Synthesis of hexagonal CoAl-layered double hydroxide nanoshales/carbon nanotubes composite for the non-enzymatic detection of hydrogen peroxide

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Abstract

A nanocomposite comprising hexagonal CoAl-layered double hydroxide nanosheets with multiwall carbon nanotubes (MWCNTs) was synthesized by reflux heating. The nanocomposite was then applied to modify a carbon paste electrode. The modified electrode was then applied to fabricate a non-enzymatic hydrogen peroxide sensor. Hydrogen peroxide was electrocatalytically oxidized on the modified electrode surface, while its electroreduction was performed by an enhanced direct electron transfer to the electrode surface. The catalytic rate constants of the hydrogen peroxide electrooxidation were processed by an active cobalt species, and the diffusion coefficient of hydrogen peroxide was reported. An amperometric method was developed for determination of hydrogen peroxide based on its electrocatalytic oxidation with a sensitivity of $118.0 \text{ mA dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}$ and a limit of detection of $10 \text{ } \mu\text{mol dm}^{-3}$. In addition, amperometric method based on hydrogen peroxide electroreduction had a sensitivity of $42.0 \text{ mA dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}$ and a limit of detection of $40 \text{ } \mu\text{mol dm}^{-3}$. The sensor had the advantages of high activity and sensitivity, with a simple fabrication method without complications of immobilization steps and using any enzyme or reagent.

Keywords: CoAl-layered double hydroxide; Multiwall carbon nanotubes; Hydrogen peroxide; Electrocatalysis.

1. Introduction

Layered double hydroxides (LDHs) or hydrotalcites have the general formula $\{[M(II)_{1-x}M'(III)_x(OH)_2]^{x+} A^{n-}_{x/n} mH_2O\}$ consisting of positively charged brucite-like layers with the anions located in the interlayers. These anionic clays have been extensively studied due to the reversible charge transfer rate kinetics, high chemical and thermal stabilities, and excellent ion exchange capability [1, 2]. Hydrotalcites have a variety of applications in supercapacitors [3], sensors and biosensors [4], pharmaceutical formulations and drug delivery [5, 6], ion exchangers [7], fire retardant additives [8], cement additives [9], electrochromism [10], catalysis and absorbents [11] and pigments [12]. Up to now, different nanocomposites of hydrotalcites with nanocarbons [13], biopolymers and biomolecules [14] and polymers [15] have been synthesized. There have appeared reports on the nanocomposite of hydrotalcites with carbon nanotubes in the literature; however, there are a few reports on the synthesis of CoAl-LDH with carbon nanotubes [13, 16], and to the best of our knowledge there is no prior report on the use of nanocomposites of CoAl-LDH with multiwall carbon nanotubes in fabrication of sensors. In one paper [13], a composite of CoAl-LDH/carbon nanotubes was synthesized by a co-precipitation method in the presence of L-cysteine. This composite was then employed as a precursor to synthesis Co-Al mixed metal oxides/carbon nanotubes nanocomposite. In the other work [16], CoAl-LDH/N-doped carbon nanotubes was synthesized by catalytic chemical vapor deposition using acetonitrile and previously synthesized CoAl-LDH. The final product of the reaction was hybrid materials containing Co nanoparticles and N-doped carbon nanotubes obtained by decomposition of the precursors. LDH-carbon nanotubes nanocomposites have been

applied as supercapacitor electrode [17, 18], battery electrode [19], reinforcing filler [20], sensor [21], CO₂ adsorbent [22], and electrochemical studies [21, 23-25].

Hydrogen peroxide is a ubiquitous compound in biological processes, as an intermediate or product in biological reactions and in all aerobic organisms. It has also wide applications in industrial processes such as medical or packaging purposes, textile industry, waste treatment, and semiconductor manufactures [26, 27]. Therefore, sensitive, reliable and rapid determination of hydrogen peroxide has received much attention in environmental, industrial, clinical, pharmaceutical and biomedical analyses [28, 29-31]. Different enzymatic and non-enzymatic biosensors for the hydrogen peroxide determination have been developed [32, 33]. Non-enzymatic hydrogen peroxide biosensors have the advantages of simplicity, high sensitivity, high stability, low cost and easy handling [28, 32-34]. In order to attain the advantages of non-enzymatic electrochemical hydrogen peroxide biosensors, the synthesis and application of novel shaped and sized nanomaterials has attracted tremendous attention. Nanostructures of noble metals, metal oxides, metal hexacyanoferrates, carbonaceous nanomaterials and conducting polymers have been applied in fabrication of hydrogen peroxide sensors [35-37].

