Advanced Materials Research Vol. 1133 (2016) pp 447-451
© (2016) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/AMR.1133.447

Submitted: 2015-02-24
Revised: 2015-03-16
Accepted: 2015-09-23
Online: 2016-01-04

Optical and Electrochemical Properties of Co_3O_4/SiO_2 Nanocomposite

GOMAA A. M. Ali[1,2,a], OSAMA A. Fouad[3,b], SALAH A. Makhlouf[4,5,c], MASHITAH M. Yusoff[1,d], KWOK Feng Chong[1,e*]

[1] Faculty of Industrial Science and Technology, University Malaysia Pahang (UMP), 26300, Kuantan, Pahang, Malaysia

[2] Chemistry Department, Faculty of Science, Al–Azhar University, Assiut branch, Assiut 71524, Egypt

[3] Central Metallurgical Research and Development Institute, CMRDI, P.O. Box 87, Helwan 11421, Egypt

[4] Physics Department, Faculty of Science, Assiut University, Assiut 71516, Egypt

[5] Deanship of Scientific Research, Al Imam Mohammad Ibn Saud Islamic University (IMSIU), Riyadh, 11463, Saudi Arabia

[a] gomaasanad@azhar.edu.eg, [b] oafouad@yahoo.com, [c] smakhlouf@gmail.com, [d] mashitah@ump.edu.my, [e] ckfeng@ump.edu.my

Keywords: Co_3O_4/SiO_2, nanocomposites, citrate–gel, optical, pseudocapacitance

Abstract. Co_3O_4/SiO_2 nanocomposite was obtained via citrate–gel method. 22 nm in size of Co_3O_4 particles in an amorphous SiO_2 matrix were obtained. Co_3O_4:SiO_2 wt. ratio was verified using EDX and found to be close to the 80 % nominal ratio. The UV–Vis measurement showed broad absorption bands at around 440 and 790 nm. The optical band gap values were 1.95 and 1.35 eV respectively, being close to those observed for pure Co_3O_4 nanoparticles. The electrochemical measurements in 5 M KOH solution were performed using a three–electrode type system. Co_3O_4/SiO_2 nanocomposite exhibited high specific capacitance reaching 758 Fg^{-1} at 2.5 mVs^{-1}. Very small solution and electrode–electrolyte interfacial charge transfer resistances were obtained when impedance spectra were analysed.

Introduction

Pseudocapacitors possess high capacitances because they can store charge via electron transfer reactions that produce chemical or oxidation state changes in these electroactive materials. On the other hand, electro double layer capacitors (EDLCs) store charge in its electrical double layer due to electrostatic charge separation between electrolyte ions and electrodes [1]. Transition metal oxides (TMO) having different oxidation states are suitable candidates for pseudocapacitance applications. TMO such as MnO_2, NiO, CuO, Fe_2O_3 and Co_3O_4 [2–5] are particularly favored for supercapacitance applications due to their cost reduction over noble metal oxides such as RuO_2. Among all TMO, Co_3O_4 is a promising electrode material for pseudocapacitance applications due to its environmental friendliness, easy preparation, very high theoretical specific capacitance (3560 Fg^{-1}), high surface area, good redox, easily tunable surface and structural properties [6]. Many methods have been reported for preparation of Co_3O_4 such as template–free growth method, facile homogeneous precipitation process under hydrothermal conditions and chemical deposition [4, 7, 8]. Coating nanoparticles with SiO_2 was found to enhance their specific capacitance and energy density, improving their electrochemical capacitance properties [9]. Co_3O_4/SiO_2 nanocomposites have been prepared by different methods such as sol–gel, citrate–gel, facile solvothermal route and chemical vapor deposition, showing a porous structure and rather narrow size distribution of highly dispersed Co_3O_4 [5, 10–14].

In this work Co_3O_4/SiO_2 nanocomposite has been prepared by citrate–gel method and was characterized by X–ray diffraction (XRD), Fourier Transform Infra–Red (FTIR) and Energy Dispersive X–ray (EDX) techniques. The optical band gaps have been calculated from UV–Vis absorption data. The electrochemical properties have been tested, analyzed and discussed in view of morphological and structural properties of the prepared nanocomposite.

