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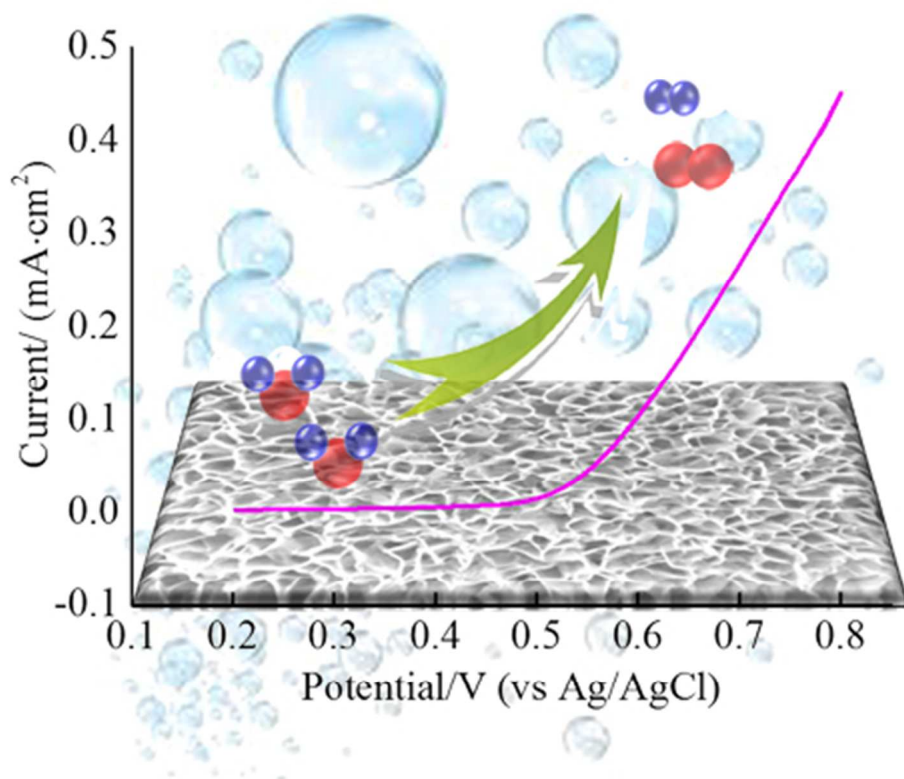


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Homogeneous Nanosheet Co₃O₄ Film Prepared by Novel Unipolar Pulse Electro-deposition Method for Electrochemical Water Splitting

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A unipolar pulse electro-deposition (UPED) method is used to prepare nanosheet Co₃O₄ film on carbon rod substrate in aqueous solution and compared with other conventional methods, i.e., cyclic voltammetry (CV) method, potentiostatic method (PM) and pulse potentiostatic method (PPM). Co₃O₄ films prepared by UPED method show more uniform structure on carbon rod and higher catalytic activity than those by other methods, and oxygen evolution reaction over it with an overpotential of 275 ± 2.3 mV results in a current density of 10 mA cm^{-2} in 1.0 mol L^{-1} KOH. Such an excellent performance should be attributed to its highly porous nanosheet structure with honeycomb-like morphology.

Introduction

The development of efficient catalyst is considered as the main topic in water electrolysis research field. In the course of seeking highly efficient electrocatalysts for water electrolysis, Pt, Ir and Ru-based compounds are found to be the most efficient electrocatalysts so far¹. Unfortunately, the scarcity and high cost hinder their commercial application in large scale. Recently, the earth-abundant Fe, Co, Ni and Mn oxides have been investigated as potential candidates for water electrolysis²⁻⁵. Among them, cobalt oxides are one of promising bifunctional catalysts under the same conditions^{4,6}. The abundant and diversiform d-orbitals endow cobalt oxides with the highly active sites for electrocatalytic water splitting^{4,7,8}. On the other hand, designing the microstructure of catalyst at nanoscale by regulating macroscopic synthesis parameters is a promising way to obtain special catalyst materials with high catalytic activity. Many researches have showed that the morphology and electrochemical performance of conductive functional materials are greatly influenced by the preparing methods and processing conditions⁹⁻¹². Hence, electrocatalysts composed of non-precious metals can also be prepared by adjusting preparation conditions and synthesis parameters to achieve high catalytic performance even to replace precious metal catalysts for water electrolysis.

