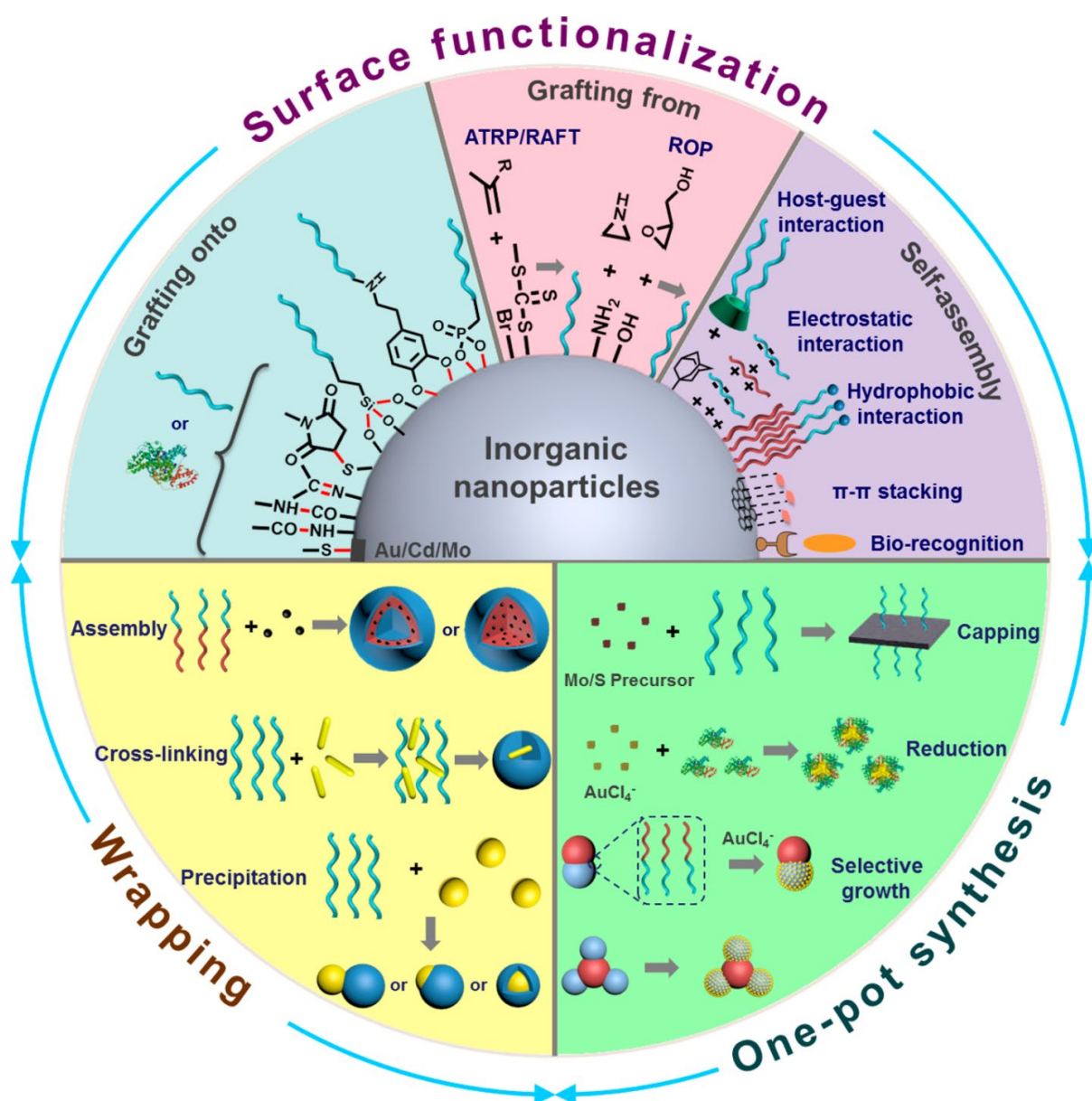
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#### 290 **4. Synthesis Approaches of OINHs**

291 Several various methods are used to synthesize organic-inorganic nanohybrids including sol-  
292 gel method, one pot synthesis, surface functionalization, and wrapping method. The most  
293 commonly used methods for the development of OINHs are presented in Figure 2 [94]. The  
294 advantages and drawbacks of each method are discussed in detail in following parts of this  
295 section. The selection of method mainly depends on target application, while the less time  
296 consuming, cheaper and more ecofriendly methods are given priority.







