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Electrocatalytic Nanomaterials for Reduction of Hydrogen Peroxide as Potential Radioprotectors

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Abstract: Nanomaterials have shown many potential application prospects in the biomedical field, such as medical imaging, drug delivery and biosensing due to their unique physical and chemical properties. In this review we focus on nanomaterials that have shown not only abilities of radiation protection, but also good electrocatalytic activities toward reduction reactions of hydrogen peroxide and oxygen. We discuss the abilities of radiation protection of these nanomaterials that are ascribed to their enzyme-like activities because their catalytic properties provide an effective pathway for scavenging free radicals *in vivo* via rapid reactions with reactive oxygen species. We also provide insights into electrocatalytic nanomaterials for the relationships between electrocatalytic activities and abilities of radiation protection that are critical for clinical translatability. Finally, we indicate current challenges and future directions in the possible use of these nanomaterials as novel radioprotectors for clinical translation as an adjuvant in radiotherapies.

Key words: nanomaterials; electrocatalysis; hydrogen peroxide; radioprotectors; reactive oxygen species
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High-energy ionizing radiations such as gamma rays and X-rays have been widely utilized in radiation therapy to destroy or damage cancer cells[1-3]. According to statistics, more than half of cancer patients get radiation therapy. Sometimes, radiation therapy is the only cancer treatment needed[4-5]. But high-energy radiations during the treatments not only kill cancer cells, but also cause inevitable damage to normal tissues. Since many free radicals including reactive oxygen species (ROS) such as peroxides, superoxide, hydroxyl radical, and singlet oxygen etc. are formed through ionizing reactions during the process of radiation therapy, these free radicals are able to react with both DNA and RNA inside the body, resulting in structural and functional changes, and affecting biological processes[6-8]. As a result, this further leads to cancer or even death. The use of radioprotectors provides a practicable method to shield normal tissues from high-energy ionizing radiations.

Radioprotectors are compounds that are administered before exposure to ionizing radiations to protect healthy normal cells and reduce the damaging effects including radiation-induced lethality[9-10]. A good radioprotector could be applied in clinical radiotherapy, space travel, radiation site clean-up, radiological terrorism and so on[11]. Amifostine (Ethyol) is a widely used prescription radioprotector in radiation medicine by scavenging oxygen-derived free radicals, but only 1 min of elimination half-life in blood limits its scavenging activities against ROS[12]. Therefore, it is highly desirable to explore new radioprotectors with capabilities of highly efficient removals of ROS, renal clearance, and low toxicities for clinical translation as an adjuvant therapy in radiotherapies.

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In recent years, some nano materials owning good electrocatalytic activities toward reduction reactions of hydrogen peroxide (H_2O_2) and oxygen show abilities of radiation protection because their catalytic properties provide an effective pathway for scavenging free radicals *in vivo* via rapid reactions with ROS, as shown in Figure 1. In this review we focus on nanomaterials which have shown not only abilities of radiation protection, but also good electrocatalytic activities toward reductions of H_2O_2 and oxygen. We also provide insights into electrocatalytic nanomaterials for the relationships between electrocatalytic activities and abilities of radiation protection that are critical for clinical translatability. Finally, we indicate current challenges and future directions in the possible use of these nanomaterials as novel radioprotectors for clinical translation as an adjuvant in radiotherapies.

1 Effectiveness of Nanomaterials Owing Electrocatalytic Activity toward Reduction of H_2O_2 as Radioprotectors

Nanomaterials have attracted much interest over the past couple of decades due to their applications in various fields, such as energy generation[13], sensing devices[14], therapeutics, and medical imaging[15-16]. Among them, some nanomaterials have shown application prospect in radiotherapies since they have intrinsic enzyme-mimetic properties under physiological conditions to maintain catalytic activities.