At present, various techniques are employed to prepare electrodes in thin film form. Among them, electrochemical methods have attractive advantages since they can anchor the desired materials onto substrates with the desired quantity and nanostructure even in one single step¹³. To date, cyclic voltammetric (CV) method, potentiostatic method (PM), and galvanostatic method (GM) have been employed for the electrodeposition of cobalt oxide thin films¹¹. However, the obtained films always have structures with irregular distribution, which lead to poor stability and repressive transports of electron, ions and generated gases in the electrode during water electrolysis. To solve these problems, Co-based materials with various nanostructure have also been prepared by modified potentiostatic and galvanostatic methods such as pulse galvanostatic method (PGM)¹⁴ and pulse potentiostatic method (PPM)¹⁵ and as such, enhanced performance can be generally obtained. It is found that uniform Co₃O₄ films can be synthesized by PGM combined with thermal oxidation¹⁶, however the obtained film has dense particle configuration with low surface area. In PGM deposition of Co(OH)₂ precursor, the corresponding reduction potential always changes with time so that it is very hard to control the deposition rate. In contrast, applied potential remains constant in PPM deposition process during each pulse duration, and the reduction rate is easy to be adjusted. However, the potential varies periodically while the redox current changes greatly during pulse cycle, as a result, the preparation process of Co(OH)₂ film is composed of not only the deposition of Co(OH)₂ during cathodic pulse duration, but also the redox process of obtained Co(OH)₂ films as applied potential changed.

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In this study, a unipolar pulse electro-deposition (UPED) method was used to prepare Co_3O_4 films on carbon rod (CR) substrate in aqueous solutions and compared with other conventional methods, i.e., cyclic voltammetry method, potentiostatic method and pulse potentiostatic method. The obtained films were characterized by measuring its morphology and catalytic activity for water electrolysis. The long-term stability was also investigated. It is expected that UPED method can be a general way to prepare high performance electrocatalytic film on the electrode for water electrolysis.

Experimental

Chemicals

Cobalt nitrate (Wako, Japan) with analytical grade was used as chemicals for the preparation of Co_3O_4 electrode. Potassium hydroxide (Sigma-Aldrich, Japan) was dissolved in deionized water as electrolyte solution for electrochemical characterization of electrodes. Carbon rods (CR, $\phi 5\text{mm}$, 10 cm length) are provided by C-task company, Japan.

Preparation of Co_3O_4 film coated electrodes

Potentiostat operated with VersaStudio software was applied to controllably deposit $\text{Co}(\text{OH})_2$ precursor and characterize the electrochemical properties of the as-fabricated electrodes. Three electrodes of platinum wire, Ag/AgCl/saturated KCl reference and CR substrate were used as counter electrode, reference electrode and working electrode, respectively. CR was pretreated in ethanol to improve its hydrophilicity at first, and the efficient deposition length is 1 cm. Electrolyte solution for synthesizing $\text{Co}(\text{OH})_2$ precursor was freshly prepared with a designed composition of 0.1 M $\text{Co}(\text{NO}_3)_2$. In this work, a series of $\text{Co}(\text{OH})_2$ film coated electrodes were prepared followed the UPED method as reported^{9, 17}. Here, the applied potentials during the on-time operation ranged from -0.8 to -1.1 V. Pulse durations of 0.2, 0.5, 1.0, 1.5 and 2.0 s were used while the off-time was fixed at 1.0 s. The number of pulse cycle was varied

from 200 to 700. For comparison, $\text{Co}(\text{OH})_2$ film coated electrodes were also prepared by the conventional method: CV, PM, PPM under the same conditions, in which the electric quantity of deposition process remained at 3.2 C.

Temperature programmed drying and calcination in air were used after the deposition step. The $\text{Co}(\text{OH})_2$ film coated electrode was heated to 65 °C with a heating rate of 0.5 °C/min and held at 65 °C for 5 h, then, it was heated to 110 °C and held at this temperature for another 5 h. Finally, it heated at a rate of 5 °C/min to final calcination temperature (ranged from 150 to 350°C), and held there for 3 h.

