Emerging applications of nanodiamonds in photocatalysis

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As a fascinating nanocarbon photocatalytic material, nanodiamonds (NDs) have attracted more and more attention recently due to their high chemical stability, high carrier mobility, narrowing band gap, easy surface modification, and mass production. This review summarizes the latest progress related to elaborated construction of NDs and NDs-based nanocomposite, including microstructure regulation of pristine NDs, elemental doping and formation a heterojunction by coupled with another semiconductor. The construction and properties of each category of NDs-based material are reviewed on their structure, preparation methods, texture control, and photocatalytic performance. Photocatalytic applications of NDs-based nanomaterials for hydrogen evolution from water splitting, organic pollution degradation, CO\textsubscript{2} reduction, N\textsubscript{2} reduction, graphene oxide reduction, and the latest advances in photocatalytic reaction mechanism have been also systematically reviewed. Finally, the challenges and prospects of the photocatalytic application of NDs are also briefly analyzed.

1. Introduction

As a metastable allotrope of carbon, Nanodiamonds (NDs) with a nanoscale level size were first synthesized by detonation in 1960 [1]. Since then, NDs were widely studied in biomedical imaging [2–6], magnetic sensors [7–9], drug delivery [10–12], quantum computing [13,14], and environmental purification techniques due to their nearly nontoxicity, low cost, easy modification, high thermal stability, and chemical stability [15–17]. More recently, NDs have been increasingly studied and developed in photocatalytic application field [18–20]. NDs can be synthesized by high-pressure high-temperature (HPHT) technique [22–24], detonation method [1,24,25], laser ablation [26–28], plasma-assisted chemical vapor deposition (CVD) [29–31], and high energy ion irradiation of graphite or carbon onions [27,32]. NDs used in photocatalytic application are mainly prepared by detonation method.

Detonation NDs have a complex structure consisting of sp\textsuperscript{3} carbon core and sp\textsuperscript{2} carbon shell, with oxygen-containing function groups covering their surface [16,33–38]. The size of NDs mostly used in photocatalytic reaction falls in the range of 5 nm in diameter [6,37,39]. The band gap of NDs is about 2–3.5 eV, which is much narrower than typical data of single-crystal diamond due to sp\textsuperscript{2} carbon shell [18–20]. The unique structure and photoelectric property of NDs endow them great potential applications in the photocatalytic field: (1) the hydrophilic surface functional groups of NDs play a great role in photocatalytic activity [40–42]; (2) sp\textsuperscript{2} carbon shell with unrivalled carrier mobility can facilitate the transfer of photogenerated carriers [43–45]; (3) sp\textsuperscript{3} carbon core with intense light scattering can enhance visible light adsorption of photocatalyst [39]; (4) Narrowing band gap of NDs can extend light adsorption range of photocatalysts [18,19]; and (5) Environmental friendliness, mass production, high chemical stability, and low cost make NDs competitive photocatalyst in practical use [16,46–48].

At present, some achievements have been made in the photocatalytic application of NDs. However, pristine NDs generally have no photocatalytic activity [19,39]. Surface functionalization is one of the most useful methods to enhance the photocatalytic activity of NDs [40,42,49]. For instance, hydrogen treated NDs have effective photocatalytic activity in hydrogen evolution from water splitting and reducing graphene oxide [49]. Comparatively, most works have focused on constructing NDs-based composite photocatalyst to optimize the photocatalytic performance of another photocatalyst in enhancing the light adsorption and reducing radiative recombination efficiency of photogenerated electron-holes pairs, where NDs act as modifiers [46,50–53]. For example, the photocatalytic hydrogen evolution activity of Cu\textsubscript{2}O was...
significantly enhanced after coupled with NDs [19]. The photocatalytic pollution degradation activity of TiO$_2$ was obviously improved after modification of NDs [41,54,55]. Accordingly, approaches to optimize photocatalytic performance of NDs-based photocatalysts have been proposed, such as element doping, regulation of surface functional group species.

In this review, we make a compendious review on the structural features of NDs, charge separation mechanism, and applications of NDs and NDs-contained photocatalysts. The application of NDs in the field of photocatalysis mainly focus on the following aspects: hydrogen generation, pollution degradation, CO$_2$ reduction, N$_2$ reduction and graphene oxide reduction. The review aims to provide a preliminary understanding of NDs in photocatalytic application. Perspectives and challenges on the design and extend application of NDs-based photocatalysts are also proposed.

