



# Cobalt nano-sheet supported on graphite modified paper as a binder free electrode for peroxide electrooxidation



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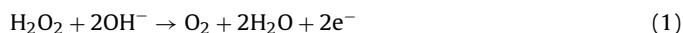
## ABSTRACT

A novel and binder free Co@graphite/paper electrode is prepared by electrodeposition Co nano-sheet on the surface of a graphite layer modified paper substrate. The morphology and phase structure of the Co@graphite/paper electrode are characterized by scanning electron microscopy equipped with energy dispersive X-ray spectrometer, transmission electron microscope and X-ray diffractometer. The catalytic activity of the Co@graphite/paper electrode for H<sub>2</sub>O<sub>2</sub> electrooxidation is investigated by means of cyclic voltammetry and chronoamperometry. The catalyst combines tightly with the paper and exhibits a good stability. The oxidation current density reaches to 580 mA cm<sup>-2</sup> in 2 mol dm<sup>-3</sup> NaOH and 0.5 mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub> at 0.5 V. Besides, we illustrate the reaction mechanization of the H<sub>2</sub>O<sub>2</sub> electrooxidation on the Co film.

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## 1. Introduction

Recently, direct peroxide-peroxide fuel cell (DPPFC) using H<sub>2</sub>O<sub>2</sub> directly as the fuel have attracted much attention due to its low cost, compact, easy operation, workable without air, and providing both power and oxygen (Eq. 1) [1–8]. Anode is one of a key factor that determines the cell performance. Therefore, the catalytic electrooxidation of H<sub>2</sub>O<sub>2</sub> has been widely studied using various catalysts to obtain a high catalytic activity [1–13].



Carbon supported noble metals [1,8,14] and their alloys [14] are widely employed for fuel cells and exhibit high catalytic activity. However, they suffer the drawback of limited reserves and high cost. Besides, the expensive binder (Eg. nafion) is absolutely essential for the preparation of the electrode [1,8,14]. The existence of the binder reduces the electric conductivity of the electrode and the activity substance may fall off during the reaction process, both of which will lead to a low catalyst utilization. Therefore, it is necessary to develop cheap electrodes prepared by base metal in a no slurry-coating way. The electrodeposition [3–7,15–17] is a kind of frequently-used method to prepare electrochemistry

catalysts directly supported on the surface of the substrate without binder. Jae Yong Song and Jongwon Kim et al. [16] reported a simple one-step electrodeposition of triangular Pd rod nanostructures on clean Au substrates and achieved a high electrocatalytic activity for oxygen reduction and methanol oxidation reactions. Our team prepared Au NTs/Ni foam electrode by one-step electrodeposition of thorn-like Au particles onto Ni foam surface without any additives for NaBH<sub>4</sub> electrooxidation [17].

In general, metallic materials (Eg. Ni foam, Cu foil, Al foil) [2,5,17–19] are widely used as the substrates of the electrodes due to their high electric conductivity. Besides, many non-conductive materials (Eg. polycarbonate membrane, anodized aluminum oxide) [15,20] are always employed as porous templates to prepare especial nano structure. However, metallic resources are finite and expensive. These porous templates are even much more expensive than the metal materials and their preparation process is complex, both of which restrict their implication.

Nowadays, many renewable substances come from our daily life have attracted scientists' attention and serve as novel electrode materials. Yi Cui et al. [21] employed textile as a three dimensional structure electrode substrate and fabricated a carbon nanotube–textile–Pt cathode for aqueous-cathode microbial fuel cells and revealed a high power density. Our team prepared a Ni@multi-walled carbon nanotubes/Sponge electrode for NaBH<sub>4</sub> electrooxidation and its catalytic activity is significantly higher than that reported for other types of Ni electrodes [22]. Recently, Teng Li and Liangbing Hu et al. [23] demonstrated that an anode

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consisting of a Sn thin film deposited on a carbon nanotubes modified hierarchical wood fiber substrate simultaneously addressed all the challenges associated with Sn anodes. The wood fiber is common in our life and exhibits a great potential for the development of the electrode materials. However, the carbon nanotubes are somewhat expensive and their preparation process is complex.

