

Enhancement of specific capacitance using hematite nanoparticles produced by green synthesis

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Abstract

Current research on iron oxide nanoparticles (Fe_3O_4 -NPs) is extremely prolific because of their unique magnetic and electrical properties with a great application potential like in energy storage. The present paper describes green synthesis technique for the production of Fe_3O_4 NPs using aqueous olive leaf extract (OLE) as surfactant agent. Various characterization techniques were performed on those mesoporous Fe_3O_4 NPs such as Raman spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction. The results demonstrate the spindle like shaped of Fe_3O_4 NPs with average particle size around 50-70 nm. The electrochemical performances of pristine activated carbon AC and the AC/ Fe_3O_4 nanocomposite were compared in order to distinguish the added value of synthesized nanoparticles in energy storage. In comparison with pure AC electrode, AC/ Fe_3O_4 nanocomposite electrodes exhibits an enhanced specific capacitance with values up to 87 F/g.

Keywords: Olive leaves extract; AC/ Fe_3O_4 Nanoparticles; Supercapacitors; Nanostructured electrodes.

1. Introduction

Energy storage has drained huge attention of researchers for the development of new materials in the context of the global crisis of energy. Nanometric semiconductor metal-oxides have been considered an appropriate candidates for energy production and environmental issues. Hematite Fe_2O_3 , with a gap of 2.1 eV, is considered to be an appropriate candidate for batteries, catalysis and sensors, because of its chemical stability, widespread availability, and high photon absorption in the visible spectral range (40% of the sunlight) [1]. It may be also considered as a promising material for supercapacitors application [2]. A huge number of physical and chemical approaches have been used for the synthesis of nanostructured materials such as hydrothermal synthesis, sol-gel process, template assisted synthesis method[3]. However, a lot of difficulties and limitation where raised, when these methods involve high temperatures, special equipment or/and the use of toxic or expensive products. Furthermore, these methods usually implicate impurities incorporation that can limit the performances. The progress in green synthesis exploiting biological efficient entities as a reducer, copper and/or stabilizer agent without using expensive, toxic chemicals to reduce metal precursors has appealed many researchers. Various plant mediated metals and metal oxides nanoparticles have been synthesized by this way. The production of NPs in these bottom-up approach using natural products or theirs extracts such as fruits, leaves,

trees/crops is eco-friendly, less expensive, free of chemical contaminations and sustainable. Recently, Bashir Ahmmad et al [4] showed that green tea extract can be used to synthesize pure mesoporous Fe_3O_4 NPs with hydrothermal method. The mesoporous nanoparticles obtained were evaluated for photo-electrochemical cells [5]. Here, we are reporting a very simple green method using olive leaves extract (OLE) in order to prepare pure mesoporous hematite $\alpha\text{-Fe}_2\text{O}_3$. The material obtained was tested for the enhancement of the specific capacitance as an electrode material in two electrodes configuration.

2. Experimental procedure and material characterization

In a typical synthesis, new composite of iron hydroxide was prepared by a green method using: iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) as a source of iron (Sigma Aldrich), extract of olive leaves as surfactant and reducer with Milli-Q water as a solvent. Initially, fresh olive leaves, collected from local region in Constantine, Algeria, were cleaned with distilled water and then dried completely. Afterward, an infusion of these olive leaves was prepared by adding 0.5 g to half liter of Milli-Q water. The infusion was heated at 100 °C for 2 hours and then filtered to remove the leaf residuals. On the other hand, 0.6 M of Iron nitrate was vigorously mixed with 30 ml of this infusion which results is an orange solution. The mixture solution was transferred into a beaker with a capacity of 100 ml and placed in a reflux system under 70 °C for 3 h. The obtained solution

was dried at 100° C. The resultant product was washed with Milli-Q water and ethanol several times and then dried at ambient temperature. Finally, the powder was transferred into an oven for calcination at 400°C for 1 hour in ambient atmosphere.

The crystallographic characterization of the powder was performed with a Panalytical EMPYREAN X-ray diffractometer in configuration with a Cu K α X-ray source. The morphology of the obtained nanostructures was investigated by Field-Emission Scanning Electron Microscopy (FESEM Supra 40 manufactured by Zeiss, equipped with EDX Si(Li) detector manufactured by Oxford Instruments.) XPS analysis was performed with a PHI 5000 VersaProbe operating with Al K α monochromatic radiation. The calibration of the binding energy scale was performed by imposing a value of 530 eV to the main peak of the O1s region, in accordance with a previously published approach [6]. Data analysis was conducted with CasaXPS software. Raman spectrum was collected using Renishaw InVia Reflex micro-Raman spectrometer (Renishaw plc, Wotton-under-Edge, UK), equipped with a cooled CCD camera was used to, with a laser excitation wavelength of 514.5 nm and a laser spot size of 10 μ m.