2. Synthesis and properties of NDs

2.1. Synthesis method

At present, NDs can be synthesized by variously method, such as HPHT, detonation method [1,24,25], laser ablation [26–28], CVD method and so on. The detonation method for synthesis NDs was first discovered in 1963 and put it into practical application in 1980s. Generally, the explosion takes place in a sealed chamber, and 4–5 nm NDs can be obtained with other impurities. Finally, pristine NDs can be obtained by the purification process, including magnetic separation, oxidation, and acid picking. Pressure and temperature are the main factors in the formation of NDs.

Laser ablation is another technique for NDs preparation. NDs are generally prepared by pulsed laser ablation in liquid, such as water or acetone. Generally, graphite in the ablation plume would turn into diamond under very high temperature and pressure. The yield of NDs using this method is usually low, compared with detonation method.

Chemical vapor deposition (CVD) is usually used to prepare crystal NDs film, high requirement for equipment. In most cases, a mixture of hydrogen and methane is needed for NDs preparation, supplying atomic hydrogen needed in the gas phase mixture and carbon atoms, respectively. The hydrogen can terminate the dangling carbon bonds on the surface of the diamond layer, cleave the neutral hydrocarbons, create reactive radicals (such as CH$_2$) to form tetrahedral sp$^3$ (ta-C) bonded carbon, and prevent the growth of graphite.

2.2. Properties of NDs

NDs have aroused growing interesting in many filed due to its high hardness, excellent chemical stability, high thermal conductivity, high refraction, easy modification, and large-scale preparation. NDs is one of the most...
stable materials at ambient temperature. NDs have an average size of 5 nm in diameter, and usually aggregation into a larger article (10–50 nm) due to their high surface energy. The type and number of surface groups over the NDs are partly depend on synthetic conditions and subsequent processing. The narrowing band gap of NDs endows it a broad absorption extending to the NIR region. For example, the value of band gap for NDs is 2.21 eV, as shown in Figure 1(a) [19]. In addition, the large refractive index makes NDs strong light scattering effect, which can enhance light absorption efficiency because of the increased optical paths and the enlarged absorption cross-section area derived from interface light scattering. The aqueous solution of NDs shows strong scattering effect under 635 nm light irradiation, as shown in Figure 1(b) [39]. Fluorescent NDs have been studied widely due to its potential in an imaging application. Color centers in diamond as photon sources have been widely reported, such as Nitrogen-vacancy (NV), Silicon-vacancy (SiV). For instance, bright fluorescent NDs can be synthesized by helium ions irradiation, as shown in Figure 1(c) [2]. There are two emission peaks in the florescent spectra of the florescent NDs under the excitation of 532 nm laser: 575 nm (N-V)⁰ and 638 nm (N-V)⁻. Surface modification is another common method to synthesize the fluorescent NDs, for example, hydrophobic blue fluorescent material (ND-ODA) by covalent linking of octadecylamine (ODA) to 5 nm ND particles emission bright blue fluorescence (450 nm) under UV light excitation (410 nm), which easily can be seen even in a very diluted colloidal solution (Figure 1(d)) [3]. These optical properties of NDs play a great role in photocatalytic application.

3. Structure and texture control of NDs

The complex production process of detonation method makes the surface of NDs rich in graphitic carbon, oxygen, hydrogen, nitrogen, and even metal elements. Therefore, the purification process is required for NDs before application, for instance, liquid oxidants (HNO₃, H₂SO₄-HNO₃ mixtures), oxidation in air [56–59]. Finally, NDs show a core-shell-like structure, sp³ carbon as the core and sp² carbon as the shell [19,60,61]. The surface of NDs is covered by functional groups, such as hydroxyl, carbonyl, carboxyl, and hydrogen bonding (Figure 2(a)). The average size of single ND grain is about 5 nm in diameter, and several or dozens single NDs generally unite into an aggregation with 10–100 nm length scale (Figure 2(b)). X-ray diffraction (XRD) patterns further prove the core-shell structure of NDs with sp³ and sp² diffraction peaks (Figure 2(c)). The type and number of surface functional groups on the surface of NDs can change in subsequent treatment conditions (Figure 2(d)) (such as annealing treatment). The unique structure endows NDs decent surface functionalization.