Paper, one of the four great inventions of ancient China, can be seen everywhere and play an important role in our daily life. What's more, it is degradable, low cost, flexible and produced easily. In recent years, the paper has been researched in laboratories for e-applications [24–36]. For example, Zhijian Chen and Qihuang Gong et al. [24] deposited an Au layer on paper by RF magnetron sputtering and employed it as the anode for solar cells. However, all of these reports must use complex or expensive method to modify the paper and form a conductive paper substrate.

In this study, we fabricate a Co@graphite/paper electrode by directly electrodepositing Co nano-sheet on the surface of a paper coated by pencil lead for the electrooxidation of  $\text{H}_2\text{O}_2$ . The support body is ordinary A4 paper and can be found in most paper shops. The whole preparation process needs no binder, which lead to a good stability during the reaction process due to its strong combining power between graphite and paper. The oxidation current density reaches to  $580 \text{ mA cm}^{-2}$  in  $2 \text{ mol dm}^{-3}$  NaOH and  $0.5 \text{ mol dm}^{-3}$   $\text{H}_2\text{O}_2$ . Besides, we discussed the possible reaction mechanization of the  $\text{H}_2\text{O}_2$  electrooxidation on the Co film.

## 2. Experimental

All chemicals were analytical grade and were used without further purification. The A4 paper ( $70 \text{ g m}^{-2}$ , Shenyang Jinxin office equipment Co. Ltd.) is commercially available printing paper, which is made up of vegetable fibres (EG. Cellulose, hemicellulose, lignin) and some calcium salts (EG.  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ). A common 8B pencil (Shanghai Yinzun company) was used to draw on the A4 paper uniformly and form a conductive graphite/paper current collector. The as-prepared graphite/paper collector was cut into  $1 \times 1 \text{ cm}^2$  and then immersed in  $2.5 \text{ mol dm}^{-3}$  KCl,  $0.4 \text{ mol dm}^{-3}$   $\text{NH}_4\text{Cl}$ ,  $0.5 \text{ mol dm}^{-3}$   $\text{H}_3\text{BO}_3$  and  $1.0 \text{ mol dm}^{-3}$   $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  for the electrodeposition of Co film on the graphite/paper substrate, which was performed using the Autolab PGSTAT302 (Eco Chemie) electrochemical workstation in a conventional three electrode electrochemical cell with a saturated Ag/AgCl, KCl reference electrode and Pt foil counter electrode. First was a 20 min 1.0V oxidation potential which made the graphite surface transform into a hydrophilic surface. Then the electrodeposition was carried out at a constant potential of  $-0.8 \text{ V}$  for 150 min to form the Co@graphite/paper.

$\text{H}_2\text{O}_2$  electrooxidation was also performed in the same three-electrode electrochemical cell using the  $1 \text{ cm}^2$  Co@graphite/paper electrode. All potentials were referred to the saturated Ag/AgCl, KCl reference electrode. The morphology of the electrodes was determined using a scanning electron microscope (SEM, JEOL JSM-6480) equipped with an energy-dispersive X-ray (EDX) analyzer and transmission electron microscope (TEM, FEI TeccaiG2S-Twin, Philips). The structure was analyzed by a powder X-ray diffractometer (XRD, Rigaku TTR-III) equipped with Cu K $\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ).

## 3. Results and discussion

Fig. 1 shows the fabrication process of the Co@graphite/paper electrode. The insert is the electrodeposition curve of the Co layer. The A4 paper, which serves as an electrode substrate, is first coated by graphite. As we know, the graphite will adhere to the surface of the paper tightly and be used as the conductive layer for the

electrodeposition of Co. Then the graphite layer will be activated at a high potential (1.0V) and some active  $-\text{COOH}$  will occur during the active process. At last, a layer of Co film will be created at a constant potential ( $-0.8 \text{ V}$ ). The Co film exhibits high electric conductivity and acts as electrochemical catalyst for the electrooxidation of  $\text{H}_2\text{O}_2$ .

