Visualization electrochromic-supercapacitor device based on porous Co doped NiO films

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1. Introduction

With the development of sustainable resources, the devices toward energy storage and conversion such as solar cell, supercapacitor and electrochromic smart windows have attracted increasing attention [1–3]. Electrochromic smart windows can change the color by reversible ion insertion/extraction under low voltages [4,5]. Supercapacitors, also known as electrochemical capacitors or ultracapacitors, store energy through reversible adsorption of electrolyte ions or redox reactions [6,7]. Thus, the electrochromic smart windows and supercapacitors have similar working mechanism and device structure. Since Wei’s group [8] successfully synthesized vanadium pentoxide network as an electrochromic supercapacitor material, the door of electrochromic-supercapacitor (ESC) was opened up due to its integrated characteristics of energy storage and electrochromism, which allowed the visualization of the charge state of the ESCs device through the color saturation degree [9–11].

Nowadays, studies on ESC are not limited to single electrode materials, but gradually turn to ESCs devices. For instance, Jia’s group [12] constructed asymmetry ESC (AESC) device using NiO/PB and WO3, which exhibited excellent electrochromic and energy storage performance. Wang’s group [13] used poly(indole-6-carboxylicacid) (PICA)/TiO2 as AESCs anode material to realize intelligent energy storage. Feng’s group [14] reported a kind of AESCs composed of viologen and EG/V2O5 hybrid nanopaper with high volumetric capacitance and ultra-fast responsive. However, in order to achieve the color change, numerous reports apply a negative voltage to the ESC devices, which limits the intelligence in the practical application. Moreover, most of the previous studies usually have a small potential window, which leads to the low current density of the ESC device. Therefore, structure design is significant to obtain a smart AESC with high performance. NiO, one of the most promising inorganic ESC material, has attracted tremendous attention due to its high theoretical specific capacitance, high transmittance modulation and low cost [15,16]. It has been report that porous NiO has significantly improved electrochromic [17] and electrochemical performance [18]. In addition, Co doping can enhance the conductivity of NiO, which is beneficial to improve the energy density [19] and electrochromic [20] performance. While there are few studies on the porous and Co doped NiO for ESC devices.

Based on the considerations mentioned above, porous Co doped NiO nanosheet growing on fluorine-doped tin oxide (FTO) glass was successfully prepared and worked as positive electrode material of the AESC devices. Fe3O4 electrode and KOH soaked white nylon membrane were used as the negative electrode and electrolyte and separator, respectively. The constructed AESC devices possess a wide
2. Experiment

2.1. Construction of the asymmetrical electrochromic-supercapacitor device

Scheme 1 illustrates the basic steps in preparing the asymmetrical electrochromic-supercapacitor (AESC) device. The Co doped NiO compound film was grown on FTO glass by simple hydrothermal and annealed. Before deposition the FTO was washed with de-ionized water, acetone, ethanol and dried at 60 °C for 2 h, then treated by plasma for 5 min under air atmosphere. The sample was prepared as follow: different weight ratio of nickel nitrate and cobalt nitrate (the weight percentage of Co is 0%, 3%, 5% and 7%) were dissolved in methanol stir 1 h, 0.6 g 2-methyl-imidazole was dissolved in 15 ml methanol solution stir 1 h, and then the two solutions were mixed. After that, the cleaned FTO was vertically into a Teflon-lined stainless-steel autoclave and added the mixed solution, subsequently sealed the vessel and heated at 120 °C for 4 h. The FTO-coated sample was wash with de-ionized water, dried in air and annealed at 300 °C in air for 2 h. The prepared films were denoted as NiO, NiO-Co3, NiO-Co5, NiO-Co7, respectively.

The Fe2O3 film electrode were synthesis according to the previous reports [21]. FeCl3.6H2O and NaNO3 were dissolved in de-ionized water stir 1 h, and then transferred to a Teflon-lined stainless-steel autoclave and added a cleaned FTO, subsequently sealed the vessel and heated at 95 °C for 10 h. The FTO-coated sample was wash with de-ionized water, dried in air and annealed at 500 °C in air for 2 h.