Elaborate strategies are generally used to regulate the microstructure for optimizing the photoelectric property of NDs, such as surface modification and elemental doping [3,62–65]. The scheme of surface functionalization of NDs is illustrated in Figure 3. The acylchloride and C-F species were formed on the surface of NDs after chlorine and fluorine treatment [66]. Hydrogen-terminated sites (C-H) were formed after hydrogen treatment [49]. High-temperature annealing (T ≥ 700 °C, vacuum or inert atmosphere) of NDs can control the degree of graphitization of NDs, namely the number of graphitic shells of
Graphitic carbon shell is beneficial to produce C-O, C-N, and C-S groups after-treatment of the corresponding organic or inorganic solution. The doping elements inside the lattice affect the photoelectric property of NDs. For example, boron doped NDs show a stronger visible light response due to their narrowed band gap.

### 4. Applications

In the field of photocatalytic application, NDs is a new favorite compared to other photocatalysts (TiO₂, g-C₃N₄). Here, NDs were reviewed by focusing on different application fields: H₂ evolution, pollution degradation, CO₂ reduction, N₂ reduction, and graphene oxide reduction.

#### 4.1. H₂ evolution

Generally, pristine NDs have no photocatalytic activity on hydrogen evolution from water splitting. Hydrogen treated NDs (HND) exhibited photocatalytic activity of hydrogen evolution from water splitting with methanol aqueous solution as sacrificial agent upon 532 nm laser pulse irradiation, which was reported by Jang et al. in 2012. As shown in Figure 4, the total H₂ evolution was about 270 μmol for HND after 3 h under the irradiation of 80 mJ per pulse laser irradiation, which was much higher than that of O₂ treatment ND (OND) and acid purified ND (PND) (Figure 4(a)). The research suggests that hydrogen-terminated sites work as reservoirs, and multiphoton absorption resulted in H₂ evolution (Figure 4(b)), as the band gap of HND (5.5 eV) was larger than photon energy (2.6 eV) used in this experiment. However, NDs are widely used as modifiers to enhance the photocatalytic activity of another semiconductor photocatalyst by forming composites. The narrowing band gap of NDs could improve visible light absorption intensity of photocatalyst, while the functional groups on the surface of NDs might provide reactive sites. For example, NDs could promote the photocatalytic H₂ evolution activity of Cu₂O under the simulated solar light irradiation. The results of XRD patterns in Figure 5(a) indicate that NDs was synthesized by laser
ablation using graphite as precursor. The size of NDs is ranging 2–4 nm (Figure 5(b)), and interplanar spacing is 0.206 nm, corresponding to the (111) lattice plane of diamond (Figure 5(c)). The XRD patterns of NDs-Cu₂O appear diffraction peaks both NDs and Cu₂O in Figure 5(d). From the SEM and TEM images in Figure 5(e,f), NDs-Cu₂O is quasi-cube shape with 50 nm in diameter. The appropriate loading amount of NDs can optimize the photocatalytic hydrogen evolution of Cu₂O (Figure 5(g)). The photocatalytic hydrogen evolution rates of NDs-Cu₂O are 1597 and 824 μmolh⁻¹g⁻¹ under the simulated solar light irradiation and visible light irradiation, respectively (Figure 5(h)). The quantum efficiency (QE) is also conducted to study the photoactivity and mechanism, and the analysis results point out that NIR absorption of NDs results from its upconversion PL behavior (Figure 5(i)). The solar to hydrogen conversion efficiency of NDs-Cu₂O was 0.85%, which is 9.3 times higher than that of Cu₂O. Analogously, the photocatalytic H₂ evolution activity of g-C₃N₄ was also enhanced after coupling with NDs, as shown in Figure 6 [39]. The hydrogen evolution rate of the optimal BDND@g-C₃N₄ composite was 96.3 μmolh⁻¹ under visible light irradiation, which is 1.5 times than that of ND@g-C₃N₄ (64.1 μmolh⁻¹). The enhanced photocatalytic activity of BDND@g-C₃N₄ was mainly due to enhanced visible light absorption efficiency of BDND.