Characterizations

The electrolysis performance was tested using the linear sweep voltammetry (LSV, scan rate: 2 mV/s) in a solution of 1 M KOH. Electrochemical impedance spectroscopy (EIS) was performed within a frequency range of 0.01 Hz–0.1 MHz in 1 M KOH solution. The morphology and element composition were investigated by a scanning electron microscope (SEM, Hitachi SU8010) equipped with a Horiba Scientific energy dispersive spectrometer (EDS) analyzer. The crystal structures of various Co_3O_4 electrodes were determined by X-ray diffraction (XRD, Rigaku SmartLab X-Ray Diffractometer) using Cu-K α ($\lambda=1.5405 \text{ \AA}$) radiation source.

Results and discussion

Jagadele et al prepared $\text{Co}(\text{OH})_2$ film coated electrodes for supercapacitor by CV and PM respectively¹¹. In this study we found that the accumulative structure was easily formed when using these two methods. To solve this problem, PPM and UPED methods were employed to prepare $\text{Co}(\text{OH})_2$ film coated electrodes at first. Fig. 1A shows the typical current-time transient curve obtained during the electrosynthesis of $\text{Co}(\text{OH})_2$ film on CR substrate by PPM in the solution containing 0.1 M $\text{Co}(\text{NO}_3)_2$. The pulse conditions include 0 V anodic potential, -1 V cathodic potential, 1.0 s anodic pulse duration and 1.0 s cathodic pulse duration. The curve shown in this

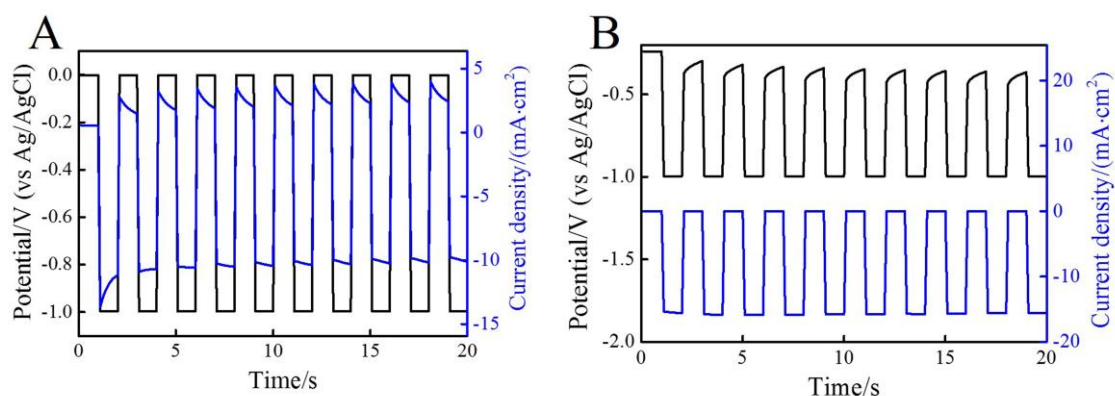
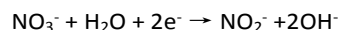
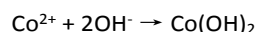


Fig. 1. (A) Potential–time (black) and current–time (blue) transient curves of initial 20 s during pulse potentiostatic electrodeposition of $\text{Co}(\text{OH})_2$ films from 0.1 M $\text{Co}(\text{NO}_3)_2$ solution. Deposition was conducted with 0 V anodic potential, -1.0 V cathodic potential, 1.0 s anodic pulse duration, 1.0 s cathodic. (B) Potential–time (black) and current–time (blue) transient curves of initial 20 s during unipolar pulse electrodeposition of $\text{Co}(\text{OH})_2$ films from 0.1 M $\text{Co}(\text{NO}_3)_2$ solution. Deposition was conducted with 1.0 s on-time, 1.0 s off-time and pulse potentials of -1.0 V.

figure corresponds to the first 20 s period. During the cathodic pulse duration, the application of potential results in the formation of hydroxyl ions on the substrate surface due to the reduction of nitrate ions as follows,



which will increase the pH value of the electrolyte near the electrode. Furthermore, the formed hydroxyl groups can react with Co^{2+} ions in the electrolyte so that cobalt hydroxide is deposited on the substrate as following reaction,



When the potential is changed from the cathodic potential to the anodic potential, the deposited Co(OH)_2 will further be oxidized to CoOOH , but it will be reduced to Co(OH)_2 again in the following cathodic pulse. Thus, such a frequently changing redox process could have negative influence on the stability, component and structure of the film. To avoid this problem, modified potentiostatic pulse UPED was employed to prepare