Experimental

Co_3O_3/SiO_2 nanocomposite has been synthesized via citrate–gel method. The cobalt chloride, TEOS, and citric acid were dissolved in absolute ethanol. The three solutions were dispersed ultrasonically for 30 minutes. The method is mainly similar to that described in our recent published work [5, 12]. Here, Co_3O_3:SiO_2 nominal weight ratio was 80 wt. %, and was verified by EDX analysis to be 82 %. Phase identification, purity, crystallinity and crystallite size of the product were studied using a Philips PW1700 diffractometer using Cu–K_α radiation (λ = 0.15418 nm) and a graphite monochromator in the 2θ range from 10 to 80°. The optical absorption spectra were measured in the wavelength range of 200–900 nm using a spectrophotometer UV–VIS Lambda 750. Measurements were made for a suspended solution of about 1 mg in 10 ml absolute ethanol in a special quartz cell. Infrared spectra were measured in the range 4000–400 cm^{-1} using an FTIR spectrometer (JASCO–480 Plus, Japan). The electrode preparation and electrochemical testing were explained in details elsewhere [5].

Results and Discussion

Crystal structure and phase analysis. Fig. 1 shows the XRD pattern for Co_3O_4/SiO_2 sample. All diffraction peaks were assigned to Co_3O_4 phase (ICDD card # 00–009–0418), indicating the formation of a pure crystalline Co_3O_4 particles in an amorphous SiO_2 matrix. The apparent crystallite size (P_S) of the Co_3O_4 particles was estimated by the Scherrer's formula to be 22 nm, with a lattice constant (a) of 0.811 nm and a unit cell volume (V) of 0.533 nm^3.

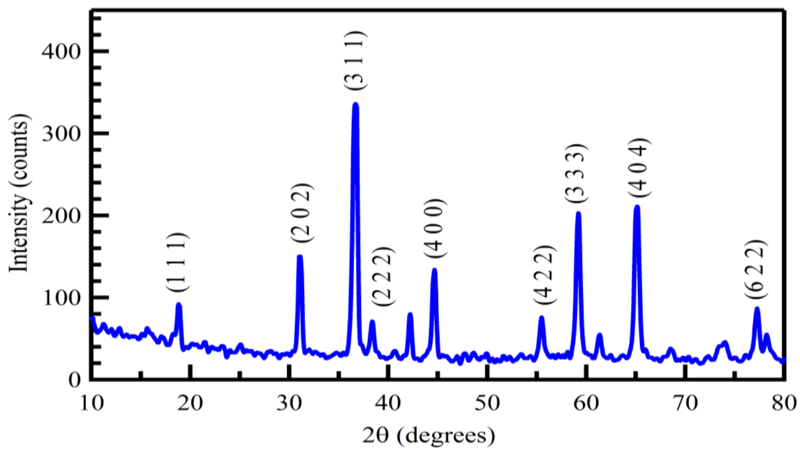

Fig. 1: XRD pattern of Co_3O_4/SiO_2.

FTIR and UV–Vis spectra. Further information about the chemical structure was obtained from FTIR data presented in Fig. 2(a). The bands at 460 and 1090 cm^{-1} can be assigned to the asymmetric stretching vibration of the bond Si–O–Si in the SiO_4 tetrahedron [8]. The weak intensity band at 840 cm^{-1} was attributed to stretching of non–bridging oxygen atoms in Si–OH bond [10]. The absorption band at 660 cm^{-1} related to the vibrations of Co(III)–O bonds in Co_3O_4 is observed. This band was assigned to the Co–O stretching in Si–O–Co network. The band at 560 cm^{-1} that was also associated with the Co–O stretching is found [10]. Fig. 2(b) shows the optical absorption spectrum of Co_3O_4/SiO_2 nanocomposite. It exhibits broad absorption bands at around 450 and 790 nm which characterisethe ligand to metal transfer transition of $(O^{-2} \rightarrow Co^{+3})$ and $(O^{-2} \rightarrow Co^{+2})$, respectively. The absorption band gap (E_g) can be obtained using the following eq. $(\alpha h\nu)^n = \beta(h\nu - E_g)$ where, $h\nu$ is the photon energy, β is a constant relative to the material, E_g is the energy band gap, α is the absorption coefficient and the exponent n take different values depending on electronic transition types [11]. Extrapolation of the linear portions to zero absorption coefficients gives the values of the optical energy gaps as shown in the inset of Fig. 2 (b). The energy gaps were found to be 1.95 and 1.35 eV suggesting direct allowed transitions, being consistent with the Co_3O_4 band structure. The energy gap values for this nanocomposite are higher than those obtained for the same samples with lower cobalt content [11], and were ascribed to the lower particle sizes of the latter [1]. Solar cells, electrochromic devices and optical gas sensors are among the potential applications of this material.