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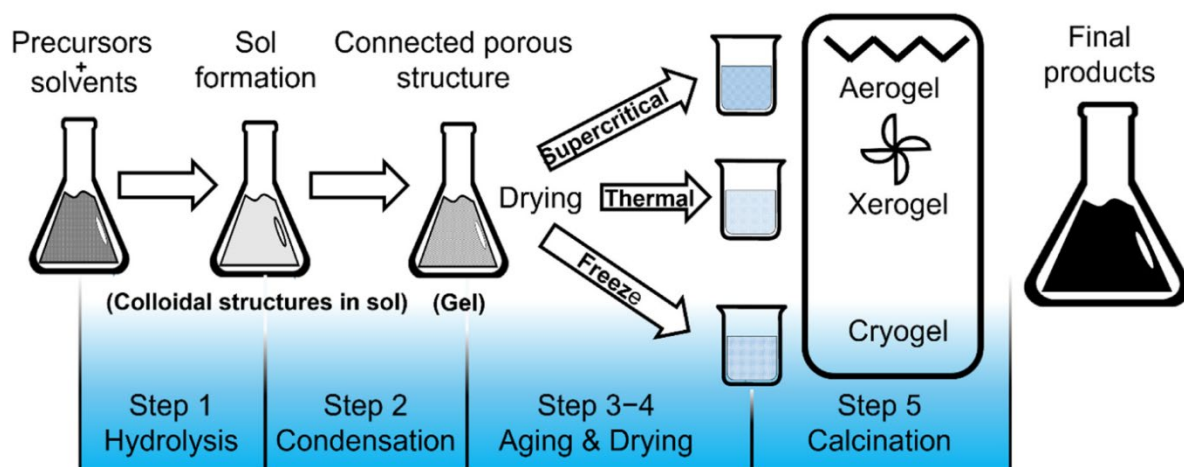
298 Figure 2: Most commonly employed methods for the development of OINHs. Reproduced

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### 300 4.1 Sol-Gel method

301 In sol-gel method, organic and inorganic components are chemically mixed at nanometric  
 302 scale [119, 120]. Typically, inorganic components are dispersed homogeneously in organic  
 303 solvent which results in the formation of metal-oxo polymers. Sol-gel method is advanta-  
 304 geous in terms of energy efficiency and control of chemical structure of product; this method  
 305 requires mild temperature (80-100°C) for synthesis of OINHs [121, 122]. Typically, sol-gel

306 method constitutes five steps including hydrolysis, polycondensation, aging, drying, and  
307 thermal decomposition, as exhibited in Figure 3 [123].



308

309 Figure 3: A schematic diagram of sol-gel method for synthesis of organic inorganic nanohy-  
310 brids[123] This is an open access article under the CC BY license  
311 (<http://creativecommons.org/licenses/by/4.0/>).

312 Chemical reaction starts from sol which is gradually converted into gel-like material. After  
313 gel formation, the reaction mixture forms a biphasic system in which sol and gel co-exist  
314 while having diverse morphology with presence of discrete particles to continuous network of  
315 polymers. Next step involves the removal of solvent followed by drying of the product. Dur-  
316 ing this step, the solvent is evaporated and the reaction mixture undergoes shrinkage and den-  
317 sification. During drying, porosity of the product can be controlled through rate at which the  
318 solvent is removed and so can the distribution of the pores. Super critical drying is considered  
319 to be the best method as it results in uniformly distributed product and prevents aggregation  
320 [124]. Zinc oxide doped polythiophene and polyimide-polydiphenylsiloxane (PI-PDPS) na-  
321 nohybrids were prepared through the same method [51, 125]. Sol-gel process is advantageous  
322 in terms of low temperature requirement, high purity product, structural control, and control  
323 of the size of material.



## 324 4.2 Surface functionalization technique

325 Surface functionalization is one of the most widely used techniques for the synthesis of  
326 OINHs as well as the target oriented functionalization of any surface. Basically, there are  
327 three strategies that are employed in surface functionalization including grafting from, graft-  
328 ing on, and the self-assembly. For integration of nanoparticles and polymers, grafting on is  
329 the easiest way in which polymer is grafted on surface of synthesized NPs. A fixed molecular  
330 weight of grafted polymer is utilized and, in case of steric hindrance, chemical substitution is  
331 employed to enhance grafted density. To obtain best performance from gold NPs, various  
332 stabilization strategies are employed[126-128]. Thiol group is well known for its attraction  
333 toward metals, thiol-ended polyethylene glycol has been used to stabilize gold NPS and this  
334 is a good example of grafting on approach [94]. Grafting on based surface functionalization  
335 offers synthesis convenience and higher levels of effectiveness. Grafting from is a type of  
336 bottom up type of surface functionalization. In this strategy, organic layer of polymers is  
337 formed through polymerization in which polymer chains are bound to functional materials  
338 [129]. In situ polymerization is also considered as grafting from strategy. Examples include  
339 clay base OINHs for various applications [130, 131]. Grafting from strategy offers control  
340 over architecture, molecular weight and composition of nanohybrids. Self-assembly is a pro-  
341 cess in which specific interaction of organic and inorganic components is employed for the  
342 spontaneous bottom up organization of OINHs.  $\beta$ -CD and hydroxypropyl- $\beta$ -cyclodextrin  
343 (HP- $\beta$ -CD) are commonly used materials to initiate synthesis of self-assembled OINHs.  $\beta$ -  
344 CD possesses hydrophilic and hydrophobic moieties for such interactions and also has favor-  
345 able size. This is also employed for gate mechanism to introduce host-guest recognition for  
346 trapping of specific molecules for catalysis [132, 133]. Surface functionalization is easy and  
347 cost effective, while providing much better control over properties of synthesized material.



