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Review

Review on fabrication of graphitic carbon nitride based efficient nanocomposites for photodegradation of aqueous phase organic pollutants

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ABSTRACT

Graphitic carbon nitride ($g\text{-}C_3N_4$) as a fascinating visible light active semiconductor photocatalyst has medium band gap, non-toxic nature, stable chemical structure and high thermal stability. Recently, intensive researches are focused on photocatalytic activity of $g\text{-}C_3N_4$ for wastewater treatment. This review demonstrates latest progress in fabrication of graphitic carbon nitride C_3N_4 incorporated nanocomposite to explore photocatalytic ability for water purification. The $g\text{-}C_3N_4$-based nanocomposites were categorized as $g\text{-}C_3N_4$ metal-free nanocomposite, noble metals/$g\text{-}C_3N_4$ heterojunction, non-metal doped $g\text{-}C_3N_4$, transition and post transition metal based $g\text{-}C_3N_4$ nanocomposite. Apart from fabrication methods, we emphasized on elaborating the mechanism of activity enhancement during photocatalytic process.

Contents

Abbreviations: NH_4F, Ammonium fluoride; AOP, Advanced oxidation process; AO, Ammonium oxalate; [Hmim]I, 1-hexyl-3-methylimidazolium iodide; (AEP), 2-aminoethylphosphonic acid; (MBT), 2-mercapto benzothiazole; AFM, Atomic force microscopy; BQ, Benzoquinone; BPA, bisphenol A; B, Boron; CNT, Carbon nano tubes; CN-U, Carbon nitride (Urea); CN-T, Carbon nitride (Thiourea); CQDs, Carbon quantum dots; CB, Conduction band; DFT, Density function theory; NH_4, 2HPO4 Diammonium hydrogen phosphate; ECL, Electrochemiluminescence; EHP, Electron–hole pair; AuNPs, Gold nanoparticles; G, Graphene; GO, Graphene oxide; GCN, Graphitic carbon nitride; HOMO, Highest occupied molecular orbital; HEDP, Hydroxyethylidene diphosphonic acid; •OH, Hydroxyl radicals; LP, Lone pair; LUMO, Lowest unoccupied Molecular orbital; MCIPs, Magnetic conductive imprinted photocatalysts; MS, Magnetically separable; MO, Methyl orange; MB, Methylene Blue; MWNTs, Multi-walled carbon nanotubes; ns, Nanosecond; NIR, Near infrared; NMR, Nuclear magnetic resonance; ORR, Oxygen reduction reaction; PRET, Plasmon resonance energy transfer; P, Phosphorous; RE, Rare-earth; rGO, Reduced graphene oxide; RhB, Rhodamine B; SEM, Scanning electron microscope; Ph_4BNa, Sodium tetraphenylborate; SHE, Standard hydrogen electrode; SRB, Sulforhodamine-B; SPR, Surface plasmon resonance; TBA, Tert-butyl alcohol; TG, Thermal gravimetric; SnS_2, Tin sulphide; TGA, Thermal gravimetric analysis; THF, Tetrahydrofuran; TEM, Transmission electron microscope; US, Ultrasonication; UV, Ultra violet; VB, Valence band; VLD, Visible light driven; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy; ZIF, Zeolitic imidazolate framework; ZnFe, Zinc ferrite; ZnO, Zinc oxide.

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Introduction

Water can be considered most valuable reserve among all natural resources that should be conserved, treated and recycled in scientific way for sustainable growth. Water pollution control is one of the big challenges in front of scientific community with its main concern for protection and conservation of natural water resources. Among various sustainable practices, semiconductor mediated photocatalysis is considered as most alluring and promising technology to directly utilize solar energy to resolve environmental issues [1–5]. Nowadays, growing industries and modern civilization are causing release of hazardous chemicals into aquatic environment causing life threat to all living species on earth [6–8]. Till now, various conventional techniques have been used for water purification *i.e.* coagulation, sedimentation, reverse osmosis, filtration, adsorption, chemical and biological methods. The efficiency of these remedial techniques is not very high for purification of water containing complex matrix of various pollutants like pesticides, pharmaceutical, organic solvents and household chemicals [9,10]. Recently, advanced oxidation processes (AOP's) have emerged as effective purification technique for wastewater containing non-biodegradable and highly stable chemicals [11,12]. In AOP's, hydroxyl radicals ($^\bullet OH$) are highly reactive species and formed *in-situ* that cause non-selective oxidation of organic pollutants to CO_2, H_2O and respective inorganic ions (Eqs. (1)–(20)). Hydroxyl radicals, with high oxidation potential of E^0 ($^\bullet OH/H_2O$) = 2.80 V/SHE, are the second strongest oxidant after fluorine (E^0 = 3.0 eV). The rate constants for reactions between $^\bullet OH$ radicals and contaminants in water are reported in range of 106–1010 L mol^{-1} s^{-1} [13]. Due to their short lifetime (ns) in water, the radicals are quickly vanished from reaction solution.

$$AOPs + OH^\bullet \xrightarrow{Pollutantmolecule} CO_2 + H_2O + Inorganicions \quad (1)$$

Charge separation pathway for ROS production

$$Photocatalyst + h\nu \rightarrow e^-(conductionband) + h^+(valence\ band) \quad (2)$$

$$O_2 + e^- \rightarrow O_2^\bullet \quad E_0' = -0.33V \quad (3)$$

$$HO_2^\bullet \rightarrow O_2^\bullet \quad pK_a = 4.8 \quad (4)$$

$$O_2^\bullet + 2H^+ + e^- \rightarrow H_2O_2 \quad E_0' = 0.89V \quad (5)$$

$$H_2O_2 \rightarrow HO_2{}^- + H^+ \quad pK_a = 11.7 \quad (6)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E_0' = 0.28V \quad (7)$$

$$H_2O_2 + e^- \rightarrow OH^- + OH^\bullet \quad E_0' = 0.38V \quad (8)$$

$$H_2O + h^+ \rightarrow OH^\bullet + H^+ \quad E_0' 2.32V \quad (9)$$

$$OH^\bullet \rightarrow O_2^\bullet + H^+ \quad pK_a = 11.8 \quad (10)$$

$$2HO_2^\bullet {}^1O_2 \rightarrow + H_2O_2 \quad (11)$$

$$O_2^{\bullet-} + h^+ \rightarrow {}^1O_2 \quad E_0' = 0.65V \quad (12)$$

Interaction between radicals

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad (13)$$

$$HO_2^\bullet + O_2^{\bullet-} + H_2O \rightarrow H_2O_2 + O_2 + OH^- \quad (14)$$

$$2OH^\bullet \rightarrow H_2O_2 \quad (15)$$

$$H_2O_2 + hv(UV) \rightarrow 2OH^\bullet \quad (16)$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow OH^\bullet + O_2 + OH^- \quad (17)$$

Energy transfer pathway for ROS production

$${}^3O_2 \xrightarrow[intersystemcrossing]{photocatalyst} {}^1O_2 \quad (18)$$