



Advances in the application, toxicity and degradation of carbon nanomaterials in environment: A review



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ABSTRACT

Carbon nanomaterials (CNMs) are novel nanomaterials with excellent physicochemical properties, which are widely used in biomedicine, energy and sensing. Besides, CNMs also play an important role in environmental pollution control, which can absorb heavy metals, antibiotics and harmful gases. However, CNMs are inevitably entering the environment while they are rapidly developing. They are harmful to living organisms in the environment and are difficult to degrade under natural conditions. Here, we systematically describe the toxicity of carbon nanotubes (CNTs), graphene (GRA) and C₆₀ to cells, animals, humans, and microorganisms. According to the current research results, the toxicity mechanism is summarized, including oxidative stress response, mechanical damage and effects on biological enzymes. In addition, according to the latest research progress, we focus on the two major degradation methods of chemical degradation and biodegradation of CNTs, GRA and C₆₀. Meanwhile, the reaction conditions and degradation mechanisms of degradation are respectively stated. Moreover, we have prospects for the limitations of CNM degradation under non-experimental conditions and their potential application.

1. Introduction

Since the advent of nanomaterials and nanotechnology, CNMs have become a hot research area because of their light weight, high strength and high conductivity (Jiang et al. 2018a). In the past few decades, nanotechnology has developed rapidly and CNMs have been widely used. With the increasing research and application of CNMs, their effects on the environment and their behavior in the environment have been obtained more and more attention (Chen et al. 2018).

CNMs are composed of carbon elements, and there is at least one dimension in the nanometer scale of new nano-materials, mainly including carbon nanotubes (CNTs), graphene (GRA) and fullerene (C₆₀) (Fu et al. 2018).

CNTs are cylindrically rolled GRA sheets with fullerene covered in the ends. CNTs include single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) (Russier et al. 2011b). In the last decades, CNTs have become a hot research area because of its unique properties and application prospects in various aspects of

nanotechnology. Owing to their unique one-dimensional nanostructures, CNTs exhibit attractive electronic and optical properties, which are different from other carbon materials and other types of nanoparticles (Gupta et al. 2018).

In addition, CNTs also have small size, good biocompatibility, good surface function and high reactivity. Therefore, CNTs can be widely used in the fields of energy (Luo et al. 2018), biomedicine (Mehra et al. 2018; Mohajeri et al. 2019), electronics (Zhang et al. 2015) and photoelectricity (Yi et al. 2018), analysis and catalysis (Chengguo and Shengshui 2009).

It is similar to CNTs, GRA is also carbon isomers, so there are many similarities between them both in structure and properties. GRA is a single plane hexagonal or multislice composed of sp² bonded C-atoms (Basheer et al. 2018). Because the carbon atoms of GRA are connected by carbon bond and the bond energy is large, the mechanical properties of GRA are much better than those of ordinary nanomaterials, which can be used to fabricate high mechanical strength composites. GRA has different sizes ranging from nanometers to microns.

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Moreover, with the change of size, their chemical properties will change accordingly (Basheer et al. 2018). The physical structure of GRA is inexplicable, with a layer of carbon atoms packed in a honeycomb lattice (Meyer et al. 2007). It is a single-layer material with low-dimensional physics (Li et al. 2008), and has excellent conductivity, optical transparency, mechanical flexibility (Mohajeri et al. 2019), thermal conductivity and low coefficient of thermal expansion (Novoselov et al. 2004). Therefore, GRA has a wide range of applications in electronic devices (Wu et al., 2018), batteries (Fu et al. 2018), wastewater treatment (Ali et al. 2019) and sensors (Jiang et al. 2018a). GRA also has a range of derivatives, including graphene oxide (GO), reduced graphene oxide (RGO), GRA nanoribbons, fluorographene and so on. The presence of these derivatives extends the scope of application of GRA (Guo et al. 2011; Yin et al., 2014; Zheng et al. 2014).

C₆₀ is a three-dimensional compound with unique cage structure. Their special physical and chemical properties may be due to the unique molecular stereotype. The three-dimensional space structure and many double bonds of C₆₀ provide a broad space for the development of fullerene science (Chen et al. 2018).

Fullerene is a magical substance. Because of its property of radical scavenging, it can be added to cosmetics, anti-aging (Benn et al. 2011). Moreover, owing to its unique physical and chemical properties, fullerene can be widely and importantly used in many fields (Prato 1997), such as biomedicine (Junaid et al. 2016; Liu et al. 2014; Markovic and Trajkovic 2008; Panchuk et al. 2015; Zhu et al. 2016), electronic devices (Yan et al. 2014), photocatalyst (Moor et al. 2015), and environment (Florescervantes 2011) and so on.

These three major kinds of CNMs are widely used, and they are ubiquitous in our lives. The application of CNMs is shown in Fig. 1. However, CNMs not only bring benefits to us, but also cause a series of environmental problems. CNMs are one of the most recalcitrant synthetic materials. With the mass production and use of CNMs, they have more and more opportunities to enter into the environment. The increase of CNMs in water environment will produce certain toxicity to aquatic organisms. Therefore, it is urgent to study the water environmental behavior of CNMs and their toxicity to aquatic organisms (Mueller and Nowack 2008). In addition, CNMs have a small particle size that can penetrate cell walls, cell membranes in a living body, triggering reactions such as lung tumors and cellular inflammation, which would produce direct damage to animals and humans (Oberdörster et al. 2006; Pangule et al. 2009). Moreover, they are likely to spread and accumulate in the food chain. (Lam et al. 2004; Wu et al. 2006). Although CNMs have strong adsorption ability and can enrich toxic and harmful pollutants in the environment, the toxic effects of CNMs adsorbed by pollutants may also be enhanced (Gosens et al.

2010; Oberdörster et al. 2005).

CNMs may be degraded in the environment, and subsequent physicochemical changes will affect their original toxicity. At present, the degradation of CNMs is mainly divided into two categories, namely, non-biodegradation and biodegradation. Non-biodegradation mainly includes chemical degradation (Liu et al. 2019; Liu et al. 2017). Biodegradation includes cell degradation, enzymatic degradation and bacterial degradation. In the research of biodegradation of CNMs, enzyme degradation is mainly used. In the enzymatic degradation process of CNMs, molecular docking (MD) technology is used to predict possible binding sites, which helps to understand its degradation mechanism (Chen et al. 2017a; Liu et al. 2018a; Liu et al. 2018b). The study of the degradability of CNMs helps to improve the safety of their application in the environment.

CNMs are an indispensable material in the development of modern science and technology, so they are widely used in many ways. However, studies have shown that CNMs are not easily degraded under natural conditions and will accumulate in the environment or combine with other substances, which may cause toxicity to organisms. This paper summarizes the toxicity of CNMs to cells, organisms and microorganisms, and briefly describes its toxicity mechanism based on the current research results. In addition, the degradation of CNMs was summarized, and the degradation mechanism of CNMs was analyzed in combination with the latest research progress, which helps to provide important guiding significance for the overall study of CNMs. In this paper, combined with the latest research progress, while expounding the application of CNMs, it mainly reviews its biological toxicity and degradation methods, which helps to provide important guiding significance for the overall research of CNMs, and provides necessary theoretical support for understanding the biotoxic effects of CNMs and degradation in the environment.

2. Application of carbon nanomaterials for pollutants removal

2.1. CNTs and their derivatives

The special and stable porous structure of CNTs has a wide range of potential applications in hydrogen storage, adsorption, catalysis and medical research (Yi et al. 2018). Among them, in terms of adsorption, the CNTs have a large specific surface area and a rich pore structure, so that they have strong adsorption properties for heavy metals, antibiotics and petroleum in an aqueous environment.

CNTs are one of the most commonly used adsorbents for the treatment of metal ions in water, and they performed remarkable stability and removal efficiency under extreme conditions (Guoqiang et al.,

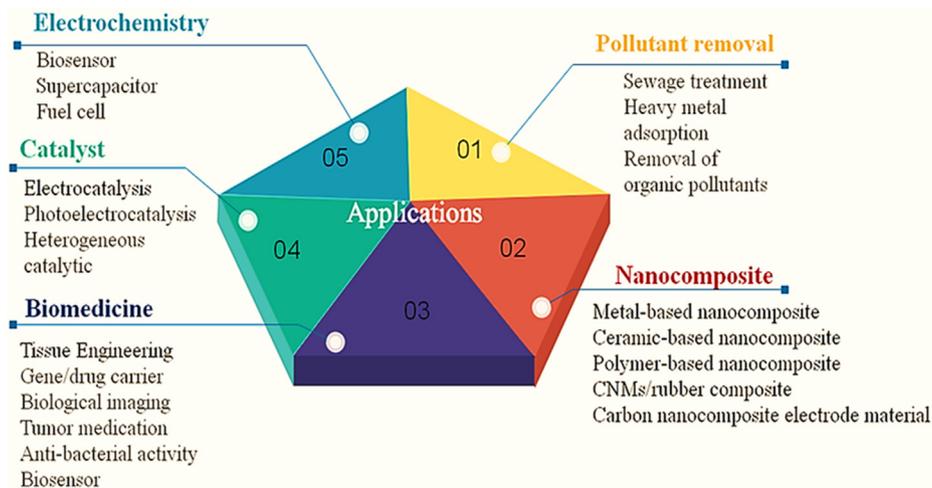


Fig. 1. Application of carbon nanomaterials.