Fig. 2 shows the SEM images (Fig. 2a–c) of the graphite/paper (Fig. 2a), Co@graphite/paper (Fig. 2b and c) and TEM image of Co nano-sheet (Fig. 2d). It is obvious that the surface of the graphite/paper is very smooth (Fig. 2a), which is favorable for the electrodeposition. The cracks existed in the surface demonstrated that the graphite layer consists of some graphite sheets. Besides, the graphite combines with the paper close, which provides a stable electrode without the fallen of activity substance during the electrochemistry test. Fig. 2b shows the low magnification SEM image of the Co film. Clearly, the Co distributes compactly in the surface of the graphite. However, the surface of the Co film is very rough and provides a large specific area, which is beneficial for the diffusion of the  $\text{H}_2\text{O}_2$  during the electrooxidation reaction. Fig. 2c shows the high magnification SEM image of the Co film. The Co film is comprised of Co nano sheets and every sheet intersects with another and has many gaps, which forms a three dimensional structure. This nano sheets framework allows easy transportation of reactants to the entire surface of the Co active material. Fig. 2d shows the TEM image of a single Co nano sheet. As can be seen, the width of the Co sheet is about 500 nm. The edge of the sheet is not straight but some twisty. This will increase the surface area of Co and the catalytic activity of Co surface active sites owing to the defects and the high surface energy.

Fig. 3 shows the XRD patterns of the paper, graphite/paper and Co@graphite/paper. These diffraction peaks between  $15^\circ$  to  $60^\circ$  can be attributed to the carbon contained calcium salt (EG.  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ; the main ingredient of the A4 paper). Compared with the bare paper, two obvious diffraction peaks can be seen at about  $26.3^\circ$  and  $54.6^\circ$ , which can be indexed to (0 0 2) and (0 0 4) plane reflections of the graphite (JCPDS Card NO. 41-1487) contained in the pencil lead (Fig. 3a). As observed in Fig. 3b, several well-defined diffraction peaks are observed at  $2\theta$  values of  $41.7^\circ$ ,  $44.2^\circ$ ,  $47.5^\circ$ ,  $51.5^\circ$ ,  $75.9^\circ$ . All of these peaks can be successfully indexed to (1 0 0), (0 0 2), (1 0 1), (2 0 0) and (1 1 0) plane reflections of the metallic Co (JCPDS Card NO. 05-0727).

Meanwhile, to characterize the distribution of the chemical element in the electrode surface, energy dispersive X-ray (EDX) spectrograms were also recorded. It can be observed from Fig. 4. Fig. 4a shows the SEM image of the Co@graphite/paper electrode. As can be seen, the surface of the electrode is covered by Co densely. Fig. 4b demonstrates that carbon element exists uniformly in the chink of the Co film. Therefore, the  $\text{H}_2\text{O}_2$  may diffuse into the chinks and the  $\text{H}_2\text{O}_2$  can contact with the catalyst fully during the reaction process. Clearly, the surface of the electrode is filled with Co element (Fig. 4c), which proves that the Co forms a film-like substance.

Few of report focus on the catalytic mechanism of Co for  $\text{H}_2\text{O}_2$  electrooxidation in alkaline electrolyte by far. In this study, we tried to get a clue about the reaction mechanism by closely examining the cyclic voltammograms (CVs) of cobalt in NaOH without and with  $\text{H}_2\text{O}_2$ . Fig. 5a shows the CVs of the graphite/paper and Co@graphite/paper in  $1 \text{ mol dm}^{-3}$  NaOH between  $-0.05 \text{ V}$  to  $0.5 \text{ V}$ . It is obvious that the graphite/paper is almost no activity in alkaline electrolyte. The Co@graphite/paper exhibits a oxidation peak at around  $0.13 \text{ V}$  in the positive going scan and a reduction peak at around  $0.07 \text{ V}$  in the negative scan, which is attributed to the redox reactions of  $\text{Co}(\text{OH})_2$  to  $\text{Co}(\text{OH})_3$  according to the previous reports [4,37]. Compared with the graphite/paper, the Co@graphite/paper exhibits much higher activity and the initial oxidation potential of  $\text{Co}(\text{OH})_2$  to  $\text{Co}(\text{OH})_3$  is about  $0.05 \text{ V}$ . Fig. 5b shows the CVs of

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