### 348 4.3. One-pot synthesis

349 One pot synthesis nanohybrids are prepared simultaneously in a single reaction. It is simple  
350 and efficient in terms of cost and strategy for synthesis of OINHs and other functional mate-  
351 rials[134]. Generally, in one pot synthesis all components are subjected to a series of succes-  
352 sive chemical reactions in single reaction chamber. Owing to absence of formation any in-  
353 termediate chemical compounds, this method helps in avoiding lengthy separation or purifi-  
354 cation process[135]. Organic molecules act as structure directing groups and it is convenient,  
355 simple and time saving method for synthesis of OINHs. In one pot synthesis, a variety of  
356 functional groups can be introduced to modify functionality of nanoparticles, which generate  
357 desirable properties in produced material. For instance, precipitation of iron oxide nanoparti-  
358 cles in the presence of carboxymethyl cellulose (CMC) enhances hydrophilicity and biocom-  
359 patibility of the product [136]. There is no need for introduction of additional chemical rea-  
360 gents such as surfactants and emulsifiers in one pot synthesis and this makes it cheap and  
361 ecofriendly method [137]. It has been also used for binding of folate molecule on the surface  
362 of  $Mn_3O_4$  without employing any linker molecule and this method proved to be cost effective  
363 [138]. Many molecules of interest can be combined in single domain through one pot synthe-  
364 sis without compromising on binding affinity of any molecule [139, 140]. Liang *et al.*, syn-  
365 thesized g- $C_3N_4$ - $Fe_2O_3$  through one-pot synthetic method and employed in photocatalytic  
366 dyes degradation for wastewater treatment along with investigation of magnetic properties.  
367 While outlining drawbacks of other methods, it has been mentioned that one pot synthesis is  
368 highly advantageous in hindering electron-hole recombination ultimately leading to higher  
369 photocatalytic properties [141]. One pot synthesis is cost effective, easy, ecofriendly and  
370 offers a higher level of control of structural and functional properties.



#### 371 **4.4 Method of wrapping**

372 In the wrapping method, inorganic molecules are encapsulated in organic matrix through self-  
373 assembly or direct encapsulation. In this method, noncovalent interactions are employed as  
374 binder for generation of OINHs. Basically, a core is generated around which organic or pol-  
375 ymer molecules start wrapping, thus ultimately resulting in a core-shell structure. In wrapping  
376 method, diversity of functional group can be added; for instance, addition of organic func-  
377 tional groups in metal organic frames containing metal ions and their core around inorganic  
378 nanoparticles result in core shell nanohybrids. Synthesis of  $\text{Fe}_3\text{O}_4@\text{OCMC}@\text{IRMOF-3}$  pro-  
379 ceeds through wrapping method in which ferrites and chitosan composites are prepared sepa-  
380 rately and then added into the organic solvent with metal organic framework precursor. The  
381 reaction mixture is poured in autoclave and placed in a heating oven at  $100^\circ\text{C}$  for 6 h after  
382 thorough sonication. A deep reddish-brown color product was obtained which was washed  
383 with ethanol and water and dried [142]. Through similar procedures, a polysacchrides@iron  
384 oxide has been prepared having core shell structure [143]. There is another technique in  
385 which solution intercalation phenomenon is used. It is widely used in wrapping of silicate  
386 where silicates are exfoliated into monolayers in the presence of polymers/prepolymers. Pol-  
387 ymers wrap around monolayers of exfoliated silicates and produce a covered nanohybrid  
388 [130, 131, 144]. Melt intercalation is a similar phenomenon except that layered silicates are  
389 in molten state and this permits higher quality interactions between the two components, thus  
390 producing exfoliated nanocomposite [145]. Although various components can be introduced  
391 in nanohybrids through wrapping method, it does not offer control over structure and compo-  
392 sition of product and can lead to compromise on properties.

#### 393 **4.5 Electrospinning of nanohybrids**

394 In this case, the polymer to be deposited is dissolved in suitable solvent and then potential  
395 difference is applied, causing charge deposition on the polymer solution droplets. Next,



396 charge on liquid droplet overcomes the surface tension of polymers solution and jumps to-  
 397 ward metal plate, thus forming nanofibers [146]. There is no need for extra step of drying  
 398 since, during the process, the solvent is evaporated and the product is collected. Electrospinning  
 399 offers formation of high surface area materials, tunable porosity and control over functionalization [147]. OINHs are synthesized by mixing of nanofibers material, polymers in  
 400 suitable organic solvent to prepare a homogenized slurry. Volatile organic solvent is employed  
 401 to obtain a stable and viscous slurry which is ejected through syringe, while potential  
 402 difference is applied [148, 149]. There are several reported reviews that elaborate on recent  
 403 advancements and application of electrospinning technique in nanofabrication. Electrospinning  
 404 is cheap, simple, ecofriendly and versatile technique, which is used to prepare particularly  
 405 nanofibers based nanohybrids for a variety of applications. Electrospinning results in formation  
 406 of nanofibers that offer expanded surface area and porosity with excellent reusability.  
 407 Li *et al.*, elaborated recent developments in field of electrospinning with outlining emerging  
 408 technologies while discussing, single needle, multi-needle, needle less technologies for electrospinning.  
 409 A detailed discussion on fibre structure, molecular orientation, optical and mechanical properties  
 410 of electrospun material has been elucidated with their application in relevant field [150].  
 411 An excellent reviews on detailed discussion on electrospun fibres and their application  
 412 in wastewater treatment technologies are available [151, 152].