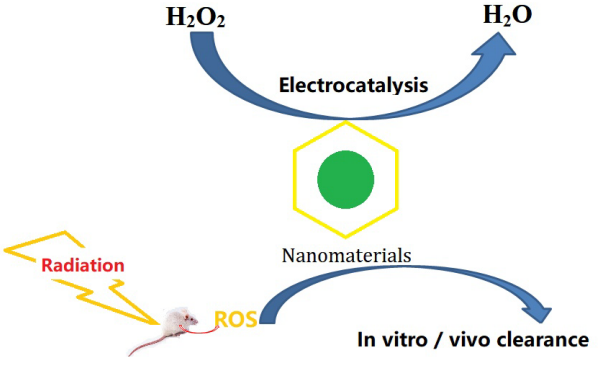

Fig. 1　Scheme of electrocatalytic nanomaterials for reduction of H_2O_2 as radioprotectors

Tarnuzzer and colleagues firstly reported that cerium oxide (CeO_2) nanoparticles (NPs) in the range of 3 ~ 5 nm could act as effective radioprotectors for normal tissues owing to a differential protection in normal cells as compared to tumor cells[7]. They proposed that CeO_2 NPs offer many active sites for free-radical scavenging because of the large surface-to-volume ratio and the presence of the mixed valence states of Ce^{3+} and Ce^{4+} induced by the oxygen vacancies on the surface. By changing their oxidation states from Ce^{3+} to Ce^{4+}, CeO_2 NPs scavenge the free radicals generated by irradiation[8].

Heckert and coworkers' research further suggested that CeO_2 NPs exhibit superoxide dismutase (SOD) and catalase (CAT) mimetic activities due to the high 3+ and 4+ oxidation states of surface "Ce" atoms presented on their surface, respectively [17-18]. Mechanism behind the switching of CeO_2 NPs between the two oxidation states is proposed to be due to the oxygen vacancy/defect in their crystal structure[19]. SOD can catalyze the dismutation of superoxide (O_2^-) radicals to either ordinary molecular oxygen (O_2) or hydrogen peroxide (H_2O_2), and CAT can break H_2O_2 down to water[20-21]. These give the explanation for why CeO_2 NPs can serve as effective radioprotectors.

Verification on the effectiveness of CeO_2 NPs as radioprotectors opens the field for further studies in nanomaterials scavenging the free radicals generated by irradiation[22]. Subsequently, more and more nanomaterials owning electrocatalytic activities for reduction of H_2O_2 have been investigated as radioprotectors, and the results indicate that they exhibit abilities of radiation protection.

Zhang and collaborators reported synthesis of ultrasmall cysteine-protected molybdenum disulfide (MoS_2) dots (sub-5 nm) as radioprotectors by combination of ultrasonication and centrifugation[23]. Surface protection with cysteine offers several indispensable merits to the MoS_2 dots. First, the ultrasmall size allows effective elimination via renal clearance [24-25]. Second, the aqueous dispersibility and stability are significantly enhanced by the surface modification, maintaining the ultrasmall size *in vivo* and preventing

aggregation. Last, nonspecific adsorption of serum proteins is largely prohibited, resulting in postponed removal from the body and a relatively longer circulation time in blood to achieve desired radiation protection. The prepared MoS_2 dots exhibit extraordinary electrocatalytic activities for hydrogen peroxide and oxygen reduction reactions, as shown in Fig. 2. With the addition of H_2O_2 or O_2, the reduction currents increase significantly and the reduction potentials shift positively compared to those without H_2O_2 or O_2, as well as with H_2O_2 or O_2 on the bare glassy carbon electrodes. Their electrocatalytic properties provide a promising and effective pathway for scavenging free radicals *in vivo* via rapid reactions with the oxygen radical superoxide ($O_2^{\cdot-}$) and the nonradical oxidant hydrogen peroxide (H_2O_2) in the blood since MoS_2 NPs possess intrinsic activities of mimicking enzymes of superoxide dismutases (SODs), catalases (CATs), and peroxidases (PODs) under moderate conditions (pH 7.4, 25 °C)[26-27]. Yang and coworkers' recent work further verified that MoS_2 nanosheets with the antioxidant-enzyme-mimetic activities can effciently remove several kinds of ROS including $O_2^{\cdot-}$, $^{\cdot}OH$ and H_2O_2[27]. MoS_2 dots improve the surviving fraction of mice that are exposed to high radiation dose of 662 keV by gamma ray because of their strong catalytic activities as multifunctional nanozymes. Furthermore, MoS_2 dots can make a contribution in cleaning up the accumulated free radicals within the body, repairing DNA damage, and recovering all vital chemical and biochemical indicators, suggesting their unique role as free radical scavengers. MoS_2 dots show rapid and efficient urinary excretion with more than 80% injected dose eliminated from the body after 24 h due to their ultrasmall hydrodynamic size, and they do not cause any noticeable toxic responses up to 30 days.

