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The Application of Nanotechnology to Ameliorate Copper Pollution of Mine Water in China

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Abstract:

Mine water pollution is a serious problem in China and has caused certain impacts on human health, water and soil. This paper talks about the applications of nanotechnology in treating copper ions in mine water, which have advantages over the traditional methods, and discusses two potential nanomaterials-graphene and zinc oxide nanoparticles based on references. The authors describe the concepts, synthesized methods, and advantages of each material. After researching, the literature revealed attractive prospects for removing copper ions from mine water using carbon nanomaterials, including the benefits of using carbon nanomaterials to adsorb copper ions, the introduction of graphene and graphene oxide, and some synthesized methods of graphene and its derivatives. In addition, the eco-friendly synthesized process of zinc oxide nanoparticles, the great performance of the absorption capacity on Cu ions, and its fundamental function in the synthesis of various nanomaterials contribute to the promising prospect of ZnO nanoparticles.

Keywords: Copper ions pollution; mine water; nano technology; adsorption; graphene.

1. Introduction

China is one of the major mining countries in the world. According to the national geological environment mapping survey of mines, there are more than 110,000 non-hydrocarbon mines in China, with a total area of about 1.04 × 10^5 km^2 and 187 types of mines, and the total amount of minerals extracted annually is estimated to be more than 1.36 × 10^{10} tons. Classified by the mining category, there are more than 16,500 energy mines such as coal, more than 10,900 metal mines, and more than 83,700 non-metallic mines such as building materials and chemical raw materials [1]. It could be seen that mine industry is an essential component of China’s national economy, which plays an important role in economic development and social stabilization.

However, while mine industry greatly contributed to the development of China, it also caused contamination to the environment of many areas and cities in China, such as Mongolia, Shaanxi, Northwest China, and Northeast China. For example, reduced state sulfide in sulfide deposits and coal seams are exposed to an oxidizing environment during mining, with oxidation, decomposition, and dissolving in mine water, ultimately forming acidic mine water. This kind of water always has a low value of pH and high mineralization, which makes the acidic water highly corrosive to mining equipment and confines the growth of plants because of the increased toxicity. Additionally, during the process of mining, heavy metals like Cu, Zn, Pb, and Hg may enter mine water as mining and transportation, thus being harmful to organisms. Almost all of the mines mentioned above have caused different levels of pollution. Hence, it has become necessary to solve the problem of mine water pollution.

Copper ion is an essential component in pollutants in most of the mines. Moreover, not only could Cu cause harmful biochemical effects, toxicity, and hazards in flora, fauna, and human beings, but also influence the toxic level of water and soil due to the increased copper ion concentration. The processing of copper-bearing minerals in Uganda has led to the accumulation of rock waste and residues near rivers, causing heavy metals to contaminate the waterways. This pollution is a result of the erosion causing the leaching of heavy metals with acid streams and transporting solid particles. Subsequent investigations have revealed higher concentrations of these toxic metals in the soil, tap water, and even the nails of residents [2].

There are already conventional methods able to solve the problem of excess copper ions to a certain extent. Precipitation is widely used in removing copper action from wastewater by reacting with lime to form its metal hydroxide nowadays. However, this way is limited by the concentration of the metal ion and pH of the solution [3]. Another technology is ion exchange which has already been used to eliminate copper ions and other heavy metals in mine water successfully, economical for the recovery and recycling of wastewater in electroplating operations. However, the ion exchange process is considered to be expensive since it needs the recharge of resin and the disposal of a substantial volume of spent and the contaminant regenerant solution [3]. Obviously, each of these approaches has its flaws. These problems could be solved to a certain extent by nanotechnologies. In recent years, nanomaterials have attracted more and more attention because of their high surface area ratio, environmental friendliness and stability. However, high cost, small production scale, difficult to recycle and many other problems still need to be solved in the future. This article will focus on the application of nanotechnology to ameliorate copper pollution of mine water in China.

