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A mimic peroxidase biosensor based on calcined layered double hydroxide for detection of H_2O_2

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ABSTRACT

An enzymeless biosensor was explored from Cu–Mg–Al calcined layered double hydroxide (CLDH) modified electrode in this study. The Cu–Mg–Al CLDH greatly promotes the electron transfer between H_2O_2 and GCE, and it is exemplified toward the non-enzymatic sensing of H_2O_2. The results indicate that the Cu–Mg–Al CLDH exhibits excellent electrocatalytic property, high sensitivity, good reproducibility, long-term stability, and fast amperometric response toward reduction of H_2O_2, thus is promising for the future development of man-made mimics of enzyme in H_2O_2 sensors. This work opens a way to utilize simply Cu–Mg–Al CLDH as an electron mediator to fabricate an efficient H_2O_2 biosensor, which exhibits great potential applications in varieties of simple, robust, and easy-to-make analytical approaches in the future.

1. Introduction

Hydrogen peroxide (H_2O_2) is a very important intermediate in environmental and biological reactions. It is widely used in many fields, including pollution control, textile and paper bleaching, sterilization and so on (Notsu et al., 2002; Tsiafoulis et al., 2005). Thus, the rapid and accurate detection of H_2O_2 is of great importance. Good selectivity and high sensitivity can be obtained with H_2O_2 enzymatic biosensors. However, their stability is limited due to easy denaturation by environmental changes since their catalytic activity originated from the intrinsic nature of enzymes (Shoji and Freund, 2001), and leakage of enzymes during their storage and immobilization procedure. Furthermore, the preparation and purification of enzymes are usually time-consuming and expensive. Therefore, considerable attention has been focused on the development of nonenzymatic electrodes to solve these problems, and the synthesis of artificial peroxidases with highly catalytic properties and widely practical applications is becoming a significant field for different purposes. Nowadays, many efforts have been made to extend the natural enzymes to enzyme mimetics (Gao et al., 2007; Wang et al., 2003; Ionescu et al., 2004). It is known that many peroxidase mimics including hemin (Fruk and Niemeyer, 2005), haematin (Zhang and Dasgupta, 1992), hemoglobin (Wang et al., 2002a,b), porphyrin (Bonar-law and Sanders, 1995; Ci et al., 1993) and cyclodextrin (Liu et al., 1999) have been applied in different fields.

It is becoming more and more significant in analytical chemistry to take advantages of various inorganic nanomaterials, because of their intrinsic advantages such as regular structure, chemical and thermal stabilities, high surface reaction activity, high catalytic efficiency, large surface-to-volume ratio and strong adsorption ability (Kaushik et al., 2008). To date, there are many reports by employing these nano-structured materials as peroxidase mimetics. In particular, electrochemically active nanomaterials consisting of metals (Park et al., 2003; Jena and Raj, 2006; Li et al., 2007; Cao et al., 2010), metallic carbon nanotubes (Ye et al., 2004; Kang et al., 2007; Rong et al., 2007), transition metal disulfide (Dai et al., 2009), transition metal oxides (Zhuang et al., 2008; Miao et al., 2008; Wei and Wang, 2008; Li et al., 2010; Jia et al., 2009; Song et al., 2010; Batchelor-McAuley et al., 2008), and conducting polymers (Farrell and Breslin, 2004) have been used in the construction of non-enzymatic electrochemical biosensors due to their unique and particular properties. However, to the best of our knowledge, there have been few reports (Wang et al., 2009) on the use of layered double hydroxides (LDHs) as peroxidase mimetics.

Layered double hydroxides (LDHs) consist of brucite-like hydroxide sheets, where partial substitution of trivalent for divalent cations results in a positive sheet charge compensated by anions within interlayer galleries (Cavani et al., 1991). They have received considerable attention because of non-toxicity and high chemical and hydrolytic stability (Shan et al., 2003), ion-exchangers, catalysts or catalyst precursors, sorbents and antacids