Analogous to MoS_2 dots, both tungsten diselenide (WSe_2) and tungsten disulfide (WS_2) dots also display potentials in protecting healthy cells and tissues against radiations via diminishing radiation-induced free radicals since they belong to two-dimensional transition-metal dichalcogenide nanomaterials and own similar electronic structure and properties[28-29].

Liu and collaborators pointed out that ultrasmall (sub-5 nm) cysteine-protected WSe_2 dots with high

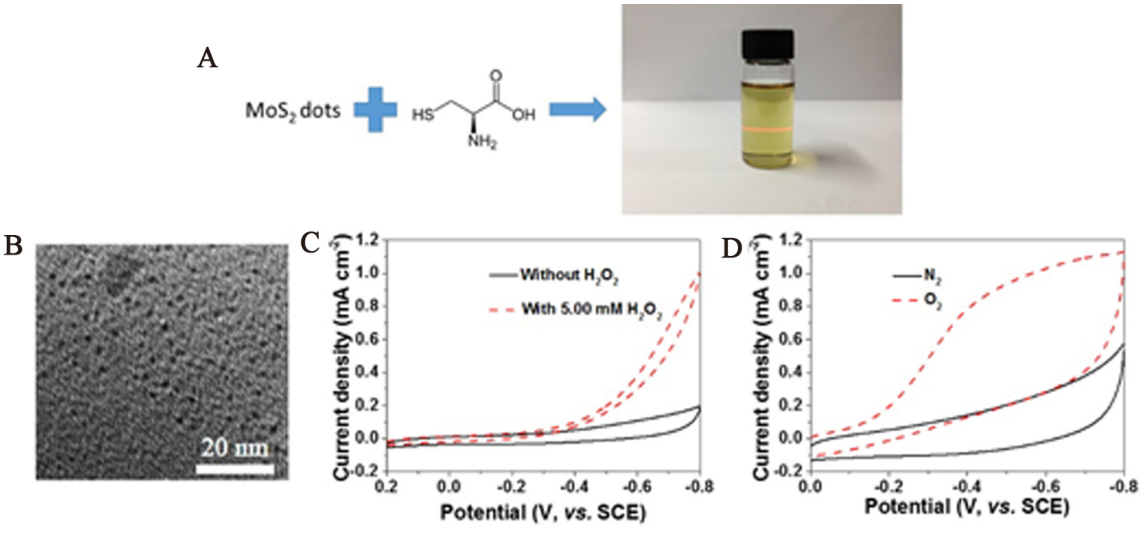

Fig. 2 Characterization and electrocatalytic properties of cysteine-protected MoS_2 dots. (A) Schematic preparation of cysteine-protected MoS_2 dots. (B) TEM image of a population of cysteine-protected MoS_2 dots with a homogeneous distribution of around 2 nm. (C) CVs of a glassy carbon (GC) electrode modified with cysteine-protected MoS_2 dots in the presence (dotted) and absence (solid) of 5.00 mmol·L^{-1} H_2O_2 in N_2 saturated 0.01 mol·L^{-1} pH 7.4 phosphate-buffered saline (PBS). Scan rates: 50 mV·s^{-1}. (D) CVs of GC electrode modified with cysteine-protected MoS_2 dots in N_2 (solid) and O_2 saturated (dotted) 0.01 mol·L^{-1} pH 7.4 PBS. Scan rate: 50 mV·s^{-1}[23].