In the present study, hexagonal CoAl-LDH nanosheets/multiwall carbon nanotubes nanocomposites (CoAl-LDH/MWCNTs) were synthesized and applied in the electrocatalytic oxidation, electroreduction and determination of hydrogen peroxide.

2. Experimental section

2.1. Materials and synthesis procedures

Graphite fine powder with a particle size of $<50\ \mu\text{m}$ was purchased from Merck. All other chemicals were of analytical grade from Merck or Sigma and used without further purification. Multiwall carbon nanotubes (MWCNTs) were obtained from US Research Nanomaterials, Inc. All solutions were prepared with redistilled water.

Before use, MWCNTs were pretreated as reported previously [38-40]. Briefly, MWCNTs were refluxed in a $2.0\ \text{mol dm}^{-3}$ nitric acid solution for 12 h, washed with redistilled water several times and dried at room temperature. MWCNTs were then sonicated in a 3:1 sulfuric/nitric acid solution for 6 h in an ultrasonic bath at room temperature, and then washed by vacuum filtration with distilled water until neutralization. The obtained sample was taken, and dried overnight at $50\ ^\circ\text{C}$. This procedure causes scission and carboxylation of MWCNTs and the tubes bear negative surface charges on the outside.

CoAl-LDH/MWCNTs nanocomposite was synthesized by reflux heating. In a typical procedure, 500 mg MWCNTs was dispersed in 200 mL degassed water by ultrasounication, while nitrogen gas was flowed through the mixture. Then, 700 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 450 mg $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added, and the mixture was ultrasounicated for 30 min with nitrogen gas flowing in the mixture. 1.8 g urea was then added and ultrasounicated in the nitrogen atmosphere. After this pre-step, the mixture was refluxed for 2h. The resultant precipitate (the nanocomposite) was separated, washed several times with water, and dried at $60\ ^\circ\text{C}$ overnight. CoAl-LDH was synthesized similarly without using MWCNTs.

2.2 Apparatus

Electrochemical studies were performed in a conventional three-electrode cell containing $1.0\ \text{mol dm}^{-3}$ NaOH solution as the supporting electrolyte powered by a μ -

Autolab potentiostat/galvanostat, type III, FRA2 (The Netherlands) run by a computer through GPES 4.9 commercial software. An Ag/AgCl ($\text{KCl } 3 \text{ mol dm}^{-3}$), a glassy carbon rode, and a carbon paste electrode (modified or else) were used as the reference, counter and working electrodes, respectively.

Field emission scanning electron microscopy (FESEM) was performed by the instrument Zeiss, Sigma-IGMA/VP (Germany) equipped with energy-dispersive X-ray spectroscopy (EDS) from Oxford Instruments. For the sample preparation, a small portion of the dried sample was placed on a piece of silver adhesive tape, followed by gold vapor sputtering.

Transmission electron microscopy (TEM) was performed by the instrument Zeiss, EM10C (Germany) with an accelerating voltage of 80 kV. For the sample preparation, a drop of the diluted and probe-ultrasonicated sample in water was dropped on a copper grid with a formvar carbon film followed by air drying.

Powder X-ray diffraction (XRD) patterns were recorded in the 2θ range from 10 to 90° at a scanning rate of $2.4^\circ \text{ min}^{-1}$ by an X-ray diffractometer (Philips X'Pert, The Netherlands) with a $\text{Cu K}\alpha$ radiation at 40 kV and 30 mA. All measurements were carried out at room temperature.