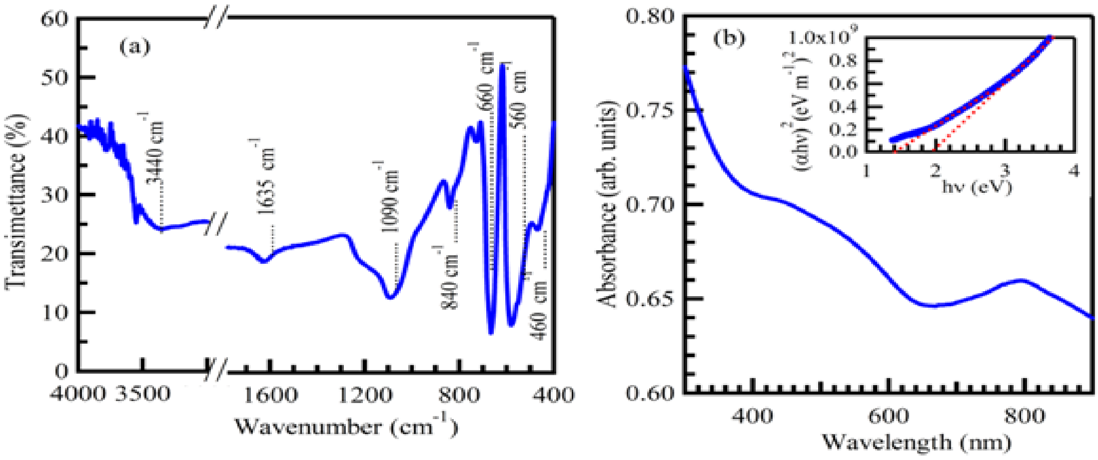

Fig. 2: FTIR (b) and UV–Vis (a) spectra, the inset shows $(\alpha h\nu)^2$ versus $h\nu$ curve of Co_3O_4/SiO_2.

Cyclic voltammetry (CV) measurements. Fig. 3(a) presents the CV curves of Co_3O_4/SiO_2 nanocomposite in the potential range of 0 to 0.60 V at different scan rates, showing nonrectangular CV shapes similar to those reported for pure Co_3O_4 [4]. Oxidation and reduction peaks were observed and ascribed to oxidation and reduction of cobalt (II, III) species. The redox reaction that occurs can be illustrated by the following equations [7, 8]:

$$Co_3O_4 + OH^- + H_2O = 3\,CoOOH + e^- \quad (1)$$

$$CoOOH + OH^- = CoO_2 + H_2O + e^- \quad (2)$$

These electrochemical charge transfer reactions occurred within Co_3O_4 support its potential use for pseudocapacitance application [4, 8], indicating that the capacitance is mainly based on the redox mechanism. In addition, both anodic and cathodic peak potentials are slightly shifted to more anodic and cathodic directions on account for the polarization in the electrode material. The specific capacitance (C_s) was calculated by integrating the area under the CV curve [5]. The C_s was found to be 758 Fg^{-1} at 2.5 mVs^{-1} and it decreases with increasing the scan rate (see Fig. 3(b)). The present C_s is higher than that reported for pure Co_3O_4 (742.5 Fg^{-1}) [6]. The results can be understood in terms of the lower particles size and high dispersion of Co_3O_4 particles in SiO_2 matrix [10–12].

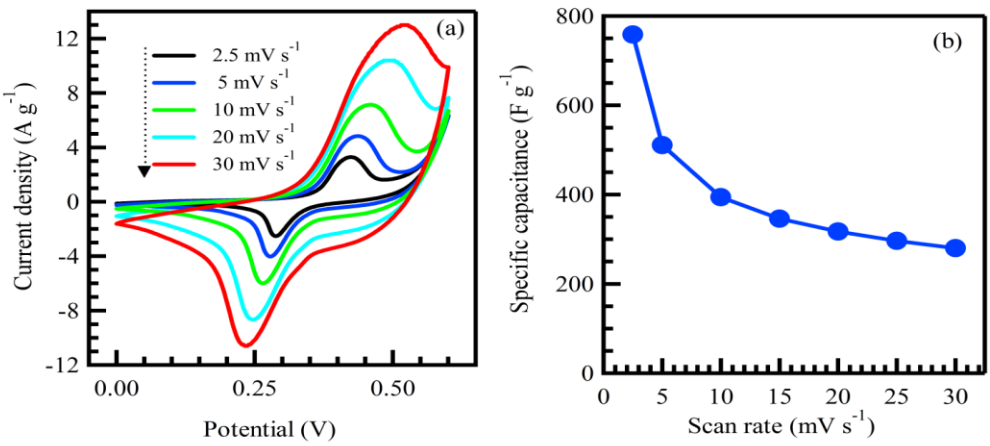

Fig. 3: CV curves at different scan rates (a) and specific capacitance (b) as a function of scan rate of Co_3O_4/SiO_2.

