Synthesis and electrochemical properties of Co-doped ZnMn$_2$O$_4$

hollow nanospheres

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Abstract. Spinel structure Co-doped ZnMn$_2$O$_4$ nanocrystals were successfully synthesized by hydrothermal method. The effects of Co doping concentration on the structure and electrochemical properties of the samples were investigated. The experimental results manifest that all samples exhibit single-phase with tetragonal structure, and the morphologies are regular hollow microspheres. The cyclic voltammetry curves for all samples are similar to rectangular shape with symmetric nature and no obvious redox peak. Galvanostatic charge–discharge curves were triangular and symmetric. The impedance spectra revealed that Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ possess low resistance. Better electrochemical properties of ZnMn$_2$O$_4$ electrode could be obtained when Co doping ratio is 0.3. Zn$_{0.7}$Co$_{0.3}$Mn$_2$O$_4$ exhibits much higher specific capacitance (306 Fg$^{-1}$) at scan rate of 5 mVs$^{-1}$, and show excellent cyclic stability, and keep 98.2% of its initial capacitance after 1000 cycles. The enhanced capacitive performance in this work can be attributed to the incorporation of Co ions are doped into ZnMn$_2$O$_4$ host lattice.

Keywords. Co-doped, ZnMn$_2$O$_4$, hollow microspheres, electrochemical properties

1. Introduction

In the past few decades, the investigation on mixed transition-metal oxides[1-2] with spinel structures have attracted growing interest because of their unique properties and numerous breakthrough applications in magnetic materials[3], electrochemical characteristic[3], photocatalytic[4-5], gas sensors [7], energy storage,
Nanoscale ZnMn$_2$O$_4$ is well known multifunctional semiconductor material with narrow band gap of 1.86 eV, belonging to I41/amd space group [10-11]. Nanoscale ZnMn$_2$O$_4$ exhibits unique properties that differ considerably from those of the bulk solid state due to their small size effect, surface effect, quantum size effect and quantum tunnelling effect [12-14]. ZnMn$_2$O$_4$ semiconductor materials have been considered as a better supercapacitor electrode material due to high specific capacitance, superior rate capability, excellent cyclic stability and high energy density [15-16].

The properties of nanomaterials primarily depend on the synthesis method as well as processing conditions. The microstructure of ZnMn$_2$O$_4$ crystals can be modified by controlling the preparation process and changing the doped transition metal element to further enhance electrochemical properties [17-19]. In recent years, in order to enhance electrochemical properties, some researchers have studied ZnMn$_2$O$_4$ microstructure doped with a small percentage of dopants, transition metal ions doped into ZnMn$_2$O$_4$ to obtain desired structural and properties by providing extra positive carriers in the host material[20-21]. Dopant ions offer a way to trap charge carriers which result in better electrochemical performances [22-23]. Unfortunately, to the best of our knowledge, there are rarely reports related to investigate the effect of transition metal ion doping on the microstructure and electrochemical properties of ZnMn$_2$O$_4$, it is still need more understanding. Therefore, the main aim of this study is to investigate the effect of dopant ions on microstructure and electrochemical properties.

In this paper, spinel structure Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ with different ratio (x=0, 0.1, 0.3 and 0.5) were prepared by a hydrothermal method. The samples were characterized by means of X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Cyclic voltammetry (CV), Galvanostatic charge-discharge(GCD) and Electrochemical impedance spectra (EIS) to investigate the effect influence of Co doped content concentration on the microstructure and electrochemical performances of Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ samples.