2. Carbon-based Nanoadsorbents

2.1 The Advantages of Carbon Nanomaterials

Carbon is an abundant, low - cost, renewable, and eco - friendly material, which has been used as an adsorbent since ancient times [4]. Compared with bulk materials, the nano-range materials' distinctive property is a much higher surface-volume ratio, which greatly increases the potential of surface applications [5]. Besides, the advantages of carbon nanomaterials in water treatment also include chemical stability, adsorption selectivity, ease of modification and compounding, renewability, and environmental friendliness. Due to the unique physicochemical properties of materials such as graphene and carbon nanotubes, they can play a significant role in adsorbing heavy metal ions and organic pollutants. Additionally, through chemical modification or functionalization, carbon nanomaterials can demonstrate high selective adsorption capabilities for specific pollutants, offering an efficient and environmentally friendly solution for water [5]. This part will focus on the usage of carbon-based nano-adsorbent materials in the management of copper ion pollution.

2.2 Graphene

2.2.1 The Introduction of Graphene and Grahene Oxide (GO)

Graphene is a carbon nanomaterial composed of tightly packed sp^2-bonded carbon atoms arranged in a honeycomb lattice crystal in two-dimensional layers, each layer one atom thick. With a sheet thickness of 0.34 nm, graphene is currently one of the strongest and thinnest nanomaterials available [6, 7]. However, because of the poor electrochemical activity, poor stability in strong acid, alkali or high temperature environment, and agglomerability caused by Vander Waals force, the usage of graphene is greatly limited [8].

A feasible approach to conquer these limitations and expand the applications of graphene is to generate graphene derivatives. Graphene oxide (GO) is a graphene material prepared by chemical oxidation and stripping graphite [9]. It introduces oxygen-containing functional groups, such as hydroxyl (-OH), epoxy (-O-), and carboxyl (-COOH) groups, which make it has a higher hydrophilicity, thus allowing it to be stably dispersed in water [10]. Hence, graphene oxide is more advantageous than graphene due to its ease of processing, large-scale production, and cheap cost of manufacture [7].

Because of their excellent surface qualities, ease of modification, large specific surface area, controlled structural variations, high chemical stability, porosity, low density,

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ease of regeneration, and reusability, carbon nanomaterials, such as graphene and its derivatives, have been used extensively as adsorbents in recent years. Furthermore, graphene oxide is characterized by strong acidity and an abundance of functional groups. Through electrostatic and hydrogen bonding interactions, graphene oxide demonstrates good adsorption for cationic and basic compounds. Therefore, it is possible for people to absorb copper ions from mine water using graphene.

2.2.2 Synthesized Methods of Graphene and its Derivatives

Currently, the most widely used method for synthesizing graphene is the oxidation-reduction method, which is an approach of reducing graphene oxide to graphene with a reducing agent, like sodium borohydride, alcohol, and phenolic, as shown in fig.1 [7]. Now, there are also two innovative ways to prepare graphene: top-down and bottom-up. Chemical synthesis, liquid-phase exfoliation, and scotch tape exfoliation, which are difficult to control the number of graphene's layers, are examples of top-down techniques. Bottom-up techniques also have flaw--it has high requirements on equipment, so it will produce high costs, like molecular beam epitaxy and CV.