414 Based on analysis of all synthetic method for OINHs, following table present advantages and  
 415 disadvantages of these methods

416 Table 2: Advantages and disadvantages of different methods for synthesis of OINHs.

Synthesis Method	Advantages	Disadvantages
Sol-gel method	Low temperature, high purity, structure and size control.	Highly sensitive to environmental conditions.



Surface functionalization	Easy to handle, cost effective with comparable control over product feature.	Limited to surface only, intrinsic features cannot be improved.
One-pot synthesis	Cost effective, higher control over structural and morphological properties.	For better performance, the product may require post-synthetic modification.
Method of wrapping	Excellent for combination of various components.	Offer less control on composition and structure of product.
Electrospinning of nano-hybrids	Cheap, eco-friendly, and versatile technique, ideal for nanofibers.	Compromised surface and physical properties, available for limited number of materials.

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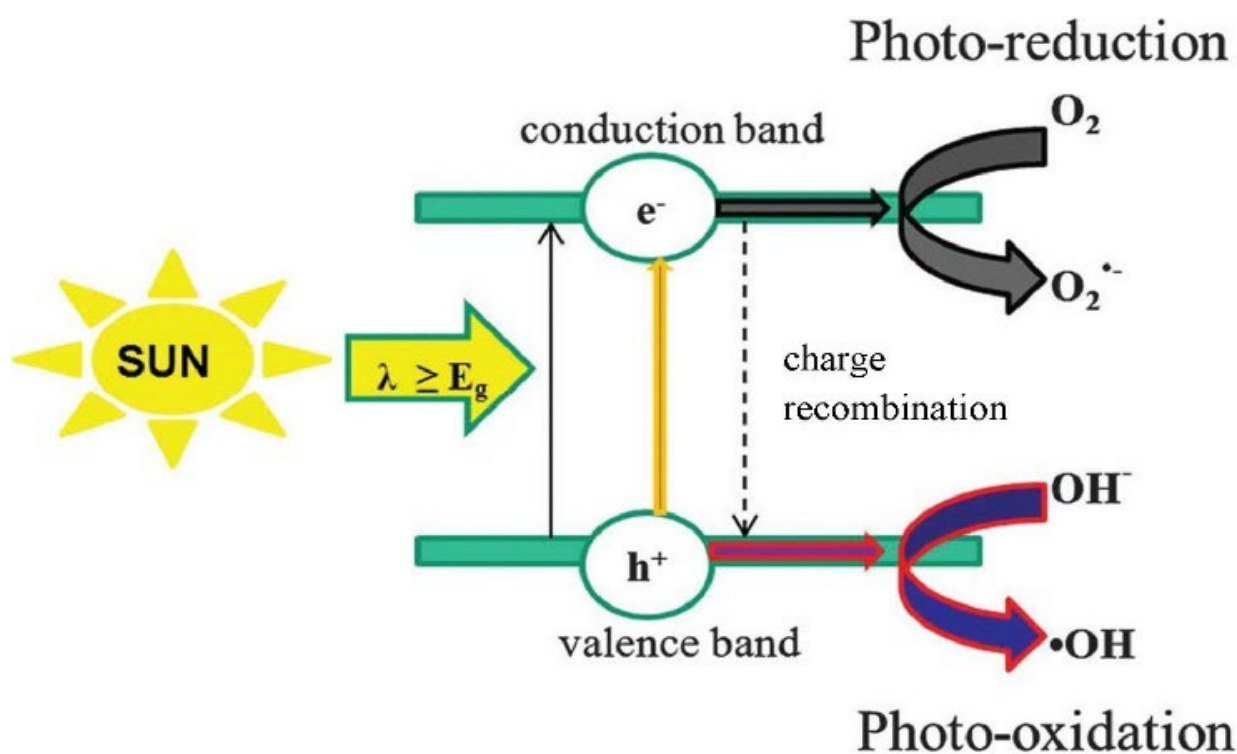
## 419 5. Photocatalysis

420 In photocatalysis, when light photon ( $h\nu$ ) with energy greater than or equal to band gap ( $E_g$ )  
421 of semiconductor photocatalyst irradiates the material, electrons ( $e^-$ ) are excited from valence  
422 band (VB) to conduction band (CB) leaving an electron hole ( $h^+$ ) in valence band. Photogen-  
423 erated electrons migrate toward the surface of photocatalyst and react with water to produce  
424 highly reactive chemical species such as  $O_2^{\bullet -}$  and  $HO^\bullet$ . These radical species react with phar-  
425 maceutical molecules and degrade them into simple molecules (Figure 4) [153]. There are  
426 two phenomena that control photocatalytic activity of semiconductor, which are the photoex-  
427 citation rate of charged carriers and their recombination rate. These two act oppositely, higher  
428 photoexcitation means higher photocatalytic activity, while higher recombination rate means  
429 loss of energy and lower photocatalytic activity. For efficient photocatalytic activity, first  
430 prerequisite is to prevent the  $e^-/h^+$  recombination. The following equations represent the re-  
431 actions occurring during the entire photocatalytic process [154, 155].