2. Experimental
2.1. Materials and Synthesis

A facile hydrothermal method was used to synthesize individual Co-doped Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ (x=0, 0.1, 0.3 and 0.5). All reagents used in this work were analytical grade products produced by ZhongQin reagent company of China. In a typical experiment, Zn(NO$_3$)$_2$, Mn(NO$_3$)$_2$, citric acid, polyethylene glycol-400 (PEG-400), Co(NO$_3$)$_2$, absolute ethyl alcohol and deionized water were used in this study were of reagent grade and used without any further purification. At room temperature, 2.25 mmol Mn(NO$_3$)$_2$ and 1.125 mmol Zn(NO$_3$)$_2$, were dissolved in 50 mL absolute ethyl alcohol and 30 mL deionized water under magnetic stirred vigorously for 30 min. Meanwhile, appropriate amount of 1.125 mmol citric acid and 0.25 mmol PEG-400 were poured dropwise into the above mixed solution under magnetic stirring for 4 hours. Subsequently, the resulting solution was transferred into a 100 mL Teflon-lined stainless steel autoclave. The hydrothermal reaction process was conducted at 423 K for 24 h in an oven, then cooled to room temperature naturally. Finally, the resultant precipitate was separated centrifugally and washed several times with distilled water and absolute alcohol, respectively, and then dried at 333 K in a vacuum oven for 10 h. Thus, Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ nanoparticles were collected and used for further studies. By comparative, Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ with different reactant concentration (x = 0, 0.1, 0.3 and 0.5) were also prepared using the above mentioned procedure. The resulting products, denoted as ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5, were collected and used for further studies.

2.2. Characterization

The crystallographic data for the products were examined by XRD with CuKα radiation at λ = 1.54056 Å. The 2θ range scanned was 20° to 80° with scanning rate 0.005°/s and step size 0.02°. The morphological study of the samples was investigated using FESEM. Elemental analysis of as prepared samples was determined by EDS.

The electrochemical tests were carried out on an electrochemical workstation (CS350, China) with electrode system in Na$_2$SO$_4$ (1 M) aqueous solution. A Pt sheet was served as the counter electrode and KCl saturated solution as the reference electrode, respectively. The work electrode was fabricated by mixing ZCMO
nanopowders, acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1 using ethyl alcohol as solvent to form slurry. The slurry was uniformly coated on the surface of nickel foam (1.5 cm×1.5 cm). Then the meshes were dried at 353 K for 12 h and pressed under 10 MPa. The mass of ZCMO on the Ni foam electrode was 2 mg/cm² as the working electrode. CV curves tests were recorded at different scanning rate between -0.1 V and 0.7 V at various scan rates ranging from 5 mVs⁻¹ to 100 mVs⁻¹ at room temperature. GCD curves were performed between 0.25 and 3.5 Ag⁻¹. EIS measurements were carried out this apparatus with a superimposed 5mV sinusoidal voltage in the frequency range of 100 kHz to 0.01 Hz. The specific capacitance C (Fg⁻¹) of ZCMO samples was calculated using the following equation:

\[ C = \frac{I \Delta t}{M \cdot \Delta V} \]  

Where C, I, Δt, M, ΔV represents the specific capacitance (Fg⁻¹) of the electrodes, discharging current (A), discharging time (s), discharging potential range (V) and mass of electro-active material (g), respectively.

3. Results and discussion

3.1 Structural Characterization

Fig. 1 (a) shows the XRD patterns of Zn₁₋ₓCoₓMn₂O₄ (x=0, 0.1, 0.3 and 0.5) samples. The diffraction peaks of all samples can be readily indexed to single-phase ZnMn₂O₄ tetragonal structures with lattice parameters a = 0.5722 nm, b = 0.5722 nm, c = 0.9326 nm, which are in agreement with the reported values of JCPDS card No. 77-2499. No extra diffraction peaks of other impurity phases such as metal clusters or metal oxides are detected when the doping atomic percentage ranges from 10% to 50% from the XRD patterns, which indicating that all Co ions are assumed to be successfully incorporated into Zn²⁺ ions sites without changing the parent ZnMn₂O₄ structure. Meanwhile, the presence of ZCMO-3 samples have been confirmed by EDS patterns as shown in Fig. 3(b).