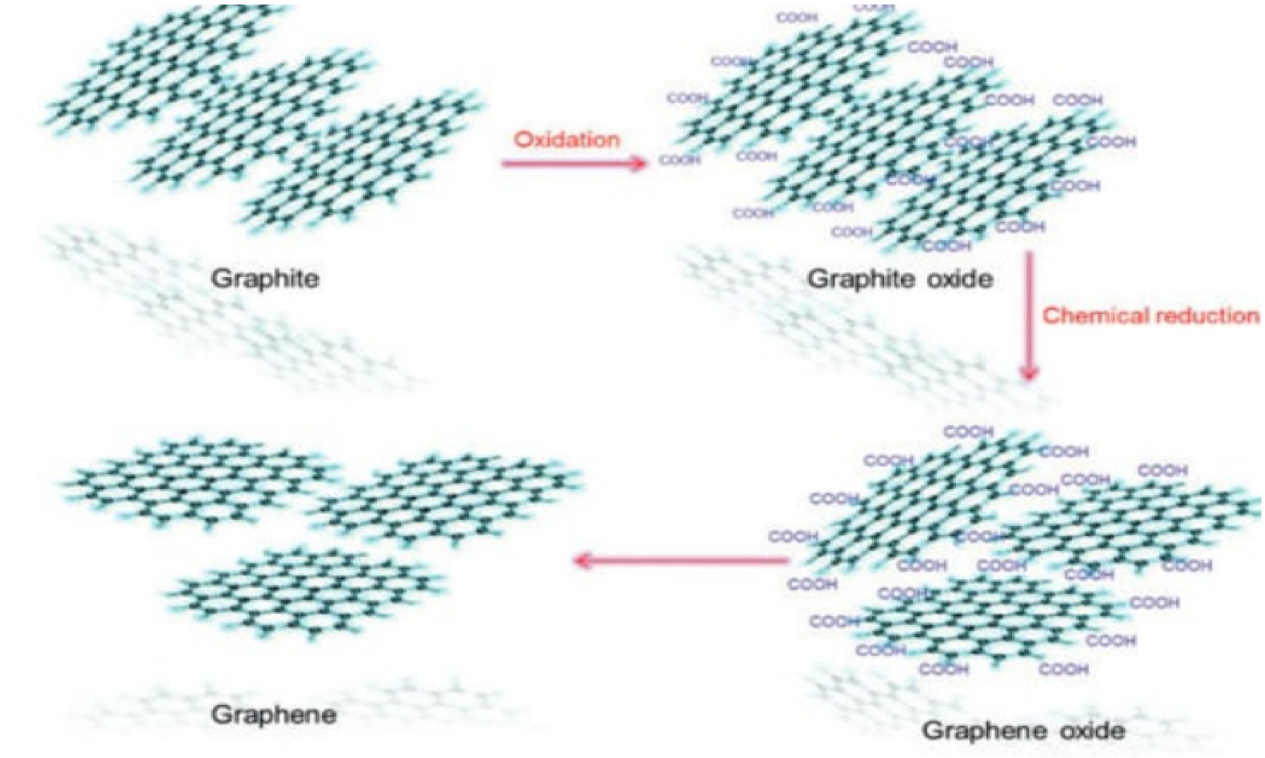

Fig. 1 Schematic of the transformation of graphite oxide to GO and graphene [11].

The preparation of graphene oxide is generally carried out via two steps of oxidant intercalation oxidation and sheet peeling, as shown in Fig. 2. Richard Offeman and Williams Hummers Jr. presented one of the oldest approaches in 1958. First, they combined concentrated sulfuric acid and oxidizers like sodium nitrate with graphite [7]. Then, added potassium permanganate while maintaining a strict temperature control, and introduced reducing and reaction-stopping chemicals such as hydrogen peroxide at the end of the process [7]. A high yield of powdered product and colloidal suspension is produced by this approach [7]. However, toxic gases were also be produced, like ClO_2, NO_2, and N_2O_4. Plus, the left Na and NO^{3+} were difficult to remove, which brought secondary pollution. Subsequent improvements to the Hummers method have been made by research teams, focusing on optimizing the temperature, duration, and precursor ratios. Notably, Marcano et al. adopted the Tours method, eliminating sodium nitrate and incorporating phosphoric acid instead. These modifications have enhanced the product quality and ease of use. Nevertheless, the improved Hummers method also has several drawbacks, including high consumption of oxidizing and intercalating agents, lengthy synthesis times, elevated costs, and limitations in large-scale applications

[12].