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(Carpani et al., 2004; Terry, 2004). It is well-known that synthesis of these materials containing transition metal ions, especially copper, in the sheets is of particular interest because of their selective oxidation properties (Lewis and Tolman, 2004). Moreover, the copper-containing hydrotalcite-like compound can be used as a catalyst for the Baeyer-Villiger oxidation of ketones (Kaneda et al., 1995), the coupling of phenylethyne (Auer et al., 1997), alkylation of phenol (Velu and Swamy, 1996) and removal of nitrogen oxides (Shannon et al., 1996). By heating LDHs above 400 °C, the interlayer CO_3^{2-} can be removed and the resulting calcination products of LDHs (CLDHs) can be used for removing inorganic anions by either adsorption on the external surface of the layers, intercalation process or reconstruction behavior (Tezuka et al., 2004). CLDHs, especially those containing Cu, were investigated for the selective hydrogenation of cinnamaldehyde (Santori et al., 2000) and good catalytic properties in catalytic oxidation for phenol (Christoskova et al., 2001; Alejandre et al., 2001; Zhang et al., 2004). Nowadays, CLDHs have been paid more attention owing to their larger surface areas, high metal dispersion, small crystallite size, stability against sintering, high thermal stability, dispersion of the active species, and less diffusion resistance than those of LDHs. Moreover, as catalysts and catalyst supports, mixed metal oxides obtained by controlled thermal decomposition of LDHs (450–600 °C) have large specific surface areas, high dispersion of M^{2+} and M^{3+} (also known as 'non-stoichiometric spinels') at an atomic level, and synergetic effects between the elements (Bellotto et al., 1996a,b). According to previous paper (Tichit et al., 1998), on calcination at a temperature of 500 °C, LDHs could convert into mixtures of basic oxides.

In the present work, the positive charged Cu–Mg–Al LDH was synthesized using coprecipitation. And then, Cu–Mg–Al CLDH was obtained by heating Cu–Mg–Al LDH at 500 °C. The key idea behind the present study is based on the Cu–Mg–Al CLDH to make a H_2O_2 biosensor, which showed attractive performance of intrinsic peroxidase-like activity toward electrocatalytic activity for H_2O_2. With the good stability, easy of production and special catalytic properties, Cu–Mg–Al CLDH can be used as an "artificial peroxidase", which implies this material has a wide range of potential applications in biosensor, biotechnology and environmental chemistry.

2. Experimental

2.1. Reagents and apparatus

Hydrogen peroxide purchased from Shanghai Biochemical Regent Co. (China). $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$ and other chemicals obtained from Chemical Reagent Company of Shanghai (China) were of pure analytical grade and used without further purification. The LDH suspension was prepared in doubly distilled water. Working solutions were freshly prepared before use by diluting the stock solution. Phosphate buffer solution (PBS) was prepared by mixing stock solution of 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4 and adjusting the pH with 0.1 M H_3PO_4 or 0.1 M NaOH. Doubly distilled and deionized water was used through this work.

Electrochemical experiments were performed with CHI660C electrochemical workstation (Shanghai Chenhua Co., China) with a conventional three-electrode cell. The working electrode is a bare glassy carbon electrode (d = 3 mm) or modified glassy carbon electrode. A saturated calomel electrode (SCE) and a platinum wire were used as reference electrode and auxiliary electrode, respectively. Powder X-ray diffraction patterns were carried out at a Rigaku D/MAX 2200PC X-ray diffractometer (Japan) with Cu Kα radiation (λ = 0.154178 nm, graphite monochromator, 28 kV and 20 mA), a 2θ range from 8° to 80° was investigated at a scanning speed of 10° min^{-1}. Scanning electron microscopy (SEM) was performed on a Hitachi S-3000N instrument (Japan).

2.2. Preparation of Cu–Mg–Al CLDH

The Cu–Mg–Al LDH was prepared similar to what reported in literature (Ai et al., 2008). In brief, 20 mL solution containing 1.208 g of $Cu(NO_3)_2$, 3.846 g $Mg(NO_3)_2$ and 3.751 g $Al(NO_3)_3$ was titrated with 20 mL mixture solution of 2.40 g NaOH and 5.30 g Na_2CO_3 under vigorous stirring. During the synthesis, the temperature was maintained at 25 °C. The resulting suspension was then maintained at 65 °C for 1 h with stirring. The obtained product was filtered and washed thoroughly with deionized water until a neutral pH was observed, then dried at 60 °C for two days in air. The Cu–Mg–Al CLDH was obtained by heating Cu–Mg–Al LDH in a muffle furnace at 500 °C for 7 h.