The capacitive behavior of the electrodes fabricated using AC/Fe₂O₃ and gel polymer electrolyte (PVA+1M KOH, Sigma Aldrich) was determined by cyclic voltammetry measurements performed with a Metrohm Autolab PGSTAT128 potentiostat. AC/Fe₂O₃ composite active material (10wt% Fe₂O₃ upon AC) was deposited on Titanium foil. The gel polymer was prepared by dissolving 2 g of PVA in 10 mL of deionized water containing 1 M KOH. After 4 h onto a hot plate at 80 °C under rigorous stirring, the PVA completely dissolves in the solution, resulting in a viscous ionically conductive gel. The obtained electrodes is shown in figure 1.



Figure 1. Photograph of the two electrodes configuration made by AC/Fe₂O₃ on Titanium foil. The specific capacitances (C_{sp}) were calculated according to:

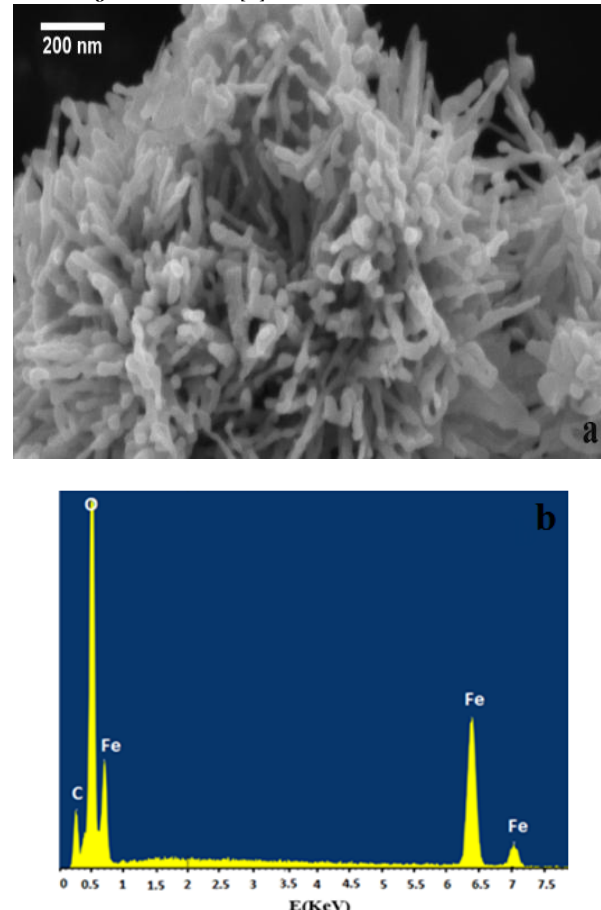
$$C_{cell} = \frac{Q}{2V} = \frac{1}{2V} \int_{-V}^{+V} i(V) dV \quad (1)$$

$$C_{sp} (F/g) = C_{cell} / m \quad (2)$$

Where I is the current, V is voltage window, v is the scan rate and m is mass of the electrodes.

3. Results and discussion

The Scanning Electron Microscopy images of hematite Fe₂O₃ nanoparticles on powder form calcined at 400°C for 1 hour are displayed in figure 2 (a). We can observe a well-defined spindle like shape nanostructures beside small spherical particles. Similar morphologies were observed by Samira Bagheri et al on hematite nanoparticles generated via Sol-Gel method [7]. The average particle size is around 40 nm. The composition of the prepared samples was confirmed by EDX spectrum showed in figure 2 (b). The EDX spectrum reveals only peaks of iron, oxygen and carbon. Carbon peak are consistent with residues from olive leaves extract. They can be reduced by increasing the temperature of calcination as it was confirmed by J. Sharmila Justus and al [8].



Figures 2. Hematite powder treated by calcination at 400°C for 1 h (a) Scanning Electron Microscopy image, (b) EDX spectrum.

The XRD pattern of Fe₂O₃ nanoparticles, shown in figure 3, was performed on the obtained powder. All the diffraction peaks can be indexed as hexagonal (rhombohedral) phase α -Fe₂O₃ (hematite, JCPDS No. 33.0664). All the expected peaks from the α -Fe₂O₃ structure are present in the pattern observed without any

detectable peak from impurities and/or other phases [9]. The strong and sharp peaks indicate that $\alpha\text{-Fe}_2\text{O}_3$ powder obtained is highly crystalline.