4.2. Pollutants degradation

NDs can generally couple with another photocatalyst to form a high-activity heterojunction photocatalyst to
degrade organic pollutants, such as gaseous toluene, diphenhydramine, rhodamine B (RhB) [22,46,53,78]. Figure 7(a,b) showed the HR-TEM images of ZnO and ZnO/ND. The lattice spacing of ZnO was 0.23 nm, corresponding to its (0001) crystallographic plane (Figure 7(a)), and ZnO was closely connected with ND.
for ZnO/ND composite, as shown in Figure 7(b). In Figure 7(c), photocatalytic degradation activity of gaseous toluene of ZnO/ND is much higher than ZnO, as the ~50 ppm toluene could be converted to CO₂ with the conversion yield of 100% within 120 min. The results of the cycle experiment (Figure 7(d)) revealed that the photocatalytic degradation ability of ZnO/ND slightly changed after successive five experiments, while that of ZnO significantly decreased under the same conditions, suggesting ZnO/ND possessed superior photocorrosion-resistance than bare ZnO. In addition, it was also reported that the face functional groups on NDs affected the photocatalytic activity of toluene of ZnO/ND, and bare ND was the optimal candidate compared with graphitized ND, oxidized ND, and acid-treatment ND [18].

Figure 7. (a, b) HR-TEM images of ND (8 wt%)/WO₃, (c) Magnified HR-TEM image from selected area (red square in panel (b)), (d) SAED pattern of the region depicted in panel (c). (e–h) EELS elemental maps of C (panel (e)), W (panel (f)), O (panel (g)), and C + W + O (panel (h)) in ND (8 wt%)/WO₃. (i) Time–dependent profiles of the photocatalytic degradation of CH₃CHO. (j) The concurrent production of CO₂ on bare WO₃, ND (8 wt%)/WO₃, and Pt (1 wt%)/WO₃ [46].

NDs loaded WO₃ exhibited an improved photocatalytic activity for the degradation of acetaldehyde (CH₃CHO) [46]. The HR-TEM images of ND/WO₃ in Figure 8(a,b) suggested that WO₃ was covered by ND. The lattice spacing is shown in Figure 8(c,d) (0.205 nm) is corresponding to the (111) plane of diamond. The electron energy loss spectroscopy (EELS) mapping analysis (Figures 8(e–h)) was performed to verify the presence of NDs and WO₃. Photocatalytic degradation activity of CH₃OH and concurrent production of CO₂ on ND/WO₃ were studied, as shown in Figure 8(i,j). ND/ WO₃ degraded CH₃CHO almost complete conversion to CO₂ within 150 min under visible light irradiation, which is comparable to Pt/WO₃ but much more efficient than pristine WO₃. The super activity of ND/WO₃ was due to the enhanced charge separation and low overpotential of O₂ reduction, which was benefited from the core–shell structure of NDs. Therefore, NDs are expected to be practical materials to replace noble-metal co-catalyst for photocatalytic pollution degradation.

NDs can also optimize the photocatalytic organic pollution degradation activity of TiO₂ [40–42,54,79,80]. TiO₂/ND with 15 wt% of NDs prepared by liquid-phase deposition method showed better photocatalytic degradation diphenylhydramine ability under near-UV/Vis irradiation than the respective bare materials [80]. Moreover, the authors pointed out NDs in composite after oxidation treatment in air at 703 K were rich in oxygen-containing surface...
species, which were beneficial for preparing TiO₂ and carbon nanocomposites. TiO₂/ND with pristine NDs obtained by detonation exhibited a high photocatalytic activity under near-UV/Vis irradiation for oxidative degradation of watersoluble pharmaceuticals diphenhydramine (DP) and amoxicillin (AMX) [41]. As shown in Figure 9(a,b), both DP and AMX can be photodegraded by NDs and TiO₂ composites. The photocatalytic efficiency of NDDT (TiO₂ combined with pristine NDs) is higher than that of NDAT (TiO₂ combined with aminated NDs), NDOT (TiO₂ combined with oxidized NDs), and NDHT (TiO₂ combined with hydrogenated NDs), and TiO₂, suggesting the photocatalytic activity of the composites is strongly dependent on the types of surface functional groups of NDs. The results of the quenching experiment indicated that generated holes were the main reactive species in pollution degradation reaction (Figure 9(c)). High rate constants remained after three-cycle experiments indicating good stability of as-prepared composites (Figure 9(d)).

NDs can reduce poisoning of photocatalyst surface with time. The photocatalytic activity of some photocatalysts (TiO₂) was decreased with time due to the accumulation of reaction intermediates, namely poisoning effect. Kim prepared TiO₂/ND composite by atomic layer deposition, which showed relative higher photocatalytic activity and less significant poisoning with time compared with P-25. They considered that the hydrophilic groups on the surface of NDs was beneficial to water absorption and creating strong oxidizing agents, such as •OH [55].