The AESC was assembled by Co doped NiO electrode and Fe2O3 electrode as asymmetric electrodes. To obtain better AESC device performance, the areal ratio of the Co doped NiO electrode and Fe2O3 electrode according to the charge balance. The charge equation can be expressed as follow [22]:

\[ q = C \times \Delta E \times S \]  

(1)

where q is the stored charges in the electrodes, C (mFcm⁻²) is the areal capacitance, \( \Delta E \) represents the potential windows, S is the areal of the electrode [22] :

\[ \frac{S_C}{S_E} = \frac{C_C}{C_E} \times \frac{\Delta E_C}{\Delta E_E} \]  

(2)

Subsequently, the nylon membrane soaked in 1 M KOH as electrolyte and separator at the same time. Finally, the device was sealed with UV curing adhesive.

3. Characterization

The phase compositions of the samples were detected by X-ray diffractometer (XRD, Japan Rigaku). The morphology and structure were characterized by scanning electron microscopy (SEM, Zeiss), transmission electron microscopy (TEM, JEOL 2010), high-resolution transmission electron microscopy (HRTEM, JEOL 2010) and selected area electron diffraction (SAED, JEOL 2010). X-ray photoelectron spectroscopy (XPS Thermo Fisher, E. Grinstead, UK) was recorded using Al Ka irradiation as the excitation source. The N2 adsorption/desorption were conducted on Brunauer–Emmett–Teller (Quantachrome Nova 2200) measurements. CHI 660E Autolab electrochemical workstation was used for electrochemical analysis. The prepared Co doped NiO film electrode (work electrode) in a three electrode configuration Pt foil, Hg/HgO and 1 M KOH served as the counter electrode, reference electrode and electrolyte, respectively. The electrochromic performance were tested by an Ocean Optics (MAYA 2000-Pro) spectrometer and CHI 660E.

4. Result and discussion

The crystallographic structure of the powders scratched from the as prepared films was carried out by XRD measurement. The diffraction peaks (Fig. 1) in all the patterns are mainly assigned to NiO (JCPDS No. 47-1049) and no cobalt oxides or other impurities peak was detected, this demonstrates that Co doping cannot alter the phase of original NiO structure.

In order to confirm the optimum doping Co content, galvanostatic charge/discharge (GCD) test (in 1 M KOH solution at different current density with potential range of 0–0.65 V versus Hg/HgO) and in-situ transmittance (in 1 M KOH solution under an applied potential of 0.3 and 0.7 V, respectively) were carried out. As shown in

![Fig. 1. XRD pattern of Co doped NiO.](image-url)
Fig. S1. NiO-Co film delivers higher areal capacitance than other samples. The areal specific capacitance of NiO-Co film are calculated to be 88.24, 83.03, 79.09, 76 and 55.53 mF cm$^{-2}$ at current density of 0.4, 0.6, 0.8, 1 and 2 mA cm$^{-2}$, respectively. Fig. S2 reports the transmittance spectra of Co doped NiO film in the wavelength range from 300 to 1100 nm. In the short wavelength, the transmittance modulation ($\Delta T$=Tb−Tc, where Tb and Tc are the transmittances of bleached and colored states, respectively) of NiO is higher than Co doped NiO and in the long wavelength, $\Delta T$ of Co doped NiO exceeding the pure NiO and NiO-Co possess the higher $\Delta T$. Based on the above results, NiO-Co and NiO were further characterized and discussed.

Fig. 2(a) illustrates the morphology of NiO-Co$_5$ growing on the FTO substrate, its displays an interconnected nanosheets structure and the thickness of nanosheets is less than 10 nm. The thickness of the NiO-Co$_5$ film is about 1 μm, which was verified by the cross-sectional SEM image (Fig. 2b). As indicating in Fig. 2(c) the mapping image suggested the film is homogeneously distributed of Co, Ni, O elements, that evidence the film containing cobalt-nickel composite. The morphology of NiO was similar to that of NiO-Co$_5$ as shown in Fig. S3(a) and (b). The surface compositions and chemical states of the NiO-Co$_5$ films were examined by XPS. Fig. 2(d) shows full range XPS spectrum. The Co 2p characteristic peaks are tested in the insert Fig. 2(d), the two peaks at 774.5 eV and 779.8 eV corresponding to the Co 2p$_{3/2}$ and 794.8 eV can be ascribed to Co 2p$_{1/2}$ [23,24], indicating the existence of Co$_2$O$_3$ in the NiO-Co$_5$ film [25]. Fig. 2(e) shows the high resolution XPS spectra of Ni, the two peaks at 853.7 eV and 855.4 eV corresponding to the Ni$^{2+}$ and Ni$^{3+}$, respectively [26].