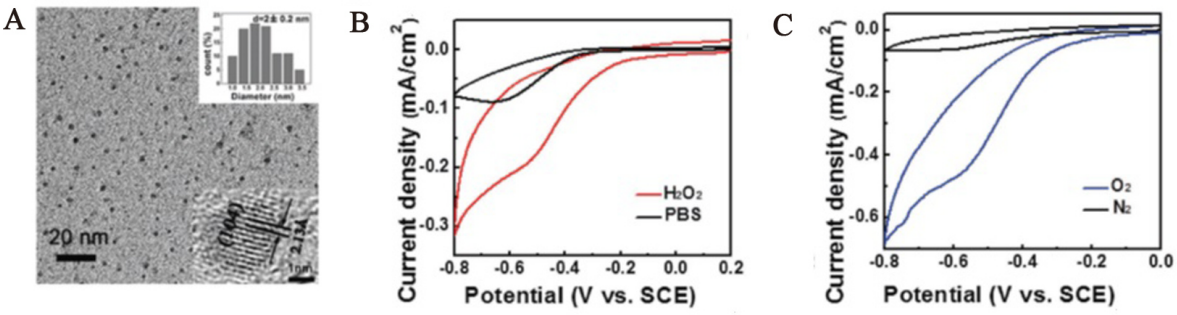

Fig. 3 Characterization and ORR activity of WSe_2 dots. (A) TEM image of WSe_2 dots. Insets of (A): size distribution and HRTEM image of WSe_2 dots with an average size around 2 nm. (B, C) CVs of GC electrode modified with cysteine-protected WSe_2 dots (B) in the absence and presence of 5×10^{-3} mol·L^{-1} H_2O_2 in N_2 saturated 0.1 mol·L^{-1} PBS solution (pH = 7.4) and (C) in N_2 and O_2 saturated 0.1 mol·L^{-1} PBS solution (pH = 7.4) at a scan rate of 50 mV·s^{-1}[28].

surface activities can recover radiation induced DNA damages and eliminate the excessive ROS generated from radiation[28]. These are attributed to their good electrocatalytic activities toward reduction reactions of H_2O_2 and oxygen, as shown in Fig. 3. They are in accordance with the reported enzyme mimic activities of WSe_2 nanomaterials, that is, possessing peroxidase-like catalytic properties[30]. *In vivo* experiments confirm that the survival rate of mice treated with WSe_2 dots is significantly elevated with radiation damages postponed under exposure to high-dose ionizing radiations. Furthermore, the free radicals in major organs and hematological system can be appreciably omitted, suggesting their unique role as free radical scavengers.

Similarly, the cysteine-protected WS_2 quantum dots also showed highly catalytic activities toward H_2O_2 and O_2 (Fig. 4) due to intrinsic peroxidase-like catalytic activities of WS_2 nanomaterials[29, 31]. Cellular experiments showed that WS_2 quantum dots can improve cell viabilities, eliminate ROS in injured cells and prevent DNA damages in irradiated cells under exposure to high energy gamma rays[29]. *In vivo* experiments displayed that cysteine-protected WS_2 quantum dots can protect the hematological system, intestine system and DNA from bone marrow cells against high-energy ionizing radiations. The biochemical mechanism verifies that cysteine-protected WS_2 quantum dots can recover SOD and remove excessive 3,4-methylenedioxyamphetamine (MDA) in liver and lung by participating in the catalytic processes and omitting ROS.

Zhang and collaborators found that Bi_2Se_3 nanoparticles (NPs) with biocompatible polyvinylpyrrolidone (PVP) surface coating (an average size of 55.6 nm) could increase the surviving fraction of mice with exposure to high-energy gamma rays [32]. Furthermore, Bi_2Se_3 NPs can minimize DNA and bone marrow that nucleated cell damages, and recover the radiation-induced damages on white blood cells and platelets. They concluded that Bi_2Se_3 NPs behave as free radical scavengers to induce increase in SOD and decrease in MDA. They believed that capabilities of Bi_2Se_3 NPs clearing ROS are ascribed to the superior electrocatalytic activity toward the reduction of H_2O_2, as shown in Fig. 5. With the addition of H_2O_2, the reduction current increases dramatically and the reduction onset potential shifts positively, which is distinctly different from the unmodified GC electrode. They have also checked *in vivo* toxicities of Bi_2Se_3 NPs at a relatively high dose of 50 mg·kg^{-1}, and the results showed that Bi_2Se_3 NPs are safe without any significant toxic responses.