Modification of carboxylated nanodiamonds (CNDs) can enhance the anti-fouling and self-cleaning properties of photocatalytic membranes. Li et al. synthesized polyvinylidene fluoride (PVDF) containing CNDs membrane (P-CND/TiO₂) by non-solvent induced phase separation, which showed much higher flux recovery ratio and lower irreversible fouling ratios than PVDF and P-TiO₂. The reasons for enhancing membrane antifouling performance of CNDs were listed below: the hydrophilic carboxyl groups on the surface of CNDs lead to a hydration water barrier that reduced foulants adsorption and increased electrostatic repulsions between the negative surface and negative foulant (humic acid) molecules [40].

Oxidized nanodiamonds/titanium dioxide (NDox-TiO₂) prepared by liquid phase deposition method showed enhanced photocatalytic activity in the oxidation of microcystin-LA (MC-LA), a cyanotoxin usually found in water [81]. The apparent first order constants (K_{app}) of NDox-TiO₂ (K_{app} = 4.4 × 10⁻¹ min⁻¹) is 15 times larger than that of pristine TiO₂ (K_{app} = 2.8 × 10⁻² min⁻¹) under visible light irradiation, and the enhanced photocatalytic degradation activity is probably attributed to electronic interphase interaction between TiO₂ and NDox phases.

NDs combined with CuFe-layered double hydroxide (LDH) was effective to enhance the activity for

![Figure 9. The enhanced photocatalytic pharmaceuticals (DP and AMX) degradation activity of treated NDs modified TiO₂ [81]. Normalized concentration of (a) DP and (b) AMX as a function of time for TiO₂ and ND-TiO₂ (1.0 g L⁻¹) composites under near-UV/Vis irradiation. (c) Effect of EDTA and t-BuOH on the photocatalytic degradation under near-UV/Vis irradiation of DP using NDDT and NDAT samples. Curves represent the fitting of the pseudo-first order equation to the experimental data. (d) Reusability of the NDDT and NDAT samples for the DP degradation in three consecutive runs.](image-url)
photoactivating H₂O₂. The migration of photoinduced charges from LDH to ND could promote the separation efficiency of electron-hole pairs, resulting in enhanced photo-Fenton efficiency on MB degradation [78].

Boron-doped NDs contained composite delivered much more improved photocatalytic activity for the organic pollution degradation under visible light irradiation than corresponding bare NDs contained composite due to their narrowing bad gap, for example, photodecomposition of RhB. Our team prepared boron-doped nanodiamonds/graphitic carbon nitride (BDND@g-C₃N₄) composite via a facile pyrolysis approach [20]. Figure 10(a) showed the XRD spectra of the materials, and relative weak characteristic peaks of BDND could be observed in BDND@g-C₃N₄, indicating two components combined closely. BDND with narrowed optical band gap (2.43 eV) extended the absorption range of g-C₃N₄ from 450 to 500 nm, resulting in improved light absorption efficiency (Figure 10(b)). The absorption intensity of RhB solution was minimized in 40 min at the presence of BDND@g-C₃N₄ (Figure 10(c,d)). The BDND@g-C₃N₄ exhibited higher photocatalytic activity for degradation of RhB than BDND and g-C₃N₄.

It is noteworthy that the photocatalytic activity of NDs modified photocatalysts is moderate compared with semiconductor photocatalysts, as shown in Table 1. More work needs to be done to improve the properties in the future.

4.3. CO₂ reduction

The photocatalytic reduction of CO₂ is extraordinarily difficult because the reduce potential of CO₂ is very high in energy compared with the conduction band of most semiconductors [86–88]. H-terminated diamond with large band gap (5.2 eV) could emit electrons into water under UV light irradiation. The electrons in water formed solvated electrons and induce reduction of CO₂ to CO₂⁻, then reduced to CO finally [89]. The photocatalytic CO₂ reduction of diamond was evaluated by fourier-transform infrared spectroscopy (FTIR), as shown in Figure 11. The CO significantly generated from CO₂ solution at the presence of diamond and light irradiation. The authors also demonstrated that the production selectivity was higher than 90% for reduction CO₂ to CO. However, only bulk and thin film samples have the ability to reduce the CO₂ to CO, but not NDs, probably because that a high crystal quantity of diamond was required in the CO₂ reduction process [90].