2.3. Preparation of Cu–Mg–Al CLDH/GCE

Before modification, the bare GCE was polished to mirror with 0.3 and 0.05 μm alumina slurry on micro-cloth pads, and rinsed thoroughly with redistilled deionized water, then washed successively with anhydrous alcohol and redistilled deionized water in an ultrasonic bath, respectively. Finally, it was dried in air before use. For preparation of modified electrode, 4 mg mL^{-1} Cu–Mg–Al CLDH were first prepared by dispersing Cu–Mg–Al CLDH in redistilled deionized water, respectively, and followed by ultrasonication for 1 h. With a microinjector, 10 μL of the above solutions were dropped on the pretreated surface of glassy carbon electrode, then allowed to dry at room temperature until complete solvent evaporation to obtain Cu–Mg–Al CLDH/GCE. For comparison, Mg–Al LDH/GCE and Cu–Mg–Al LDH/GCE were also prepared with the similar process. The modified electrodes were stored in air when they were not in use.

3. Results and discussion

3.1. Characterization of the Cu–Mg–Al CLDH

Fig. 1A showed the typical XRD pattern of Cu–Mg–Al CLDH. The sample was scanned for 2θ ranging from 10 to 80° and the XRD analysis revealed that Cu–Mg–Al CLDH was composed of CuO (JCPDS-ICDD 80-1916), which has a higher crystallinity. The calcination of LDH at calcination temperature 500 °C has destroyed its layered structure completely, and resulted in the formation of spinel phases, which accompanied by tenorite phase (CuO).

Typical SEM image of the Cu–Mg–Al CLDH was displayed in Fig. 1B. A lot of porous on the surface of Cu–Mg–Al CLDH was observed. When the calcination temperature was at 500 °C, the sample sintering occurred. Upon calcination, the production of LDH layer started to break to smaller pieces and pores appeared due to the loss of water and anions. Cu–Mg–Al CLDH film could give larger specific surface area, high surface reaction activity and efficient transmission channel for the analyzed molecules to reach the active sites, which will help to improve the stability and sensitivity of the modified electrode.

3.2. Electrochemical behavior of Cu–Mg–Al CLDH/GCE

The electrochemical properties of the Cu–Mg–Al LDH/GCE and Cu–Mg–Al CLDH/GCE were explored by cyclic voltammetry (CV). Fig. 2 depicted typical cyclic voltammograms of bare GCE (a), Mg–Al LDH/GCE (b), Cu–Mg–Al LDH/GCE (c) and Cu–Mg–Al CLDH/GCE (d) in 0.1 M pH 7.0 PBS containing 0.1 M KCl. It was clear that Cu–Mg–Al LDH/GCE and Cu–Mg–Al CLDH/GCE exhibited, respectively a pair of

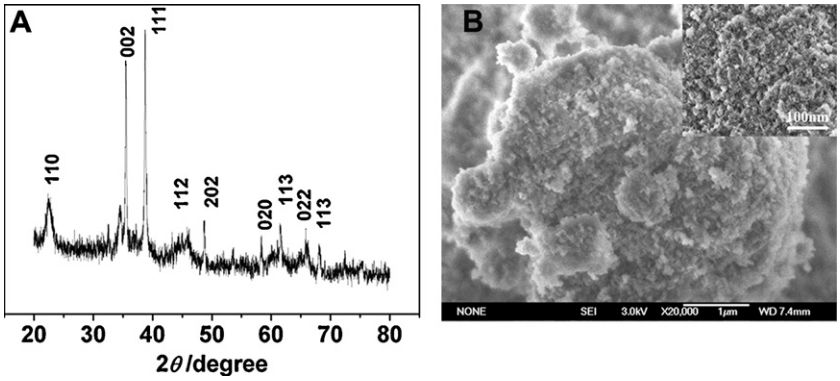

Fig. 1. The XRD pattern (A) and SEM image (B) of the Cu–Mg–Al CLDH.

well-defined redox peaks, which could be ascribed to the reversible reduction and oxidation of the Cu^{II}/Cu^{I} couple in Cu–Mg–Al LDH and Cu–Mg–Al CLDH. Because none of the brucite layer, nitrate anion and carbonate anion has redox peaks in the investigated potential range. Moreover, the redox peaks current of Cu–Mg–Al CLDH/GCE were stronger than Cu–Mg–Al LDH/GCE obviously, which can be attributed to the porous structure of Cu–Mg–Al CLDH possessing larger surface area than Cu–Mg–Al LDH.

