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Fabrication of cobalt ferrite/cobalt sulfide hybrid nanotubes with enhanced peroxidase-like activity for colorimetric detection of dopamine

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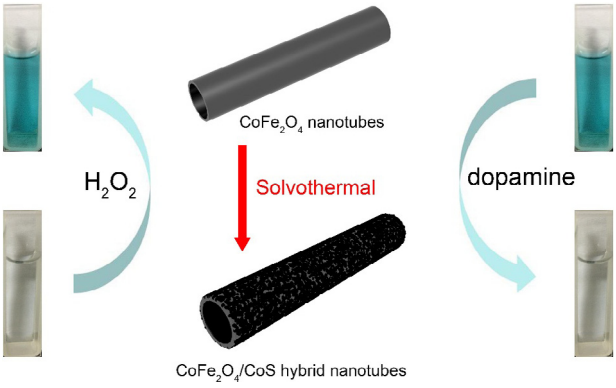
GRAPHICAL ABSTRACT

Synthesis of a novel peroxidase-like catalyst for the detection of hydrogen peroxide and dopamine.



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ABSTRACT

The development of highly sensitive and low-cost biosensors for the detection of dopamine is of paramount importance for medical diagnostics. Herein, we report the preparation of a new peroxidase-like catalyst with a uniform heterostructure by using a technique involving electrospinning, annealing and solvothermal reaction. In this catalyst system, cobalt sulfide (CoS) nanoparticles were homogenously distributed and supported on the surface of cobalt ferrite ($CoFe_2O_4$) nanotubes. The as-prepared $CoFe_2O_4$/CoS hybrid nanotubes showed remarkably high catalytic efficiency as peroxidase mimics toward the oxidation of 3,3,5,5-tetramethylbenzidine (TMB) in the presence of H_2O_2. Owing to the synergistic effect between the $CoFe_2O_4$ and CoS component, the prepared $CoFe_2O_4$/CoS hybrid nanotubes exhibited enhanced peroxidase-like activity, exceeding that of either the CoS nanoparticles or $CoFe_2O_4$ nanotubes alone. Dopamine has been widely investigated due to its unique function in the nervous system. Consequently, various approaches have been developed for the sensitive determination of dopamine. In this work, a simple and sensitive colorimetric route for the detection of dopamine was established based on the ability of dopamine to induce the reduction of oxidized TMB to TMB with consequent fading of the blue color. This method shows a wide linear range (0–50 μM) and a low detection limit of 0.58 μM.

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The unique heterostructure with spinel/sulfide interfaces represents a new concept for the construction of highly efficient and multifunctional biocatalysts.

1. Introduction

Natural enzymes have been exploited for hundreds of years and are widely studied owing to their immense catalytic activity and extraordinarily high substrate specificity. However, the inherent shortcomings of natural enzymes, including the high cost of synthesis and purification, poor operational stability, as well as the sensitivity of the catalytic performance to environmental conditions, have enormously limited their practical applications [1–3]. As potential solutions to the issues mentioned above, artificial enzymes have been rapidly developed in the past decades as alternatives to natural enzymes [3–7]. A variety of novel synthetic methods have been developed for the fabrication of highly efficient artificial enzymatic catalysts, providing the basis for their application in the fields such as sensors, medical diagnosis, biotechnology, and environmental monitoring [8–14]. In recent years, nanomaterial-based artificial enzyme mimics have attracted extensive attention due to their tunable catalytic activity, excellent stability and low preparation cost. Among these enzyme mimics, transition metal sulfide nanomaterials constitute a significant branch of artificial enzyme research, and have gained increasing interest in recent times. For example, researchers have reported that FeS nanosheets [15], CuS nanoparticles [16] and concave polyhedral superstructures [17], MoS_2 nanosheets [18] and CoS nanospheres [19] function as good peroxidase mimetic catalysts with favorable catalytic activity and high stability. To further increase the peroxidase-like activity of metal sulfides, they are generally combined with other functional materials to achieve a synergistic effect between the components [20–22]. For instance, we have found that the modification of the surface of graphene nanosheets with CuS nanoparticles provided enhanced catalytic activity relatively to the individual CuS nanoparticles or graphene alone [20]. Another example showed that the combination of Cu_9S_5 nanoparticles with polyaniline (PANI) nanowires produced considerably better peroxidase-like catalytic activity than either the Cu_9S_5 nanoparticles or PANI nanowires [21]. Therefore, it is a meaningful objective to fabricate functional nanocomposites with a synergistic effect to enhance the peroxidase-like activity of enzyme mimics.