Graphene is used to help improving the performance of many materials and substances due to its peculiar structure and properties. Nanohybrids (M@Cs) formed by one single-layer graphene encapsulating metal nanoparticles Fe and CoNi alloy possess outstanding catalytic activities toward the oxygen reduction reaction and oxygen evolution reaction processes,

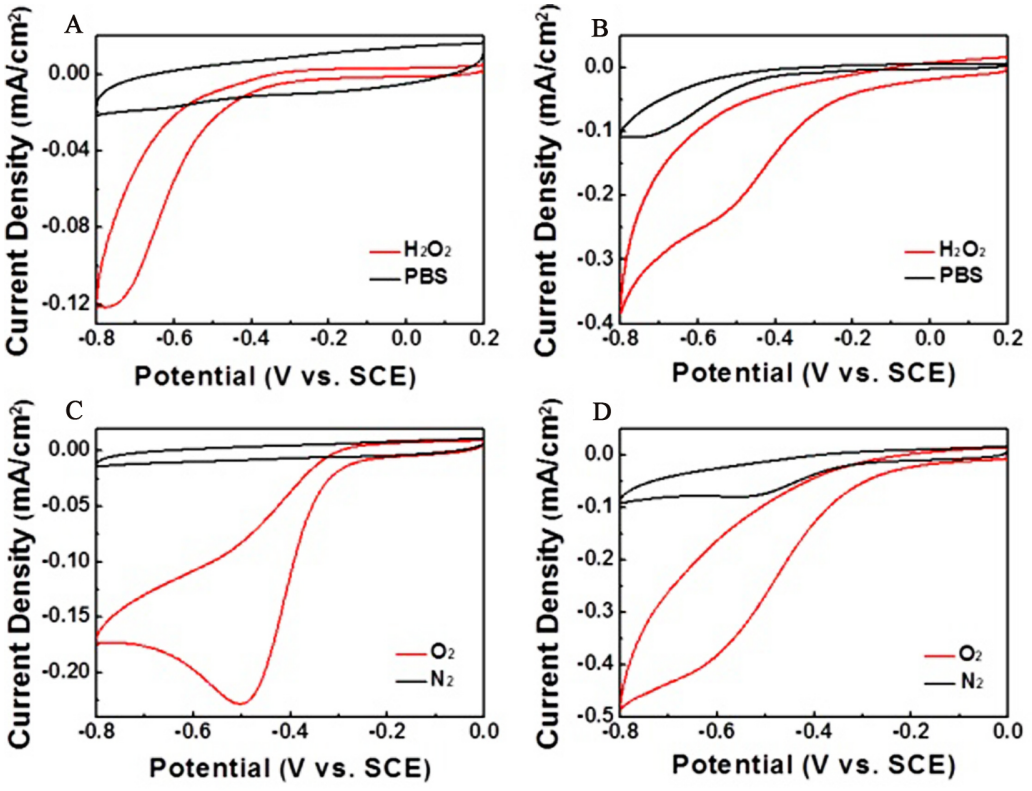

Fig. 4 Electrocatalytic properties of WS_2 quantum dots. (A) CVs of GC electrode in the absence and presence of 5 mmol·L^{-1} H_2O_2 in N_2 saturated 0.1 mol·L^{-1} PBS (pH 7.4). (B) CVs of GC electrode modified with WS_2 quantum dots in the same condition. (C) CVs of GC electrode in O_2 and N_2 saturated 0.1 mol·L^{-1} PBS (pH 7.4) at a scan rate of 50 mV·s^{-1}. (D) CVs of GC electrode modified with WS_2 quantum dots in the same condition[29].

providing a route to scavenge oxygen free radicals[33]. The synthesized M@Cs can considerably reduce the amount of radiation-induced oxygen free radicals in cells and prevent DNA damage. *In vivo* radiation protection experiments showed a survival rate of 90% for the irradiated mice. Evaluation of SOD and MDA levels indicate that M@Cs lead to the increased SOD levels and decrease the harmful MDA content via scavenging of oxygen free radicals. Long-term monitoring showed that the highly catalytical active nanohybrids can repair radiation damage in the peripheral blood system while exhibiting minimal toxicities over 30 days. These are consistent with electrochemical characterizations and DFT calculations, that is, the M@C nanomaterials have strong catalytic activities toward O_2, H_2O_2 and O_3, and they can efficiently convert ROS into O_2 and H_2O.

