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Preparation and application of magnetic zinc pyridinedicarboxylic acid nanocomposite (Zn-$(PDC)_2$@Fe_3O_4)

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Abstract Nano-scaled Fe_3O_4 were synthesized using solvothermal synthesis, and amino-modification of nano-scaled Fe_3O_4 was conducted with APTES. With Fe_3O_4-NH_2 and Zn^{2+} as the metal centers, 2,6-pyridinedicarboxylic acids as the organic ligand, and using the one-step ultrasonic-assisted method, a new magnetic zinc pyridinedicarboxylic acid nanocomposite (Zn-$(PDC)_2$@Fe_3O_4) was synthesized. The structure, composition and morphology of the products were characterized using methods such as X-ray single crystal diffraction, Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction, and scanning electron microscope. The results showed that the Zn-$(PDC)_2$ was almost an octahedron, and the Zn-$(PDC)_2$@Fe_3O_4 looked like a nanoflower. The mimetic peroxidase properties of Zn-$(PDC)_2$@Fe_3O_4 were studied with H_2O_2 solution and TMB solution as the substrates, and the results showed that: the Michaelis constant of H_2O_2 by Zn-$(PDC)_2$@Fe_3O_4 was: K_m = 0.411 mM, the maximum reaction rate: v_{max} = 3.440 × 10^{-8} M s^{-1}; the Michaelis constant of TMB by Zn-$(PDC)_2$@Fe_3O_4 was: K_m = 0.189 mM, and the maximum reaction rate: v_{max} = 2.419 × 10^{-8} M s^{-1}, both of which were lower than those of H_2O_2 and TMB by Fe_3O_4 and Horseradish Peroxidase (HRP). Based on the reduction of the absorbance of original solution due to the consumption of H_2O_2 in oxidation-reduction reaction between SO_3^{2-} and H_2O_2 under acid conditions, a new method for determining the content of SO_3^{2-} was established. The linear range of SO_3^{2-} was 8 × 10^{-7}~8 × 10^{-5} mol/L, the detection limit of SO_3^{2-} was 8 × 10^{-8} mol/L, and the RSD of SO_3^{2-} was 2.7–9.2%.

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1. Introduction

Sulfite is a traditional food additive, having antiseptic, antibacteria and bleaching functions. However, containing certain toxicity, once taken in excessively, it will reduce the number

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of hemoglobin and red blood cells, and bring damages to human brain, heart, liver, stomach, kidney and other organs and the reproductive system (Ma et al., 2013).

Therefore, it is important to find a simple, sensitive, low cost and efficient method todetermine the content of sulfite for food quality and safety control. There are many methods for doing this job, and the current methods at home and abroad mainly include the pararosaniline hydrochloride direct colorimetric method, the distillation iodimetry method of GB/T5009.34--2003 (GB/T5009.34--2003) and the distillation colorimetric method of Japan Food Hygiene Association. Besides, some other methods for determining the content of sulfite have appeared in recent years, which include the mercury free salt colorimetric method, the potentiometric drop method, the extraction spectrophotometry, the flow injection analysis and the ion chromatography, but these methods have disadvantages such as complexity, high cost, and low sensitivity.

With a strong reducibility, the original solution's absorbance was reduced due to consumption of H_2O_2 in the oxidation-reduction reaction between SO_3^{2-} and H_2O_2 under acid conditions. Different amounts of SO_3^{2-} caused different absorbance reduction, which could even be observed with the naked eye. The experiment found that there was a good linear relationship between the two within a certain scope. Therefore, a new method for determining the content of SO_3^{2-} was established: the mimetic peroxidase colorimetric method.

In recent years, the mimetic peroxidase colorimetric method has drawn attention from many scholars. In this method, hydroxyl radical (OH) is first produced by the catalyzation of H_2O_2 with the mimetic peroxidase to oxidize substrates such as TMB, OPD, ABTS and luminol, which can change their colors or fluorescence characteristics (Luo et al., 2015), thus determining the contents of H_2O_2 and substance in relation to H_2O_2 in the samples. Compared with natural enzymes, the mimetic peroxidase has advantages such as simple preparation, low cost, good stability, and tolerance to extreme reaction conditions, and is morefavored.