2.3. Working electrodes preparation

Unmodified carbon paste electrode (UCPE) was prepared by hand-mixing carbon powder and Nujol with an 80:20 weight ratio. The paste was carefully mixed and homogenized in an agate mortar. The resulting paste was kept at room temperature in a desiccator before use. The paste was packed firmly into a cavity (2 mm in diameter and depth) at the end of a Teflon tube. Electrical contact was established by a copper wire connected to the paste in the inner hole of the tube. The

electrode surface was gently smoothed by rubbing on a piece of weighing paper just prior to use. This procedure was also used to regenerate the surface of the electrode.

Modified carbon paste electrodes with CoAl-LDH (LDH-CPE), MWCNTs (MWCNTs-CPE) and the nanocomposite (MCPE) were prepared by mixing carbon powder, Nujol, and the modifiers with weight ratios of 75:20:5 in an agate mortar until a uniform paste was obtained. The paste obtained in this way was packed into the cavity at the end of the Teflon tube.

2.4. Procedures

The calibration curve for hydrogen peroxide in 1.0 mol dm^{-3} NaOH solution was measured by amperometric technique. Two potential steps of 250 and -350 mV were applied for amperometric measurements separately at these potentials, and the transient currents were allowed to decay to steady-state values.

Three river water samples and three wastewater samples were taken from three different local rivers and three different textile factories. The samples were left standing undisturbed for three days to settle, and then filtered by filter paper. The amperometric responses of MCPE were measured by hydrogen peroxide addition of known concentrations to these samples.

3. Results and discussion

Fig. 1 shows powder XRD patterns of CoAl-LDH/MWCNTs (A), MWCNTs (B) and CoAl-LDH (C). In the diffractograms of CoAl-LDH/MWCNTs and MWCNTs, the diffraction peaks located at 2θ of 27 and 54° corresponded to (002) planes of the stacked graphene layers in MWCNTs and (004) reflection, respectively [34]. The diffractograms of CoAl-LDH/MWCNTs and CoAl-LDH contained the main

peaks located at 12, 24, 35, 40 and 47°. They were related to (003), (006), (012) and (015) reflections, respectively. The peaks can be indexed as a rhombohedral structure of CoAl-LDH [41]. The pattern of CoAl-LDH/MWCNTs confirmed the deposition of the layered double hydroxide on MWCNTs.

Fig. 2 shows FESEM images of CoAl-LDH/MWCNTs at different magnifications and a FESEM image of CoAl-LDH, and the corresponding EDS spectra. In the images of CoAl-LDH/MWCNTs (Fig. 2A-C), the adhered MWCNTs to the hexagonal nanoshales of the double hydroxide can be observed. The nanotubes have an average diameter of about 55 nm, and the nanoshales have a few μm^2 with an apparent thickness of about 40 nm. Figure 2D shows an EDS spectra of CoAl-LDH/MWCNTs. Cobalt, aluminum, carbon and oxygen were the main detected elements in the nanocomposite. FESEM image of CoAl-LDH shows irregular-shaped nanolayers of the sample, and its EDS spectrum contains peaks related to cobalt, aluminum and oxygen. The gold peaks in the EDS spectra resulted from gold coating during sample preparation for FESEM.

Fig. 3 shows TEM images of CoAl-LDH/MWCNTs at different magnifications (A-G), and a TEM image of CoAl-LDH (H). While irregular-shaped microparticles are observed for CoAl-LDH, the adherence of MWCNTs with an average diameter of ≈ 55 nm to the hexagonal nanoshales of the double hydroxide is clearly observed for CoAl-LDH/MWCNTs. It is obvious that the hexagonal nanoshales of the double hydroxide have an atomic thickness, and in the SEM images, the adherence of multi-layers of the nanoshales is apparent. This is due to the differences between sample preparation procedures employed for TEM. The formation mechanism of CoAl-LDH and CoAl-LDH/MWCNTs involves dissolution and re-crystallization processes [42], after thermal decomposition of transition metal nitrates resulting in the metal oxides

[43-45]. For CoAl-LDH/MWCNTs, the initially formed CoAl-LDH seeds adhered to the MWCNTs surface, through electrostatic attractions [46], and it was followed by heterogeneous growth.