To further investigate the morphology and the microstructure of the NiO-Co$_5$ film, TEM test was employed. As shown in Fig. 3(a), the sample shows sheet-like morphology and the deep black parts suggest the interconnected features of the sample, which is good consistent with the SEM results. In the insert of Fig. 3(a), the mesoporous structures with pore size of 3–8 nm is observed. HRTEM images shows the porous NiO-Co$_5$ nanosheets (Fig. 3b) fringe spacing of 0.256 nm larger than NiO (0.249 nm, Supporting information Fig. S4a), corresponding to the (111) plane spacing of cubic NiO. The SAED pattern (Fig. 3b, insert) demonstrates the polycrystalline nature of NiO and the diffraction rings corresponding to (111), (200), and (220), respectively, which is agreement with the XRD results. To estimate the surface area and porosity property of the NiO-Co$_5$, N$_2$-adsorption/desorption was performed. As shown in Fig. 2(c), N$_2$-adsorption/desorption curves can be assigned to IV type isotherm. The measured BET specific surface of NiO-Co$_5$ was 173 m$^2$ g$^{-1}$, which is larger than that of NiO (105 m$^2$ g$^{-1}$, based on Fig. S4b). In addition, the pore size of the NiO-Co$_5$ is about 5–10 nm in diameter (Fig. 3d), identify with the TEM observation. Such large planer spacing, porosity and high surface area facility for ion and electronic transmission channel and enable the achievement of high electrochemical and electrochromic performance [27]. In the following, the electrochromic and electrochemical performance of NiO-Co$_5$ were further investigated.

In order to evaluate the charge storage level of NiO-Co$_5$ film, cyclic voltammetry (CV) was performed. Fig. 4(a) shows the typical CV curves of NiO-Co$_5$ film at different scan rates from 1 to 20 mV s$^{-1}$ with a potential range of 0~0.8 V (vs. SCE) in 1 M KOH. As shown in the CV curve, the film shows a pair of redox peaks for the different scan rate corresponding to the Faradaic redox reaction of Ni$^{2+}$. 

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Fig. 2. Characterizations of the NiO-Co$_5$ film (a) SEM image; (b) cross-sectional SEM image; (c) Elemental mapping of Co, Ni, O; (d) XPS survey spectrum and Co 2p (insert d) and O 1s (e).
With the scan rate increases, both redox peaks shift more negative and more positive direction may due to the polarization effect of the electrode [28]. To further investigation the electrochemical performance of the NiO-Co₅ film, galvanostatic charge-discharge (GCD) was executed in 1 M KOH solution at different current density with potential range of 0 ~ 0.65 V. All GCD curves presented excellent symmetry indicated the high electrochemical reversibility [29].

**Fig. 3.** (a) TEM image (inset: corresponding magnified image) and (b) high-resolution TEM image (SAED pattern in the insert b) of NiO-Co₅; (c) Nitrogen adsorption-desorption isotherms and corresponding the pore size distributions (d) of NiO-Co₅.

**Fig. 4.** Electrochemical and electrochromic performance of the NiO-Co₅ film: (a) Cyclic voltammetry curves; (b) the galvanostatic discharge-charge curves; (c) Nyquist plots of EIS; (d) Cycle stability; (e) Transmittance spectra; (f) the switching response curves. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article)
EIS was carried out to evaluate the resistive of NiO-Co film with a frequency range of 100 kHz to 0.01 Hz. As shown in Fig. 4(c), the intercept of the semicircle with the real axis indicate the equivalent series resistance (Rs), the Rs value was 7.25 Ω means low internal resistance of the electrode and the small semicircle diameter in the high frequency region indicates a low charge-transfer resistance (Rct) on the electrode/electrolyte interface. The stability is also an important factor for supercapacitor, stability of NiO-Co film was evaluated by GCD cycle at current density of 0.8 mA cm$^{-2}$, as shown in Fig. 4(d), the NiO-Co electrode retains 100% of the initial capacitance after 10,000 cycles.