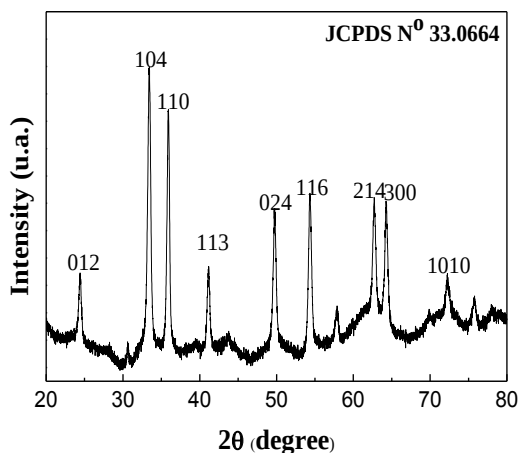


Figure 3. XRD pattern of hematite Fe_2O_3 nanoparticles.

Raman spectroscopy is often used to identify hematite iron oxide phases. Figure 4, shows the Raman spectrum of powder obtained after calcination at 400°C for 1 hour. All the Raman bands of crystalline hematite structure are present in the spectrum. Six Raman active bands from the seven lines predicted by group theory were observed with closely the same intensities, namely two A_{1g} modes (225.5 and 495.9 cm^{-1}) and four E_g modes (245.6 , 292.3 , 409.3 and 612.8 cm^{-1}) [10], the interaction between two magnons, created on sites close to spin anti-parallel of hematite, at 1319.2 cm^{-1} caused by two magnon scattering bands were observed and closely matched those in the hematite spectrum of Froment et al [11], Raman results is in good agreement with XRD observations.

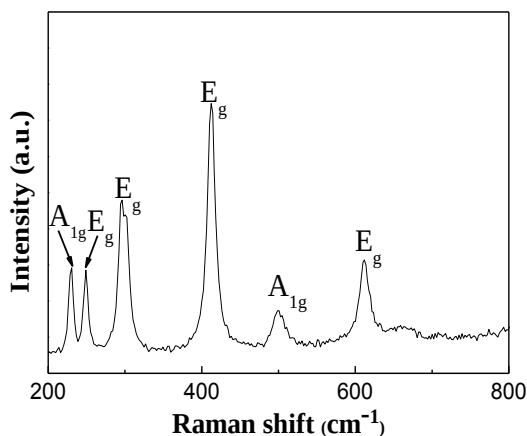
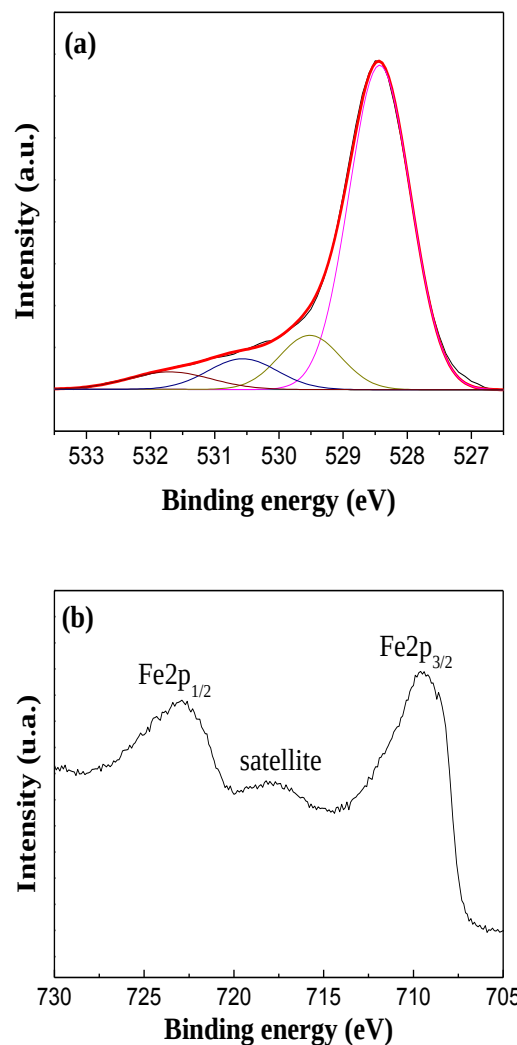


Figure 4. Raman spectrum of hematite Fe_2O_3 nanoparticles powder calcined at 400°C for 1 hour.