4.4. N₂ reduction

Poor binding of N₂ to photocatalyst and high-energy intermediates in reduce reaction are the main two problem in the photocatalytic reduction N₂ [91,92]. The hydrogen-terminated diamond used to reduce CO₂ mentioned above was also applied in N₂ reduction [93]. The electrons emitted from hydrogen-terminated diamond
formed solvated electrons in water, which reducing N₂ to NH₃ at ambient temperature and pressure. Similarly, NDs could not be as successful as bulk and thin film diamond [90].

4.5. Graphene oxide reduction

ND could be used as a photosensitizer for reduced graphene oxide (RGO) [49]. As shown in Figure 12(a), the color of graphene oxide (GO) turned black in the presence of hydrogen (H₂) treated NDs (referred as HND) sample under 532 nm laser pulsed irradiation, indicating RGO was formed. The TEM image suggested HND was homogeneously attached to the RGO sheets, which might result from electrostatic adsorption between positively charged HND and negatively charged RGO sheets (Figure 12(b)). The thickness was 4 nm for RGO and the diameter was 5 nm for NDs (Figure 12(c)). The current of HND-RGO devices showed significantly change upon illumination of 514 nm Ar ion laser irradiation, suggesting ohmic contact of devices (Figure 12(d)). As shown in Figure 11(e), the current of was increasing/decreasing flashy when the light was in on/off, suggesting excellent stability of HND-RGO sample. The effective transfer of photogenerated charge carriers from HND to RGO resulted in high photocurrent.

4.6. The stability of ND-based photocatalysts

The stability plays an important role in the practical application for photocatalysts. Delightfully, several consecutive recycle experiments, NDs-based nanocomposite photocatalysts exhibit excellent photostability. HND show negligible reduction of the photocatalytic activity toward hydrogen evolution after three-times recycling, as shown in Figure 13(a) [49]. Figure 13(b) suggests that NDs-Cu₂O also possesses good stability even after five cycle experiments [19]. Analogously, as shown in Figure 13(c), after four recycles, there only 8.85% of H₂ production amount loss, suggesting satisfactory stability of ND@g-C₃N₄ photocatalyst [39]. The crystalline structure of ZnO/ND negligibly changed after photocatalytic reaction, while the peak intensity of ZnO was obviously weakened, indicating quite a stability of ZnO/ND photocatalysts, as shown in Figure 13(d) [89].

5. Photocatalytic reaction mechanism

Pristine NDs generally show no photocatalytic activity in photocatalytic application mentioned above. Thus, NDs are mostly used as modifiers to enhance the photocatalytic efficiency of another semiconductor photocatalyst by synthesizing composites.
**Figure 11.** The photochemical reduction performance of diamond analyzed FTIR spectra: FTIR spectra of gaseous headspace demonstrating reduction of \( \text{CO}_2 \) to \( \text{CO} \) by illuminated diamond, along with control samples [86].

**Figure 12.** The character of NDs in photocatalytic reduce RGO [49]: (a) Photograph of the GO, HND, and 1:5 ratio of GO:HND (dispersed in water) before and after laser irradiation. (b) TEM image of HND-RGO composites. (c) AFM image and height profile of the photodetector device consisting of 10 nm (avg.) thick HND-RGO. (d) I–V characteristics of the RGO and HND-RGO under 514 nm Ar ion laser irradiation and in the dark, and (e) their Di-t curves under chopped irradiation.
The optical band gap of NDs with relative size (about 5–10 nm) is 2–3.5 eV, which is much narrower than typical data (5.5 eV). Therefore, the electrons in the valence band can be excited by visible light and transited to its conduction band. As shown in Figure 14(a), the absorption of NDs-Cu$_2$O is obviously stronger than of Cu$_2$O, ND, and the mixture of both. Accordingly, the narrower band gap of NDs-Cu$_2$O (2.28 eV) compared with Cu$_2$O can enhance light absorption intensity (Figure 14(b)). For a composite photocatalyst, photogenerated electron-hole pairs can be separated by a built-in electric field formed at the interface of different components. The same process can happen to NDs contained composites [18,19,39,41]. For instance, the photocurrent density of ZnO/ND is obviously improved compared to ZnO (Figure 14(c)), suggesting charge separation efficiency is much improved with the addition of ND. In addition, EIS Nyquist plots were also performed to evaluate the advantage of composite photocatalysts in charge separation. As displayed in Figure 14(d), smaller arcs observed for ZnO/ND compared to that of ZnO suggest lower charge transfer resistance, resulting in a higher transfer rate of photogenerated charges in ZnO/ND composite.

