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Metal Doping Significantly Affects The Peroxidase-Like Activity of CeO2 Nanoparticles

Ali Reza Hormozi Jangi[1], Mohammad Reza Hormozi Jangi[2]*

[1,2]Hormozi Laboratory of Chemistry and Biochemistry, Iran.

[*]**Corresponding author:** Mohammad Reza Hormozi Jangi, Hormozi Laboratory of Chemistry and Biochemistry, Iran.

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Abstract

In this study, the effect of metal doping on the peroxidase-like activity of CeO_2 nanoparticles was investigated. In this regard, different metals including Cr, Mn, Co, Ni, and Ag were used to synthesize the metal/ CeO_2 nanoparticles. Thereafter, the peroxidase-like activity of each metal/ CeO_2 nanoparticle was calculated using the TMB standard assay. Notably, the bare CoO_2 nanoparticles were used as the control and its activity was considered as 100%. The results revealed that although the presence of Cr, Co, and Ag in the nanozyme structure led to enhancement of the peroxidase-like activity of the CeO_2 nanoparticles, by doping the Mn and Ni in the nanozyme structure, a significant decrease in the peroxidase-like activity was observed. The Cr/CeO_2 nanoparticles showed the highest activity which was 4.0-fold higher than that of the bare CeO_2 and 2.0-fold higher than that of the CO/CeO_2 and Ag/CeO_2 nanoparticles. Besides, the specific enzyme-like activity of the nanozymes was found to be 0.427 µM/min, 0.256 µM/min, 1.710 µM/min, 0.812 µM/min, 0.256 µM/min, and 0.854 µM/min for the CeO_2, Ni/CeO_2, Cr/CeO_2, Ag/CeO_2, Mn/CeO_2, and Co/CeO_2, in order. The results of this study proved that co-doping a suitable metal in the structure of CeO_2 nanoparticles can significantly affect their peroxidase-like activity.

Keywords: Metal/ CeO2 nanoparticles; bimetallic nanozymes; CeO2 nanoparticles; Peroxidase-like activity

1. Introduction

Nanozymes are a variety of highly stable, low-cost, and efficient nanosized materials that show significant intrinsic enzyme-like properties [1-9]. The nanozymes were introduced as powerful alternatives to native enzymes for overcoming the current drawbacks of native free enzymes such as their instability and difficult recovery [10-20]. Besides, they attracted good attention to be used to solve the significant disadvantage of the immobilized enzymes, i.e., lower activity than the native enzymes and higher cost than intrinsic enzyme-like nanozymes [21-24]. Notably, with the fast development of nanoscience in recent years, a wide veracity of nanomaterials with unique spectral, optical, catalytic, and stability has been introduced [25-38]. Among these nanostructures reveal significant enzyme-like activity for instance peroxidase-like, oxidase-like, urease-like, and catalase-like, etc. [39-51]. Nanozymes have been used for different applications such as dye degradation and the battery industry, as well as, sensing and detection [51-58], especially after the first report of COVID-19 [59, 60], they applied for its clinical sensing [61-65]. Among different nanozymes, CeO_2 nanoparticles attracted good attention for application in different fields such as sensing, detection, catalysis, and cancer treatment. Hence, herein, the effect of metal doping on the peroxidase-like activity of CeO_2 nanoparticles was investigated. In this regard, different metals including Cr, Mn, Co, Ni, and Ag were used to synthesize the metal/ CeO_2 nanoparticles. Thereafter, the peroxidase-like activity of each metal/ CeO_2 nanoparticle was calculated using the TMB standard assay. Besides, the specific enzyme-like activity of the nanozymes was also quantified.

2. Experimental

2.1. Synthesis of peroxidase-like Metal/CeO_2 nanoparticles

The metal/CeO_2 nanoparticles were prepared using a simple low-cost coprecipitation method. To do this, initially, 50 mg of citric acid and 70 mg of EDTA (0.073 g) were added into 12.0 mL water under stirring. After that, 800 mg of each metal slat and 780 mg of $Ce(NO_3)_3$•$6H_2O$ were added to the mixture. Then 0.3 mL ammonium hydroxide was added to the reaction media under vigorous stirring, followed by stirring for 2 h at room temperature. Afterward, the precipitate of metal/CeO_2

nanoparticles was collected, washed, dried, and calcined at 550 °C for about 4 h.