438





439

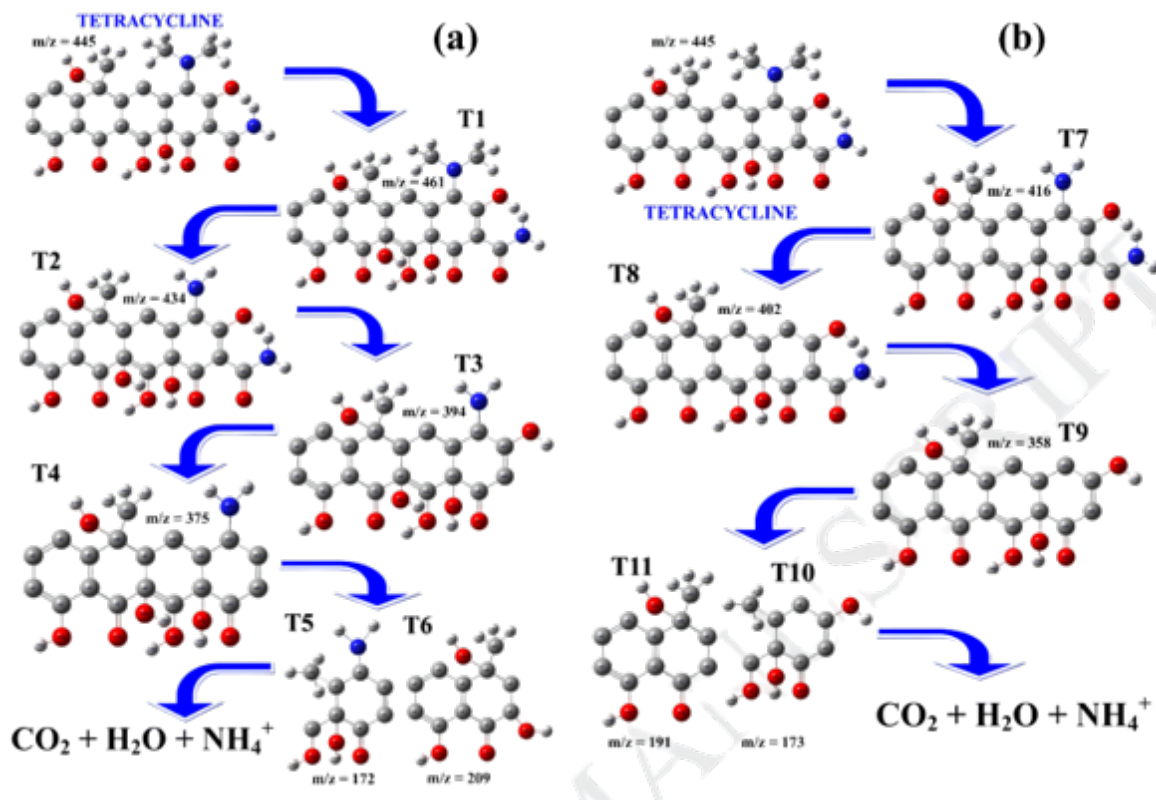
440 Figure 4: Schematic representation of photocatalytic process [153]. This is an open access  
 441 article under the Creative Commons Attribution 3.0 Unported License  
 442 (<https://creativecommons.org/licenses/by/3.0/>).

443 OINs based photocatalysts undergo same reaction steps (1-6) for photocatalytic mineraliza-  
 444 tion of pharmaceutical drugs. There are many research papers which report photocatalytic  
 445 mineralization of various pharmaceuticals such as DCF [84], ibuprofen, sulfamethoxazole  
 446 [156], paracetamol [157], ciprofloxacin [158], naproxen [78], tetracycline [81] etc. Owing to  
 447 complex chemistry and different chemical structure there are different mechanisms of photo-  
 448 catalytic degradation of different pharmaceuticals. To investigate degradation reaction path-  
 449 ways, intermediates are determined and on the basis of their chemistry, the respective mecha-  
 450 nism is developed. On the other hand, reactive oxygen species (ROSs), as well as  $h^+$  and  $e^-$   
 451 contribution to the degradation mechanism are studied by means of scavenging tests as well  
 452 as EPR technique.

453 Mechanism of degradation of TC is determined first based on the proportion of formed reac-  
454 tive oxygen species. Later degradation by-products (typically by chromatographic techniques  
455 coupled to mass spectrometry) are analyzed to define degradation pathways. As photocatalyt-  
456 ic mineralization is determined by analysis of intermediates, different pathways are possible  
457 owing to diversity of intermediates. Shanavas *et al.* proposed two mechanisms for the visible  
458 light driven degradation of tetracycline using Cu/Bi<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>/rGO (*Figure 5*). The process pro-  
459 duces hydroxyl and superoxide radicals and electron holes after sunlight radiation of the sur-  
460 face of the photocatalyst. These radicals attack TC molecules and its intermediates ultimately  
461 leading to the formation of carbon dioxide, water and ammonium ion. To be specific, there  
462 are four active species that are produced by photocatalyst on incessant striking of sunlight on  
463 its surface and these include  $\cdot\text{OH}$ ,  $\cdot\text{O}_2^-$ ,  $\text{h}^+$  and  $\text{e}^-$ . These active species attack TC and convert  
464 it into by-products with lower molecular weight. The degradation mechanism starts with cy-  
465 cloaddition of  $\cdot\text{OH}$  radical at 11C-12C double bond of TC leading to the formation of T1 in-  
466 termediate with m/z of 461. Two methyl groups are removed from tertiary amine of T1 and  
467 T2 intermediate having m/z of 434. T3 intermediate having m/z of 394 is formed through the  
468 removal of formamide and T4 with m/z of 375 is formed by further removal of hydroxyl  
469 group. T5 (m/z; 172) and T6 (m/z; 209) intermediates are formed by cleavage of 5C-6C and  
470 11C-12C of T4, respectively. In a final step, these intermediates are converted into water,  
471 carbon dioxide, and ammonium ions. Second mechanism of degradation starts with removal  
472 of methyl groups from TC and Produce a T7 with m/z of 416. Further degradation proceeds  
473 with removal of amino group from 5C and formamide leading to formation of T8 (m/z; 402)  
474 and T9 (m/z; 358), respectively. Second, last step is similar in both mechanism as thy involve  
475 cleavage of 5C-6C and 11C-12C leading to formation of T10 (m/z; 173) and T11 (m/z; 191),  
476 respectively. A CO<sub>2</sub>, H<sub>2</sub>O, and NH<sub>4</sub><sup>+</sup> are final products in both mechanisms (*Figure 5*) [159].  
477 Along with these two possible mechanism of TC degradation, the literature reports several