Table 1
Application of CNTs in heavy metal adsorption

CNTs	Heavy metal elements	Adsorption capacity(mg/g)	Refs
F- MWCNTs	Cu(II)	118	(Gupta et al., 2017a)
MWCNTs	Cr(III)	66	(Marques Neto et al., 2019)
MWCNTs	Cr(VI)	449	(Marques Neto et al., 2019)
MWCNTs	Cd(II)	181	(Bhanjana et al., 2017)
MWCNTs-SH,	Pb(II)	187	(Li et al., 2017)
F-CNTs, MWCNTs	Ni(II)	18	(Mehrmand et al., 2018)
MWCNTs-Fe ₃ O ₄	Hg(II)	238	(Sadegh et al., 2018)
PdO-MWCNTs	V(V)	57	(Gupta et al., 2017b)
CNTs	Mn(VII)	147	(Yadav and Srivastava, 2017)
MWCNTs	Au(III)	28	(Jose Alguacil, 2018)

2018). Chromium (Cr) is often in the form of Cr(III) in the environment. Trivalent chromium is hypotoxicity, but once converted to Cr(VI), it becomes high-toxic (Maitlo et al., 2019). The removal of Cr(VI) is very necessary (Jiang et al., 2018b). Researchers have used carboxylated MWCNTs treated with chitosan to develop a fast and effective method for Cr(VI) removal, and the adsorption of Cr(VI) is more easily achieved in an acidic aqueous solution. Among them, the maximum adsorption amount is as high as 140 mg/g or more (Huang et al., 2018). The main mechanism by which CNTs remove heavy metals from water is due to the interaction between heavy metal ions and oxygen-containing functional groups on the surface of CNTs (Vilardi et al., 2018). The adsorption of CNTs on other heavy metals is shown in Table 1.

With the widespread use of antibiotics, their residues in the environment are increasing (Ncibi and Sillanpaa, 2015). Antibiotics are difficult to be biodegraded in the environment (Shao et al., 2019a; Shao et al., 2019b). Nowadays, the pollution of antibiotics to water environment become a serious problem (Shao et al., 2018). Since antibiotics have low biodegradability in water environment, low cost and simple adsorption operation are widely used in antibiotics. Some adsorbents also cause secondary pollution after treatment, and CNTs are widely used due to their environmental friendliness. The mechanism of CNTs adsorbing organic pollutants is mainly hydrophobic interaction, π - π electron donor-receptor (π - π EDA), and π - π electron coupling stacking, etc. The main reason for the adsorption of chlortetracycline hydrochloride (CTC) and tetracycline hydrochloride (TCN) is the π - π interaction between the adsorbents (Xiong et al., 2018). The adsorption of CNTs for other antibiotics is shown in Table 2.

The leakage of crude oil has occurred from time to time, and the degradation of oil in water is also a difficult problem. CNTs have a strong adsorption capacity and are capable of adsorbing oil. Fard et al. used two types of CNTs (P-CNTs and C-CNTs) for comparing the adsorption of emulsified oil. The results showed that the repulsive force between produced CNTs (P-CNTs) and oil droplets is smaller, and the adsorption is stronger. P-CNTs had better emulsified oil removal efficiency than commercial CNTs (C-CNTs). And P-CNTs has a large oil absorption capacity, which can even reach 17 times of their own weight (Fard et al., 2016).

In addition, CNTs can be used as a water purification membrane to purify water and remove pollutants from water.

Table 2
Application of CNTs in antibiotic adsorption

CNTs	Antibiotics	Adsorption capacity(mg/g)	Refs
SWCNTs	Oxytetracycline	554	(Ncibi and Sillanpaa, 2015)
SWCNTs	Ciprofloxacin	724	(Ncibi and Sillanpaa, 2015)
SWCNTs	Lincomycine	115	(Kim et al., 2014)
MWCNTs	Lincomycine	18	(Kim et al., 2014)
MWCNTs	Oxytetracycline	391	(Ncibi and Sillanpaa, 2015)
MWCNTs	Ciprofloxacin	475	(Ncibi and Sillanpaa, 2015)
MWCNTs	Tetracycline hydrochloride	368	(Xiong et al., 2018)
MWCNTs	Chlortetracycline hydrochloride	254	(Xiong et al., 2018)

The special shape of CNTs and their unique physical antibacterial action provide a new perspective for the inhibition of microorganisms. Brady-Estévez et al. (2008) have developed a SWNTs filter. SWNTs filters can effectively retain and inactivate bacteria and viruses. CNTs also can be applied to remove surfactants in water. Since the MWCNTs are hydrophobic, the surface of MWCNTs are engaged in hydrophobic binding with the tail of the surfactant (Ncibi et al., 2015). In the filtration treatment of personal care products (PPCP) and drugs, MWCNTs are used due to their selectivity. Because of the hydrogen bonding between MWCNTs and PPCPs, filtration of these wastewaters with selected membranes can remove PPCP well (Wang et al., 2016b). In the adsorption of drugs, porosity plays an important role. Compared with mesoporous activated carbon, CNTs have higher efficiency in removing drugs from water (Ncibi and Sillanpaa, 2017).

CNTs can not only adsorb pollutants alone, but also combine with other materials to form composites with stronger adsorption capacity (Yu et al., 2016). In order to better utilize the adsorption properties of the CNTs, the surface of the CNTs is functionalized, which can improve the dispersion in the medium, thereby enhancing the interaction between the contaminants and the CNTs (Fatemi and Foroutan, 2016). The carbon nanotubes-chitosan (CNTs-CS) composite electrode has good capacitance. Compared with the conventional electrode, the CNTs-CS composite electrode has a larger electroadsorption capacity and a faster electroadsorption rate, and its good mesoporosity improves the capacitive water desalination performance. Due to its excellent electroadsorption performance, CNTs-CS composite electrode has a good application in the purification and treatment of sewage (Ma et al., 2016).

2.2. Graphene and their derivatives

GRA is the first synthesized two-dimensional atomic crystal, which has attracted much attention because of its excellent properties, such as, high strength, stiffness, elasticity, and good mechanical properties (Di Bartolomeo, 2016). In addition, the thermal conductivity and electron mobility of GRA are extremely high, and the band gap is adjustable (Wang et al., 2011). Many excellent properties appear in one kind of materials, which can replace other materials in many applications, and bring a series of technical breakthroughs for related applications.

Table 3
Toxicity impact of carbon nanomaterials

Materials	Results	Refs
Cytotoxicity		
C ₆₀	The ROS produced by C ₆₀ can attack organisms directly	(Hebard et al., 1994)
C ₆₀	Unmodified C ₆₀ molecules can exchange electrons with nucleotides	(Nogueira et al., 2015)
C ₆₀	Electrostatic and cellular structures causing damage	(Gieldon et al., 2017)
Aqu- C ₆₀	DNA damage potential	(Matsuda et al., 2011)
GRA	The sharp edge of the graphene can cut the cell wall of the algae cell	(Song et al., 2018)
GRA	Affect the metabolic activity of fish cells	(Kalman et al., 2019)
GRA	Oxidative stress reaction, causing cytotoxicity	(Chng and Pumera, 2013)
GO	Significant mechanical damage to cells	(Efremova et al., 2015)
MWCNTs	DNA repair mechanism	(Martinez-Paz et al., 2019)
MWCNTs	MWCNTs has phagocytic activity and cytotoxicity against HL-60 cells	(Tabei et al., 2019)
Toxicity to animals and humans		
SWCNTs	SWCNTs has a great effect on the development of <i>Artemia salina</i> in seawater	(Jang and Hwang, 2018)
SWCNTs	Hormone regulation affecting the brain of zebrafish	(da Rocha et al., 2019)
CNTs	CNTs can enhance the toxicity of Cu and Cd	(Shvedova and Kisin, 2008; Wang et al., 2016)
CNTs	CNTs can enter the body through the respiratory tract and deposit in the lungs, causing granuloma, fibrosis or inflammation in the lungs	(Kayat et al., 2011; Panchapakesan et al., 2005; Qinglin et al., 2015)
GRA	Destroying the ultrastructure and physiological characteristics of the lungs, playing a toxic role	(Keelan, 2011; Usenko et al., 2007)
GRA	Neurotoxicity to zebrafish embryo development	(Yang et al., 2019)
GRA	GRA can enter fetal blood via placenta to influence fetal growth and development	(Su et al., 2016)
GO	Reduce the fecundity of <i>Spodoptera litura</i>	(Martins et al., 2019)
C ₆₀	Produces inflammation in rat lung tissue	(Myojo and Ono-Ogasawara, 2018; Shinohara et al., 2010)
nC ₆₀	Non-derivative C ₆₀ suspension was found to be toxic to fish by oxidative stress	(Liu et al., 2010)
nC ₆₀	nC ₆₀ can produce acute and chronic toxicity to large cockroaches	(Deryabin et al., 2015)
GRA	Chronic toxicity to large leeches	(Fan et al., 2016)
Toxicity to microorganism		
C ₆₀	C ₆₀ can cause toxic effects on <i>Escherichia coli</i> , and charge transfer occurs between the two	(Dharni et al., 2016)
MWCNMs	CNMs can inhibit the growth of certain bacteria and fungi	(Chung et al., 2011)
MWCNTs	High concentration of MWCNTs inhibit the biomass and activity of microorganisms in the soil	(Jin et al., 2014)
SWCNTs	The concentration of SWCNTs was negatively correlated with the biomass of soil microbial community	(Oyelami and Semple, 2015)
CNMs	Biomass and community structure affecting microbial communities	(Chen et al., 2019)

GRA has a wide range of applications in the preparation of semiconductor photocatalysts due to its excellent properties, such as high transparency and high specific surface area. Graphene-based photocatalysts can reduce heavy metals, disinfect wastewater and degrade organic pollutants in the environment.