According to the Bragg formula: \( 2d_{hkl} \sin \theta = \lambda \), where \( d_{hkl} \) denotes the crystalline plane distance for indices \((hkl)\) and \( \theta \) is the diffraction angle of the (211) peak. It can be observed that the diffraction angle of the (211) peak for all samples is slightly shifted towards lower angle with the increase of Co doping content, which
indicating that Co is successfully substituted for Zn in the host lattice. The decrease in disorder may be attributed to the incorporation of Co ions are doped into ZnMn$_2$O$_4$ host lattice, and ionic radius of Co$^{2+}$ (0.72 Å) smaller than Zn$^{2+}$ (0.74 Å), which eventually led to the lattice distortion and contraction. As tetragonal crystal structure: 

$$\frac{1}{4 \pi} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

, the lattice parameter (a) can be calculated from measured values of the (211) plane spacing. The lattice constant of doped samples decrease as compared to that of undoped ZnMn$_2$O$_4$ with Co doped content increase in Table 1.

The crystallite size of the samples is calculated from the full width at half maximum (FWHM) and the peak position using the most intense diffraction peak (211) by following Scherrer formula: $D = \frac{K \lambda}{B \cos \theta}$, where $D$ represents the crystallite size, $K=0.9$ is the Scherrer constant, $\lambda$ is the wavelength of X-ray (Cu Ka, 1.54056 Å), $\theta$ is the Bragg diffraction angle and $B$ is FWHM in radians of the (211) plane. The crystallite size of the samples was summarized in Table 1. It can be clearly seen that the crystallite size gradually decreases with the increase of Co-doping amount.

3.2. Morphological Studies

The FESEM image of pure ZnMn$_2$O$_4$ sample is showed in Fig. 2 (a). It is clearly visible that the morphology of pure ZnMn$_2$O$_4$ is regular porous microspheres architecture mainly composed of many nanoparticles, the diameter of the rough and porous microspheres in the range of 300-500nm, with average diameter is about 400 nm. Fig. 2 (b) presents FESEM image of the ZCMO-3 sample, showing loose and irregular microsphere morphology composed of massive nanoparticles. With the increase of Co-doping content, the edges of the microsphere become more loose and hollow, and some stacked microspheres appear breakage and exhibit hollow microspheres. The hollow microspheres grow bigger in size and more rough and irregular in morphology. This loose hollow microspheres structure contributes to improving the electrochemical performance.

Fig. 3 (a) shows the EDS patterns of pure ZnMn$_2$O$_4$ sample to further clarify the chemical components of the as-prepared samples. It is easily found that pure ZnMn$_2$O$_4$ mainly exhibits peaks characteristic of Zn, Mn and O elements. Fig.3 (b)
confirms the presence of Co elements besides Zn, Mn and O elements for ZCMO-3 sample, whereas the spectrum of pure ZnMn$_2$O$_4$ not find the presence of Co elements. In order to more accurately observe the doped cobalt element, EDS element scanning mapping was used to detect the ZMO sample. Fig.4 clearly shows the cobalt distribution in the ZCMO-3 microsphere structure. The EDS results further verify XRD conclusion, which indicates that Co-doped ZnMn$_2$O$_4$ were synthesized by hydrothermal method, and Co$^{2+}$ are successfully substituted as dopant in ZnMn$_2$O$_4$ matrix. It is evident that the synthesize condition helps to further study the influence of Co doping concentration on the properties of Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ microspheres.

3.3. Electrochemical characterization

Fig.5 (a), (b), (c) and (d) shows the CV curves of Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ (x=0, 0.1, 0.3, 0.5) electrodes in the potential window of -0.1~0.7 V at different scan rates ranging from 5 mVs$^{-1}$ to 100 mVs$^{-1}$. It is obviously that all samples exhibit similar CV curves with a couple of symmetric quasi-rectangular shapes without any redox peaks, which indicating that the ZnMn$_2$O$_4$ electrode exhibit excellent electrochemical reversibility, easy ion transport and fast charge propagation due to electric double-layer capacitance (ELDC) feature, implying good electrical capacitive behavior for active capacitor materials.