Improvement in the electrocatalytic properties of nanomaterials toward reduction reactions of H_2O_2 and O_2 can effectively enhance corresponding antioxidant activities and radioprotection effects *in vivo*. Therefore, rational designs of electrocatalytic nanomaterials by modifying and doping with other substances or changing surface morphologies are good choices for enhancing the radioprotection effect of nanomaterials.

Ultrasmall Au-MoS_2 clusters display higher catalytic activities toward reduction reactions of H_2O_2 and O_2 compared to Cys-MoS_2[34] (Fig. 6). As a result, the improvement in the electrocatalytic activities of MoS_2 by modification with Au-NCs can effectively enhance its antioxidant activity and radioprotection effect. Cellular experiments indicate that Au-MoS_2 could improve cell viabilities, remove ROS in irradiated cells and prevent DNA-associated damages induced by high energy gamma rays, which outperforms MoS_2 counterpart. Meanwhile, Au-MoS_2 can also recover the SOD and MDA levels in organs by

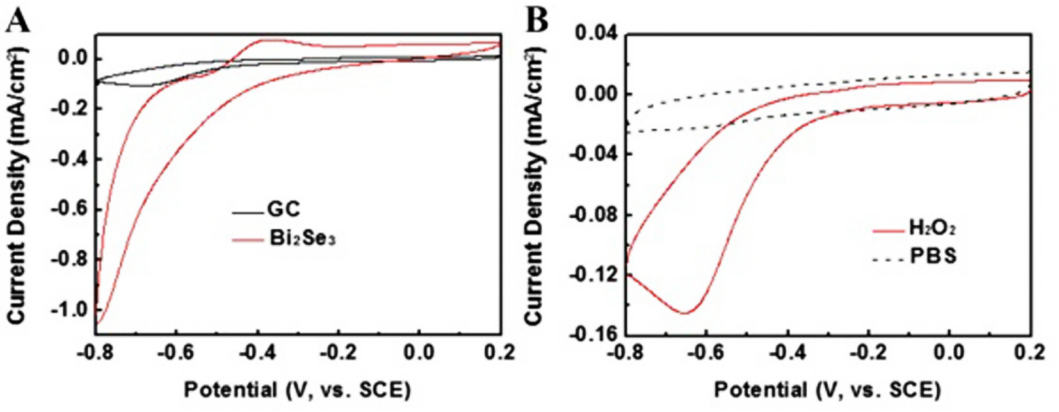

Fig. 5 CVs of (A) GC electrode modified with Bi_2Se_3 nanoparticles and (B) bare GC electrode with or without 5 mmol·L^{-1} H_2O_2 in N_2 saturated 0.1 mol·L^{-1} PBS solution (pH = 7.4) at a scan rate of 50 mV·s^{-1}[32].

removing free radicals and protecting the hematopoietic system of mice from radiation. Therefore, enhancement of the catalytic activities of MoS_2 nanoparticles modified with Au-NCs is very important. Au-MoS_2 is considered as a promising radioprotectro to be employed in clinical applications such as tumor chemotherapy, mutagenesis prevention, anti-cell transformation and reduction of carcinogenesis.

Catalytic nanomaterials for reduction reactions of H_2O_2 and O_2 have demonstrated to function as promising antioxidants to scavenge ROS. Pt-based nanomaterials are widely used as excellent electrocatalysts for oxygen reduction reaction[35-36]. In order to significantly enhance the catalytic performances, rational design of surface morphologies and appropriate doping is a good choice. PtPdRh nanocubes prepared through a simplified approach of one-pot synthesis display enhancement of ORR with remarkable catalytic properties of decomposing H_2O_2 via enhanced oxygen reduction reactions, as shown in Fig. 7, resulting in enhanced catalytic performance and capacity of free radical scavenging via bond breaking mechanism[37]. An enhanced survival percentage (50%) of mice has been obtained by using these hollow PtPdRh nanocubes. Both *in vitro* and *in vivo* experiments along with theoretical calculation reveal that the radiation protection effect is ascribed to the high catalytic performance of the hollow PtPdRh nanocubes in scavenging accumulated ROS since these nanocubes possess strong and specific catalytic activities for H_2O_2, O_2 and $O_2^{\cdot -}$, and they can function as catalase, peroxidase and SOD analogs. Furthermore, all the re-