GRA has great potential in the development of nanotechnology, energy technologies and environment, and it is considered to be an important achievement. As a tool to enhance photocatalytic performance and solar photovoltaic efficiency, GRA is widely used in photocatalysis. There are many methods to remove the heavy metal in water. Compared with other chemical methods, photocatalytic removal of toxic heavy metal ions has the advantages of low energy consumption, mild reaction conditions, and high efficiency, and can be used to remove Cr(VI) pollution from water. Wang et al. (Zhou et al., 2010) studied the photocatalytic reduction of Cr(VI) by graphene-titanium dioxide composites. The synthesized GO/TiO₂ composite exhibits excellent photocatalytic oxidation ability in the reduction conversion of inorganic pollutants such as Cr(VI) (Fardos and Bahamonde, 2017). GRA materials have important research value and application prospect in heavy metal ion adsorption. Three dimensional GRA/polypyrrole sponge was prepared by covalent assembly of GO and pyrrole by Li et al. (Li et al., 2013). And this material have a very large adsorption capacity and adsorption rate to oil (> 100 g/g) and organic solvents. Besides, under different sunlight irradiation time, the GO/TiO₂ film is reduced and used as a catalyst for degrading *Escherichia coli*. [67].

In addition, GRA also shows great application potential in atmospheric treatment. GRA has large specific surface area, high carrier mobility and high sensitivity. It can detect the properties of a single molecule or atom and be used to prepare a highly sensitive gas sensor. Al mashat et al. prepared an H₂ sensor using GRA polyaniline nanocomposite as the medium. Its sensitivity to H₂ is much higher than that of the intrinsic GRA H₂ sensor (Almashat et al., 2010). GRA based materials can adsorb some greenhouse gases and other gases, such as

NH₃. NH₃ is more easily adsorbed when the water vapor content in the atmosphere is high, and the interaction between NH₃ and graphite oxide will occur. The carboxyl group reacts with the hydroxyl group, but the adsorption weakens when the water content is too high (And and Badosz, 2007). The GRA sheet has a stronger adsorption capacity for gas after modification. For example, GRA modified by polyaniline has higher adsorption of CO₂ than unmodified raw GRA because of the amine group. There is a reaction between them, the surface alkalinity of the complex is higher. And CO₂ is an acid gas, it is more likely to react between the two to form carbon oxide compounds.

2.3. C₆₀ and other carbon-based materials

C₆₀ is the third carbon isomorphism, and its structure is similar to that of football. The unique structure of C₆₀ molecules determines their colorful physical and chemical properties (Yan et al., 2015). In terms of physical properties, C₆₀ molecules are nonpolar, with large π bond spherical molecules, easily soluble in aromatic solvents containing large π bonds, such as benzene, and toluene, etc. C₆₀ exists in solid form at room temperature and atmospheric pressure. C₆₀ is a good electron acceptor in both ground state and excited state. C₆₀ has super conductivity (Avanasi et al., 2014). At present, the chemical properties of C₆₀ mainly focus on molecular modification. Through the study of C₆₀ and its derivatives, it has been found that C₆₀ and its derivatives have good application prospects in electronic light sensitivity devices, superconductors, luminescent materials, molecular magnets, catalysis, biomedicine and so on.

C₆₀ is known as “pioneers of materials in the 21st century”. Studies have shown that C₆₀ has aromatic properties and a certain adsorption effect on small organic molecules. Amer et al. (Amer and El-ashry, 2006) have found that the entropy effect and the enthalpy effect play an important role in the selective adsorption of methanol and water by C₆₀ in a methanol/water mixtures with different mixed components. This

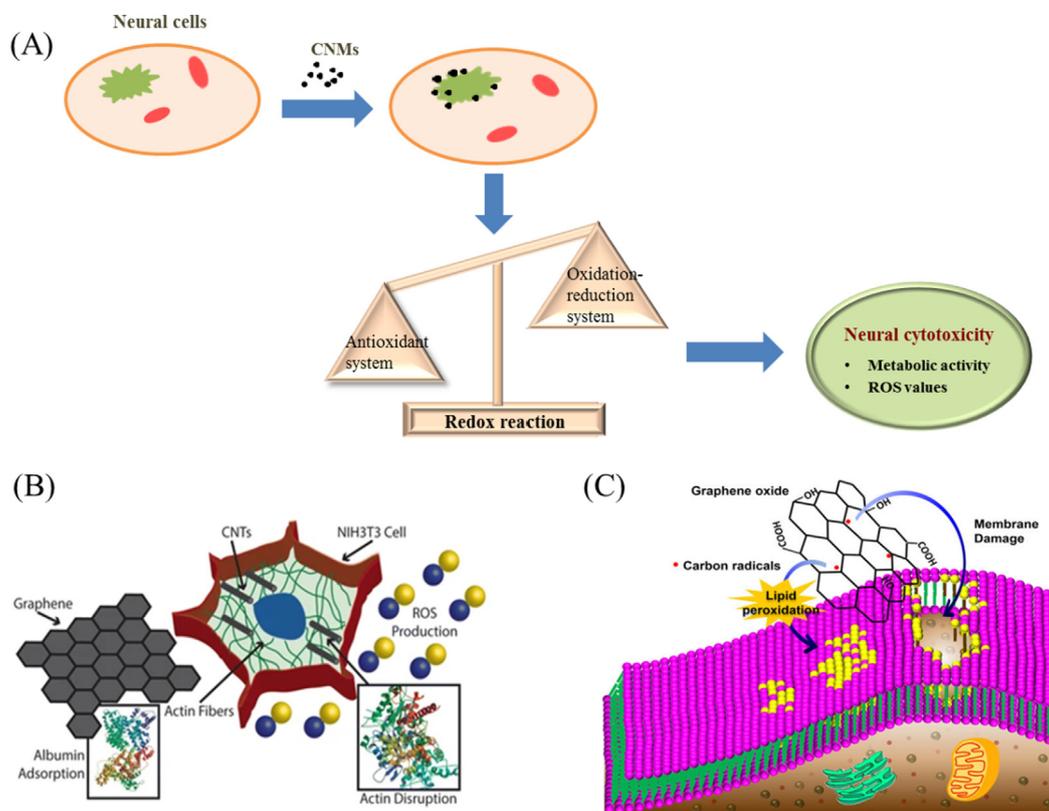


Fig. 2. Toxicity mechanism of CNMs to cells. (A) The equilibrium state of the ROS in the cells is broken by the addition of CNMs, resulting in the production of large amounts of oxidants and affecting cellular metabolic activity. (B) Toxic effects of CNMs on NIH3T3 cells: agonistic protein destruction and ROS production. (C) Toxic effects of GO on macrophages: lipid peroxidation and membrane damage. Reproduced with permission from Ref. (Li et al. 2018; Pastrana et al. 2019).

property can be applied to the adsorption of volatile organic compounds (VOCs) in the atmosphere. C_{60} can react with other substances in the adsorption of atmospheric pollutants. Although the adsorption amount of VOCs in the atmosphere is large, there is no targeted absorption, C_{60} is also in the aspect of adsorbing VOCs in the atmosphere (Fagan et al., 1991). There has a large room for improvement. In addition, the adsorption of C_{60} is related to the geometry of their surface. Santos et al. (Santos et al., 2008) performed classical annealing to explore and find the optimal geometry of ascorbic acid molecules in the study of the adsorption of C_{60} to ascorbic acid.