Fig.6 (a) shows the plots of the specific capacitance values for different Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ samples in proportion to CV profile. It is easily found that the specific capacitance of ZCMO electrodes decreases gradually with the increase of the scan rate. On the one hand it can be ascribed to insufficient ion transfer at the electrode-electrolyte interface and the electrode possess lower energy storage efficiency, on the other hand the charge transfer decreasing the diffusion rate of electrolyte into each electrode materials at higher scan rate. Moreover, the specific capacitance of doped ZCMO samples is clearly superior to that of undoped ZCMO electrode at given scan rate. The estimated highest specific capacitance of ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5 are 168 Fg$^{-1}$, 207 Fg$^{-1}$, 306 Fg$^{-1}$ and 279 Fg$^{-1}$ at scan rate 5 mVs$^{-1}$. In addition, the ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5 samples maintain 64.8%, 73.8%, 76.8% and 72% capacitance retention as the scan
rate increased from 5 to 200 mVs$^{-1}$, respectively. Meanwhile, the specific capacitance of ZCMO-3 is clearly superior to other ZMO electrode materials at given scan rate. Obviously, Co doped concentration not only influence the morphology and structures, but also affect the specific capacitance of ZCMO samples. Compared with the ZCMO-0, ZCMO-1 and ZCMO-5 samples, the superior specific capacitance of ZCMO-3 can mainly be attributed to its loose and porous microsphere architecture, which provides more active sites for Faradaic reactions, enhance the ion and electron movement, and consequently promote the electrochemical performance.

In order to further investigate the advantages of ZCMO samples, the CV curves of ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5 samples were recorded at scan rate 5mVs$^{-1}$ as shown in Fig.6 (b). Obviously, the specific capacitance is proportional to the average area of a CV curve, and the CV loop area of ZCMO-3 is the largest, corresponding to the excellent specific capacitance than ZCMO-0, ZCMO-1 and ZCMO-5 samples. From above XRD results, it is found the existence of the lattice distortion for Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ samples at the peak of the (211) plane, because the lattice constant of Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ samples appears different levels of disturbance due to Co$^{2+}$ successfully substituted for Zn$^{2+}$ into ZnMn$_2$O$_4$ host lattice. Obviously, the values of specific capacitance are attributed to an effective synergistic effect between Co ions and ZnMn$_2$O$_4$ host lattice, and the suitable lattice disturbance may be beneficial to electrochemical performance. Nevertheless, ZCMO-3 exhibits an excellent electrochemical performance, manifesting an optimum doped content of Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ samples at x=0.3.

Fig.7 (a), (b), (c) and (d) present the GCD curves for ZCMO samples obtained in the voltage window between 0 and 0.48 V at different current densities from 0.25 Ag$^{-1}$ to 3.5 Ag$^{-1}$. All curves clearly exhibits resemble each other quite closely with a nearly linear and isosceles triangle, and the charge curves are symmetric to the discharge curves at all current densities. The linear characteristic of the charge-discharge curves suggests that the electrochemical reaction takes place due to the super capacitance behavior, and this result is concordant with the CV results shown in Fig. 5. The GCD curves for ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5
electrode materials are acquired at current density of 2.5 Ag\textsuperscript{-1} are illustrated in Fig.7 (e). All of the GCD curves are obviously symmetric during the process of charge and discharge, resulting in perfect super capacitance property.