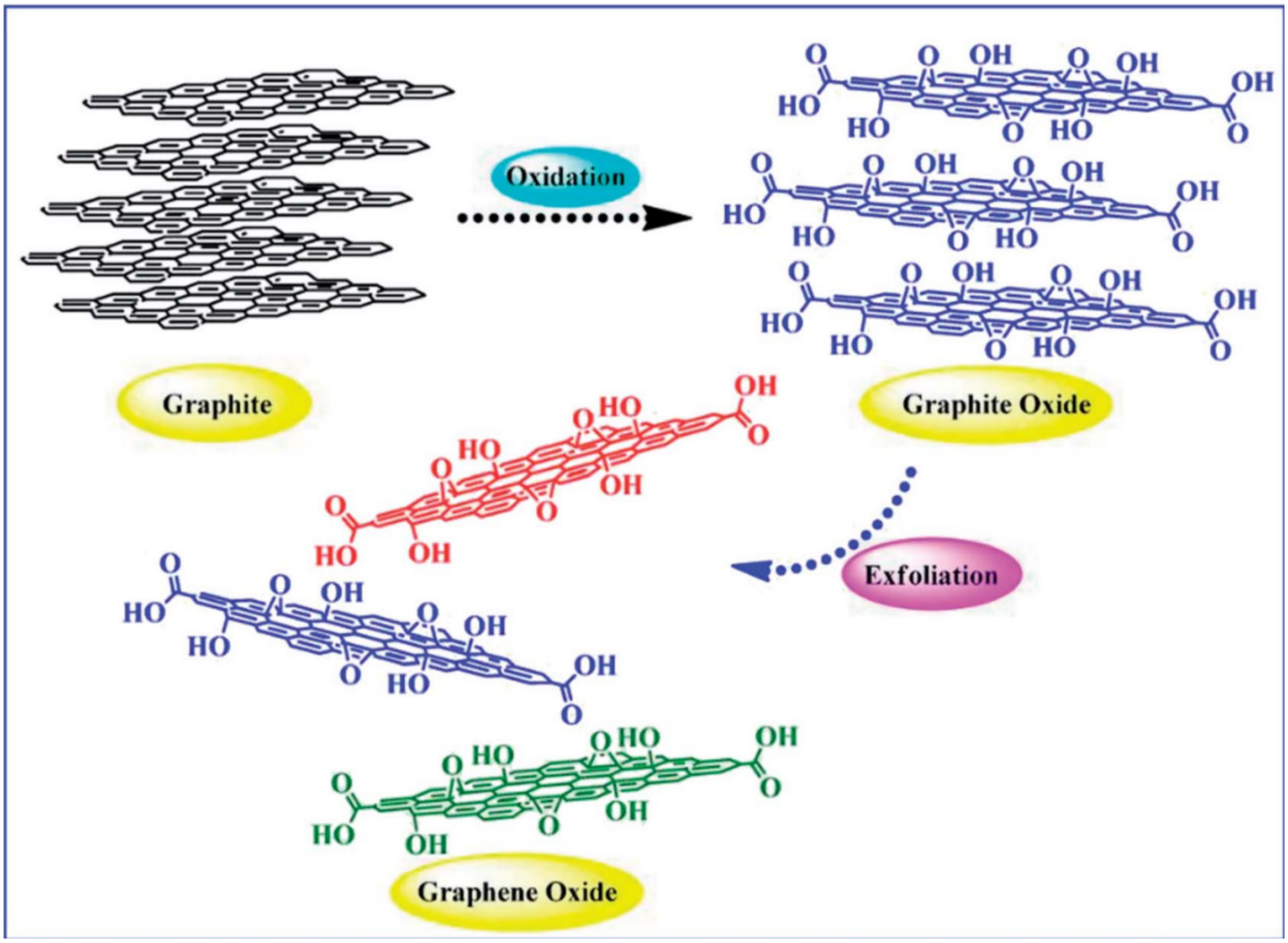

Fig.2 Preparation of graphene oxide [7].

In response to these challenges, the latest advancements in the Hummers method aim to reduce the usage of concentrated sulfuric acid and partially replace potassium permanganate (KMnO4) with potassium ferrate (K_2FeO_4). As Fig.3.shows, these modifications have effectively shortened the synthesis time and lowered the ratio of auxiliary agents to graphite, thereby improving the overall efficiency and economic viability of the process.

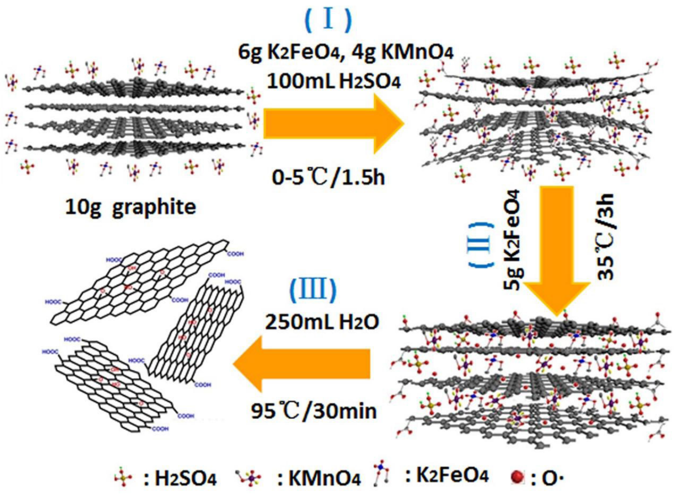

Fig. 3 The Illustration of the preparation of GO [12]