3. Toxicity impact of carbon nanomaterials

3.1. Cytotoxicity

CNMs have received wide attention due to their unique physical and chemical properties. When they are widely used, people begin to study the possible environmental pollution and hazards. As a result, scientists have conducted a series of experiments on the toxicity of CNMs (Table 3). The toxicity study of MWCNTs by Tabei et al. (2019) showed that it has extremely high phagocytic activity for undifferentiated HL-60 cells and a certain cytotoxicity for already differentiated HL-60 cells. In addition, MWCNTs have a certain genotoxicity, which will affect the DNA repair mechanism. Martinez-Paz et al. (Martinez-Paz et al., 2019) using molecular larval studies at aquatic levels to showed that MWCNTs affect the transcription of genes involved in apoptosis. Moreover, the structure, diameter, and length of CNTs are also important factors for their toxicity. The longer the length of the CNTs, the stronger the toxicity (Sato et al., 2005). For example, it has been suggested that macrophages will absorb short CNTs, while long ones will not (Shi et al., 2017). In addition, the toxicity of two CNTs of different lengths was compared experimentally, and long CNTs were found to have a

higher inflammatory response (Poland et al., 2008).

The cytotoxicity of GRA and its related materials is related to its physicochemical properties. Studies by Chng et al. (Chng and Pumera, 2015) have shown that GRA is capable of forming GRA aggregates, so GRA is more toxic to CRL-2522 cells than GO. Studies also have shown that GRA and GO are cytotoxic to human skin and produce different interactions with different cells (Chng and Pumera, 2013; Liao et al., 2011). Graphene-related materials also have an effect on the metabolic activity and lysosomal function of fish cells, and the degree of graphitization is closely related to toxicity, and the two are inversely proportional (Kalman et al., 2019). In addition, Efremova et al. (Efremova et al., 2015) used *Escherichia coli* to study the toxicity of GO. The results showed that the change of physicochemical properties of GO was decisive for its toxicity (Akhavan and Ghaderi, 2010; Liu et al., 2011), and GO will adhere a lot to the surface of bacteria and charge neutralization. In addition, GO's excellent mechanical strength causes significant mechanical damage to cells (Zhang et al., 2010).

The toxicity of C_{60} is mainly related to surface charge. Gieldon et al. (Gieldon et al., 2017) studied the effect of C_{60} on protein. The results showed that C_{60} aggregates are cytotoxic and can disrupt cell structure. In addition, C_{60} is insoluble in water, but can be stably dispersed in water, thus becoming an aquatic pollutant, aqu- C_{60} . The data indicates that aqu- C_{60} has potential for DNA damage (Matsuda et al., 2011).

These studies have shown that the three nanomaterials, GO, SWCNTs and C_{60} , have certain cytotoxicity. Among them, SWCNTs and C_{60} can significantly cause the translocation of BAX proteins related to apoptosis in mitochondrial membranes, which are toxic to cells by inducing apoptosis. C_{60} can cause cytotoxicity and DNA damage in organisms. Because C_{60} has good light sensitivity, it is easy to produce excited fullerenes under the condition of light excitation, which is the key of the toxicity of C_{60} to organisms. The reactive oxygen species (ROS) can attack organisms directly, resulting in a series of changes

such as protein oxidation, DNA destruction, membrane degradation and so on, thus causing damage to organisms (Ausman, 2005). When the formation of ROS exceeds the antioxidant defense ability of the organism, the organism will be in the state of oxidative stress, resulting in cell mitochondrial damage, lipid peroxidation and protein oxidation, thus causing cytotoxicity. In addition, C₆₀ can produce certain genetic toxicity to organisms. Unmodified C₆₀ molecules can accept electrons and exchange electrons with nucleotides, thus causing damage to DNA (Hebard et al., 1994).

The mechanism of toxic effects of CNMs on cells is mainly the mechanism of oxidative stress toxicity (Pastrana et al., 2019). And the mechanism is shown in Fig. 2. The active oxygen free radicals in the organism remain in equilibrium when they are undisturbed. Once this balance is broken, it will accumulate a large amount of oxidant. Glutathione, which causes an increase in oxidative stress in the cell, which subsequently leads to loss of function of the cell, which ultimately leads to cell death (Lee et al., 2019). In addition, since the CNMs particles are small, they can directly enter into the cells, and the entry of the CNMs into the immune cells induces an accelerated inflammatory reaction (Vasyukova et al., 2015). Besides, the entry of CNMs destroys the integrity of the cells and produces toxicity. Some studies believe that CNTs can directly damage the cell membrane of bacteria, causing their nucleic acid leakage and metabolism to decline. GRA has different toxicity mechanisms to cells. The edge of the GRA sheet is sharp. When exposed to algae cells, GRA flakes may damage the cell wall (Nogueira et al., 2015), and cause some mechanical damage to the cells.

The derivative of C₆₀, nano-C₆₀ (nC₆₀), also produces certain toxic effects in the environment. Prylutska et al. (Prylutska et al., 2017) found that the concentration of nC₆₀ aqueous solution has a strong correlation with the genotoxicity of human lymphocytes. The cytotoxicity of nC₆₀ is related to the chemical properties of the surface of C₆₀, and its toxicity is due to the complex formed by charge transfer of C₆₀ with solvent water, tetrahydrofuran (THF) and so on. Although the pathways for possible uptake, distribution, metabolism, and excretion of nC₆₀ in organisms are unclear, nC₆₀ has toxic effects at different molecular levels (Ausman, 2005).

3.2. Toxicity to animals and humans

CNTs are insoluble in water and deposited in sediment, which are toxic to benthic animals in rivers, and also affect the transport of other co-existing pollutants (Mueller et al., 2013; Song et al., 2018). Some researchers have studied the toxicity of CNTs to aquatic organisms. Zhu et al. have found that SWCNTs has a great effect on the development of artemia salina in seawater, and that the higher concentration of SWCNTs, the higher larval mortality (Zhu et al., 2018). da Rocha et al. (2019) studied the toxicity of CNTs to zebrafish. The results showed that SWCNTs regulate the release of hormones by affecting the brain of zebrafish, which is neurotoxic. Jang and Hwang (2018) proved that F-MWCNT in aquatic environment can alleviate the toxicity of lead in the environment. However, Kim et al. (Kim et al. 2009) found that CNTs can enhance the toxicity of copper. Wang et al. (2016) found that the cadmium (Cd) toxicity in daphnia magna would be enhanced in the presence of F-MWCNT. Lam et al. did the toxicity test of CNTs with mice. It was found that CNTs reaching the lungs would produce strong toxicity, and the damage caused by CNTs would be aggravated with the passage of time, and long-term inhalation of CNTs would be extremely harmful to health (Panchapakesan et al. 2005). In the actual environment, CNTs do not exist alone, and have a certain degree of adsorption to other environmental pollutants, so it is impossible to accurately estimate the damage caused by CNTs to the environment.

Direct contact with CNTs is also a potential hazard to human health (Beard et al., 2018). The mechanism of the damage may be related to the physical and chemical properties of CNTs, especially the small size effect. Because CNTs are light, they can enter into the body through the respiratory tract and deposit in the lungs, causing pulmonary

granuloma, fibrosis or inflammation (Shvedova and Kisin, 2008). CNTs are cleared through alveolar macrophages when they enter into the lungs. After the CNTs were swallowed by macrophages, most of them deposited in the alveolar septum and alveolar cavity, and granulomatous inflammation occurred. The deposit would deeply and easily to penetrate into deep lung tissue (Kayat et al., 2011). Russ et al. (Russ et al., 2019) have found that inhalation of MWCNTs can trigger an inflammatory response in the lungs, and lead to disturbances in pulmonary mechanics and airway epithelial function, leading to changes in lung function ultimately. It is shown that the smaller the size of CNTs, the more difficult it is for macrophages to clear them quickly. The size and number of CNTs are closely related to the lung damage. The smaller size of CNTs, the larger the amount of contact with alveolar epithelial cells and macrophages, and the more likely it is to cause bursts of inflammatory cells in the lungs (Zhao and Liu, 2012).

GRA is a good biocompatible CNMs. However, some studies have found that GRA has certain biological toxicity. The biotoxicity of GRA mainly depends on its physical and chemical properties and is closely related to its dosage. With the increasing production and use of GRA, they will inevitably enter the environment, which brings risks to the ecological environment and human health.

Placental barrier is an organ in which maternal and fetal nutrients and metabolites are exchanged, which can prevent harmful substances from entering the fetus. Placental barrier is an essential defensive barrier to protect the fetus during maternal pregnancy. Studies on embryotoxicity of nanomaterials have shown that nanoparticles below 100 nm can enter fetal blood via placenta to influence fetal growth and development (Keelan, 2011). GRA can not only penetrate the physiological barrier, but also produce a series of systemic toxicity.

Most GRA nanoparticles inhaled into the lungs pass through the upper respiratory tract and deposit in the lungs (Su et al., 2016). GRA induced lung injury is the main symptom of toxicity in animals (Qinglin et al., 2015). In addition, GRA can also produce certain toxicity to the central nervous system, and will affect the reproduction and development of animals. Yang et al. (Yang et al., 2019) studied the effects of GO on embryonic development of zebrafish. Studies have shown that GO in the environment is acutely toxic to zebrafish embryos. After treatment with 10 µg/ml GO, the hatching rate and survival rate of zebrafish embryos decreased significantly, and the deformity rate was as high as 11.11%. Besides, the presence of GO can cause motor disturbances and may cause neurotoxicity.