It is well known that dopamine is an indispensable neurotransmitter that can affect the emotions and perceptions of humans. In addition, dopamine is known to be involved in the delivery of information in the brain, and abnormal levels of dopamine in the brain can cause numerous diseases, such as the well-known Parkinsonism's disease. Therefore, it is crucial to determine dopamine levels with a high sensitivity [23–27]. To date, various strategies, including electrochemical approaches [23,24], fluorescence methods [25–27], chromatography [28,29], capillary electrophoresis [30], have been developed for the determination of dopamine. However, each method has its limitations, such as complexity, high costs, or strict requirements on equipment. In contrast, colorimetric detection is a simple, rapid, and effective method of assaying the levels of dopamine in samples [31]. As the interaction with dopamine induces a fading of the color of the oxidized peroxidase substrate, a reliable sensing platform for the colorimetric detection of dopamine can be developed based on this approach [32,33].

Considering the high stability and the resistance of $CoFe_2O_4$ nanotubes as catalyst carriers and the photocatalytic performance of $CoFe_2O_4$-based nanocomposites, which may facilitate the transfer of photo-induced electrons, it is anticipated that the combination of transition metal sulfides and $CoFe_2O_4$ nanotubes may provide an effective platform for achieving outstanding enzyme mimics [34]. In this study, we fabricate a heterostructure comprising of $CoFe_2O_4$ nanotubes decorated with CoS nanoparticles via an electrospinning technique followed by calcination in air and subsequent solvothermal reaction. The as-prepared $CoFe_2O_4$/CoS hybrid nanotubes exhibit enhanced peroxidase-like activity compared to pure CoS nanoparticles or $CoFe_2O_4$ nanotubes due to the synergistic effect. On the basis of the inhibition of the peroxidase-like catalytic activity of dopamine, a simple approach for the colorimetric detection of dopamine is developed. This work offers a new route for the fabrication of spinel-supported metal sulfide nanomaterials and creates new opportunities for their application in biosensing and medical diagnostics.

2. Experimental

2.1. Chemicals and materials

Poly(vinylpyrrolidone) (PVP, Mw = 1300000) and L-cysteine were purchased from Sigma-Aldrich. $Fe(NO_3)_3{\cdot}9H_2O$ and hexamethylenetetramine (HMTA) were obtained from Tianjin East China reagent factory. $Co(Ac)_2{\cdot}4H_2O$ and 3,3′,5,5′-tetramethylbenzidine (TMB) were purchased from Sinopharm Reagent Co., Ltd., Beijing. $Co(NO_3)_2{\cdot}6H_2O$ was obtained from Xilong Chemical Co., Ltd. Dopamine hydrochloride (DA) and dimethyl sulfoxide (DMSO) were bought from Aladdin. N, N′–dimethylformamide (DMF) was commercially obtained from Tianjin Tiantai Fine Chemicals Co., Ltd. H_2O_2 (30%) and ethanol were bought from Beijing Chemical Works. All other reagents were used without further purification.

2.2. Preparation of $CoFe_2O_4$ nanotubes via electrospinning followed by calcination process

In a typical experiment, 1.64 g of PVP was added to a conical flask containing 11.4 g of ethanol and 7.8 g of DMF. Subsequently, 0.50 g of $Fe(NO_3)_3{\cdot}9H_2O$ and 0.154 g of $Co(Ac)_2{\cdot}4H_2O$ were introduced into the above solution. The mixture was stirred vigorously for about 12 h at room temperature for homogenization. The homogenized solution was electrospun under an applied voltage of 15 kV supplied by a high-voltage DC power supply that was connected to an aluminium foil collector, and the distance was fixed at ~20 cm. The as-prepared fibrous membrane was subsequently calcined at 550 °C in air for 3 h using a confirmed program. Ultimately, $CoFe_2O_4$ nanotubes with a black color were obtained.

2.3. Fabrication of $CoFe_2O_4$/CoS hybrid nanotubes

3 mg of the as-prepared $CoFe_2O_4$ nanotube sample was dispersed in a mixture of 8 ml of H_2O and 4 ml of ethanol under ultrasonic for a few minutes. Subsequently, 25 mg of $Co(NO_3)_2{\cdot}6H_2O$, 30 mg of HMTA, and 18 mg of L-cysteine were added to the mixture, followed by ultrasonic dispersion to produce a uniform dispersion. Herein, HMTA was used as structure-directing agent and L-cysteine served as an effective sulfur source. The mentioned solution was transferred to a 50 ml Teflon-lined autoclave and maintained at 200 °C for 12 h. After cooling, the as-prepared sample was collected from the mixture with a magnet and washed