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2.2.3 Adsoprtion Mechanism and its Effects

Since graphene oxide (GO) is an oxidized version of graphene with oxygen-containing groups present, it has hydrophilic characteristics. It makes graphene oxide nanosheets possible to effectively generate metal complexes by electron pair sharing in order to absorb metal ions [13]. A team conducted an experiment and the following equation was utilized to determine the efficiency of Cu (II) removal by GO and experiments showed that the R of GO was 68.2%, which shown noticeably great efficiency of removing the Cu (II) [13].

2.3 Future Perspectives

Carbon-based nanomaterials present significant advantages in treating polluted water. However, it also faces challenges in the future. First of all, after treatment, nano particles are difficult to separate from adsorbed substances to recycle and reuse. Besides, the existing synthesis route is complex, high cost and small yield. Hence, scientists still need to overcome technological and economic challenges in the future.

3. Zinc Oxide Nanomaterials

3.1 The Introduction and Advantages of ZnO-NPs and its Derivatives

Zinc oxide (ZnO) is an environmentally benign substance that has a lot of functional groups, such as hydroxyl groups, on its surface that can act as adsorption sites. Therefore, ZnO with micro/nanostructure may be a viable option for treating copper ions in wastewater as an adsorbent because of its high specific surface area and surface activity [14] Moreover, the nanostructure makes ZnO-NPs easy to separate from liquid, thus avoiding secondary pollution. However, powered zinc oxide or porous nanoplates of ZnO tend to agglomerate, which greatly reduce the surface area that exposure to the liquid. Obviously, stacking or pileup of the porous nanoplates will not occur, and the surface area within the porous nanoplates will be adequately exposed to the solution, if we assemble these porous nanoplates into a micro/nanostructure and all the porous nanoplates are vertically standing and cross-linked [14]. Thus, the structurally improved adsorption performance would be demonstrated to a sufficient degree.

Hence, scientists create ZnO hollow microspheres with exposed porous nanosheet surfaces using a modified hydrothermal process and citrate acting as a structural director [14]. Compared to porous nanoplates or conventional ZnO nanopowders, scientists have shown that this material sufficiently demonstrates structurally increased adsorption ability for heavy metal cations [14].

3.2 The Adsorption Mechanism of ZnO Nanomaterials on Copper Ions

When ZnO is exposed to the surrounding air or water, hydroxyl groups will accumulate on its surface, creating a negatively charged surface, as shown in fig.4 [14]. Water adsorption and partial dissociation of water molecules are the causes of the formation of hydroxyl groups on the surface of ZnO NPs, according to Yin et al. [15]. Hence, those hydroxyl groups would function as actively adsorptive sites and engage in Lewis interaction with Cu to create Cu-O bonds [15]. Hence, copper ions can be absorbed to the surface of ZnO-NPs. According to fig. 4, Cu^{2+} with high electronegativity can adsorb on the active sites of ZnO NPs because of the existence of hydroxyl groups on the surface of ZnO NPs.

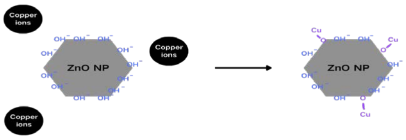

Fig.4 An illustration of the adsorption mechanism of ZnO NPs

3.3 The Synthesis of ZnO Nanomaterials on Copper Ions

3.3.1 ZnO-NPs

Indeed, the traditional synthesis method of ZnO-NPs--hydrothermal method has matured. However, it needs to react under high temperature and high pressure, which make it has high requirements to equipment and needs lots of energy. Therefore, scientists have developed eco-friendly routes to synthesize ZnO-NPs. The amount of Cu^{2+} ion adsorbed at the end of the adsorption experiment and the ion percentage removal (%) by the ZnO nanoparticles were calculated applying Equations (1, 2), respectively [16]:

$$q = \frac{(c_o - c_f)}{m} \cdot V \tag{1}$$

$$Removal(\%) = 100 \cdot \frac{(c_o - c_f)}{c_o} \tag{2}$$

where q is the amount of ion adsorbed by the adsorbent in mg g^{-1}, Co is the initial ion concentration in contact with the adsorbent (mg. L^{-1}), Cf is the ion concentration (mg. L^{-1}) after the batch adsorption process, m (g) is the mass of adsorbent and V (L) is the volume of ion solution [16].