3.3. Peroxidase-like of CLDH electrocatalysis toward H_2O_2

For use of Cu–Mg–Al CLDH nanostructures as biocatalysts for reagentless amperometric biosensors, its electrocatalytic activity toward reduction of H_2O_2 was examined by cyclic voltammetry, which was a convenient and efficient tool for the characterization of electrocatalytic activity of materials. Moreover, the reduction behavior of H_2O_2 on Cu–Mg–Al LDH modified electrode was also investigated in this work. As can be clearly witnessed from Fig. 3B, when H_2O_2 (1.0 mM) was added to 0.1 M PBS containing 0.1 M KCl, the voltammetric characteristics of the Cu–Mg–Al CLDH/GCE changed significantly, the reduction peak current on the Cu–Mg–Al CLDH/GCE increased obviously with a reduction potential at −0.14 V, accompanied by a decrease of the oxidation peak current. However, the cyclic voltammogram of the Cu–Mg–Al LDH/GCE modified GCE in 0.1 M PBS (pH 7.0) showed a weak reduction peak at 100 mV s^{-1} (Fig. 3A). Thus, the ability to catalyze the reduction of H_2O_2 of Cu–Mg–Al CLDH was stronger than Cu–Mg–Al LDH. The catalytic mechanism for the reduction of H_2O_2 was Cu (II) reduced electrochemically to Cu (I), which reacted chemically with H_2O_2 and resulted in the H_2O_2 revert to H_2O and in the regeneration of the catalyst (see Supporting Information, Scheme 1S).

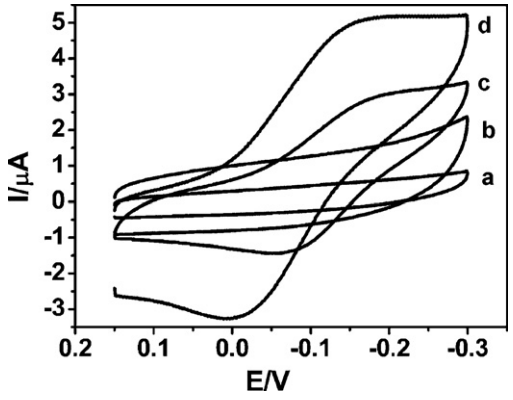

Fig. 2. Cyclic voltammograms of (a) GCE, (b) Mg–Al LDH/GCE, (c) Cu–Mg–Al LDH/GCE and (d) Cu–Mg–Al CLDH/GCE in 0.1 M PBS containing 0.1 M KCl. Scan rate: 100 mV s^{-1}.

3.4. Effect of scan rate

To further investigate the characteristics of Cu–Mg–Al CLDH/GCE, the effect of scan rate on the voltammetric behavior of Cu–Mg–Al CLDH was studied. Fig. 4A showed cyclic voltammograms of Cu–Mg–Al CLDH/GCE in 0.1 M pH 7.0 PBS containing 0.1 M KCl at various potential scan rates in the range of 20–200 mV s^{-1}. Both the cathodic and anodic peak currents were linearly proportional to the square root of scan rate ($v^{1/2}$) in the range from 0.02 to 0.2 mV s^{-1}, as demonstrated in Fig. 4B, suggesting a typical diffusion controlled process. The regression equations were $I_{pa} = 0.3345v^{1/2} - 0.7386$ (μA, V s^{-1}, $R = 0.9950$) and $I_{pc} = -0.4383v^{1/2} - 0.2343$ (μA, V s^{-1}, $R = 0.8800$). It suggested that the electrode reaction corresponded to a diffusion controlled process. As shown in Fig. 4C, a graph of $E_p = f(\log v)$ yields two straight lines with slopes of $-2.3RT/\alpha nF$ and $2.3RT/(1-\alpha)nF$ for cathodic peak and anodic peak, respectively. So the value of α can be estimated as 0.54 from the slopes of the straight lines based on the following equation (Laviron, 1979a):

