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Construction of surface charge-controlled reduced graphene oxide-loaded Fe_3O_4 and Pt nanohybrid for peroxidase mimic with enhanced catalytic activity

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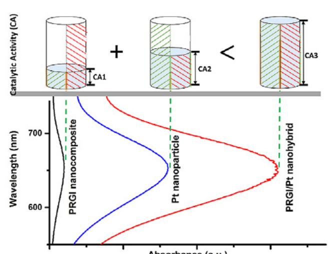
HIGHLIGHTS

- A nanohybrid of reduced graphene oxide anchoring iron oxide and Pt nanoparticle was first used as a peroxidase mimic.
- A synergistic effect existed between PRGI nanocomposite and Pt nanoparticle.
- An effective way of electrostatic assembly was developed to construct enhanced nanozymes.

GRAPHICAL ABSTRACT



PRGI/Pt nanohybrid showed higher catalytic activity than the sum of PRGI nanocomposite and Pt nanoparticle.

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ABSTRACT

Hybrid nanomaterials with synergistic effect are highly potential for developing advanced nanozymes. Herein, we designed a nanozyme assembled by polyethylenimine (PEI)-protected reduced graphene oxide anchoring iron oxide (PRGI) and Pt nanoparticle using electrostatic interaction, PRGI/Pt nanohybrid. The different ratio of PRGI nanocomposite and Pt nanoparticle could control PRGI/Pt nanohybrid's surface charge and stability, which determined PRGI/Pt nanohybrid's catalytic activity. At the mass ratio of 0.8, the as-obtained PRGI/Pt nanohybrid showed the highest catalytic ability, and was better than Pt nanoparticle at different pH and temperature, although the PRGI/Pt nanohybrid showed lower affinity for TMB than Pt nanoparticle, which maybe attributed to the fact that PRGI/Pt nanohybrid possessed better product desorption ability or larger contact area. Furthermore, PRGI/Pt nanohybrid showed much higher catalytic activity than the sum of PRGI nanocomposite and Pt nanoparticle, indicating the strong cooperation between PRGI nanocomposite and Pt nanoparticle. Our study also provided a new way to conveniently construct nanozyme based on hybrid nanomaterials.

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1. Introduction

Recently, enzyme mimics based on nanomaterials (nanozymes) are widely explored [1–4], due to their significant advantages than natural enzymes, such as strong stability, low cost, facile preparation and purification, which can mimic many kinds of natural enzymes, including peroxide [5–7], catalase [8,9], esterase [10,11], nuclease [12–14] and so on. As a result, they are used for biosensor [15,16], prodrug activation [17,18], immunoassay [6,19], pollutant removal [20,21], etc. According to structure and composition, the common nanozymes can be constituted by the following types of nanomaterials. 1) Metal or metal compound nanoparticles, such as Pt [22], Fe_3O_4 [6,23] and $Cu(OH)_2$ [7]. 2) Catalytic core-shell nanoparticles, including Zn(II)-triazacyclononane-gold nanoparticle [24], Cp*Ru(cod)Cl-gold nanoparticle [17] and so on. 3) Carbon nanomaterials, such as graphene oxide [25] and carbon nanodots [26]. 4) Hybrid nanomaterials [27,28].

With the development of nanotechnology, plenty of hybrid nanomaterials were successfully synthesized [29–31]. More importantly, the hybrid nanomaterials possessed the significantly improved performance in different areas. In biomedical application, the nanohybrid of gold nanoparticle and graphene (or graphene oxide) performed better photothermal conversion ability for improving tumor cell ablation [30,32]. Likewise, nanozymes based on hybrid nanomaterials also showed enhanced catalytic properties. For example, Qu et al. prepared a kind of synergistic catalyst with high peroxidase activity in broad pH range, by combining graphene oxide with gold nanoclusters [27]. Chen et al. demonstrated the graphene oxide-Fe_3O_4 magnetic nanocomposites owned improved catalytic activity [28]. However, there were no cases of researching on combining Fe_3O_4 and Pt nanoparticle as a new nanozyme. And, hybrid nanomaterials assembled by electrostatic interaction for nanozymes are less investigated, even though such way could construct nanozymes based on hybrid nanomaterial more conveniently.

It was reported that the surface charge of nanozymes could greatly influence their catalytic activity for different substrates [23,33]. For example, 3, 3′, 5, 5′-tetramethylbenzidine (TMB) was easier to be catalyzed by negatively charged nanozymes, while 2, 2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) was more sensitive to positively charged ones [23]. Therefore, it is important to control the surface charge of nanozymes for optimizing their catalytic properties. However, most nanozymes were prepared without controlling their surface charge on purpose. Considering that there are a lot of well-designed nanozymes with different surface charges, the electrostatic interaction could be used to assemble two kinds of individual nanozymes to form hybrid nanozymes. Meanwhile, such way could easily regulate nanozyme's surface charge by changing mixing ratio of two independent nanozymes.