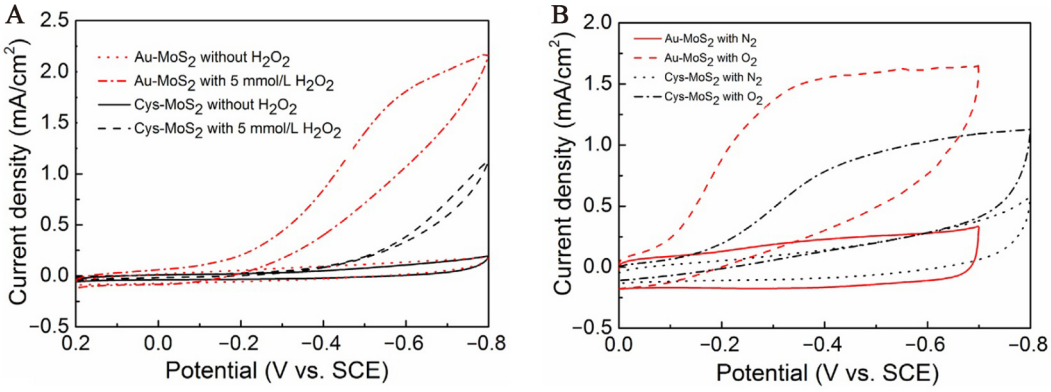

Fig. 6 Electrocatalytic activities of Au-MoS_2 clusters. (A) CVs of the GC electrode modified by Au-MoS_2 clusters and Cys-MoS_2 with and without 5.00 mmol·L^{-1} H_2O_2 in N_2 saturated 0.1 mol·L^{-1} PBS at a scan rate of 50 mV·s^{-1}. (B) CVs of the GC electrode modified by Au-MoS_2 clusters and Cys-MoS_2 in N_2 and O_2 saturated 0.1 mol·L^{-1} PBS at a scan rate of 50 mV·s^{-1}[34].