Co(OH)_2 film coated electrode here. Fig 1B shows the typical current–time transient curve obtained in UPED process during the electrosynthesis of Co(OH)_2 film coated electrode in the same conditions as PPM. Especially, it should be noted that the pulse waveform of UPED consists of an applied cathodic potential during the on-period and an open-circuit potential (OCP, zero current) during the off-period. In this case, the OCP during the off-time can be controlled automatically. In addition, compared to PPM, the potential changes between the upper limit potential (pulse potential) and the lower limit potential (OCP) are much smaller (Fig 1A and B). This mode is expected to avoid the frequent redox of Co(OH)_2 film efficiently.

Fig. 2 shows SEM images of Co(OH)_2 films coated on CRs (Fig. 2 A1 – D1) prepared by different electrodeposition methods and the corresponding Co_3O_4 films after calcined in air (Fig. 2 A2 – D2). One can see that all Co(OH)_2 films have porous nanosheet structure. However, for the films prepared by CV and PM methods, there are many aggregations accumulated on the surface of film. In contrast, the film prepared by PPM becomes more uniform, suggesting that the transitory pulse duration can restrain the generation of particles accumulation. In this case, during the periodic pulse process, Co^{2+} and NO_3^- ions could periodically be assembled and scattered on the electrode surface, avoiding the appearance of agglomeration. Interestingly, when UPED method was applied, much more uniform Co(OH)_2 film was formed on CR. This also should be attributed to the transitory pulse duration, in addition, during UPED process the current during off-time is zero, and the OCP could be tuned gradually and controlled automatically in the deposition process. As such, the sudden potential changing can be avoided effectively, resulting in gentle assemblage and scatter of Co^{2+} and NO_3^- ions, so that a uniform porous structure is formed on CR. Furthermore, as shown in Fig 2 A2 –

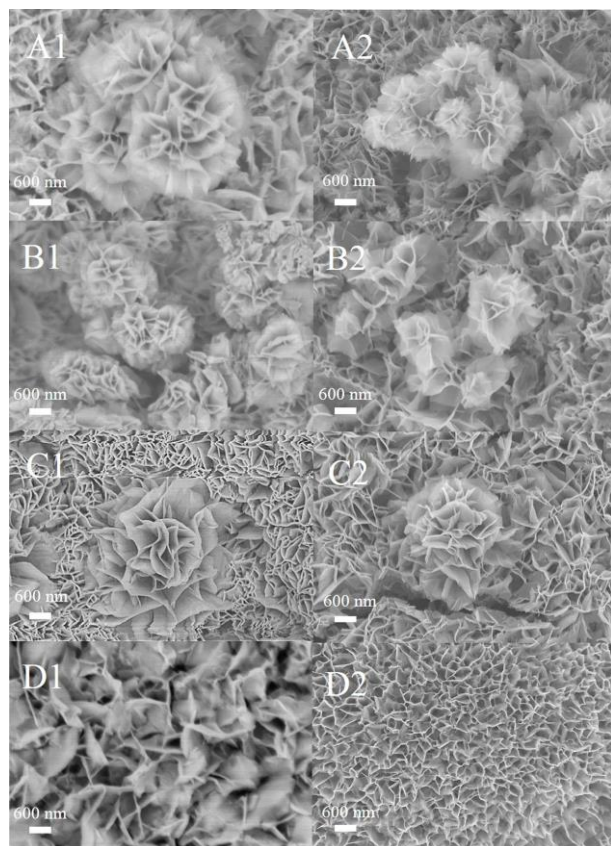


Fig. 2. SEM images of Co(OH)_2 films (A1 – D1) and corresponding Co_3O_4 films (A2 – D2) prepared by CV (A1, A2), PM (B1, B2), PPM (C1, C2), UPED (D1, D2).