Galvanostatic charge–discharge (GCD). Fig. 4(a) shows the GCD curves for the nanocomposite at indicated discharge current densities. The nonlinearity in the discharge curves suggests pseudocapacitance behavior of Co_3O_4 resulting from the electrochemical adsorption–desorption or redox reaction at the electrode–electrolyte interface. The data shows an almost neglected iR drop. C_s of the nanocomposite electrode was also calculated and found to be 623 and 460 Fg^{-1} at current densities of 0.5 and 1 Ag^{-1}, respectively (see Fig. 4(b)). These results are much higher than those reported for Co_3O_4 nanowires (336 Fg^{-1} at 1 Ag^{-1}) [1] and layered parallel folding structure of mesoporous Co_3O_4 (202.5 Fg^{-1} at 1 Ag^{-1}) [8]. The higher values of C_s of the present sample result from the smaller crystallite size and more accessible surface sites.

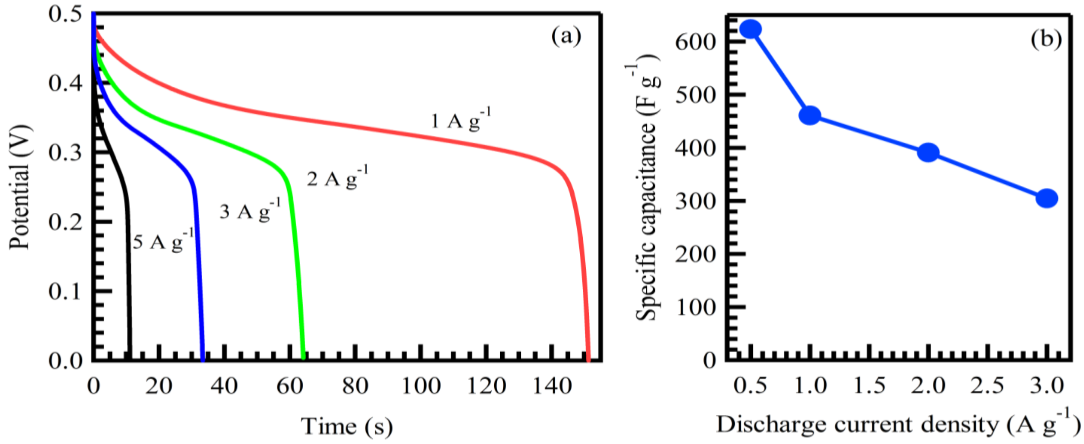

Fig. 4: GCD curves (a) at the indicated current densities, and specific capacitance (b) as a function of discharge current density of Co_3O_4/SiO_2.

Electrochemical impedance spectroscopy (EIS). EIS were collected to gain more information about capacitive behavior. Fig. 5 shows the *Nyquist* plot for Co_3O_4/SiO_2 nanocomposite, the inset is the expanded high frequency region. The equivalent circuit is composed of a solution resistor (R_s), an electrode–electrolyte interfacial charge transfer resistor (R_{ct}), a double layer capacitor (C_{dl}), a Warburg diffusion element (W), and a faradic pseudocapacitor (C_{ps}). C_{dl} and C_{ps} were found to be 0.27 and 19.76 mF, respectively. Very small R_s of 0.28 and R_{ct} of 0.57 Ω were obtained indicating good conductivity and consequently good electrochemical performance of this material.

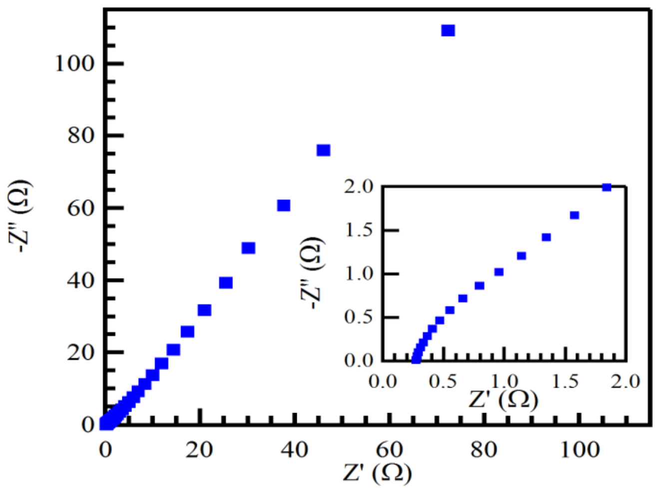

Fig. 5: *Nyquist* plot, the inset is the expansion of the high frequency region of Co_3O_4/SiO_2.

