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Peroxidase-like properties of Ruthenium nanoframes

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Abstract This work reports the inherent peroxidase-like properties of Ruthenium (Ru) nanoframes. After templating with Palladium (Pd) seeds, Ru nanoframes with an octahedral shape, average edge length of 6.2 nm, and thickness of 1.8 nm were synthesized in high purity (>95 %) and good uniformity. Using the oxidation of 3,3′,5,5′-tetramethylbenzidine (TMB) by H_2O_2 as a model catalytic reaction, the Ru frames were demonstrated to be approximately three times more active than natural peroxidases in catalyzing the formation of colored products. As compared to their natural counterparts, Ru frames have a stronger binding affinity to TMB as well as a weaker binding affinity to hydrogen peroxide during the catalysis. The Ru frames as peroxidase mimics proved to be chemically and thermally stable. This work represents the first demonstration of Ru nanostructure-based peroxidase mimics and is therefore expected to inspire future research on bio-applications of Ru nanomaterials.

Keywords Ruthenium · Nanoframes · Peroxidase · Enzyme mimic · Catalysis

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1 Introduction

Peroxidase mimics of inorganic nanomaterials hold great potential for replacing natural peroxidases in diagnostic, sensing, and imaging applications, providing enhanced performance [1–8]. Since the first demonstration of ferromagnetic nanoparticles as peroxidase mimics [9], a vast variety of inorganic nanomaterials have been reported to show peroxidase-like properties, including nanostructures made of metal oxides [10–14], noble metals [15–21], carbon materials [22–24], and a combination of them [25, 26]. Among them, noble-metal mimics are particularly intriguing because: (1) they are ultra-stable owing to their chemical inertness, enabling them to survive harsh environments; and (2) their surfaces can be conveniently functionalized with biomolecules by means of metal-thiolate bonding [27], facilitating biomedical applications. While peroxidase-like properties have been demonstrated for noble-metal nanostructures of Au, Pt, Pd, Ir and their alloys [15–21], to the best of our knowledge, there is no literature report on Ru nanostructure-based peroxidase mimics. Ru is quite unique compared to other noble metals. For example, Ru is chemically super stable and is even invulnerable to aqua regia [28]; Ru is the only noble metal that normally takes the hexagonal close-packed (hcp) crystal structure [29]. These unique features of Ru inspired us to explore Ru nanostructure-based peroxidase mimics.

In this work, we demonstrate the peroxidase-like properties of Ru nanoframes with an octahedral shape and size <10 nm. Specifically, uniform Ru nanoframes were first synthesized using a method based on seeded growth and chemical etching [29]. The peroxidase-like activity of the frames was then demonstrated by the catalytic reactions between hydrogen peroxide and different peroxidase substrates. Using 3,3′,5,5′-tetramethylbenzidine (TMB [30]) as

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a model substrate, we have quantified the catalytic efficiency of the Ru frames. Finally, superior stabilities of the Ru frames as peroxidase mimics were demonstrated. This work represents the first attempt to explore Ru-based peroxidase mimics and, in a sense, offers a promising prospect for the application of Ru nanomaterials in biocatalysis.

2 Materials and methods

2.1 Chemicals and materials

Ruthenium (III) chloride hydrate ($RuCl_3{\cdot}xH_2O$), sodium tetrachloropalladate(II) (Na_2PdCl_4, 98 %), potassium bromide (KBr, ≥99 %), L-ascorbic acid (AA, ≥99 %), poly(vinylpyrrolidone) (PVP, $M_W \approx 55{,}000$), hydrochloric acid (HCl, 37 %), iron(III) chloride ($FeCl_3$, 97 %), 3,3′,5,5′-tetramethylbenzidine (TMB, >99 %), 3,30-diaminobenzidine (DAB, > 99 %), *o*-phenylenediamine (OPD, > 98 %), hydrogen peroxide solution (30 wt. % in H_2O), sodium chloride (NaCl, 99.5 %), sodium phosphate dibasic (Na_2HPO_4, 99 %), potassium phosphate monobasic (KH_2PO_4, 99 %), tris base (99.9 %), citric acid (99 %), acetic acid (HOAc, 99.7 %), and sodium acetate (NaOAc, 99 %) were all obtained from Sigma-Aldrich. Ethylene glycol (EG) was obtained from J. T. Baker. All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.0 MΩ cm.