$$\log\frac{v_a}{v_c} = \log\frac{\alpha}{1-\alpha} \quad (1)$$

In order to calculate the value of apparent heterogeneous electron transfer rate constant (k_s), the following Laviron equation was used (Laviron, 1979a):

$$\log k_s = \alpha\log(1-\alpha) + (1-\alpha)\log\alpha - \log\frac{RT}{nFv} - \frac{\alpha(1-\alpha)nF\Delta E_P}{2.3RT} \quad (2)$$

where α is the electron transfer coefficient, n is the number of electron, ΔE_p is the separation of the redox peaks, v is the scan rate. k_s can be calculated to be $6.49 \pm 0.2\ s^{-1}$.

According to Laviron equation (Laviron, 1979b), $I_p = n^2F^2A\Gamma v/4RT$, the surface coverage ($\Gamma$) of Cu–Mg–Al CLDH immobilized on the surface of the modified electrode could be calculated to be 7.378×10^{-10} mol cm^{-2}.

3.5. Effects of pH and temperature on Cu–Mg–Al CLDH based sensor for H_2O_2

Fig. 5 showed the effects of pH and temperature on the electrocatalytic activity of the Cu–Mg–Al CLDH, in which the relative activity was defined as the ratio of the electrocatalytic response at a given condition to the maximum electrocatalytic response. It was found that the ratio of the electrocatalytic response increased with the increasing pH of detection solution from 4.0 to 7.0, then decreased (Fig. 5A). Thus, the maximum catalytic activity toward the reduction of H_2O_2 occurred at approximately pH 7.0. The electrocatalytic activity on temperature in the range of 10–70 °C also

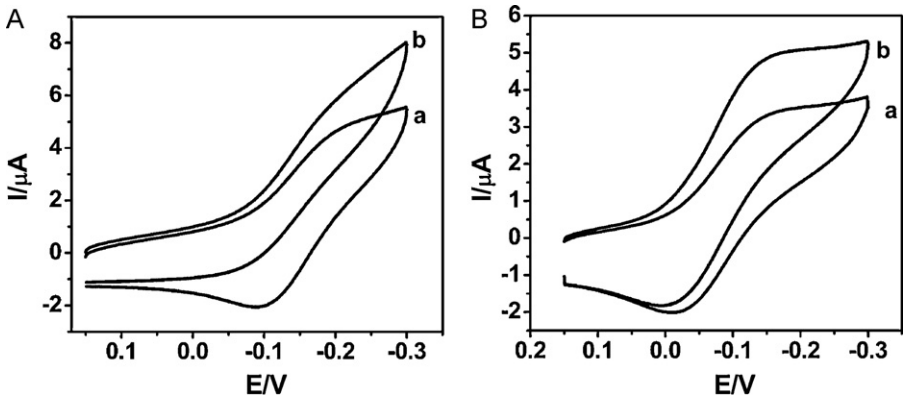

Fig. 3. Cyclic voltammograms of (A) Cu–Mg–Al LDH/GCE electrode and (B) Cu–Mg–Al CLDH/GCE electrode in 0.1 M PBS containing 0.1 M KCl in the absence (a) and presence (b) of 1.0 mM H_2O_2. Scan rate: 100 mV s^{-1}.