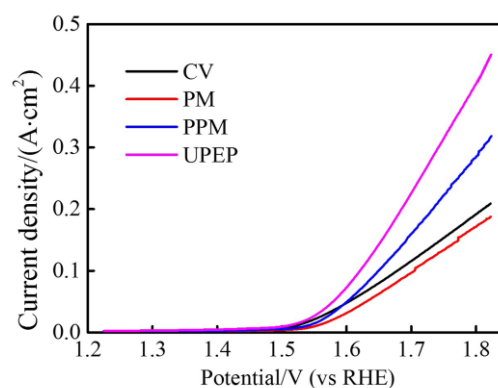


Fig. 3. Polarization curves of Co_3O_4 film coated electrodes prepared by different methods

Table 1. Summary of O₂ productivity of Co₃O₄ electrodes prepared by different methods

Method	CV	PM	PPM	UPED
O ₂ productivity [cm ³ /(min·cm ²)]	0.96	0.8	1.1	1.5

D2, compared with Co(OH)₂ films, after calcination, Co₃O₄ particle seems to shrink to some extent. This shrink after calcination should be owed to the reconstructing of the materials during the thermal oxidation of Co(OH)₂ to Co₃O₄. Especially, for the films prepared by UPED method, after calcination, more compact and regular morphology of Co₃O₄ film with a uniform honeycomb-like structure is obtained. Such a highly porous and uniform nanosheet structure with honeycomb-like morphology should be benefit for the improvement of the electrochemical properties of the obtained electrode.

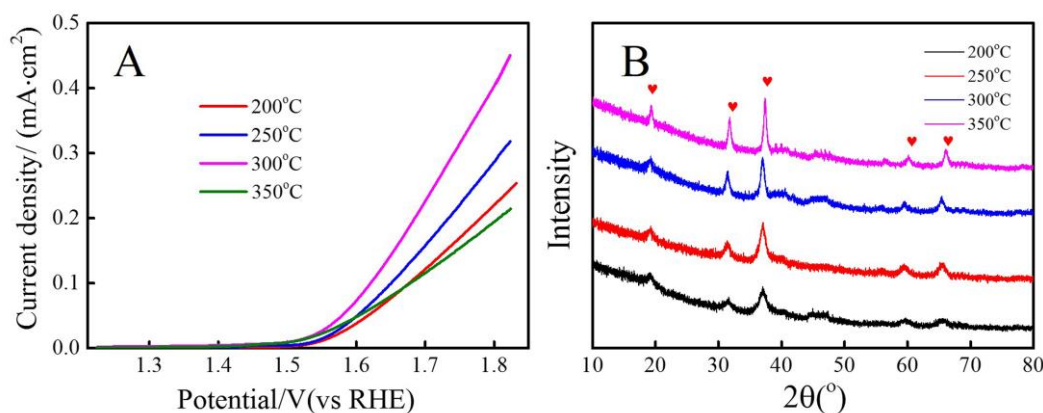
Fig. 3 shows the catalytic performance of different Co₃O₄ film coated electrodes prepared by different methods for the water electrolysis using the linear sweep voltammetry (LSV). We can see that electrode prepared by UPED show higher polarization current than those by other methods. However, Minguzzi et al.²⁶ considered that the recorded current should include the capacitive contribution of the double-layer charging. In order to confirm the dependability of polarization curves, we had tested the oxygen productivity of electrodes prepared by different methods at 1.8V (vs RHE). As shown in Table 1, the electrodes prepared by UPED shows the highest O₂ productivity and the results are corresponding to polarization curves. Thus we consider that comparison of catalytic activity of different electrodes by polarization curves is feasible. In addition, revealed from Fig 3 the overpotentials

of the electrodes prepared by CV, PM and PPM to drive current density of 10 mA/cm² are 290 ± 3.2, 323 ± 2.7, 308 ± 3.7 mV respectively. In contrast, only an overpotential of 275 ± 2.3 mV is needed for the electrode prepared by UPED method to afford the same current density. This overpotential is also lower than those most reported OER catalysts in alkaline conditions, including CCHH/MWCNT (285 mV)¹⁸, NiCo₂O₄ (320 mV)¹⁹, Co₃O₄ (320 mV)⁴, CuCo₂O₄/NrGO (360 mV)²⁰, Cu/(Cu(OH)₂-CuO) (417 mV)²¹, Mn₃O₄/CoSe₂ (450 mV)⁵, α-Fe₂O₃ NA/CC (417 mV)², NiCo-LDH (420 mV)²², α-MnO₂-SF (490 mV)²³. It should be attributed to its uniform porous nanosheet structure with a honeycomb-like morphology which could provide more active sites and facilitate the transport of electron, ions and generated gases during water electrolysis.