A cyclic voltammogram of MCPE recorded in the supporting electrolyte with a potential sweep rate of 50 mV s⁻¹ is shown in Fig. 4A. In this voltammogram, **one pair of peaks** appear with a formal potential of about 200 mV (as an average mid peak of cyclic voltammograms recorded at slow potential sweep rates of <10 mV s⁻¹). The redox reaction dominated in the voltammogram are attributed to the Co(II)/Co(III) redox pair at the MCPE surface via the following reaction [47, 48]:

The anodic-to-cathodic peak potential separation for the redox transition in the voltammogram of MCPE at the potential sweep rate of 50 mV s⁻¹ is greater (≈55 mV) than that for adsorbed redox species (theoretically equal to zero). This indicates a small limitation in the rate of charge transfer process of the redox transition. In addition, the average value of full width at half height of the cathodic and anodic peaks is estimated to be greater than the theoretical value for non-interacting one-electron surface redox sites (theoretically equal to 90 mV) [49]. It confirms domination of site-site repulsion for the redox centers [50].

Cyclic voltammograms of MCPE (A), UCPE (B), LDH-CPE (C) and MWCNTs-CPE (D) in the absence and presence of 5 mmol dm⁻³ hydrogen peroxide are shown in Fig. 4. In the voltammogram of UCPE, negligible anodic or cathodic currents related to the electrooxidation or electroreduction of hydrogen peroxide at two positive and negative edges of the voltammograms are observed. For LDH-CPE, the anodic peak current of the redox transition of cobalt species in the presence of

hydrogen peroxide increased, and the corresponding cathodic current decreased. This indicates that hydrogen peroxide was oxidized on the LDH-CPE surfaces with a surface mediation electrooxidation mechanism. In the voltammogram of MWCNTs-CPE, increments in the anodic and cathodic currents at the two edges of the voltammogram are observed. Both currents are higher than those observed for UCPE, due to an electrocatalytic effect of MWCNTs on both the electroreduction and electrooxidation of hydrogen peroxide. These electrocatalytic effects are due to changes in the surface state of the electrode and electrode entity upon modification with MWCNTs. On the other hand, hydrogen peroxide underwent both oxidation and reduction processes on the MCPE surface. In the presence of hydrogen peroxide, in the voltammogram of MCPE, the anodic peak current of the redox transition increased, and simultaneously, the cathodic current of this transition decreased. In addition, a cathodic peak appeared in the voltammograms related to the electroreduction of hydrogen peroxide. These results indicated that hydrogen peroxide was oxidized and reduced on the MCPE surfaces with a process involved surface mediation of immobilized cobalt species, and an enhanced direct electron transfer process, respectively. The estimated potential of hydrogen peroxide electroreduction on the MCPE surface is about 220 and 125 mV less than UCPE and MWCNTs-CPE, respectively. In addition, the electroreduction current for MCPE is about 1.6 times of UCPE, and almost equals to MWCNTs-CPE. Therefore, for the electrooxidation of hydrogen peroxide, the redox transitions of the cobalt species,

is coupled to the chemical oxidation of hydrogen peroxide via the cobalt species:

and the electroreduction of hydrogen peroxide is:

which occurs at less negative potentials on MCPE, compared to MWCNTs-CPE.

In order to study the kinetics of electrocatalytic oxidation and direct reduction of hydrogen peroxide, chronoamperometry was employed. Chronoamperograms recorded using MCPE in the absence and presence of different hydrogen peroxide concentrations at two different potential steps of 230 and -350 mV (corresponding to electrooxidation or of hydrogen peroxide) are shown in Fig. 5. In both chronoamperogram sets, the transient currents were decayed in a Cottrellian manner (Fig. 5A inset A1 and Fig. 5B inset) and confirmed that both electrooxidation and electroreduction processes were diffusion-controlled. In addition, the mean diffusion coefficient of hydrogen peroxide was obtained based on Cottrell's equation [51]:

$$I = nFAD^{1/2}C\pi^{-1/2}t^{-1/2} \quad (5)$$

as $2.35 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. This value is in close agreement with that reported elsewhere [27]. The catalytic rate constants of hydrogen peroxide oxidation by active cobalt species can also be obtained based on the following equation [51]:

$$I_{cat}/I_d = \gamma^{1/2}[\pi^{1/2}\text{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2}] \quad (6)$$

where I_{cat} and I_d are the currents in the presence and absence of hydrogen peroxide, respectively, and $\gamma = k_{cat}Ct$ is the argument of the error function, k_{cat} is the catalytic rate constant, and t is elapsed time. When $\gamma > 1.5$, $\text{erf}(\gamma^{1/2})$ is almost equal to unity, and Equation (6) is reduced to:

$$I_{cat}/I_d = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} (k_{cat}Ct)^{1/2} \quad (7)$$

Using the plot of I_{cat}/I_d versus $t^{1/2}$ (Fig. 5A inset A2), k_{ca} is obtained as $5.45 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This value is about 40 times higher than that obtained for Cobalt oxide nanoparticles anchored to multiwall carbon nanotubes [34].

Based on the above results, MCPE can oxidize or reduce hydrogen peroxide, and it can set up amperometric sensors for hydrogen peroxide based on its either oxidation or reduction. In order to determine hydrogen peroxide using MCPE, the amperometry technique was employed. Amperometric signals of MCPE toward the successive increments of hydrogen peroxide concentrations at two different potentials of 230 and -350 mV are represented in Fig. 6. The corresponding calibration plots are also shown in the insets. Based on the results, the limits of detection (LOD) and quantitation (LOQ) of the procedures were calculated according to the $3SD/b$ and $10SD/b$ criteria, respectively, where SD is the standard deviation of the intercept and b is the slope of the calibration curves [52]. The determined parameters for the calibration curve of hydrogen peroxide using MCPE are reported in Table 1. The detection limits of some different sensors for hydrogen peroxide are also presented in Table 2. A comparison between amperometric measurements of hydrogen peroxide at two different potentials of 230 and -350 mV revealed that the calibration curve recorded at the negative potential (based on H_2O_2 electroreduction at the MCPE surface) had a lower sensitivity, while the calibration sensitivity at the positive potential (based on H_2O_2 electrocatalytic oxidation at the MCPE surface) was higher. On the other hand, hydrogen peroxide sensing based on its electroreduction leads to production of water, rather than molecular oxygen. This causes more stability of the electrode and the electrolyte species. Moreover, hydrogen peroxide sensing at negative potentials suffered less from the interference compounds.

Fig. 7 shows amperometric signals of MCPE toward different species of glucose, ethanol, ascorbic acid, dopamine and uric acid of 100 μM concentration at both the potentials of 230 (A) and -350 mV (B). No chemical interferences were observed for all these compounds, and MCPE can be considered to be selective.

In order to verify the applicability of MCPE electrode in detection of hydrogen peroxide in real matrices, three different river samples and three different wastewater samples were analyzed by the amperometry method at -350 mV. The recovery results of hydrogen peroxide determination for the river samples were 102.28%, 101.54% and 100.96%, and for the wastewater samples were 99.1, 99.8, 98.8%. Therefore, MCPE represented an excellent sensing capability in detecting hydrogen peroxide in real samples.

In order to verify the durability of MCPE, 100 consecutive cyclic voltammograms were recorded and it was found that the peak currents changed slightly (<4%). MCPE was stored in 100 mmol dm^{-3} NaOH solution when not in use and retained its electrochemical reactivity for at least four weeks.

4. Conclusion

A nanocomposite of hexagonal CoAl-LDH nanosheets and MWCNTs was successfully synthesized. The method could be expandable to synthesis of nanocomposites of other LDHs nanosheets with MWCNTs, or CoAl-LDH nanosheets with other carbon nanostructures. CoAl-LDH/MWCNTs then applied to modification of a carbon paste electrode. CoAl-LDH/MWCNTs was characterized and then employed for the electrocatalytic oxidation and electroreduction of hydrogen peroxide. Cobalt species catalyzed the electrooxidation reaction, and CoAl-LDH enhanced the electroreduction process. The interference-free current generated from

the oxidation and reduction of hydrogen peroxide was used for quantification of hydrogen peroxide. The modified electrode showed remarkable activity, stability, and high sensitivity toward hydrogen peroxide.