In this study, we prepared a nanohybrid of polyethylenimine (PEI)-protected reduced graphene oxide anchoring iron oxide (PRGI) and Pt nanoparticle by electrostatic interaction. The mass ratio of PRGI and Pt could determine the surface charge and stability of PRGI/Pt nanohybrid, leading to catalytic activity dependent on mass ratio, which could reach the maximum at the ratio of 0.8. The as-obtained PRGI/Pt nanohybrid could catalyze TMB oxidation more effectively, which was higher than the sum of individual PRGI and Pt, so there was synergistic effect between PRGI and Pt in PRGI/Pt nanohybrid. Furthermore, the PRGI/Pt nanohybrid showed higher maximum initial velocity than Pt nanoparticle, which was consistent with PRGI/Pt nanohybrid's stronger catalytic activity. Nevertheless, the PRGI/Pt nanohybrid performed weaker binding affinity for TMB than Pt nanoparticle. Thus, the enhanced activity might be attributed to PRGI/Pt nanohybrid's large contact area or fast product desorption rate. Our study also demonstrated that the electrostatic assembly was a potential way for constructing nanozymes based hybrid nanomaterials with controllable surface charge, which supplied another perspective for improving nanozyme activity.

2. Materials and methods

2.1. Materials

Polyethyleneimine (PEI_{800}, PEI_{1800}, PEI_{25000}), 3, 3′, 5, 5′-tetramethylbenzidine (TMB), 2, 2′-azino-bis (3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) and L-ascorbic acid ($C_6H_8O_6$) were purchased from Sigma-Aldrich (USA). Sodium citrate ($Na_3C_6H_5O_7$), sodium bicarbonate ($NaHCO_3$), hydrogen peroxide (H_2O_2), dimethyl sulphoxide (DMSO), H_2PtCl_6 and $FeCl_3 \cdot 6H_2O$ were obtained from Beijing Chemical Works (China). All chemicals were used without any further purification. All experiments used 18.2 MΩ of ultrapure water.

2.2. Characterization

High-resolution transmission electron microscopy (HRTEM) images were acquired by JEM-2100F high-resolution transmission electron microscopy. The absolute content of iron and Pt were quantified by inductively coupled plasma mass spectrometer (ICP-MS). The dynamic light scattering (DLS) size and zeta potential were measured by Nano ZS (Malvern, UK). The UV-Vis absorbance was measured by Cary 500 UV–Vis–NIR spectrometer (Varian). X-ray photoelectron spectroscopy (XPS) assay was performed by ESCALAB-MKII spectrometer (VG Co., United Kingdom) using Al KαX-ray radiation as excitation source.

2.3. Preparation of Pt nanoparticle, PRGI nanocomposite and PRGI/Pt nanohybrid

The Pt nanoparticle was prepared according to the previous description [34]. Briefly, 0.6 mL of sodium citrate solution (40 mM) was added into 10 mL of H_2PtCl_6 aqueous solution (2 mM) with rigorous stirring. Then, 1.125 mL of $NaBH_4$ solution (112 mM) was dropped into the above mixture slowly.

The PRGI nanocomposite was synthesized by hydrothermal method [35]. Typically, 5 mL of sodium bicarbonate (12.6 mg mL^{-1}) was added into 2.5 mL of mixture solution of $FeCl_3$ (18 mg mL^{-1}) and graphene oxide (2 mg mL^{-1}) with rigorous stirring. After 20 min, 1 mL of L-ascorbic acid (2.936 mg mL^{-1}) was dropped into the former solution and keep stirring for another 10 min. Then, 800 μL of PEI (25%) was added into the mixture. Finally, the solution was transferred into autoclave, and the autoclave was placed in the oven. Keep the temperature at 150 °C for 6 h, then the mixture was cooled down, ultrasonicated and purified by centrifugation.

The PRGI/Pt nanohybrid was prepared just by mixing PRGI nanocomposite and Pt nanoparticle at different mass ratio, such as 4, 2, 1, 0.8, 0.6, 0.4. In brief, fixing the Pt nanoparticle (270 μg mL^{-1}) at 100 μL, PRGI nanocomposite (270 μg mL^{-1}) of 400, 200, 100, 80, 60 and 40 μL was mixed with Pt nanoparticle solution, respectively, and then add moderate double-distilled water (ddH_2O) to keep all of them at 500 μL.

2.4. Evaluation of pH- and temperature-dependent catalytic activity

In order to investigate the pH-dependent catalytic activity, 1 μL of TMB solution (0.8 M in DMSO) and 10 μL of H_2O_2 solution (1 M) were added into the NaAc-HAc buffer with different pH, including