478 other routes where photocatalyst of different nature involved and produce varying proportion  
479 of reactive species. Tan *et al.* reported two different degradation pathways taking place dur-  
480 ing application of Z-scheme  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> heterojunctions with 3D mesoporous SiO<sub>2</sub> nano-  
481 spheres as photocatalyst where deamination and demethylataion has been the first step of two  
482 methods initiating a series of steps toward formation of mineralized product [160]. In another  
483 study, degradation of TC was assisted by carbon quantum dots-decorated BiOCl  
484 nanosheet/carbonized eggshell membrane composite. In this study a three different pathways  
485 were reported. A dehydration, dealkylation, and hydroxylation has been reported as first step  
486 [161]. There is also a study where a synergistic effect between photocatalysis and adsorption  
487 for TC degradation has been reported [162]. In this case a 1D/2D La(OH)<sub>3</sub>/(BiO)<sub>2</sub>OHC1 het-  
488 erostructures were used. Although, all these studies reported different pathways for degrada-  
489 tion of TC, at the end, they all result in the total mineralization with formation of CO<sub>2</sub>, H<sub>2</sub>O,  
490 and NH<sub>4</sub><sup>+</sup>.



491

492 Figure 5: Two possible degradation reaction pathways for the photocatalytic degradation of

493 TC. Reproduced from [159] with permission from Elsevier. License number:

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## 496 6. Application of OINs for the removal of pharmaceuticals

497 OINs are classified into three classes on the basis of their organic component. Among g-  
498 C<sub>3</sub>N<sub>4</sub> based OINs, nitrogen doped carbon dot decorated Bi<sub>2</sub>MoO<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> showed highest  
499 photodegradation efficiency for the removal of ciprofloxacin (CIP). Synthesized photocata-  
500 lyst had band gap of 2.07 eV and showed 99% photocatalytic degradation of model pollutant  
501 in aqueous solution, in 30 min. There are five factors that make this photocatalyst better than  
502 others: (1) hydrophilicity, (2) large surface area (43.7 m<sup>2</sup>/g), (3) higher light absorption, (4)  
503 low impedance, (5) good crystallinity. Hydrophilicity coupled with oxygenated surface en-  
504 hances the adsorption of target pollutant for degradation. Large surface area is beneficial in  
505 terms of providing more active sites and enhanced photocatalytic activity. Photoexcitation of  
506 charged carriers solely depends upon absorption of sunlight, higher sunlight absorption  
507 means higher rate of photocatalytic activity. Photoexcitation of electrons is not the only fac-  
508 tor that heavily influences photocatalytic efficiency. Migration of charged carriers and pre-  
509 vention of their recombination are also an important factor. Moreover, low impedance sup-  
510 ports a robust electron-hole pairs migration and good crystallinity facilitates the prevention of  
511 their recombination[163]. Coupling of conducting polymers and functional material has been  
512 widely used for a variety of applications including photocatalytic removal of pharmaceuticals  
513 from wastewater. Mohamed *et al.* synthesized PAN-MWCNT/TiO<sub>2</sub>-NH<sub>2</sub> OINs to combine  
514 individual properties of polyaniline as an excellent stabilizer, MWCNT to improve tensile  
515 strength and electron conduction and cost effectiveness, ecofriendly nature and higher photo-  
516 catalytic activity of TiO<sub>2</sub> [164-168]. As synthesized photocatalyst was employed for the deg-  
517 radation of three pharmaceutical pollutants that are commonly present in wastewater includ-  
518 ing ibuprofen, naproxen, and cetirizine, 99% of pollutants were degraded in the presence of  
519 UV irradiation. Different parameters were studied and optimized conditions were reported for



520 practical applications. Photocatalyst was highly stable as it showed minor loss of its activity  
521 even after 5<sup>th</sup> cycle[169].

522 In a nutshell, production of OINs for photocatalytic degradation of pharmaceuticals in  
523 wastewater is an excellent technique for environmental remediation that needs to be executed  
524 at large scale. In OINs, synergistic impact of each component is vital factor that mainly  
525 promotes photocatalytic activity of the material.