The effect of the calcination temperature on the crystalline structures of the Co₃O₄ films is shown in Fig. 4A in terms of the XRD patterns. All of the samples reflects the formation of Co₃O₄ with cubic crystal structure [JCPDS card no. 42-1467]. The diffraction peaks at angles (2θ) of 31.4, 37.1, 59.6 and 65.5 are assigned to the (220), (311), (511) and (440) planes of the Co₃O₄ crystal lattice. However, it should be noted that as the temperature increases, the intensities of the peaks increase. The crystallite size can be estimated by using Scherrer's formula,

$$D = (0.89\lambda) / (\beta \cos\theta)$$

Where 'D' is crystallite size, 'β' is full width at half maxima, 'λ' is wavelength of X-ray used and 'θ' is diffraction angle. It is found that the average crystallite sizes of Co₃O₄ calcined at 200, 250, 300, 350°C are about 12 ± 0.3, 16 ± 0.3, 21 ± 0.2 and 33 ± 0.2 nm, respectively, suggesting that the crystallite size is increased with the increase of the calcination temperature. Fig

Fig. 4 Polarization curves (A) and XRD patterns (B) of Co₃O₄ film coated electrodes prepared at different calcination temperature.

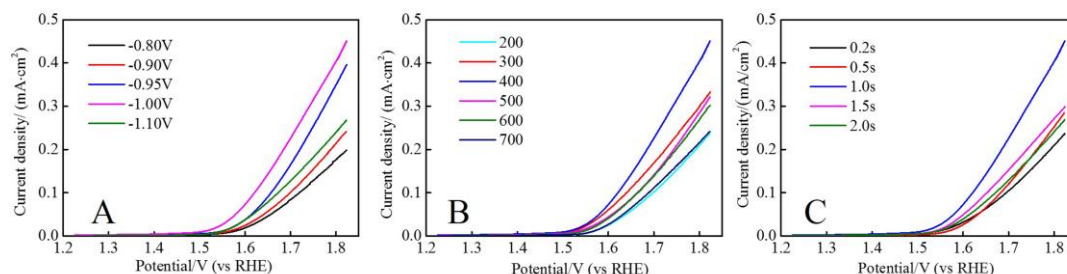


Fig. 5. Polarization curves of Co_3O_4 film coated electrodes prepared by different potentials (A), pulse cycles (B) and potential duration (C).

4B shows the activity of Co_3O_4 film coated electrodes calcined at different temperatures. One can see that the performance is highly dependent on the calcination temperature and the electrode with highest performance is the one obtained at electroactivity of Co_3O_4 ²⁴.

The preparation parameters such as pulse potential, pulse cycles, pulse duration will influence the electrolysis performance of Co_3O_4 film coated electrodes. Fig 5A shows the catalytic activity change of the electrodes at various cathodic potential of -0.80, -0.90, -0.95, -1.00 and -1.10 V. One can see that the activity is strongly dependent on the cathodic potential. It is believed that the cathodic potential will affect the growth situation of $\text{Co}(\text{OH})_2$ film on the electrode, and consequently influence the OER performance of the final film. If the potential is too high, it is hard for the reduction of nitrate ion. In other words, the nitrate reduction can be accelerated at more negative potentials. On the contrary, if the potential is too low, the growth rate of $\text{Co}(\text{OH})_2$ film will be very fast so that the accumulative structure is easily to form. As a result, when the potential is decreased under -1.0 V, the activity of the electrode decreased sharply, as the accumulative structure with lower the transport ability of electron, ions was formed in it.

In general, the amount of catalyst can be regulated by tuning the pulse times. As such, the performance of Co_3O_4 film coated electrode could be controlled by adjusting the pulse cycles during the deposition process. As demonstrated in Fig. 5B, the activity of electrode increases with the increase in the pulse cycle at first, due to more Co_3O_4 effective component formed during this process. However, the activity begins to decrease after 400 pulse cycles, because the film became thicker and denser with the increase in the pulse cycles, resulting in the blockage of electrolyte diffusion through it during water electrolysis¹⁷. Fig. 5C shows the effect of pulse duration on the catalytic activity of the obtained film. One can see that the pulse duration also greatly influences the activity of the obtained Co_3O_4 film coated electrode. This is because the