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Figure Legends:

Fig. 1: Powder XRD patterns of CoAl-LDH/MWCNTs (A), MWCNTs (B) and CoAl-LDH (C).

Fig. 2: FESEM images of CoAl-LDH/MWCNTs at different magnifications (A-C), an EDS spectrum for CoAl-LDH/MWCNTs (D), a FESEM image of CoAl-LDH (E), and an EDS spectrum for CoAl-LDH (F).

Fig. 3: TEM images of CoAl-LDH/MWCNTs at different magnifications (A-G), and a TEM image of CoAl-LDH (H).

Fig. 4: Cyclic voltammograms of MCPE (A), UCPE (B), LDH-CPE (C) and MWCNTs-CPE (D) in 1.0 mol dm^{-3} NaOH solution in the absence (blue curve) and presence (red curve) of 5.0 mmol dm^{-3} hydrogen peroxide. The potential sweep rate was 50 mV s^{-1} .

Fig. 5:

(A, Main panel) Chronoamperograms for MCPE in 1.0 mol dm^{-3} NaOH solution in the absence (a) and presence of 0.05 (b) 0.1 (c), 0.2 (d), 0.5 (e), 0.75 (f), 1.0 (g), 1.5 (h), 2.0 (i), 3.0 (j) and 5.0 mmol dm^{-3} (k) hydrogen peroxide. The applied potential step was 230 mV. Inset A1: The Cottrell plot for curve (j) in the main panel. Inset A2: Dependency of I_{cat}/I_L on the square root of time for curve (j) in the main panel.

(B, Main panel) Chronoamperograms for MCPE in 1.0 mol dm^{-3} NaOH solution in the absence (a) and presence of 0.05 (b) 0.1 (c), 0.2 (d), 0.5 (e), 0.75 (f), 1.0 (g), 1.5 (h), 2.0 (i), 3.0 (j) and 5.0 mmol dm^{-3} (k) hydrogen peroxide. The applied potential step was -350 mV. Inset: The Cottrell plot for curve (j) in the main panel.

Fig. 6: Amperometric signals of MCPE in 1.0 mol dm^{-3} NaOH solution toward the successive increments of hydrogen peroxide concentrations (A, B). The working potentials were 230 (A) and -350 (B) mV. Insets: The corresponding calibration curves.

Fig. 7: Amperometric signals of MCPE in 1.0 mol dm^{-3} NaOH solution toward $100 \text{ } \mu\text{mol dm}^{-3}$ hydrogen peroxide and some other interfering species (GL: glucose, EtOH: ethanol, AA: ascorbic acid, DA: dopamine, UA: uric acid). The working potentials were 230 (A) and -350 mV (B).

Table 1: The determined parameters for the calibration curve of hydrogen peroxide using MCPE.

Potential / mV	230	-350
Linear range / mmol dm ⁻³	0.1-4.0	0.1-4.0
Sensitivity (Slope) / mA dm ³ mol ⁻¹ cm ⁻²	118.0	42.0
Intercept / μA cm ⁻²	12.4	0.09
R ²	0.9991	0.9996
LOD / mmol dm ⁻³	0.005	0.01
LOQ / mmol dm ⁻³	0.01	0.04
RSD%	3.71	3.48

Table 2: Comparison of some different hydrogen peroxide sensors.