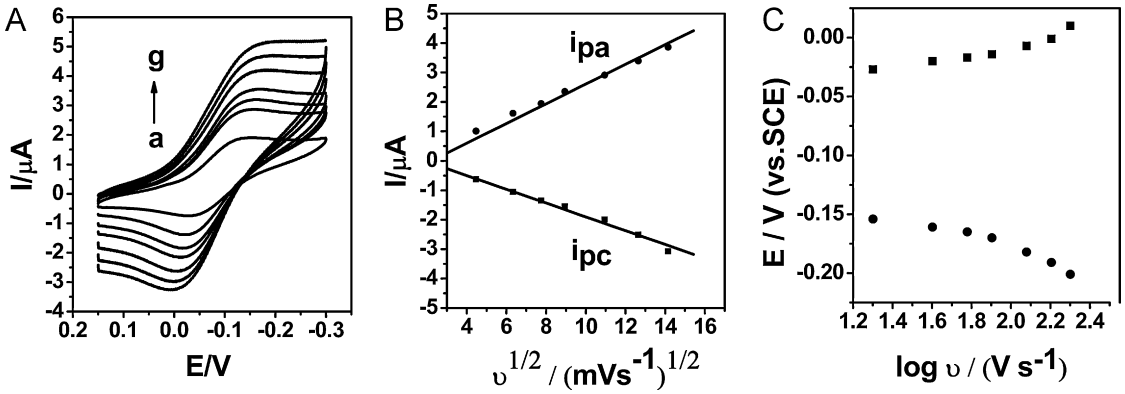

Fig. 4. (A) Cyclic voltammograms of Cu–Mg–Al CLDH/GCE in 0.1 M pH 7.0 PBS containing 0.1 M KCl at various scan rates of (from inner to outer) 20, 40, 60, 80, 120, 160 and 200 mV s^{-1}; (B) plots of anodic and cathodic peak currents versus the square root of scan rate; (C) variation of anodic and cathodic peak potentials versus the logarithm of scan rate.

showed similar appearance (Fig. 5B). The maximum catalytic activity was obtained at 40 °C. These optimal conditions were similar to the values for the electrocatalytic reduction of H_2O_2 by immobilizing horseradish peroxidase (HRP) on different films (Dai et al., 2004; Lei et al., 2004; Liu et al., 2005; Wang et al., 2002a,b).

3.6. Amperometric response of the proposed H_2O_2 biosensor

Fig. 6 illustrated current–time plot for the Cu–Mg–Al LDH/GCE and Cu–Mg–Al CLDH/GCE through successive adding H_2O_2. Insets were their corresponding calibration curves, respectively. Under the optimized experimental conditions with successive additions of H_2O_2, the reduction current also increased. In addition, there was no obviously amperometric response for the dissolved oxygen in buffer on the modified electrodes, which means that hydrogen peroxide can be determined without inhibition of oxygen using this electrode. It may be due to the specific structure of Cu–Mg–Al CLDH and the condition in near neutral or alkaline working solution (Karyakin et al., 1998). As shown in Fig. 6B, 5.0 μL 1.0 mM H_2O_2 was injected into a 5.0 mL 0.1 M pH 7.0 PBS containing 0.1 M KCl at −0.1 V, the steady-state currents reached another steady-state value (95% of the maximum) in less than 6 s at the Cu–Mg–Al CLDH/GCE. The electrochemical response to H_2O_2 showed a linear range of 1–100 μM with the calculated detection limit of 0.5 μM at a signal-to-noise ratio of 3. The sensitivity of the proposed biosensor was estimated to be 29.51 μA mM^{-1}. However, the catalytic responses of H_2O_2 at Cu–Mg–Al LDH/GCE (Fig. 6A) were smaller than that at Cu–Mg–Al CLDH modified GCE, indicating that

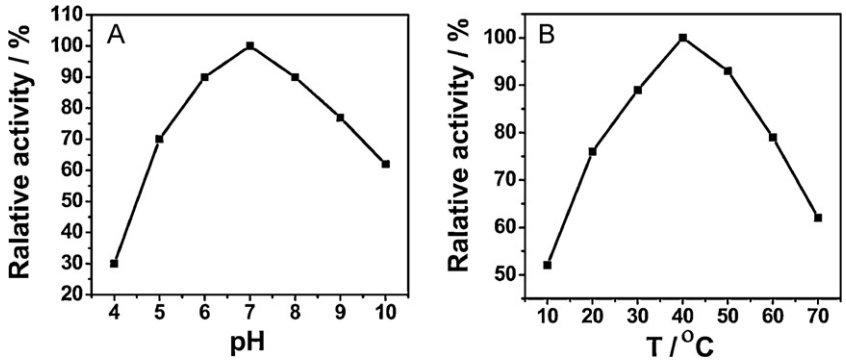

Fig. 5. Effects of (A) pH and (B) temperature on the electrocatalytic response of Cu–Mg–Al CLDH to H_2O_2 reduction.