amount of $\text{Co}(\text{OH})_2$ deposition in one pulse period usually, depends on the pulse duration and the concentrations of Co^{2+} and NO_3^- ions. Here, the concentrations of the ions near the electrode could be equal to its bulk concentration and independent of mass-transport limitations²⁵. If the pulse duration is too short, the ions on the surface of the electrode have no enough time to complete the reaction so that the amount of $\text{Co}(\text{OH})_2$ deposition is limited. On the contrary, if the pulse duration is too long, the formed $\text{Co}(\text{OH})_2$ could become too large, and as a result, the final Co_3O_4 particles with larger size would be formed after the calcination, and occlude the ion transfer and electrolyte diffusion when it is used for water electrolysis. Above results reveal that suitable calcination temperature, pulse potential, pulse cycles, pulse duration were important for obtaining Co_3O_4 electrode with ideal performance.

Fig. 6A shows the electrochemical impedance spectroscopy (EIS) of Co_3O_4 electrodes. The resistance shown in the high frequency region is related to the uncompensated solution resistance (R_s , ohmic resistance) and the charge transfer resistance (signed as R_{ct}) can be calculated from the arc radius of the Nyquist plot²³. As listed in Table 1, the Co_3O_4 film coated electrode prepared by UPED method exhibits the lowest R_s of 0.37Ω and R_{ct} of 0.35Ω , which imply the enhanced electrical

Table 2. Summary of electrochemical impedance spectroscopy of Co_3O_4 electrodes prepared by different methods

Deposition method	R_s (Ω)	R_{ct} (Ω)
CV	0.44 ± 0.010	0.42 ± 0.017
PM	0.42 ± 0.012	0.43 ± 0.018
PPM	0.40 ± 0.011	0.42 ± 0.015
UPED	0.37 ± 0.009	0.35 ± 0.020

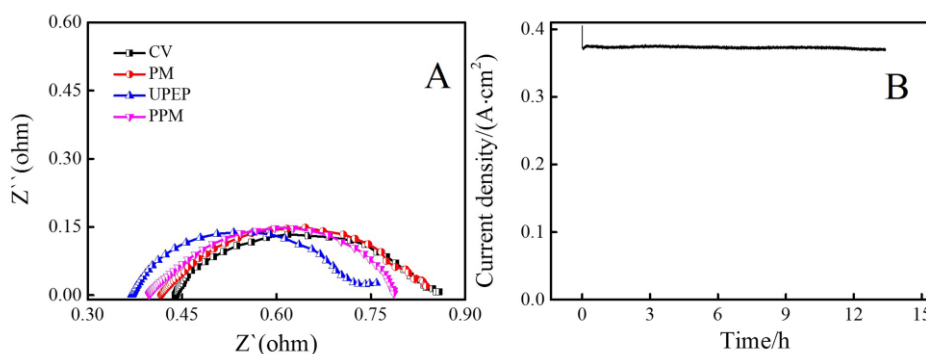


Fig. 6. (A) Nyquist plots of Co_3O_4 film coated electrodes prepared by different methods. (Overpotential is 0.4 V). (B) Time dependence of current density for Co_3O_4 film coated electrode in 1 M KOH electrolytes over 50,000 s.

transport property, charge-transfer rate and improved catalytic activity for this kind of film. Fig. 4B shows the durability of Co_3O_4 electrode prepared by UPEP method. Here, the time-dependent current density curve was collected at 0.8 V where the cell shows a high hydrogen evolution rate. One can see that Co_3O_4 film coated electrode has an excellent stability during 14 h test. Therefore, the Co_3O_4 film prepared by this method should be an ideal selection for oxygen and hydrogen evolutions from water electrolysis.

Conclusions

In summary, Co_3O_4 film with homogeneously porous nanosheet structure can be synthesized by a facile electro-deposition combined with thermal oxidation method. The morphology and microstructure of the obtained films are highly dependent on the preparation methods. It is found that the honeycomb-like one can be successfully obtained by UPEP method. Benefit from its highly porous nano-size structure, the remarkably enhanced catalytic performance of this film for OER is obtained. In addition, the obtained electrode reveals low charge transfer resistance and excellent long-term durability. In view of the facile and efficient fabrication process and the low-cost nature of Co oxides, this film has great potential to be an inexpensive catalyst toward electrochemical water splitting.

Acknowledgements

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