Like many other nanomaterials, C₆₀ are likely to be exposed to workers through direct skin absorption or oral feeding from the source of production. During the production, transportation, storage and consumption of C₆₀, overflow C₆₀ may pollute the air and water environment (Sanchis et al., 2018). C₆₀ in cosmetics which are used by humans, like other chemicals in cosmetics, may be released in water, discharged into sewers, and released into the environment after cleaning their skin. In some cosmetics, C₆₀ can stay in the environment for a long time (Benn et al., 2011). From a consumer's point of view, the use of products containing C₆₀ makes consumers exposure to C₆₀, especially those in direct contact with the human body, such as sunscreen and cosmetics, which are popular with female friends (Benn et al., 2011).

C₆₀ also has a certain effect on lung tissue. In the toxicity evaluation experiment of rats, Myojo et al. Myojo and Ono-Ogasawara (2018) injected C₆₀ into the body by inhalation and intraluminal injection, and the results showed that the lung tissue of the rats would have an inflammatory reaction. As shown in Fig. 3, Shinohara et al. (Shinohara et al., 2010) used inhalation and intratracheal injections to infect rats, and found that a small fraction of C₆₀ is deposited on the surface of the lungs and can be present for a long time. In addition, C₆₀ has a certain influence on the embryonic development of mammals. Vasyukova et al. (Vasyukova et al., 2015) conducted in vivo and in vitro studies using mice, and the results showed that C₆₀ had harmful effects on mouse embryos.

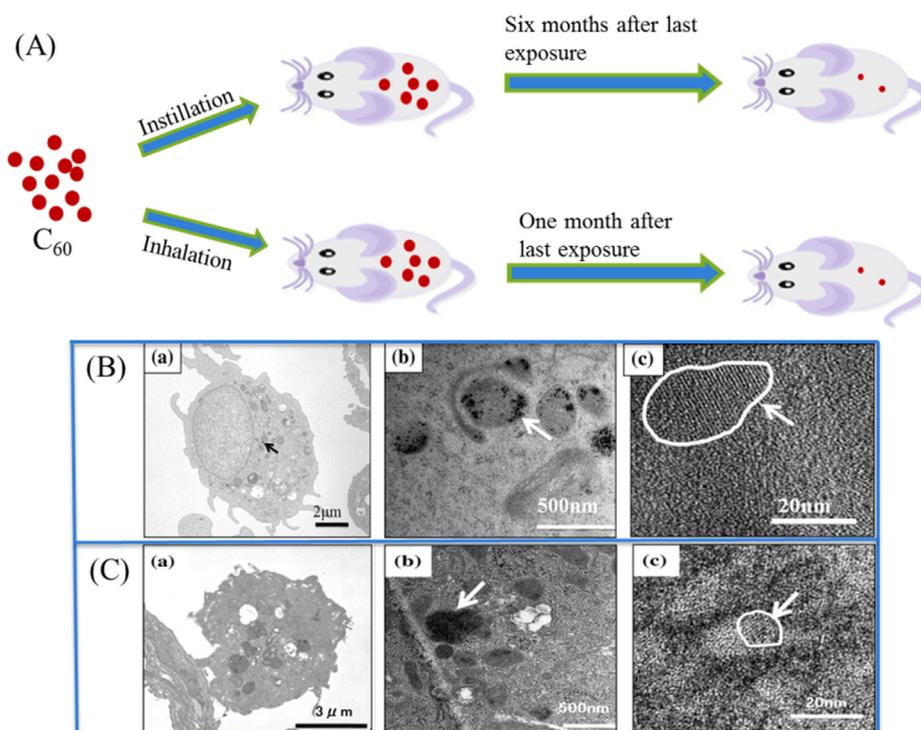


Fig. 3. Toxicity study of C₆₀ on rat lung. (A) The elimination process of rats after injection by inhalation and inhalation of C₆₀. (B) and (C) are TEM images of alveolar macrophages after injection and inhalation, respectively. Reproduced with permission from Ref. (Shinohara et al. 2010).

In addition, the application of C₆₀ in the environment makes it possible to leak in the water environment. C₆₀ can form stable water-soluble nanoparticles in water, thus increasing their mobility and biological exposure in the environment. In the water environment, C₆₀ can be transported/diffused into organisms and may eventually act on humans and some advanced consumers through food chain accumulation. Non-derivative C₆₀ suspension was found to be toxic to fish by oxidative stress (Usenko et al., 2007). Studies have shown that nC₆₀ can produce acute and chronic toxicity to large cockroaches who play an important role in maintaining the balance of aquatic ecosystems, and their exercise capacity is significantly weakened, which in turn affects the predation activities of large cockroaches and even causes large cockroaches to die (Lovern et al., 2007).

3.3. Toxicity to microorganisms

Microorganisms are an indispensable part of nature and are closely related to our lives. Microorganisms are different from animals and humans. They have no complicated cell structure. Although the structure is different, the toxicity mechanism of CNMs on microorganisms is similar to that of animals (Chen et al. 2018). CNMs can interfere with their metabolic processes by affecting microbial enzymes and cause damage to microorganisms (Chen et al. 2019). Direct contact with microorganisms by CNMs can cause damage to the cell membrane and then lead to microbial death. In addition, reactive oxygen species produced by oxidative stress in CNMs induce a series of phenomena, such as protein denaturation, DNA damage, etc, which can also cause damage or death of microbial cells (Gieldon et al., 2017; Hebard et al., 1994). *Escherichia coli* (*E. coli*) is a microorganisms in the ecosystem, which can degrade GO under certain conditions. However, C₆₀ can cause toxic effects on *E. coli*, and charge transfer occurs between them (Deryabin et al., 2015). CNMs exposed to the environment can have an indirect effect on microbial communities in the soil. Studies have shown that the presence of CNTs in the soil affects microbial carbon, reducing its content and affecting soil microbes (Kang et al., 2019).

Microorganisms are the most important decomposers in nature and

play an important role in maintaining material circulation and decomposing animal and plant remains. Some autotrophic microorganisms, such as cyanobacteria and some planktonic microorganisms, are the starting segments of the food chain. The concentration of CNMs is closely related to the survival of microorganisms. When the concentration is high, it inhibits the growth of most microorganisms, and also has an important impact on the biomass and community structure of microbial communities. The effects of CNMs on microorganisms can interfere with their decomposition and thus have an indirect effect on the environment. Chung et al. (Chung et al., 2011) studied the effects of MWCNTs on soil microbes. The results showed that the high concentration of MWCNTs inhibited the biomass and activity of microorganisms in the soil. In addition, CNMs also have a certain effect on the biodiversity of microorganisms, which may inhibit the growth of certain bacteria and fungi (Dharmi et al., 2016). The concentration of SWCNTs was negatively correlated with the biomass of soil microbial community, and SWCNTs in soil had a certain influence on the microbial community composition (Jin et al., 2014). There are more and more researches on the effects of CNMs on soil microbes. Oyelami et al. (Oyelami and Semple, 2015) have found that CNMs have no significant effect on soil microbial activity in a short period of time, but refractory CNMs are exposed to the environment in large quantities. Some of the toxic mechanisms are still unclear, so we should minimize the release of CNMs in the environment.

4. Degradation of carbon nanomaterials

4.1. Chemical degradation

The chemical degradation of CNMs mainly includes photodegradation and chemical degradation (Hou et al., 2015; Xing et al., 2014). Photodegradation relies mainly on light, while chemical degradation relies primarily on chemical reagents. The chemical degradation of CNMs is induced by the production of reactive oxygen species. In general, the light that causes the degradation of CNMs is ultraviolet light because it has high energy and can excite electronic transitions

(Hou et al., 2015). Light will act on the surface of the CNMs, inducing the production of reactive oxygen species and electron-holes, causing degradation and transformation of the material. Under light conditions, CNMs will produce CO_2 when it is degraded and converted into small molecules. Under the premise of illumination, the addition of other chemicals will increase the degradation rate of CNMs. Studies have shown that in the photodegradation process of GO, the simultaneous addition of H_2O_2 can increase the degradation rate of 15% (Xing et al., 2014). In addition to chemical reagents, pH and the size of CNMs is also an important factor affecting their degradation. In general, the efficiency of photodegradation is still relatively high, but only UV light can degrade CNMs (Ren et al., 2015), and in the natural environment, CNMs will react with other substances, so the degradation of CNMs by UV light will be affected by these factors.