Graphitic carbon nitride based OINs											
Nanohybrid Photocatalyst	Method of synthesis	Band Gap (eV)	Pollutant	Conditions					Degradation Effectiveness (%)	Rate Constant	References
				Catalyst Dosage	Pollutant concentration	pH	Irradiation Time (min)	Light Source			
CeVO <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	Hydrothermal method	1.99	CIP	0.5 g/L	6.6 mg/L	3	70	Visible light	92	0.2504 min <sup>-1</sup>	[85]
CdS-g-C <sub>3</sub> N <sub>4</sub>	Chemical precipitation method	2.45	CTX	0.06 g/L	15 mg/L	10.5	81	Visible light	93	0.0336 min <sup>-1</sup>	[170]
N-doped Carbon dot/g-C <sub>3</sub> N <sub>4</sub> / BiMoO <sub>6</sub>	Hydrothermal method	2.07	CIP	1 g/L	5 mg/L	8	30	Visible light	99	0.13 min <sup>-1</sup>	[163]
SmVO <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	Hydrothermal method	2.41	CP	0.4g/L	20 mg/L	3	105	Visible light	94	0.2704 min <sup>-1</sup>	[85]
g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub> /Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	Sol-gel route	N/A	IBP	1 g/L	2 mg/L	7	15	Visible light	97	N/A	[83]
rGO/ Fe <sub>2</sub> O <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	Hydrothermal	1.82	TC CIP	0.1 g/L	50 mg/L	7	60	500 W halogen lamp	98 97	0.7088 min <sup>-1</sup> 0.5187 min <sup>-1</sup>	[92]

Fe <sub>3</sub> O <sub>4</sub> /CeO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Hydrothermal	1.50	TCH	1 g/L	50 mg/L	2.7	180	300 W xenon lamp	97	0.0533 min <sup>-1</sup>	[93]
g-C <sub>3</sub> N <sub>4</sub> /Bi <sub>2</sub> WO <sub>6</sub> /rGO	Microwave-assisted rout	N/A	IBP	0.5 g/L	5 mg/L	4.3	60	Visible light	93	0.011 min <sup>-1</sup>	[110]
g-C <sub>3</sub> N <sub>4</sub> /NiO/ZnO/ Fe <sub>3</sub> O <sub>4</sub>	Hydrothermal	2.8	ESP	0.7 g/L	30 mg/L	6	70	23 W white LED bulb	95	0.06616 min <sup>-1</sup>	[86]
CdS/g-C <sub>3</sub> N <sub>4</sub> /4AZ	Chemical precipitation method	2.10	CFP	0.4 g/L	17 mg/L	9	80	Visible light	93	3.71 × 10 <sup>-2</sup> min <sup>-1</sup>	[171]
Ultrathin porous P-doped g-C <sub>3</sub> N <sub>4</sub>	One-step thermal polymerization method	N/A	DCF	0.4 g/L	5 mg/L	4.34	20	LED light	99	0.1248 min <sup>-1</sup>	[172]
g-C <sub>3</sub> N <sub>4</sub> @ZnO	Thermal atomic layer deposition method	2.27	CEX	0.3 g/L	10 mg/L	N/A	60	Sunlight	99	0.0735 min <sup>-1</sup>	[94]
Fe <sub>3</sub> O <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub> /MoO <sub>3</sub>	Calcination method	N/A	TC	0.4 g/L	40 mg/L	7	120	1000 W xenon lamp	94	1.63 x 10 <sup>-2</sup> min <sup>-1</sup>	[173]
Ce <sub>2</sub> (WO <sub>4</sub> ) <sub>3</sub> @ g-C <sub>3</sub> N <sub>4</sub>	Hydrothermal route	2.69	MXF	0.5 g/L	10 mg/L	N/A	60	Visible light	94	0.0594 min <sup>-1</sup>	[174]
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Solvothermal method	2.76	IBF	1 g/L	5 mg/L	N/A	60	Visible light	95	0.03833 min <sup>-1</sup>	[175]
TiO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	Ultrasonication method	2.02	DCF	0.1 g/L	10 mg/L	6.4	30	Visible light	98.2	0.1796 min -1	[176]
CoWO <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	Hydrothermal method, followed by ultra-sonication	1.85	NOR	0.5 g/L	10 mg/L	N/A	80	Visible light	97	0.000471 min <sup>-1</sup>	[68]