Fig.7(f) shows specific capacitance versus current densities for ZCMO samples. With the increase in the current density, the specific capacity for all samples display decreasing trend, which may be due to an increase in ionic resistivity and a decrease in charge diffusion to the inner active sites and the redox reaction rate. Moreover, ZCMO-3 showing more stable relative to the other three samples, the reducing trend of the capacitance is relatively moderate with the increase of current density. In addition, the specific capacitance of doped ZCMO electrode at given current density is obviously higher than that of undoped ZCMO electrode. The highest specific capacity is observed for ZCMO-3 sample, reaching about 296 Fg\textsuperscript{-1} at current density of 0.25 Ag\textsuperscript{-1}, the specific capacity still reaches 200 Fg\textsuperscript{-1} at a high current density of 3.5 Ag\textsuperscript{-1}. This suggests that the ZCMO-3 electrode maintains an excellent electrochemical performance under high charge-discharge current densities. These results can be explained by the fact that doped ZCMO sample possess loose hollow microspheres structure and thus can provide more available surface active sites for the electrochemical reaction, which further indicating that doped ZCMO sample possess better electrochemical behavior.

The electrochemical cycling stability for ZCMO samples as electrode material were evaluated by the repeated charge-discharge measurement at constant current density of 2.5 Ag\textsuperscript{-1} for 1000 cycles, as shown in Fig.8. Fig.8 exhibits plot of specific capacitance retention as a function of the charge-discharge cycling number. The initial cycle specific capacitance for ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5 samples are 134, 169, 241 and 229 Fg\textsuperscript{-1} at current density of 2.5 Ag\textsuperscript{-1}, respectively. After 1000 cycles, the specific capacitances for ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5 samples still remain at about 130, 166, 236 and 224 Fg\textsuperscript{-1}, and maintain about 96.8%, 97.9%, 98.2% and 97.8% of its initial value, respectively, doped ZCMO samples exhibit better electrochemical performance compared with pure ZCMO. The excellent electrochemical stability and good reversibility of ZCMO-3 is superior to other
ZCMO electrode materials can be ascribed to the synergistic effect. This demonstrates that Co doped concentration make a great influence on the electrochemical performances of the samples. On one hand, the Co$^{2+}$ acts as active sites substituted for Zn$^{2+}$ into ZnMn$_2$O$_4$ host lattice and the integration of Co$^{2+}$ with ZnMn$_2$O$_4$ can supply more active sites due to the coexistence of tetrahedral sites and octahedral sites, which can facilitate fast electrochemical reaction of active material and enhance rapid electron transportation from electrode material to the current collector. On the other hand, the loose hollow microspheres structure of Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ contribute to improving electrochemical behavior, which provide more pathways for charge transfer in electrolyte. This is beneficial to obtain a better supercapacitor electrode material.

EIS measurements were carried out in the frequency range from 0.01 Hz to 100 kHz. Fig.9 shows Nyquist spectra and the inset shows the enlarged high frequency region of the spectra and the equivalent circuit for ZCMO samples. The Nyquist plots of the impedance spectra are clearly similar in shapes, which indicating the existence of equivalent diffusion ability for ZnMn$_2$O$_4$ samples. All the impedance curves composed of one semi-arc at the high frequency region and almost similar straight line at the low frequency region.

The equivalent circuit as shown in Fig. 9, including the solution resistance ($R_s$), charge-transfer resistance ($R_{ct}$), double layer capacitance(Cdl), pseudo capacitance ($C_p$) and Warburg impedance (W). The inset of Fig. 9 shows the spectra at the high frequency region, where the diameter of the semicircle indicates the charge-transfer resistance at the electrode-electrolyte interface ($R_{ct}$). The slope of the straight line at low frequency represents the Warburg impedance (W) for the diffusion of the electrolyte ions into the electrode, which the higher is the slope the easier is the ion diffusion process. The $R_{ct}$ for ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5 samples are 0.59 Ω, 0.67 Ω, 0.86 Ω, 0.79 Ω. The diameters of the semicircle for all ZCMO samples are found to be very small (inset of Fig. 9), indicating the $R_{ct}$ value is small, and the electrode possess better electrical conductivity. These findings reveal that the faradic reaction is easy to proceed with a high reversibility, and ZCMO samples
materials would be suitable for used as electrodes due to super capacitor with good frequency response characteristics. The phase angle of Nyquist spectra for all ZCMO samples in the mid frequency region are observed to be higher than 45º as seen from the inset to Fig. 9, indicating an important capacitive behavior for ZCMO samples.