Chemical degradation relies on some chemical agents with strong oxidizing properties, such as O_3 , to directly oxidize CNMs by means of dipolar addition, electrophilic substitution, or indirect oxidation of negative ions during oxidation (Labille et al., 2009). During chemical degradation, CNMs undergo redox reactions with chemical reagents, which change their physicochemical properties. Both strongly oxidizing O_3 and H_2O_2 and reducing S^{2-} can degrade CNMs (Xia et al., 2015). The surface of SWCNTs has a π -conjugated structure. When O_3 degrades SWCNTs, this structure is removed and then reacted. The surface of SWCNTs generates a large number of carboxyl groups, so the oxygen content is greatly increased (Simmons et al., 2006). The chemical degradation of CNMs is affected by its own stability, and the more stable it is, the more difficult it is to degrade (Labille et al., 2009). Although chemical degradation is more efficient, in the natural environment, CNMs usually combine with other pollutants to form new and more difficult to decompose complexes, and the chemical degradation of CNMs requires the use of a large number of chemical reagents, and some reagents also process the CNMs (Du et al., 2017). It will cause secondary pollution, so it is very important to study the efficient and environmentally friendly degradation methods of CNMs.

4.2. Biodegradation

The biodegradation methods of CNMs mainly include enzymatic degradation, cell degradation and bacterial degradation. Among them, enzymatic degradation is the most widely studied in the biodegradation of CNMs (Table 4), and we can see the main mechanism of catalytic degradation of CNMs in Fig. 4.

4.2.1. CNTs biodegradation

With the wide application of CNTs in various fields, people have more and more understanding of CNTs as a new nanomaterial. The study of CNTs biodegradation is always associated with various kinds of enzymes.

Scientists have demonstrated that CNTs can be biodegraded in the natural environment by enzyme catalysis (Allen et al., 2008; Andon et al., 2013; Russier et al., 2011a). Most previous studies have focused

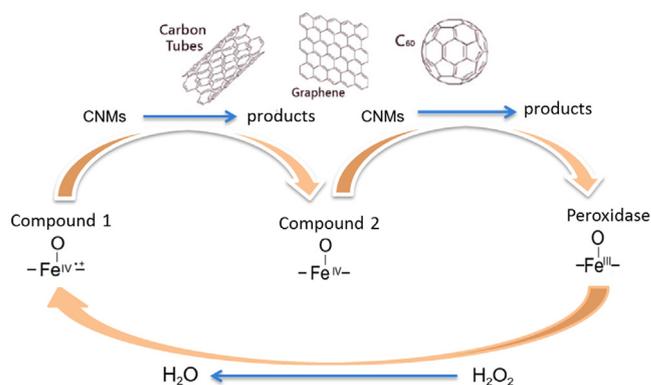


Fig. 4. The main mechanism of enzyme biodegradation of CNMs.

on the degradation of CNTs, which have better biocompatibility and are more likely to react (Bianco et al., 2011; Niyogi et al., 2002). The degradation of SWCNTs is relatively simple. Myeloperoxidase (MPO) in human neutrophils can promote the biodegradation of SWCNTs, but SWCNTs can't be completely degraded in macrophages. Because MPO contains hypochlorite and reactive free radical intermediates, acidic conditions are conducive to the degradation of CNTs. In addition, the existence of free radicals will promote the effective degradation of CNTs. In addition to degradation in vivo, SWCNTs can also be degraded under certain conditions in vitro. In vitro culture of human neutrophils, the presence of MPO, hypochlorite and H_2O_2 can also completely degrade SWCNTs. EPO, like other peroxidases, predominantly catalyzes a two-electron redox reaction, using H_2O_2 to oxidize a halide to its corresponding hypohalous acids, and produce reactive radical intermediates. It can be seen that both human eosinophil peroxidase (EPO) (in vivo) and EPO activated in vitro can catalyze the oxidative degradation of SWCNTs (Andon et al., 2013).

When MPO was proved to be able to oxidize and degrade SWCNTs, some scholars studied the degradation mechanism of SWCNTs. The degradation of CNTs by MPO mainly depends on the hypochlorite produced in vivo. The carboxyl functional groups of SWCNTs can interact electrostatic with protein's Arg residues, and there is a π - π stacking interactions between them and the Tyr residues of the protein. These two reactions combine SWCNTs with human serum albumin (HSA) and greatly promote the biodegradation of SWCNTs (Naihao et al., 2014). Lu et al. studied the effect of HSA on the biodegradation of SWCNTs by MD technique. As is shown in Fig. 5(A), the results showed that there were two potential sites to bind to oxidized SWCNTs, and the oxidative SWCNTs at the two binding sites was stabilized by electrostatic interaction (Lu et al., 2014). In combination with previous studies, it has been shown that carboxyl groups on CNTs make them interact with a variety of proteins.

Moreover, Chen et al. (2016) used two different enzymes to study the molecular basis of SWCNTs degradation. The two enzymes were manganese peroxidase (MnP) capable of degrading SWCNTs and lignin

Table 4

Enzymatic degradation of carbon nanomaterials

Enzyme	CNMs	Theory	Refs
MPO	SWCNTs, GO	The degradation of CNTs by MPO mainly depends on the hypochlorite produced in vivo	(Andon et al., 2013; Naihao et al., 2014)
HRP	MWCNTs	MWCNTs is oxidized by HRP and H_2O_2 , which leads to many defects	(Modugno et al., 2016; Yong et al., 2011)
HRP	SWCNTs	There is a strong interaction between SWCNTs and proteins which makes the active sites of HRP close to the carboxylated SWCNTs substrates	(Allen et al., 2009)
LPO	SWCNTs	LPO combination with NaSCN and H_2O_2 can form the hypothiocyanous acid which is capable to modify the phospholipids adsorbed to the SWCNTs	(Bhattacharya et al., 2015; Chen et al., 2017)
MnP	SWCNTs	The conformational change in MnP can be enhanced by SWCNTs	(Chen et al., 2016)
HRP	GO	There is electron transfer between graphene and bacteria	(Liu et al., 2015)
LIP	GRAs	LIP is a peroxidase with stronger redox properties than HRP and MPO	(Zhao et al., 2018)

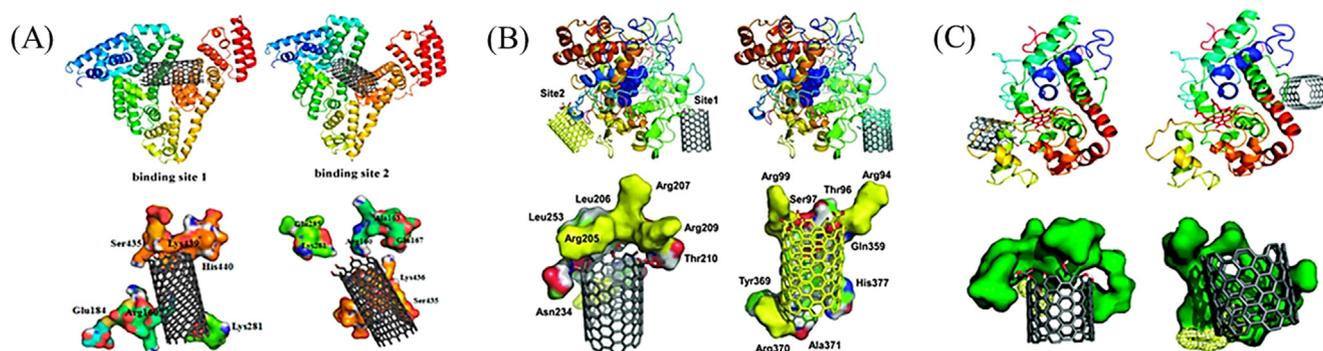


Fig. 5. A molecular model of the interaction between enzymes and SWCNTs. (A) Interaction between SWCNTs and HSAs and possible sites of action. (B) The interaction site of SWCNTs on EPO. (C) Modified and original binding sites of SWCNTs and HRP. Reproduced with permission from Ref. (Allen et al. 2009; Andon et al. 2013; Lu et al. 2014).

peroxide (LiP) which could not degrade SWCNTs. The analysis shows that SWCNTs can prevent the natural conformation of LiP from changing, so that it can avoid its degradation, while MnP can undergo a conformational transition. The conformational change occurs in the presence of SWCNTs. The conformational change of MnP is enhanced, which plays a key role in the biodegradation of SWCNTs. Although LiP can't degrade the original SWCNTs, it can degrade the treated carboxylated SWCNTs. Therefore, LiP also has a certain ability to degrade SWCNTs.

CNTs usually needs to be functionalized before degradation, because the original CNTs is difficult to be degraded by naturally occurring animal and plant enzymes under normal circumstances, but it can be degraded after functionalization. The biodegradation of CNTs mainly depends on a variety of enzymes. Chen et al. (2017b) studied the molecular basis of CNTs degradation by functionalization using two known biodegradative enzymes, horseradish peroxidase (HRP) and lactoperoxidase (LPO). The results show that the functionalization energy can change the properties of CNTs itself, such as enhancing the stability of the complexes produced by enzyme and substrate reactions through carboxylation.

Under the condition that only H_2O_2 is used as an auxiliary reactant, MPO degrades SWCNTs into small molecule products after 6 days (Vlasova et al., 2011), MnP has no degradation to SWCNTs after 14 days of reaction (Zhang et al., 2014), LiP can effectively degrade SWCNTs after 20 days (Lalwani et al., 2014), while HRP takes 10 days to completely degrade SWCNTs (Allen et al., 2009). However, according to the current study, among these four enzymes of HRP, MPO, LiP and MnP, since the reaction conditions of each enzyme are different, there is no comparative experiment in which the four enzymes degrade the same carbon nanomaterial under the same reaction conditions.