2.2 Preparation of Ru nanoframes

Ru nanoframes were prepared using our recently published procedure with minor modifications [29]. In brief, Ru was selectively deposited to the edge and corner sites of Pd truncated octahedra as the seeds, leading to the formation of Pd–Ru core-frame octahedra. The Pd cores were then removed through chemical etching, leaving Ru octahedral nanoframes as the final product. Specifically, three steps were involved in a standard synthesis:

1. Preparation of 5.6 nm Pd truncated octahedra to be used as the seeds. The Pd seeds were produced according to our previously published procedure [31]. The final Pd seeds were dispersed in 1.0 mL of EG for future use. Particle concentration for the Pd seeds was estimated to be 7.8×10^{-6} M (1 M = 1 mol L^{-1}) with the combination of transmission electron microscope (TEM) imaging and ICP-OES analysis [31].
2. Deposition of Ru on Pd seeds. 8 mL of an EG solution containing 105 mg of PVP and 66.6 mg of AA was combined in a 50-mL three-neck flask and preheated to 200 °C in an oil bath under magnetic. Then, 1.0 mL of the already synthesized Pd seeds were added to the flask using a pipette. After 5 min, 10.0 mL of $RuCl_3{\cdot}xH_2O$ solution (0.4 mg/mL, in EG) was injected to the flask at a rate of 2.0 mL/h using a syringe pump. The products (i.e., Pd–Ru core-frame octahedra) were collected by centrifugation, washed once with acetone, twice with water, and finally re-dispersed in 1.0 mL of DI water.
3. Removal of Pd cores from Pd–Ru core-frame octahedra. KBr (200 mg), PVP (40 mg), $FeCl_3$ (40 mg), HCl (0.2 mL, 37 %), DI water (3.8 mL), and an aqueous suspension of the as-prepared Pd–Ru core-frame octahedra (0.5 mL) were mixed together in a 20-mL glass vial under magnetic stirring at room temperature for 10 min. Then, the solution was heated to 80 °C in an oil bath under magnetic stirring. After 1 h, the solution was cooled down with a water bath to room temperature and the products (i.e., Ru frames) were collected by centrifugation, washed once with ethanol, twice with water, and finally re-dispersed in 0.5 mL of DI water or EG for future use.

2.3 Evaluation of the peroxidase-like activities of Ru frames

The experiments were performed at room temperature in 1.5 mL tubes. The catalytic reactions were carried out in different buffer solutions (i.e., 1.0 mL 0.2 M NaOAc/HOAc buffer solution pH 4.0 for TMB, 1.0 mL 0.2 M Na_2HPO_4 + 0.1 M citric acid buffer solution pH 7.8 for DAB, and 1.0 mL Tris–HCl + 0.15 M NaCl buffer solution pH 7.8 for OPD). Each contained ~1×10^{-11} M Ru frames, 2 M H_2O_2, and 0.8 mM TMB, DAB, or OPD. Control experiments were conducted under the same conditions except for the absence of Ru frames.

2.4 Kinetic assays

The steady-state kinetic assays [9, 20] were performed at room temperature (~22 °C) in 1.0 mL 0.2 M NaOAc/HOAc solution (pH 4.0). Upon the addition of substrates (TMB and H_2O_2) in the buffer system containing Ru frames (1.06×10^{-11} M), the absorbance at 653 nm of the reaction solution as a function of time were recorded using a spectrophotometer for 2 min (interval of 6 s). The initial reaction velocity (v) was derived through $v = \text{Slope}_{\text{Initial}}/(\varepsilon_{\text{TMB-653 nm}} \times l)$, where $\text{Slope}_{\text{Initial}}$ was obtained from the first derivation of each "absorbance vs. time" plots, $\varepsilon_{\text{TMB-653 nm}}$ was the molar extinction coefficient of TMB at 653 nm that equals 3.9×10^4 M^{-1} cm^{-1} [32], and l is the length of cuvettes that equals 1.0 cm. The "v versus substrate concentrations" plots were then fitted with the