The proposed mechanism of photocatalytic degradation of toluene upon ZnO/ND photocatalyst, are shown in Figure 15 [18]. Both ZnO and NDs could generate electron-hole pairs under UV-365 nm light irradiation. Excited electrons of NDs are transferred to ZnO, while the holes of ZnO are transferred to NDs. Therefore, the separation efficiency of photogenerated charge carriers is enhanced, resulting in finally improved photocatalytic degradation toluene. The similar separation regulation of photogenerated electron-hole pairs occurred in BDND@g-C$_3$N$_4$ photocatalyst (Figure 16) [20]. The photogenerated electrons and holes transferred in opposite directions, reducing recombination efficiency of photogenerated electron-hole pairs.

The species and number of surface functional groups play a great role in the photocatalytic performance of NDs [18,40,41,49]. The hydrophilic oxygen-containing groups on NDs surface can affect the pollutants absorption ability of photocatalysts [40]. As shown in Figure 17, carboxylated NDs have a significant enhancement in self-cleaning anti-fouling catalytic membrane due to its hydrophilicity and negative.

NDs can enhance the light adsorption efficiency due to its relative narrowed band gap resulting from the unique core-shell structure and light scattering effect [18,19,39]. The main reasons might be due to that numerous defect energy trapping sates are introduced in the forbidden gap resulting from the electron redistribution and electronic coupling between sp$^3$ carbons and sp$^2$ carbons. Therefore, NDs could generate electron-hole pairs under visible light irradiation, which is beneficial to enhance visible light adsorption efficiency for NDs modified composite photocatalysts. Much large refractive index (approximately 2.42) endows NDs effective light scattering ability, which is another reason for...
enhancing light absorption [39]. As shown in Figure 18, significant light scattering effect of NDs leads to expanding absorption range over the entire wavelength range for ND@g-C_3N_4 composite (Figure 15(a)). The finite difference time domain simulation (FDTD) simulation results about ND@g-C_3N_4 are showed as in Figure 18(b),
a large portion of redirected lights together with rectilinearly propagating parts appeared in the field pattern suggesting enhanced internal scattering at the interfaces of NDs and g-C$_3$N$_4$.

6. Conclusion and perspective

In summary, NDs are becoming more and more valuable photocatalysts because of their large-scale production, earth-abundant nature, visible light response, easy modification, and effective light scattering. At present, the applications of NDs in photocatalysis field mainly focus on photodegradation of pollutants in water and photodissociation water to produce hydrogen. Notice that pristine NDs generally have no photocatalytic activity, but they can be activated via surface functionalization. Mostly, NDs can be used as a modifier to enhance the photocatalytic activity of another semiconductor by constructing composites, which show reduced charge transfer.
recombination. In addition, the narrowed band gap of NDs can enhance the visible light absorption of composite. The effective light scattering of NDs can significantly improve light utilization of composites containing NDs. Moreover, the species and number of the surface functional groups of NDs play an important role in their photocatalytic activity. Many strategies, such as surface modification, doping, heterojunction design have been proposed to explore the application potential of NDs. However, the research achievements of NDs in photocatalysis application is few compared with other carbon materials, such as carbon nanotubes.

More works are needed to further enhance the photocatalytic activity of NDs and explore the photocatalytic reaction mechanism. To enhance visible light adsorption, one may accurately control the band gap of NDs by doping method such as doping with phosphorus (P), nitrogen (N), and boron (B). In terms of the photocatalytic mechanism, some achievements have been made in the surface functionalization of NDs, but what roles do different types of surface functional groups play in photocatalytic reactions need more studies in the future. The applications of NDs in the fields of photocatalytic reduction of carbon dioxide, photocatalytic sterilization, and photocatalytic nitrogen fixation is still scarce, which are worth exploring. In addition, the photocatalytic activity of NDs might be beneficial to its antibacterial effect. However, to our best knowledge, the works direct correlation between photocatalytic activity and antibacterial activity has not been reported.

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