The degradation of MWCNTs is different from SWCNTs. Because SWCNTs have only one layer, while MWCNTs are composed of multiple layers, which would affect the secretion of HRP. The degradation rate of MWCNTs is related to their own carboxylation degree. Compare with SWCNTs, it takes longer to degrade MWCNTs with HRP. And the degradation usually begins at the defect point on the MWCNTs (Yong et al., 2011). Modugno et al. used HRP to study the biodegradability of double-walled CNTs and MWCNTs covalently oxidized with different lengths and degrees of oxidation. The results showed that double-walled CNTs can't be biodegraded because of their ability to resist the degradation of HRP, but MWCNTs can be partially degraded (Modugno et al., 2016). As is shown in Fig. 5(C), Allen et al. used MD technique to analyze the conformation of the interaction between HRP and SWCNTs in order to find the most priority binding sites under different conditions (Allen et al., 2009). It has been mentioned in previous studies that there is attraction between carboxyl groups of SWCNTs and positively charged structural regions of proteins. This molecular model also verifies this point. There is a strong interaction between SWCNTs and

proteins. This attraction makes the active sites of HRP close to the carboxylated SWCNTs substrates, thus making the oxidative degradation of SWCNTs possible.

Different cells have different principles for the degradation of CNTs. Some cells degrade CNTs through their own peroxidase, while phagocytic cells degrade CNTs through phagocytosis and a series of reactions. *Eosinophils* can produce EPO in the presence of NaBr or H_2O_2 , and the enzymes can degrade CNTs (Andon et al., 2013). The interaction site of SWCNTs on EPO is shown in Fig. 5(B). Before phagocytic cells degrade CNTs, CNTs need to be modified to form defect sites. After their original structures are destroyed, MWCNTs are more susceptible to degradation by phagocytic cells (Elgrabli et al., 2015). In addition, the degradation mechanism of SWCNTs by neutrophils is similar to that of macrophages (Kagan et al., 2014), and its degradation mechanism is shown in Fig. 6(A).

Bacteria are widely found in nature, and the degradation of CNTs by bacteria takes a long time. Because CNTs are biocompatible, they can adsorb bacteria on the surface, and the reaction of bacteria with CNTs begins at the defect, edge or surface. Bacteria can stress MWCNTs and then produce peroxidase. The conformation of this active site has a strong affinity, which enhances the ability of bacteria to degrade MWCNTs (Chouhan et al., 2016). Bacterial degradation of MWCNTs produces CO_2 . When a single strain degrades MWCNTs, the amount of CO_2 is small. When a variety of bacteria coexist, the amount of CO_2 produced will increase significantly (Zhang et al., 2013). The CO_2 in the degradation process is not all derived from MWCNTs, and sometimes an external carbon source is needed to ensure the smooth progress of the degradation process.

4.2.2. GRA biodegradation

With the increasing commercialization of GO and GRA, eco-friendly methods are urgently needed to oxidize and degrade graphitized materials for two main reasons. Firstly, it is essential to develop a mild, green graphite oxide method. Because GO is generally made by potassium permanganate, depending on the high concentration of potassium permanganate and sulfuric acid caused by the intense oxidation of graphite. Heavy use of strong oxidants and concentrated acids can increase costs and threaten the environment (Likens and Bormann 1974). Secondly, once graphitized materials are released in large quantities into the environment, they are likely to be toxic to flora and fauna (Dreher 2004; Lowry et al., 2012). For example, GRA sheets may cause physical damage when entering cells. There is an urgent need for an environmentally friendly method for degradation of GRA nanomaterials.

In terms of biodegradation of GRA, some researchers have found that microbial bacteria can oxidize GRA materials. Liu et al. (2015) have isolated naphthalene degrading bacteria from graphite ores, which are exposed to GRA materials. There is electron transfer in GRA, which results in the reduction of the volume of the material and the

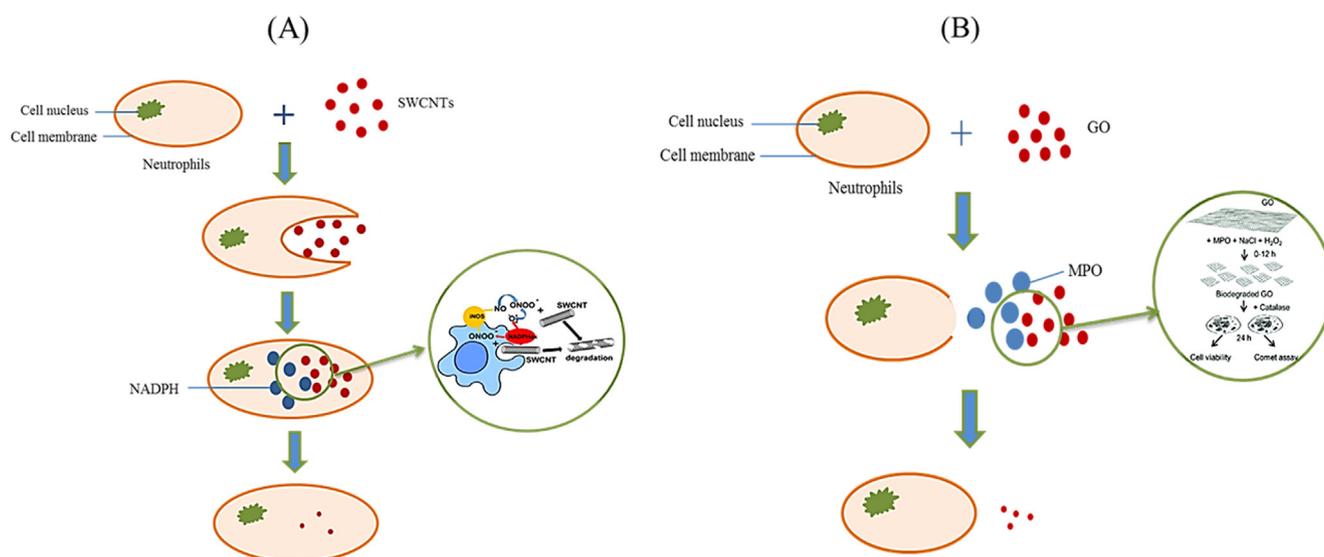


Fig. 6. Degradation of CNMs by neutrophils. (A) Neutrophils degrade SWCNTs by endocytosis. (B) Neutrophils degrade extracellular GO by producing extracellular trapping networks containing proteases such as MPO. Reproduced with permission from Refs. Kagan et al. (2014); Mukherjee et al. 2018).

degradation of the material. In addition, there are several enzymes that can degrade GRA. HRP was originally used to degrade carbon materials and then used in biodegradation of CNTs and GRA. HRP needs to be activated in the presence of H_2O_2 and then converted (Kurapati et al., 2018). GO is oxidized by two successive electron transfer processes. The oxidation reaction destroyed the crystal structure and resulted in defects which promoted the biodegradation of GO. HRP can also degrade three-dimensional GRA materials in engineering applications. It is stripped off and dissolved one by one. After the GRA sheet is gradually corroded into a single layer, the edge slowly dissolves and eventually degrades to CO_2 .

The degradation of GO by MPO in myeloid cells mainly depends on the production of strong oxidant hypochloric acid, and then reacts with the functional group in GRA to break it, thus achieving the purpose of degradation. The degradation of GRA by MPO mainly depends on its hydrophilicity, colloid stability and surface negative charge. The more dispersed the GO, the easier it is to be degraded. The most likely place for degradation of GRA materials is on the oxygen-containing groups on the surface of GRA materials, while hydrophilic functional groups will make the GRA materials gather together, thus reducing the stability of colloids, producing precipitation and making the degradation process difficult (Kurapati et al., 2015). In addition, LiP secreted by white rot fungi can also degrade GRA materials. This is a peroxidase with stronger redox properties than HRP and MPO, which can effectively degrade GRA, which is widely present in the environment (Zhao et al., 2018).

In addition to the use of some bacteria or enzymes to degrade GRA, we can also look for the degradation method from GRA itself. The physical and chemical properties of GRA materials are changed by doping heterogeneous atoms or surface modification. Doping heterogeneous atoms will change the physical and chemical properties, photochemical properties and electromagnetic properties of the materials, resulting in defects in the structure of GRA materials, which plays a key role in the enzymatic degradation of GRA. However, at present, this method is mainly used in battery, capacitor and so on (Wang et al., 2014), and there are many details worth our further study.