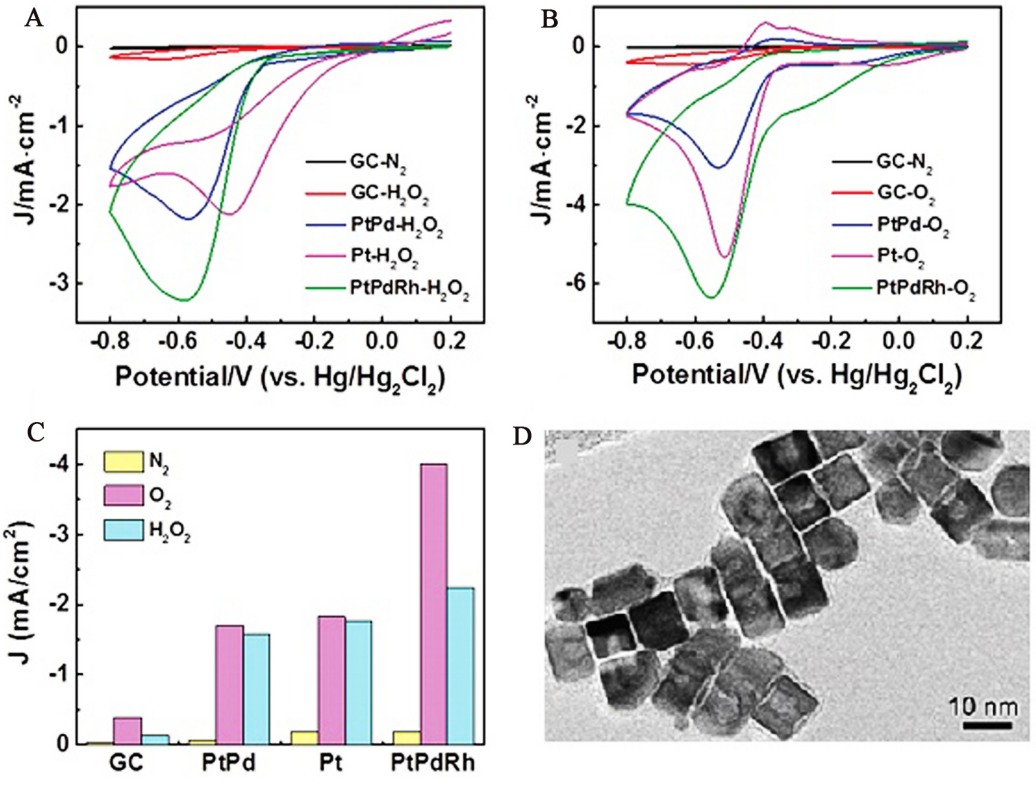

Fig. 7 Catalytic and peroxidase-like activities of the hollow PtPdRh nanocubes. (A) CVs of GC electrode modified with as-prepared Pt, PtPd, or PtPdRh nanocubes in the absence and presence of 5.00×10^{-3} mol·L^{-1} H_2O_2 in N_2 saturated 0.01 mol·L^{-1} PBS (pH 7.4). (B) CVs of GC electrode modified with as-prepared Pt, PtPd, or PtPdRh nanocubes in O_2 saturated 0.01 mol·L^{-1} PBS (pH 7.4) and pure GC electrode in N_2 saturated 0.01 mol·L^{-1} PBS (pH 7.4). (C) Current density of different samples at the potential of -0.8 V obtained from panels (A) and (B). Unmodified GC electrode was used as a control. (D) TEM image of the hollow PtPdRh nanocubes[37].

sults of enhanced SOD activity, decreased MDA amount and prevented damages in DNA and bone marrow nucleated cells illustrate that the hollow PtPdRh nanocubes could protect normal body tissues from free radical injuries.

2 Conclusions and Outlook

Nanomaterials have shown many potential application prospects in the biomedical field, such as medical imaging, drug delivery and biosensing due to their unique physical and chemical properties. Intriguingly, some electrocatalytical nanomaterials for reduction reactions of H_2O_2 and O_2 have been found to possess abilities of radiation protection because of their enzyme-like activities. They can eliminate the excessive ROS generated from radiation, which has provided a good idea for exploring new radioprotectors. Moreover, improvement in electrocatalytic activitie s of nanomaterials for reduction reactions of H_2O_2 and O_2 can effectively enhance their antioxidant activity and radioprotection effect, which has given a good way to improve the performance of radioprotectors. Therefore, there exist many opportunities for the development of novel radioprotectors based on electrocatalytic nanomaterials. Nanomaterials are helpful to function as radioprotectors to protect patients against the damaging and lethal effects of ionizing radiations. However, there are also hurdles to be overcome to realize optimal catalytic activity and radioprotective efficacy *in vivo* as well as good safety. The current challenges for the possible use of these nanomaterials as novel radioprotectors are to achieve the macroscopic-quantity preparation with homogeneousness and to develop the corresponding characterization methods. Future directions should focus on develop-

ing radioprotectors based on catalytic nanomaterials with the maximal radioprotective efficacy and minimal toxicity, as well as long-term therapeutic effects, which will pave a way to clinical translatability. Furthermore, we believe that rapid advances in materials science and biomedicine will accelerate the development of improved materials with enhanced catalytic activity and radioprotective efficacy *in vivo*.

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电催化过氧化氢还原的纳米材料作为潜在的辐射防护剂

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摘要: 纳米材料由于独特的物理化学性质,在生物医学领域显示出许多潜在的应用前景,诸如医学成像、药物输运和生物传感等. 这篇综述总结了对过氧化氢和氧还原表现出好的电催化活性的一些纳米材料显示了辐射防护性能. 作者讨论了这些纳米材料的辐射防护性能来源于它们的类酶活性,因为它们的催化性质表现为和活性氧的快速反应,为清除体内的自由基提供了一条有效通道. 作者也提出了纳米材料的电催化活性和作为临床转化关键的辐射防护性能之间关系的见解. 最后,作者指出了这些纳米材料作为新的辐射防护剂用于辐射防护治疗辅助成份所面临的挑战和将来的研究方向.

关键词: 纳米材料;电催化;过氧化氢;辐射防护剂;活性氧