The transmittance modulation range of NiO-Co film at 630 nm is 52% (Fig. 4(e)) and the color of NiO-Co films change from brown (colored) to yellow (bleached), as shown in insert Fig. 4(e). The response time is also an important parameter that determines the electrochromic performance which is defined as require the time to up to 90% of the total ΔT. Switching phenomenon was conducted by monitoring the transmittance at 633 nm under the application of a square wave voltage between 0 and 0.7 V vs Hg/HgO. The response time of NiO-Co for coloration and bleaching are 5.9 s and 7.1 s at 633 nm, respectively (Fig. 4f).

To evaluate the practical application of supercapacitor is composed of NiO-Co electrode, an AESC device was fabricated and the electrode was determined by the charge balance (according to Eqs. 1 and 2). Before the assembly, CV curves of the NiO-Co and Fe$_2$O$_3$ electrode were measured in a three electrode system with scan rate of 5 mV s$^{-1}$ in 1 M KOH to estimate their operating potential windows. As shown in Fig. 5(a), the working potential windows of Fe$_2$O$_3$ and NiO-Co were −1.0 V and 0.0 to 0.8 V vs Hg/HgO, respectively. The CV curves of the AESC device at a scan rate of 5 mV s$^{-1}$ testify that the operation potential can reach 1.8 V (Fig. 5b), the AESC operating potential windows is decided by the sum of the Fe$_2$O$_3$ and NiO-Co operating potential windows, this is consist with the literature reports [30].

The electrochemical performance of NiO-Co/Fe$_2$O$_3$ AESCs was evaluated by CV and GCD tests. Fig. 5(c) shows the CV curves of the AESC device at different scan rate from 5 to 100 mV s$^{-1}$. All the curves show a pair of redox peaks, indicating typical Faradaic redox reactions for pseudocapacitive behavior. The GCD curves (Fig. 5d) with different current density were similar in shape, indicating that NiO-Co/Fe$_2$O$_3$ AESCs can work stably. During the discharge, the GCD curves were approximately triangular revealed the pseudocapacitive characteristics. The Cs of the AESC was 10.8 mF cm$^{-2}$ at a current density of 0.4 mA cm$^{-2}$ (Fig. 5e), the energy density and the average power density of the device are calculated to be 3.84 × 10$^{-3}$ mW h cm$^{-2}$ and 0.10 mW cm$^{-2}$, respectively. The AESCs stability was examined by GCD tests at current density of 0.8 mA cm$^{-2}$, after 2000 charge/discharge cycle, the AESC retained 84.5% of its initial capacitance.

In order to prove the intelligent, the energy storage states were directly reflected by color change. As shown in Fig. 6(a), the AESC...
device exhibits ‘yellow→light brown→brown→dark brown’ as voltage increase from 0 to 1.8 V. When discharging, the color of the device changes from dark brown to yellow. Moreover, two series AESC devices can light up two red LED (Fig. 6b), and with the output of the AESC devices, the AESC device color becomes shallow (Fig. 6c), the details process shows in Video S1. These results suggest the AESCs device with smart features.

5. Conclusion

In this work, an AESC device based on porous Co doped NiO film as positive electrode was designed and fabricated, which exhibits a large potential window of 1.8 V. The AESC device has high areal specific capacitance, high energy density and excellent cycle stability. For the practical application, the device is able to light up LED and monitoring the energy storage state through color change. It can potentially be used for application in smart electronics.

CRediT authorship contribution statement

Junying Xue: Conceptualization, Methodology, Software, Writing – original draft. Zhang Xiang: Grammar check of revised draft. Li Wenjie: Validation, Formal analysis, Data Curation. Ying Song: Writing – review & editing. Zhao Jiupeng: Supervision, Project administration, Writing – review & editing. Li Yao: Funding acquisition, Project administration, Software.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2020.158087.

References