MoS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub> / Bi <sub>24</sub> O <sub>31</sub> Cl <sub>10</sub>	Impregnation-calcination method	N/A	TC	0.01 g/L	20 mg/L	N/A	50	Visible light	98	0.06429 min <sup>-1</sup>	[80]
g-C <sub>3</sub> N <sub>4</sub> /Zn doped Fe <sub>3</sub> O <sub>4</sub>	Solvothermal route	N/A	CEX	0.5 g/L	10 mg/L	6	30	Visible light	91	0.0645 min <sup>-1</sup>	[177]
Polymer based OINHs											
PPy-ZnO	Polymerization method	1.81	DCF	1 g/L	10 mg/L	6	60	UV-Vis Light	81	0.986 min <sup>-1</sup>	[19]
PANI/LaFeO <sub>3</sub> /CoFe <sub>2</sub> O <sub>4</sub>	In situ polymerization	2.25	CZP	0.3 g/L	50 mg/L	6	120	Visible light	94	0.0248 min <sup>-1</sup>	[82]
Chitosan-glyoxal/Polyvinylpyrrolidone/MoS <sub>2</sub> (CSG/PVP/MoS <sub>2</sub> )	Hydrothermal-ultrasonic method	2.12	DCF	0.1 g/L	100 mg/L	5	50	UV-light	95	0.0195 min <sup>-1</sup>	[178]
ZnFe <sub>2</sub> O <sub>4</sub> @CMC	Hydrothermal	1.4	CIP	0.3 g/L	5 mg/L	7	100	6 W UV lamp	87	0.277 min <sup>-1</sup>	[179]
POPD/Sb <sub>2</sub> O <sub>3</sub>	In-situ oxidative polymerization method	1.35	IBP	N/A	50 mg/L	N/A	60	Sunlight	91	0.1725 min <sup>-1</sup>	[118]
Pt@PPy-C/ZnO	Sol-gel route and ultrasonication methodology	2.65	LIZ	0.1	20 mg/L	N/A	40	Visible light	94	0.066 min <sup>-1</sup>	[122]
PAN-MWCNT/TiO <sub>2</sub> -NH <sub>2</sub>	Polymerization method	N/A	IBP	0.3 g/L	5 mg/L	2	120	UV Light	99	N/A	[169]
			NPX				25				

			CIZ				45					
rGO/PANI/C-ZnO	Polymerization method	2.80	ACP	0.1 g/L	10 mg/L	N/A	100	Solar light	47	0.0055	[180]	
										min <sup>-1</sup>		
Fe <sub>2</sub> O <sub>3</sub> @PPy/rGO	Chemical reflux	N/A	ACP	0.6 g/L	1 mg/L	7.4	120	UV- Light	84	N/A	[181]	
PANI/ZrO <sub>2</sub>	Hydrothermal method	3.16	CIP	1g/L	13 mg/L	N/A	120	UV-light	96	N/A	[182]	

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## 531 7. Current challenges and future recommendations

532 Although there has been a lot of developments in the OINHS field for photocatalytic degrada-  
533 tion of pharmaceutical pollutants from water bodies, these developments are far from practi-  
534 cal application. Currently this field faces challenges from two sides, one issue is related to  
535 synthesis of photocatalysts and mechanism of photocatalysis, while the second is the diversi-  
536 ty of pharmaceuticals. Synthesis is highly expensive, complicated and time consuming. These  
537 are big challenges that must be addressed through the development of properly optimized  
538 synthesis methods. In many cases, such aspects are not reported in the papers; authors omit to  
539 discuss the issues and limitations of developed materials. In the current review work, only lab  
540 scale applications have been studied and there has been no investigation of OINHS in real  
541 water matrices which are highly complex mixtures of various compounds, this needs to be  
542 addressed for practical applications. Photocatalysts efficiency can be enhanced by preventing  
543 recombination of electron and hole pairs and this can be achieved by band engineering and  
544 selection of suitable semiconductor materials. Second major challenge comes from diverse  
545 structure of pharmaceuticals that may be treated by a limited number of photocatalysts. There  
546 is a limited number of reports in which photocatalytic degradation of more than one pharma-  
547 ceutical pollutant was investigated. It seems that only best results are reported, instead of crit-  
548 ical evaluation of universal character/selectivity of the catalyst. Diverse structure of pharma-  
549 ceutical and resulting intermediates are huge challenges, which can create more toxicity in  
550 comparison to the parent chemicals. To overcome this challenge there is need of development  
551 of methodology to control nature of intermediates and end product. Currently, risks of nitro-  
552 derivatives as by-products in AOPs are widely reported[183, 184]. This aspect should be ad-  
553 dressed in respect to OINHS based processes. Table 1 reveal that most studies report photo-  
554 catalytic degradation of NSAIDs [118, 169], no doubt they are widely used pharmaceuticals  
555 but there is need to work on degradation of other pharmaceutical and related pollutants such



556 as antineoplastic, beta blockers, steroids, hormones, psychotropic, and personal care products.  
557 To address current challenges and advancement in the field, future researches should be fo-  
558 cused on development of cost effective, ecofriendly, simple, and mild condition method for  
559 synthesis of OINs having fully optimized crystallinity and band structure. For practical ap-  
560 plication, work should be done on diversification of pharmaceuticals.

## 561 **8. Conclusions**

562 Diseases are integral part of life which are cured through pharmaceuticals. Excessive and  
563 uncontrolled use of these pharmaceutical results in their release in environment particularly in  
564 water bodies and cause harms to human, animals, aquatic life and ecosystems. This review  
565 summarizes latest literature on removal of these toxic pharmaceutical from water bodies via  
566 advanced oxidation process based on photocatalysis. This review provides reader with vital  
567 information about OINs as photocatalyst for photocatalytic removal of pharmaceutical from  
568 water bodies. OINs are excellent photocatalytic materials owing to their novel properties  
569 for photocatalytic removal of pharmaceuticals and they can be optimized for large scale ap-  
570 plication. We believe, this review provides enough information for future researchers and we  
571 hope future researches will be focused on synthesis of OINs photocatalyst and diversifica-  
572 tion of pharmaceutical to achieve industrial scale applications.

## 573 **Acknowledgements**

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