



The intrinsic oxidase-like activity of Ag₂O nanoparticles and its application for colorimetric detection of sulfite

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ABSTRACT

Ag₂O nanoparticles (Ag₂O NPs) were found to possess intrinsic oxidase-like activity and could catalyze the oxidation of typical peroxidase substrates, such as guaiacol, *o*-phenylenediamine (OPDA), and 3,3',5,5'-tetramethylbenzidine (TMB), to form colored products under atmospheric O₂ without addition of exogenous H₂O₂. Furthermore, a simple method for the colorimetric detection of sulfite was developed based on the finding that the oxidase-like activity of Ag₂O NPs was inhibited by sulfite.

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1. Introduction

Natural enzymes have been extensively studied and widely used due to their high substrate specificity, high catalytic efficiency and mild reaction conditions. However, the catalytic activity of natural enzymes can be easily affected by environmental conditions, such as high acidity, strong basicity and high temperature. Moreover, the high cost of preparation, purification, storage and transportation conditions also prevent natural enzymes from wide application [1]. Therefore, considerable attentions have been paid to the stabilization of natural enzymes by various techniques and methods, including protein engineering [2], chemical modification [3], immobilization [4] and addition of stabilizers [5]. Moreover, remarkable progress has also been made to construct and discover new enzyme mimics with high catalytic activity and chemical stability, such as myoglobin variants [6], cytochrome *c* variants [7], hybrid of cytochrome *c* and horseradish peroxidase [8], hemin [9], porphyrin [10], cyclodextrin [11], phthalocyanine [12] and polymers [13].

Inorganic nanomaterials have attracted much interest due to their size, morphology and composition-dependent properties. However, the potential enzyme-like activity of inorganic nanomaterials had not been recognized until ferroferric oxide nanoparticles (Fe₃O₄ NPs) were discovered to possess intrinsic peroxidase-like activity in 2007 [14]. Since then, several kinds of metal oxides,

such as Co₃O₄ [15], CeO₂ [16], V₂O₅ [17] and CuO [18], have been found to possess enzyme-like activities. These studies show that nanomaterial-based enzyme mimics have the advantages of easy preparation, low cost and high stability for use as enzyme mimics.

Ag₂O, a brown powder with a simple cubic structure, has been widely used in many industrial fields, such as antibacterial materials [19], catalysts for alkane activation and olefin epoxidation [20], as well as photocatalyst [21]. However, the oxidase-like activity of Ag₂O nanoparticles (Ag₂O NPs) has not yet been reported. In the study, we report that Ag₂O NPs has intrinsic oxidase-like activity; it can catalyze the oxidation of typical peroxidase substrates under atmospheric O₂ without addition of exogenous H₂O₂.

2. Experimental

Ag₂O NPs were prepared via a typical solution precipitation method. Typically, 100 mL NaOH solution (1.5 mol L⁻¹) was added dropwise into 50 mL AgNO₃ solution (0.1 mol L⁻¹) under magnetic stirring. The brown Ag₂O precipitate was collected by filtration, washed with deionized water until the pH of the aqueous effluent was neutral, and then dried at 60 °C.

Powder X-ray diffraction (XRD) datum was recorded on a Rigaku Dmax/Ultima IV X-ray diffractometer. Scanning electron microscopy (SEM) measurements were carried out on an FEI Inspect F50 microscope. High-resolution transmission electron microscopy (HRTEM) was measured on an FEI Tecnai F20 microscope. X-ray

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photoelectron spectroscopy (XPS) was performed on a Kratos XSAM800 XPS spectrometer.

The oxidase-like activity of the as-prepared Ag_2O NPs was investigated by the oxidation of guaiacol, OPDA and TMB under atmospheric O_2 at 25°C without addition of exogenous H_2O_2 . For the oxidation of guaiacol and OPDA, 5 mg Ag_2O NPs was dispersed in 100 mL deionized water, and then 60 μL of 100 mM guaiacol or 2 mL of 50 mM OPDA was added to start the reaction under magnetic stirring. For the oxidation of TMB, 5 mg Ag_2O NPs was dispersed in 100 mL acetic acid/sodium acetate buffer solution (100 mM, $\text{pH}=4.0$), and then 100 μL of 50 mM TMB solution (dissolved in DMF) was added to initiate the reaction.

3. Results and discussion

Fig. 1A shows the XRD pattern of the as-prepared Ag_2O sample. All the diffraction peaks could be indexed to Ag_2O crystal (JCPDS No. 41-1104) with a cubic structure ($a=b=c=4.726\text{ \AA}$). SEM images showed that the Ag_2O sample was composed of irregular particles with diameters mainly in the range of 200–500 nm (Fig. 1B and C). The HRTEM image showed the d -spacing of 0.238 nm, which could be assigned to the (200) crystal plane of

cubic Ag_2O (Fig. 1D). The corresponding FFT pattern (inset in Fig. 1D) indicated the good crystallization of the Ag_2O NPs.