X-ray photoelectron spectroscopy (XPS) was performed to examine the coordination within nanocrystals and to confirm the chemical composition of the powder obtained. Figures 5 (a-b) shows the XPS signals of O1s and Fe2p curves of hematite respectively. The presence of Fe and O

in this spectrum is obvious, C1s peak can also be observed in the survey spectrum. The O1s is detected at 528.5 eV (Fig 5-a). It is known that the binding energy of O in crystal lattice is $528.5\sim 529.7\text{ eV}$ and the binding energy of absorbed oxygen is $530.5\sim 533.7\text{ eV}$. The binding energy of $\text{Fe}2p_{3/2}$ is at about 711.2 eV and the binding energy of $\text{Fe}2p_{1/2}$ is at about 724.6 eV (Fig 5-b) as it has been reported by several researchers [12] and the satellite peak is located around 719.4 eV . XPS results is in accordance with XRD and Raman results shown previously and with the literature.



Figures 5. O1s (a) and Fe2p (b) curves of hematite Fe_2O_3 nanoparticles powder calcined at 400°C for 1 hour.

To investigate the potential applications of the obtained material as supercapacitors electrode, we have compared the results of pristine activated carbon deposited on Ti foil and composite of the $\text{AC}/\text{Fe}_2\text{O}_3$ in symmetric configuration. In this way it is possible to discriminate the contribution achieved by Fe_2O_3 addition. Figure 6a), shows CV curves of the composite of $\text{AC}/\text{Fe}_2\text{O}_3$ on Ti foil substrate at different scan rates: 5, 10, 50 and 100 mV/s respectively. The voltammograms exhibit quasi-rectangular

shapes even at high scan rates, which is characteristic of electric double layer formation. This demonstrates a high rate capability and higher specific capacitance as compare to the pristine activated carbon electrode, as shown in Figure 6 b). The specific capacitances were calculated from the CV curves according to equations (1) and (2). The calculated capacitances were plotted as a function of the scan rate in Figure 6 b) and it arises that composite material shows 5-6 times higher specific capacitance than pristine activated carbon, approaching a value of 87 F/g. This higher specific capacitance of AC/Fe₂O₃ can be explained by considering the synergistic contribution from both electrochemical double-layer capacitance (EDLC) and pseudo-capacitance. This is possibly due to the fine and well dispersed Fe₂O₃ grains in the active carbon which could provide more active sites for redox actions and yield a high capacitance [13]. Activated carbon, which act both as EDLC material and as conductive matrix, directly contacts with iron oxides nanoparticles, could allow easy electron transport and enhance the electrochemical performances of the nanocomposites [14]. This demonstrates that green synthesized hematite in composite with some porous carbon material is a potential candidate for supercapacitor application.

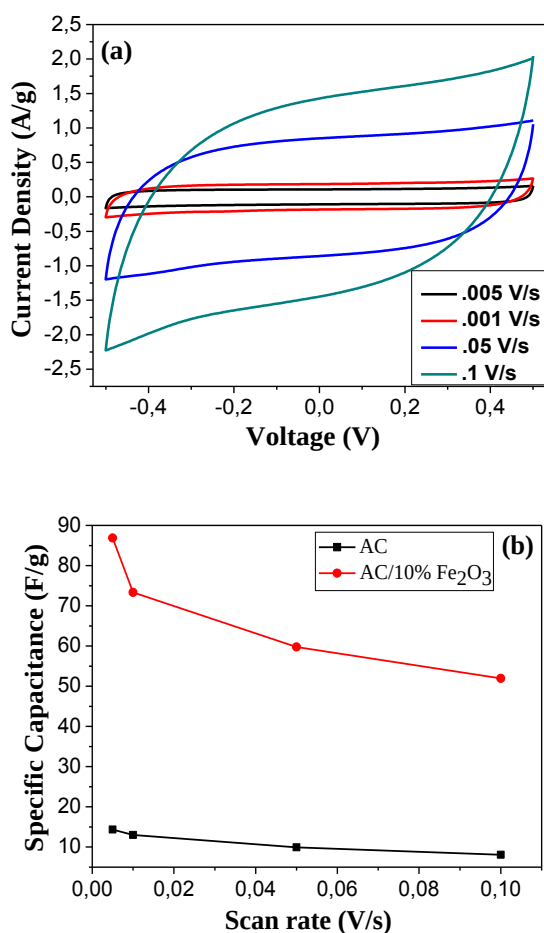


Figure 6. a) CVs of AC/Fe₂O₃ composite as function of scan rates, b) comparison of specific capacitance of pristine activated carbon and composite (AC/Fe₂O₃).

4. Conclusion

Hematite Fe₂O₃ NPs have been successfully synthesized via green chemistry using olive leaves extract as a source of polyphenol component which contain O-H function and iron nitrate as iron source. Several techniques were carried out to characterize the final product and to confirm its phase formation. This material was considered as a promising material for supercapacitance performance. It has been shown that hematite Fe₂O₃ produced via simple green method can be chosen as an appropriate candidate to facilitate and to enhance the charges transport within a slurry of some porous structure for supercapacitors fabrication.

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