2.2. Enzyme assay

TMB assay was used for determining the enzyme-like activity of peroxidase-like graphene oxide/gold nanoparticles as a standard method. Briefly, 20 µL of each nanozyme solution was added to the acetate buffer (pH, 6.0). Then, 0.2 mL TMB solution and 0.2 mL H_2O_2 solution were added to the solution. After reacting for 30.0 minutes, the absorbance of the colored product was measured at 650 nm.

3. Results and discussion

In this study, the effect of metal doping on the peroxidase-like activity of CeO_2 nanoparticles was investigated. In this regard, different metals including Cr, Mn, Co, Ni, and Ag were used to synthesize the metal/ CeO_2 nanoparticles, and their enzyme-like activity was calculated.

3.1. Effect of metal doping on peroxidase-like activity of CeO_2 nanoparticles

The peroxidase-like activity of each metal/ CeO_2 nanoparticle was calculated using the TMB standard assay. It should be mentioned that the peroxidase-like activity of nanozymes was determined using the following equation;

$$\text{Activity} = (A/A_{con})\times 100$$

which A and Acon are represented by the activity of each nanozyme and the activity of control, respectively. Notably, the bare CoO_2 nanoparticles were used as the control, and their activity was considered 100%. The peroxidase-like activity of different metal/CeO_2 nanoparticles toward TMB oxidation compared to the bare CeO_2 is shown in Figure 1.

These results revealed that although the presence of Cr, Co, and Ag in the nanozyme structure led to enhancement of the peroxidase-like activity of the CeO_2 nanoparticles, by doping the Mn and Ni in the nanozyme structure, a significant decrease in the peroxidase-like activity was observed. Minimal activity was found for the Ni/CeO_2 and Mn/CeO_2, which showed about 60% of the activity of bare CeO_2. In fact, doping Ni and Mn into CeO2 reduced their activity by about 40% which is a significant value. Besides, doping Ag and Co showed that these metals can enhance the peroxidase-like activity of the bare CeO_2 nanozymes by about 200% of their initial activity (bare CeO_2 is considered 100%). The Cr/CeO_2 nanoparticles showed the highest activity which was 4.0-fold higher than that of the bare CeO_2 and 2.0-fold higher than that of the CO/CeO_2 and Ag/CeO_2 nanoparticles.

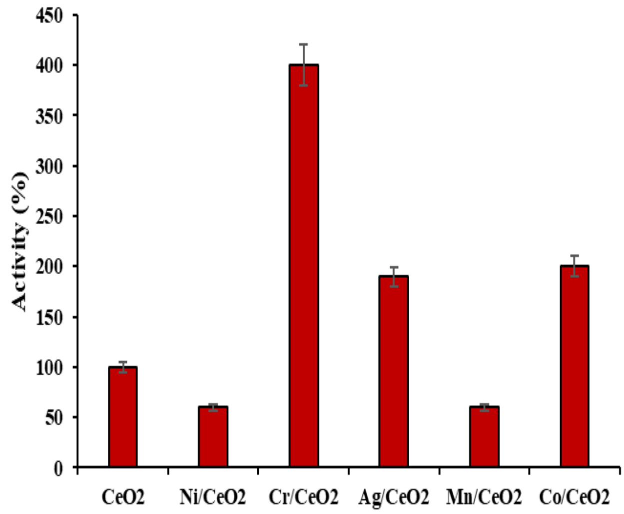

Figure 1. Peroxidase-like activity of different metal/CeO_2 nanoparticles toward TMB oxidation.

3.2. Evaluating the specific activity of nanozymes

Although the relative activity can provide a good insight into the effect of metal doping on the peroxidase-like activity of CeO_2 nanoparticles, it cannot be considered a reliable index for quantitative comparisons. Hence, the specific activity of nanozymes was calculated as per µM/min unit. The radar plot of the specific enzyme-like activity of different nanozymes is shown in Figure 2. As can be shown in this plot, the Cr/CeO_2 showed maximal specific activity, and the Ni/CeO_2 had minimal specific activity.