Fig. 2 shows the high-resolution XPS spectra of Ag 3d and O 1s. The Ag 3d spectrum consisted of two peaks at 373.9 and 367.9 eV with a doublet separation of $\Delta=6\text{ eV}$, which corresponded to the binding energies of Ag $3d_{3/2}$ and Ag $3d_{5/2}$, respectively (Fig. 2A) [22]. The strong peak of O 1s at binding energy of 530.6 eV could be assigned to the lattice oxygen of Ag_2O . The weak peak at binding energy of 532.6 was 2 eV higher than the oxide peak (Fig. 2B), which might be attributed to adsorbed oxygen or hydroxyl groups on the surface of Ag_2O NPs according to previous studies [23].

The oxidase-like activity of Ag_2O NPs was examined using guaiacol, OPDA and TMB as typical chromogenic substrates, which have been widely used to investigate the oxidase- and/or peroxidase-like activities of natural enzymes or enzyme mimetics [7,24–27]. In the presence of Ag_2O NPs, the solutions of guaiacol, OPDA and TMB changed to brown, yellow and blue, respectively, by reaction with atmospheric O_2 for 15 min (Fig. 3A). In contrast, the solutions were still colorless in the absence of Ag_2O NPs (Fig. 3B).

The absorption spectrum of guaiacol oxidized by atmospheric O_2 in the presence of Ag_2O NPs showed a broad band at $\sim 415\text{--}470\text{ nm}$

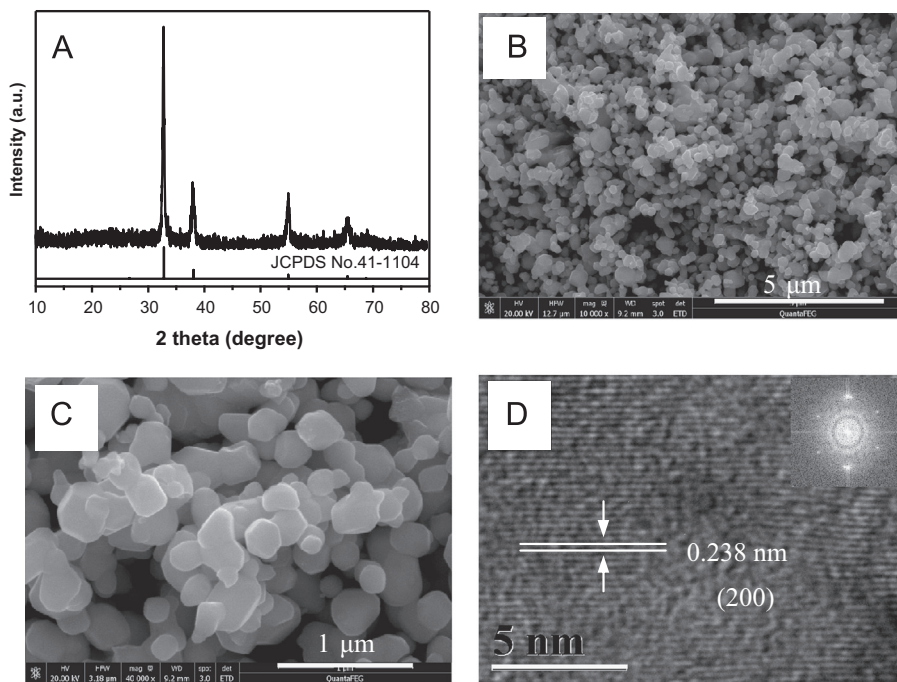


Fig. 1. XRD pattern (A), SEM images (B and C), HRTEM image (D) and FFT pattern (inset of D) of the as-prepared Ag_2O powders.

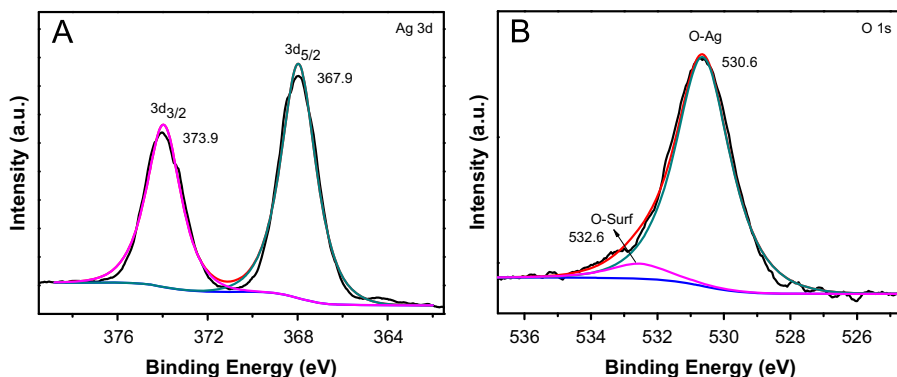


Fig. 2. XPS spectra of Ag 3d (A) and O 1s (B).

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