Moreover, the resistance \(Z_w\) value of ZCMO-0 is larger than that of ZCMO-1, ZCMO-3 and ZCMO-5 sample, demonstrating the lowest impedance caused by the ion diffusion within the electroactive materials. In addition, the intersection of the plot at the x-axis represents represents the internal resistance \(R_s\), including the ionic resistance of the electrolyte, the intrinsic resistance of electrode materials and the contact resistance at the electrode-electrolyte interface. It can be seen that the \(R_s\) for ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5 samples about 3.37, 3.39\(\Omega\), 3.35\(\Omega\) and 3.40\(\Omega\), respectively. The \(R_s\) value for ZCMO-3 sample is the lowest, suggesting ZCMO-3 sample exhibits rapid electron transfer and optimal conductivity, as well as excellent specific capacitance.

4. Conclusions

We successfully synthesized Co-doped ZnMn_2O_4 as electrode materials in supercapacitors via a facile hydrothermal method. All samples exhibit single-phase spinel tetragonal with well crystallization, and the morphologies are loose hollow microspheres structure. The CV curves are similar to rectangular shape without significant redox peaks. ZCMO-3 electrode exhibits better specific capacitance and excellent cyclic stability, and keeps 98.2% of its initial capacitance after 1000 cycles. The electrochemical impedance spectroscopy with lower resistance reveals doped ZCMO samples exhibits ideal electron conductivity. The excellent electrochemical behavior of ZCMO-3 is superior to other ZCMO electrode materials ascribed to the synergistic effect. All these results demonstrate that Co-doped spinel ZnMn_2O_4 microspheres are a meaningful choice for the further enhancement of capacitive performance for supercapacitors application.
Acknowledgements

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References


**Figure captions**

Fig.1 XRD patterns of Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ (x=0, 0.1, 0.3 and 0.5) samples

Fig.2 FESEM images of (a) ZCMO-0 and (b) ZCMO-3 samples

Fig.3 EDS patterns of (a) ZCMO-0 and (b) ZCMO-3 samples

Fig.4 Element scan mapping patterns of ZCMO-3 samples

Fig.5 CV curves of (a) ZCMO-0, (b) ZCMO-1, (c) ZCMO-3 and (d) ZCMO-5 samples at different scan rates of 5-100 mV/s

Fig.6 (a) Variations in the specific capacitance of samples at different scan rates derived from CV, (b) CV curves of ZCMO samples at scan rate of 5mV/s

Fig.7 Galvanostatic charge-discharge curves of (a) ZCMO-0, (b) ZCMO-1, (c) ZCMO-3 and (d) ZCMO-5 samples at different current from 0.25 to 3.5A/g, (e) ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5 samples at the current densities of 2.5A/g, (f) Variations in the specific capacitance of samples at different current

Fig.8 Cycle stability of ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5 samples at current density of 2.5A/g over 1000 cycles

Fig.9 Nyquist plots of ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5 samples and its equivalent circuit model.
Fig. 1 XRD patterns of Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ (x=0, 0.1, 0.3 and 0.5) samples
Fig. 2 FESEM images of (a) ZCMO-0 and (b) ZCMO-3 samples
Fig. 3 EDS patterns of (a) ZCMO-0 and (b) ZCMO-3 samples

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Fig8 Cycle stability of ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5 samples at current density of 2.5A/g over 1000 cycles
Fig. 9 Nyquist plots of ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5 samples and its equivalent circuit model.

(The inset shows the high frequency portion of the Nyquist plots of ZCMO-0, ZCMO-1, ZCMO-3 and ZCMO-5 samples.)
Table Captions

Table1 XRD result of Zn$_{1-x}$Co$_x$Mn$_2$O$_4$ (x=0, 0.1, 0.3 and 0.5) samples

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