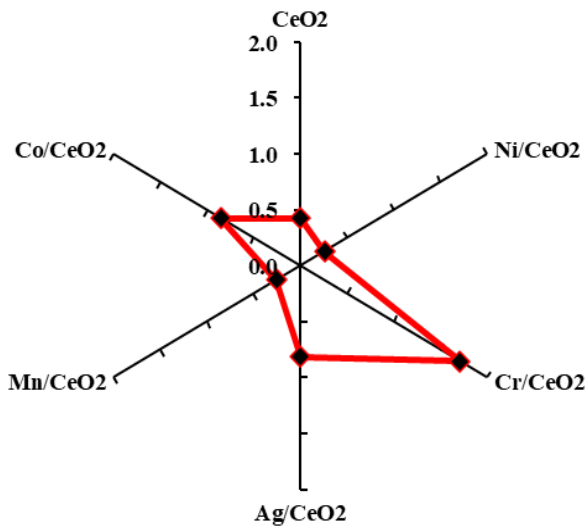

Figure 2. Radar plot of the specific enzyme-like activity of

different nanozymes.

To provide a more precise investigation, the histogram of specific enzyme-like activity of the nanozymes was constructed. The results are shown in Figure 3. According to the results of Figure 3, the specific enzyme-like activity of the nanozymes was found to be 0.427 µM/min, 0.256 µM/min, 1.710 µM/min, 0.812 µM/min, 0.256 µM/min, and 0.854 µM/min for the CeO_2, Ni/CeO_2, Cr/CeO_2, Ag/CeO_2, Mn/CeO_2, and Co/CeO_2, in order. The specific activity of Ni/CeO_2, Cr/CeO_2, Ag/CeO_2, Mn/CeO_2, and Co/CeO_2 nanozymes was found to be 0.6-order, 4.0-order, 1.9-order, and 2.0-order of the specific activity of the bare CeO_2 nanoparticles. The results of this study proved that co-doping a suitable metal in the structure of CeO_2 nanoparticles can significantly affect their peroxidase-like activity.

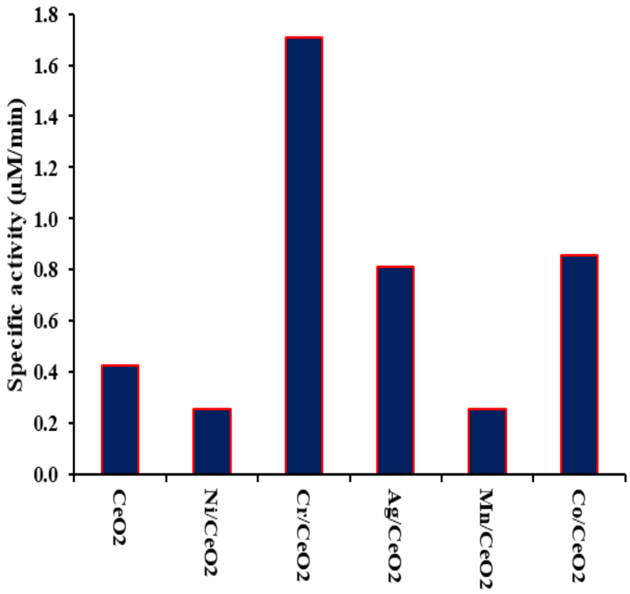

Figure 3. Comparing the specific peroxidase-like activity of metal/CoO_2 nanoparticles

4. Conclusions

In this study, the effect of metal doping on the peroxidase-like activity of CeO_2 nanoparticles was investigated. In this regard, different metals including Cr, Mn, Co, Ni, and Ag were used to synthesize the metal/ CeO_2 nanoparticles. Thereafter, the peroxidase-like activity of each metal/ CeO_2 nanoparticle was calculated using the TMB standard assay. Notably, the bare CoO_2 nanoparticles were used as the control and its activity was considered as 100%. The results revealed that although the presence of Cr, Co, and Ag in the nanozyme structure led to enhancement of the peroxidase-like activity of the CeO_2 nanoparticles, by doping the Mn and Ni in the nanozyme structure, a significant decrease in the peroxidase-like activity was observed. The Cr/CeO_2 nanoparticles showed the highest activity which was 4.0-fold higher than that of the bare CeO_2 and 2.0-fold higher than that of the CO/CeO_2 and Ag/CeO_2 nanoparticles. Besides, the specific enzyme-like activity of the nanozymes was found to be 0.427 µM/min, 0.256 µM/min, 1.710 µM/min, 0.812 µM/min, 0.256 µM/min, and 0.854 µM/min for the CeO_2, Ni/CeO_2, Cr/CeO_2, Ag/CeO_2, Mn/CeO_2, and Co/CeO_2, in order. The results of this study proved that co-doping a suitable metal in the structure of CeO_2 nanoparticles can significantly affect their peroxidase-like activity.

Acknowledgment

None.

Conflict of interest

None.

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