Many nanomaterials have been reported to have the peroxidase activity. For example, gold, silver, platinum, nickel oxide, cerium dioxide, magnetite, copper sulfide, conductive polymer, carbon nanotube and nano-metal–organic framework are found to be able to catalyze H_2O_2 to produce hydroxyl radical (OH) to oxidize substrates such as TMB, OPD, ABTS and luminol, the actions of which may then change the colors of the substrates. The mimetic peroxidase can catalyze H_2O_2 to produce hydroxyl radical (OH) with a strong oxidation capacity, so it can be used to degrade organic pollutants and kill human cancer cells. Thanks to these advantages, nano-mimetic peroxidases are widely used in the determination of heavy metals in the environment, the determination and degradation of organic pollutants, the detection of food additives, detection analyses and the treatment of tumors (Zhang et al., 2012).

Because nano-scaled Fe_3O_4 have advantages such as magnetic properties, mimetic peroxidase properties, biocompatible properties, and can be separated, recovered and reused from complex matrices by external magnetism, while MOFs have advantages such as large specific surface area, porosity, the capacity to carry specific substances for site-specific delivery, and high stability, MMOFs are designed to be made of both magnetic materials and MOFs, which enables it to have the structures and properties of MOFs and magnetic properties, allowing it to be widely used in catalytic chemistry, biomedicine, environmental treatment and other fields (Li, 2014). In this paper, based on the characteristics of nano-scaled Fe_3O_4 and MOFs, with nano-scaled Fe_3O_4 and Zn^{2+} as the metal centers, and 2,6-pyridinedicarboxylic acid as the organic ligand, a new magnetic zinc pyridinedicarboxylic acid nanocomposite (Zn-$(PDC)_2$@Fe_3O_4) was prepared.

2. Experiments

2.1. Experimental reagents and apparatuses

2,6-pyridinedicarboxylic acid, ferric chloride hexahydrate (AR, Xiya Chemical Reagent Factory); zinc sulfate heptahydrat (AR, Xilong Chemical Co., Ltd.); anhydrous sodium acetate, hydrochloric acid, acetic acid, ethanol, 30% H_2O_2, anhydrous sodium sulfite (AR, Guangzhou Chemical Reagent Factory); polyethylene glycol 6000 (AR, Tianjin Kermel Chemical Reagent Co., Ltd.); polyvinylpyrrolidone (PVP), 3-aminopropyl triethoxy silane (APTES), 3,3′,5,5′-tetramethyl benzidine (TMB) (AR, Aladdin Industrial Corporation); glycol (AR, Sinopharm Group Chemical Reagent Co., Ltd.); pure nitrogen (≥99.99%, Gas Plant, Sanshui District, Foshan City); deionized water; water from Xijiang River (collected from Zhaoqing section, stored at 4 °C); lake water (collected from the Calligraphy Pond of Zhaoqing University, stored at 4 °C); hylocereus undatus 1, hylocereus undatus 2, tremella fuciformis and Chinese wolfberry (purchased from school supermarket).

AUY120 type electronic balance (SHIMADZU), HH-S2 thermostatic water bath (Universal Scientific Instruments Factory, Jintan City, Jiangsu Province), PHS-3C pH meter (Shanghai Rex), vortex mixing (Haimen Qilinbeier Instrument Manufacturing Co., Ltd.), 149A0279 type ultrasonic cleaner (Shanghai Kudos Ultrasonic Instrument Co., Ltd.), vacuum drying oven (Shanghai Yiheng Technical Co., Ltd.), electric constant temperature drying oven (Shanghai Sumsung Laboratory Instrument Co., Ltd.), PTEF autoclave (Shanghai Sumsung Laboratory Instrument Co., Ltd.), pipette and UV-2600 UV–VIS Spectrophotometer (SHIMADZU), APEX ⅡQUAZAR X-ray single crystal diffractometer (Bruker, German), IRT racer-100 Fourier transform infrared spectrometer (SHIMADZU), D/max 2000 X-ray powder diffractometer (XRD) (Rigaku), SUPRA 55 SAPPHIRE Fs-SEM (Carl Zeiss Jena), etc.

2.2. Synthesis and activation of nano-scaled Fe_3O_4

Synthesis of nano-scaled Fe_3O_4 using the hydrothermal and solvothermal method (Hu and Lou, 2013): 2.70 g $FeCl_3{\cdot}6H_2O$ (iron source) was weighed, and dissolved in 60 mL ethylene glycol solvent, and the mixture solution was stirred for 30 min to form a clear bright yellow solution. Then, 7.20 g sodium acetate (electrostatic stabilizer) and 1 g (polyethylene glycol stabilizer) were added, and the mixture solution was stirred for 30 min. The mixture solution finally formed was put into two 50 mL PTEF lined reaction kettles to react (solvothermal reduction) at 200 °C for 9 h, and then cooled

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