After calculating, scientists came to a conclusion that the adsorption rate constant of Zn-ST (2.65g mg^{-1} h^{-1}) is larger than Zn-AL's (1.52g mg^{-1} h^{-1}) [16]. The adsorption efficiency is limited by the concentration of copper ions. Under the condition of low concentration of copper ions (~ 40 mg/L), the adsorption efficiency of zinc oxide nanoparticles synthesized by the two methods is close to 100%. Under the condition of high concentration of copper ions (> 80 mg/L), the adsorption efficiency of Zn-AL is higher than that of Zn-ST [16]. Besides, under different pH conditions, the percentage of adsorption efficiency is also various. When pH=4, the adsorption efficiency of the two particles is roughly equal, approaching to 100%. However, when pH=6, the efficiency will reduce to a certain extent [16].

3.3.2 ZnO Hollow Microspheres

Mix the two solutions and stir for 30 minutes. Transfer the mixed solution to a 65 mL Teflon lined autoclave, following hydrothermal treatment at 160°C for 12 hours. After the reaction was finished, the white product was cooled to room temperature and washed with distilled water and ethanol for many times. Finally, calcined at 400°C for 2 hours. Through the above steps, ZnO hollow microspheres can be obtained [14]. After researching, the adsorption capacity of ZnO hollow microspheres to copper exceeds 1400mg Cu/g, which is much higher than commercial ZnO nano powder [14].

3.4 Future Perspectives

ZnO hollow microspheres exhibit significant practical application prospects in wastewater treatment due to their high adsorption performance, easy separation, environmental friendliness, wide applicability, and structural stability, making them an efficient and eco-friendly adsorbent for heavy metal ions. However, their widespread adoption still faces challenges such as cost, stability, regeneration and recycling, large-scale production, environmental adaptability, and safety assessment. To fully realize the potential of ZnO hollow microspheres, further optimizations are needed, including refining the synthesis process to reduce production costs, investigating their stability under various environmental conditions, exploring effective regeneration and recycling techniques, developing suitable large-scale production methods, and conducting comprehensive long-term safety assessments. These efforts will contribute to the wider application and promotion of ZnO hollow microspheres in wastewater treatment.

4. Comparison of the Two Nanomaterials

From the view of adsorption efficiency alone, the adsorption efficiency of zinc oxide nanoparticles is higher than that of graphene, but zinc oxide nanomaterials are also facing more challenges: its synthesis path is more complex, the production scale is smaller, and the safety factor is not as high as graphene. So, in the future, if people want to use zinc oxide nanomaterials to treat water pollution on a larger scale, we need to continue to work hard.

Hence, as for the choice of the two materials, if funds are sufficient, the sewage that needs to be treated is small, and the treatment efficiency needs to be high, zinc oxide nanoparticles can be selected. However, if the capital is less but the treating efficiency does not need to be very high, graphene would be a better choice.

5.Conclusion

In China, which is a country rich in minerals and has a well-developed mining industry, the problem of mine water pollution is inevitably. When clean water flows through a mining area, the water becomes contaminated and eventually ends up in rivers and lakes, which can be harmful to human beings, plants, soil, and many other aspects. This paper focuses on the study of copper ions, a very important pollutant in mine water. Considering the drawbacks of conventional methods, this thesis attempts to remedy these shortcomings using nanotechnology. Graphene and zinc oxide nanoparticles mentioned in the paper are both promising in the author's opinion. Nanomaterials have high adsorption efficiency, are environmentally friendly, and produce less secondary pollution, all of which are somewhat superior characteristics to traditional methods. However, nanotechnology also faces challenges: the current production scale of nanomaterials is still small, the technology is complex, and the used material is difficult to separate and recycle, all of which require our future disdainful efforts to make nanotechnology benefit more people.

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