Summary

Well crystalline and highly dispersed Co_3O_4 particles in an amorphous SiO_2 matrix were prepared successfully via citrate–gel method. The XRD particle size of Co_3O_4 was 22 nm. The optical band gaps obtained from UV–Vis measurements were 1.95 and 1.35 eV. Co_3O_4/SiO_2 nanocomposite shows high specific capacitances of 758 and 623 F g^{-1} at a scan rate of 2.5 mV s^{-1} and a current density of 0.5 A g^{-1} in 5 M KOH, respectively. Impedance measurements show very small resistances indicating good electrochemical performance.

Acknowledgement

The funding from the Ministry of Education Malaysia in the form of MTUN–COE grant RDU121212 and RDU121213.

References

[1] S.K. Meher, G.R. Rao, Effect of microwave on the nanowire morphology, optical, magnetic, and pseudocapacitance behavior of Co_3O_4, J. Phys. Chem. C 115 (2011) 25543–25556.

[2] C.D. Lokhande, D.P. Dubal, O.S. Joo, Metal oxide thin film based supercapacitors, Curr. Appl Phys. 11 (2011) 255–270.

[3] G.A.M. Ali, L.L. Tan, R. Jose, M.M. Yusoff, K.F. Chong, Electrochemical performance studies of MnO_2 nanoflowers recovered from spent battery, Mater. Res. Bull. 60 (2014) 5–9.

[4] J. Xu, L. Gao, J. Cao, W. Wang, Z. Chen, Preparation and electrochemical capacitance of cobalt oxide (Co_3O_4) nanotubes as supercapacitor material, Electrochimica Acta. 56 (2010) 732–736.

[5] G.A.M. Ali, O.A. Fouad, S.A. Makhlouf, M.M. Yusoff, K.F. Chong, Co_3O_4/SiO_2 nanocomposites for supercapacitor application, J. Solid State Electrochem. 18(9) (2014) 2505–2512.

[6] X. Wang, A. Sumboja, E. Khoo, C. Yan, P.S. Lee, Cryogel synthesis of hierarchical interconnected macro–/mesoporousCo_3O_4 with superb electrochemical energy storage, J. Phys. Chem. C 116 (2012) 4930−4935.

[7] Y. Li, K. Huang, Z. Yao, S. Liu, X. Qing, Co_3O_4 thin film prepared by a chemical bath deposition for electrochemical capacitors, Electrochim Acta. 56 (2011) 2140–2144.

[8] D. Wang, Q. Wang, T. Wang, Morphology–controllable synthesis of cobalt oxalates and their conversion to mesoporous Co_3O_4 nanostructures for application in supercapacitors, Inorg. Chem. 50 (2011) 6482–6492.

[9] K.C. Leonard, W.E. Suyama, M.A. Anderson, Improvement of electrochemical capacitor electrodes using SiO_2 nanoparticles, Electrochimica Acta. 56 (2011) 10137–10144.

[10] O.A. Fouad, S.A. Makhlouf, G.A.M. Ali, A.Y. El–Sayed, Cobalt/silica nanocomposite via thermal calcination–reduction of gel precursors, Mater. Chem. Phys. 128 (2011) 70–76.

[11] G.A.M. Ali, O.A. Fouad, S. A. Makhlouf, Structural, optical and electrical properties of sol–gel prepared mesoporous Co_3O_4/SiO_2 nanocomposites, J. Alloys Compd. 579 (2013) 606–611.

[12] O.A. Fouad, G.A.M. Ali, M.A.I. El–Erian, S.A. Makhlouf, Humidity sensing properties of cobalt oxide/silica nanocomposites prepared via sol–gel and related routes, Nano. 7 (2012) 1250038–1250049.

[13] R. Xie, D. Li, B. Hou, J. Wang, L. Jia, Y. Sun, Solvothermally derived Co_3O_4–SiO_2 nanocomposites for Fischer–Tropsch synthesis, Catal. Commun. 12 (2011) 380–383.

[14] L.B. Backmana, A. Rautiainen, M. Lindblad, O. Jylhä, A.O.I. Krause, Characterisation of Co/SiO_2 catalysts prepared from $Co(acac)_3$ by gas phase deposition, Appl. Catal. A 208 (2001) 223–234.