Electrode	Potential / V	Papers		Linear range / $\mu\text{mol dm}^{-3}$	Reference
		Sensitivity / $\mu\text{A dm}^{-3} \text{mol}^{-1} \text{cm}^{-2}$	LOD / $\mu\text{mol dm}^{-3}$		
Pd NPs	-0.45 ^a	-	0.68	1.0-820	[53]
Ag NPs	-0.3 ^b	-	33.9	100-180000	[54]
Fe ₃ O ₄ -Ag	-0.5 ^b	0.012	1.2	1.2-3500	[55]
Ppy-Cu/Au	-0.3 ^a	-	2.3	7.0-4300	[56]
HRP-sol gel	-0.25 ^b	-	12.89	0.01289-10.6	[57]
Graphene-Pt	0.0 ^b	0.1415	0.5	2-710	[58]
Ag-SWCNTs	-0.3 ^a	1.092	2.76	16-18000	[59]
Au nanowires	-0.2 ^b	-	1.2	0.0012-0.8	[60]
Ag NPs/PoPD	-0.5 ^a	-	1.5	6.0-67300	[61]
Pt Nanoflower	-0.2 ^b	-	60	100-900	[62]
Pt-carbon paste	0.8 ^b	-	5	-	[63]
PtPd/MWCNTs	0.25 ^a	-	1.2	2.5-125	[64]
Pt NPs/SWCNTs	0.55 ^b	-	0.025	0.025-0.01, 0.1-2	[65]
MnO ₂ -MWCNTs	0.45 ^b	-	0.8	0.0012-1.8	[66]
Co ₃ O ₄ /MWCNTs	0.19 ^b	0.729	4.87	20-430	[34]
Co ₃ O ₄ /MWCNTs	-0.19 ^b	1.00	2.46	20-430	[34]
Pt-coated Au ANPs	0.08 ^b	-	0.18	1-450	[67]
Pt NPs-MWCNTCs	-0.4 ^b	-	1.23	5-2000	[68]
Pt/MWCNTs-PANI	-0.25 ^a	-	2.0	7.0-2500	[69]
Pt/Carbon nanofibers	0.0 ^b	0.829	0.6	0.001-0.8	[70]
Se/Pt nanocomposites	0.0 ^b	-	3.1	0.01-15	[71]
Pt NPs-PPy nanowires	-0.3 ^a	-	1.2	3.5-9900	[72]
Macroporous Au/Pt NPs	0.1 ^b	0.264	50	-	[73]

Pt NPs-Poly(ionic liquid)	-0.24 ^b	0.346	0.08	0.1-3200	[74]
Graphene/Au NPs/chitosan	-0.2 ^b	-	-	0.2-4.2	[75]
Pt hierarchical nanoflowers	0.21 ^b	1.39	1.05	10-400	[28]
Pt NPs-micro carbon pillars	-0.4 ^b	1.28-1.75	9.6-17.7	to 7000	[76]
Ni/Al layered double hydroxide	0.06 ^b	-	0.009	0.036-175	[77]
Co/Al layered double hydroxide	0.06 ^b	-	0.05	0.2-674	[77]
Ag NDs/layered double hydroxides	-0.3 ^b	-	2.2	10-19330	[78]
CoAl-LDH/MWCNTs	0.23	118.0	5.0	100-4000	This work
CoAl-LDH/MWCNTs	-0.35	42.0	10	100-4000	This work
Routine methods					
Method	Interferences		Limit of quantitation	Linear range	Reference
Cobalt Bicarbonate	Reducing agents		0.1 mg dm ⁻³	-	[79]
Iodometric Titration	Other oxidizing agents		mg dm ⁻³ levels		h2o2.com
Peroxidase enzyme catalyzer	-		0.1 mg dm ⁻³	-	h2o2.com
Spectrophotometry by titanium oxalate	-		50 mg dm ⁻³	0.1-50 mg dm ⁻³	h2o2.com

a Potential versus SCE.

b potential versus Ag/AgCl

Abbreviations:

MWCNTs: Multi wall carbon nanotubes

PANI: Polyaniline

NPs: Nanoparticles

SWCNTs: Single wall carbon nanotubes

PoPD: Poly(o-phenylene diamine)

PPy: Polypyrrole

NDs: Nanodendrites

Figure 1

Figure 2

(A)

(B)

(C)

(D)

2 μm

(E)

(F)

Figure 3

(A)

(B)

(C)

(D)

(E)

(F)

(G)

(H)

Figure 4

Figure 3B

Figure 6A

Figure 6B

Figure 7

Figure 5A