Some researchers have also studied a new “design degradation” strategy, which has been applied to GO degradation. Some molecules are coupled to the surface of GO to increase the attraction of GO to the enzyme near the active site, or to increase the oxidation rate of the enzyme by guiding the electron transfer between GO and the enzyme. The results show that covalently bound GO is more easily

biodegradable. Kurapati et al. (2018) have studied four different GRA oxidation models using GO model and construction function provided by pymol to evaluate the ability of functional groups. They used the MD method to study the interaction between GO and HRP. The results showed that the more the residual number was, the better the biodegradation of GO was. As shown in Fig. 7, compared with natural GO, the addition of coumarin and catechol groups can accelerate the degradation rate of GO and make it almost completely degrade. In addition, most of the additional amino acids can catalyze the oxidation reaction. The biodegradation of GO mainly depends on the functional groups attached to the surface. The covalent modified GO can bind to the protein better than the unmodified one (Kurapati et al., 2018).

The degradation mechanisms of CNMs by cells and bacteria are similar. At present, there are few studies on the degradation of GRA by cells. Phagocytic cells and neutrophils can degrade GO, and the degradation mechanism is the same as that of CNTs, as shown in Fig. 6(B). Bacterial degradation of GO, after the reaction, many pores will form on the surface, because the chemical bond is broken, CO_2 will be produced during the degradation process, and GO will gradually become fragmented as the degradation reaction progresses (Liu et al., 2015). Both *E. coli* and *Shewanella* bacteria can effectively degrade GO, provide electrons and transfer electrons extracellularly to restore GO (Akhavan and Ghaderi 2012). Oxygen is an important factor in the degradation of CNMs by bacteria. Some bacteria can only degrade GO in an anaerobic environment, and studies have shown that the presence of oxygen can accelerate the reduction of GO.

4.2.3. C_{60} biodegradation

The biodegradation of CNTs and GRA is mainly enzymatic degradation. At present, there is not much research on C_{60} biodegradation, and the mainly reported ones related to bacteria. C_{60} can be mineralized in soil, especially clay and organic blower soil, which can promote the rapid and complete mineralization of C_{60} . In the presence of soil bacteria, C_{60} is difficult to be degraded (Avanasi et al., 2014). In the organic-rich clay, due to the presence of agricultural soil bacteria, the mineralization degradation rate of C_{60} is greatly improved, and more than 50% of C_{60} can be mineralized in 65 days (Berry et al., 2017).

The coupling process between photochemistry and biodegradation has the potential to greatly accelerate the degradation of C_{60} , possibly due to the destruction of stable condensed aromatic structures by photochemistry. The degradation of C_{60} by chlorobacterium and

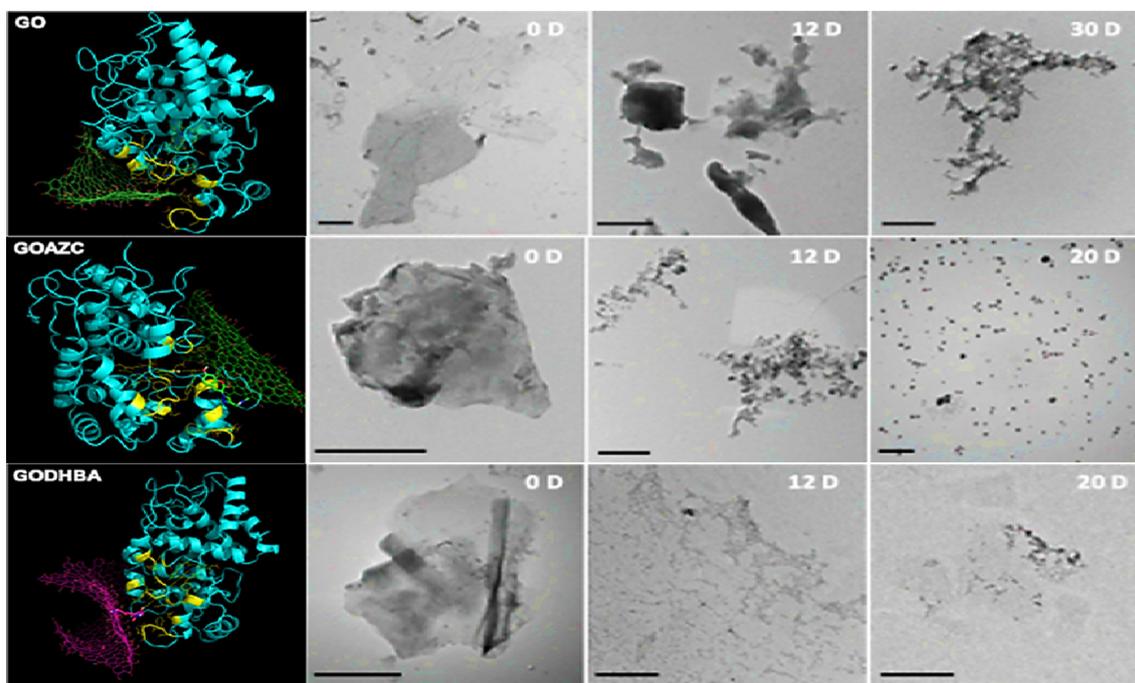


Fig. 7. Molecular simulations show possible binding positions of HRP and functionalized GO samples and the TEM images of GO, GOAZC and GOTEG during HRP/ H_2O_2 degradation at different time points. Reproduced with permission from Ref. Kurapati et al. (2018).

hydrolysable sp^3 and sp^2 oxygenated carbon (Berry et al. 2017). At 350 nm illumination, C_{60} can't be degraded by photo-conversion. However, when it is used as a hydroxylation intermediate reaction product, C_{60} has a great mineralization potential after long-term infrared radiation (Hwang and Li 2010).

Moreover, Chae et al. used the strain of the genus coriobacter to degrade C_{60} . It was found that the volume of C_{60} aggregates would decrease under the condition of microorganism. The hydroxylation of C_{60} and the activity of photosensitivity reaction will be enhanced, but the degradation is slow and there is no obvious phenomenon (Chae et al., 2014). The biodegradation of CNMs by bacteria is mainly related to electron transfer. The transfer of electrons causes the C–C chemical bond to break, forming a large number of pores, causing the surface structure of the CNMs to be damaged and degraded. When the surface of CNMs is negatively charged, bacteria can act as electron acceptors. When the surface of CNMs is positively charged, bacteria can transfer electrons to them (Liu et al., 2015). At the point of electron transfer, bacterial degradation of CNMs is subject to oxygen interference (Salas et al., 2010).

The enzymes that degrade CNMs are mainly HRP, MPO, MnP and LiP. These four enzymes require H_2O_2 to participate in the degradation of CNMs. The negatively charged functional group on the surface of CNMs is the key to its binding to enzymes. The enzyme has positively charged amino acid residues, which are bound by electrostatic interaction. The combined complex depends on the heme in the enzyme. Unfunctionalized CNMs may not be easily degraded, and their degradation begins at the defect. The treated CNMs have more defects, which is more conducive to the combination with the enzyme.

Biodegradation is an environmentally friendly degradation method. However, there is still a gap between experimental research and actual conditions. CNMs are easily adsorbed together with other pollutants in the environment, which makes difficulty for the practical degradation of CNMs in the environment. Therefore, more researches are still need, especially in the actual situation, to study the CNMs degradation.

5. Conclusions

CNMs can be applied not only in industrial manufacturing, but also

in the treatment of environmental pollution. With the increasing use of CNMs, people gradually began to study its toxicity. In recent years, researchers have learned a certain understanding of the toxicity of CNMs. It can pollute the ecological environment and has toxic effects on animals, and humans. CNMs are easy to combine with other substances in the environment, and there are few studies on the toxicity of conjugates in the toxicity study on CNMs. It requires further exploration and analyze of the migration of CNMs in organisms and the environment.

The toxicity of CNMs limits its application in vivo. The research on the degradation of CNMs is also to reduce its biological toxicity and facilitate the biomedical applications of CNMs. The physico-chemical degradation of CNMs relies mainly on ultraviolet light and chemical reagents. Photodegradation is affected by many factors, such as pH and the size of CNMs. Although chemical degradation is more efficient, it may cause secondary pollution. The biodegradation of CNMs relies mainly on enzymes, cells and bacteria. The degradation of CNMs is mainly based on enzymatic degradation. The activity of enzymes is affected by many factors such as temperature and pH. Therefore, the requirements for enzymatic degradation are strict. Under natural conditions, CNMs will adsorb substances in the environment, and their degradability will change accordingly. Therefore, we also need to explore the degradation of CNMs in the presence of different contaminants and find a highly efficient green degradation method.

Therefore, the following four points are proposed for the research of CNMs:

1. When CNMs are combined with other substances in the environment, their structure will change accordingly, which will change the toxicity. Therefore, researchers need to further explore the laws of CNMs structural changes and provide effective support for the toxicity research of CNMs.
2. The toxicity of CNMs is related to its structure and length. In subsequent studies, exploring ways to reduce its toxicity can promote its application in biomedicine.
3. In the degradation process of CNMs, biodegradation method and non-biodegradation method can be combined to reduce the generation of pollution while improving the degradation efficiency.

4. The current biodegradation of C₆₀ is mainly based on bacterial degradation, and further research is needed for the novel degradation method of C₆₀.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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