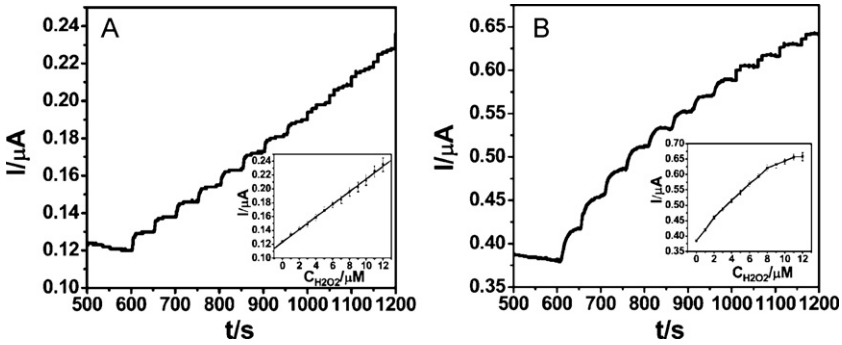

Fig. 6. (A) Amperometric response of Cu–Mg–Al LDH/GCE electrodes to successive additions of 5 μL 1.0 mM H_2O_2 into 5.0 mL 0.1 M pH 7.0 PBS containing 0.1 M KCl at an applied potential of −0.1 V. Inset: the corresponding calibration curves of Cu–Mg–Al LDH/GCE. (B) Amperometric response of Cu–Mg–Al CLDH/GCE electrodes to successive additions of 5 μL 1.0 mM H_2O_2 into 5.0 mL 0.1 M pH 7.0 PBS containing 0.1 M KCl at an applied potential of −0.1 V. Inset: its corresponding calibration curves of Cu–Mg–Al CLDH/GCE.

Cu–Mg–Al CLDH had a better catalytic activity, which might result from the larger surface area of Cu–Mg–Al CLDH than Cu–Mg–Al LDH. The analytical performances of the proposed biosensor were compared with other sensors reported in the literatures. Characteristics such as the sensitivity, linear range, and the limit of detection of the biosensors were all summarized in Supporting Information, Table 1S. As can be observed, the proposed mimic peroxidase sensor (CLDH/GCE) exhibited excellent performance in terms of wide linear range and low limit of detection. These results indicated that the proposed CLDH/GCE is an excellent platform for the detection of H_2O_2 detection.

3.7. Stability and reproducibility

The stability of the Cu–Mg–Al CLDH/GCE was examined by monitoring the remained amount of current response after successive cycling the modified electrode in the potential range of −0.15 to +0.3 V for 300 circles. It was found that the peak current for 1.0 mM H_2O_2 reduction retained 91% of its initial value and no obvious potential shift was observed, which indicated that the Cu–Mg–Al CLDH on the surface of GCE was quite stable. The reproducibility of Cu–Mg–Al CLDH/GCE electrode was investigated by comparing the amperometric current response to H_2O_2 at seven modified electrodes prepared independently, and the relative standard deviation (R.S.D.) was 2.3% at a H_2O_2 concentration of 1.0 mM, which indicated that the modified electrode displayed an acceptable reproducibility.

3.8. Selectivity of the developed H_2O_2 biosensor

Selectivity is also important in practical use of the biosensors. Four such substances were used to evaluate the selectivity of the electrode: ascorbic acid, glucose, dopamine, L-tyrosine, and uric acid were tested at the 0.1 mM level. The amperometric responses of the biosensor got to the consecutive injection of 0.1 mM H_2O_2 and 0.1 mM the above interfering species (see Supporting Information, Fig. 1S). It was evident that the influence of interfering species tested on the H_2O_2 response was negligible, indicating a high selectivity of the proposed biosensor.

4. Conclusions

This work has successfully demonstrated a promising H_2O_2 biosensor based on the Cu–Mg–Al CLDH modified GCE. The Cu–Mg–Al CLDH possesses unique peroxidase-like activity, which can be used as an amperometric sensor for routine analysis of H_2O_2. With adsorbability, thermal stability and low cost, the designed biosensor can be considered as a mimic peroxidase, and is thus further used as a man-made mimic enzyme for the development of biocatalysts and electrochemical biosensors. These experimental results indicate that the Cu–Mg–Al CLDH modified electrode holds the prospect for effective non-enzymatic determination of H_2O_2 at a low detection limit with very high sensitivity. In summary, the biosensor proposed in this study is very promising in the pharmaceutical, clinical and industrial detection of H_2O_2 due to the advantages of easy fabrication, a low cost, fast response and high sensitivity.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bios.2010.12.043.

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