



Article Highly Wrinkled Porous Polypyrrole for the Enhancement of the Performance of an Fe₂S₃-Fe₂O₃/poly-O-amino Benzenethiol Supercapacitor from a Basic Medium

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Abstract: In this study, *O*-amino benzenethiol (OABT) was oxidized in one pot using $Fe(NO_3)_3$ to produce a novel Fe_2S_3 - Fe_2O_3 /poly *O*-amino benzenethiol (POABT), which showed a highly uniform morphology. At the same time, from SEM analysis, highly wrinkled porous polypyrrole (Ppy) and porous ball-like POABT structures prepared from the $K_2S_2O_8$ route were evidenced by SEM and TEM analyses. A nanocomposite pseudo-supercapacitor (SC) was fabricated using Fe_2S_3 - Fe_2O_3 /POABT, and its performance was tested with and without incorporating Ppy in the paste. The results indicate that Ppy significantly increased the specific capacitance (C_S) values, indicating an enhancement in charge storage. At a current density of 0.2 A/g, the C_S values were 44 F/g and 161 F/g for the paste without and with Ppy, respectively. Additionally, the E was calculated, and the incorporation of Ppy resulted in a significant increase in E, reaching 30 W.h.kg⁻¹; this was significantly higher than the value of 8.18 W.h.kg⁻¹ observed without Ppy materials. This effect is likely due to the improved charge transfer facilitated by the presence of Ppy, as evidenced by the Nyquist plot, where the R_{ct} values were 1.1 Ω and 2.1 Ω with and without Ppy, respectively. Overall, the low cost and significant technical advantages of this capacitor make it a promising candidate for commercial applications.

Keywords: Fe₂S₃-Fe₂O₃; poly-O-amino-benzenethiol; polypyrrole; nanocomposite

1. Introduction

The pressing demand for energy arises as a direct consequence of continuous global population growth, creating a palpable energy deficit in numerous nations across the globe [1–3]. To mitigate this shortfall, researchers have pioneered the development of energy storage devices, with supercapacitors (SCs) emerging as a particularly intriguing technology owing to their significant attributes such as high energy density and prolonged lifespan [4–7]. Notably surpassing the energy density of conventional capacitors, SCs represent a promising technological advancement that addresses the escalating energy requisites of storage systems [8,9].

Energy storage devices can be categorized into two primary types: double-layer electrochemical storage devices and pseudostorage devices [10]. The latter involve electrodes in these devices undergoing oxidation and reduction reactions with electrolyte ions, leading to chemical transformations [11]. Countless experiments and research efforts have been dedicated to developing superior electrode materials for capacitors. While a range of metal oxides have been explored, ferric oxide has garnered attention due to its relative scarcity, coupled with its non-toxicity and affordability, rendering it a subject of study as a supercapacitor (SC) material [12–15]. Recent studies have focused on nanoscale ferric oxides, highlighting their potential [16,17].



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Ferric oxide's utilization as an anode material has been favored owing to its costeffectiveness, potent power generation capabilities, and low toxicity. The nanostructure of ferric oxide, often described as a hybrid nanostructure, results from the gradual oxidation of iron, yielding diverse sizes and augmented capacity. Within this category, one can find notable examples like nanoporous materials, tendrils, and nanotubes [18]. In some instances, metals are enhanced through amalgamation with metal–organic framework (MOF) materials [19,20].

The amalgamation of metal oxides and polymers in SC pastes has yielded a promising field of study, exploring how these materials synergistically impact SC performance [21–23]. Here, polymers play a role in augmenting the charge that surpasses that of oxide materials [24,25]. For instance, the enhancement in capacitance has seen CoO/CuO achieving 40 F/g, with Gd composites only reaching 2.5 F/g [26]. The pursuit of an optimal capacitor necessitates a focus on the reproducibility of oxidation and reduction reactions alongside high charge storage capacity. Solely relying on polymers within SC pastes does not yield sufficient capacitance, with certain studies even reporting values as low as 0.03 F/g.

In this study, the research revolves around an innovative Fe_2S_3 - Fe_2O_3 /POABT nanocomposite distinguished by its unique properties. The synthesis of this nanocomposite employs a one-pot approach, characterized by its cost-effective and high-yield nature. The fabricated SC is simple to produce and cost-effective, making it a promising candidate for practical applications. The device is tested using a basic medium of 1.0 M NaOH both with and without the addition of Ppy. The morphology of the material is highly conducive to creating a high surface area, thanks to the wrinkled surface morphology of the polymer material with a positive effect on the performance of the SC. Under a current density of 0.2 A/g, the CS values are measured at 44 F/g for the paste lacking Ppy and notably elevated to 161 F/g with the incorporation of Ppy. Furthermore, the E achieves a remarkable 30 W.h.kg⁻¹, showcasing a substantial increase compared to the baseline value of 8.18 W.h.kg⁻¹ observed in the absence of Ppy materials. Due to its great performance, this SC is expected to have great application potential in industrial energy storage devices. Its high capacitance charge storage and low fabrication cost make it an attractive option for practical use.

2. Results and Discussion

The structural characterization of the POABT and Fe₂S₃-Fe₂O₃/POABT nanocomposite was performed using FTIR and XRD analyses as illustrated in Figure 1a,b, respectively.

The FTIR (black curve) confirms well the POABT groups, in which S-H and C-H are located at 3373 cm⁻¹ and 3743 cm⁻¹, correspondingly. The organic C-H group is located at 1304 cm⁻¹, while the ring benzenoid or quinoid C=C appear well at 1380 and 1514 cm⁻¹, correspondingly. This quinoid structure supports the promising role of this polymer for semiconductor device applications.

The FTIR of the Fe_2S_3 - Fe_2O_3 /POABT nanocomposite was confirmed well, in which the great band at 3364 cm⁻¹ was related to OH⁻ and S-H group formation in the Fe(OH)₃ and POABT. The other groups in the POABT appeared again in this composite, with a blue–red shift that confirmed composite formation. The band at 3754 cm⁻¹ was for the N-H group of the composite, with a blue shift at 3743 cm⁻¹. The C=C quinoid structure was observed at 1607 cm⁻¹, with a long band that confirmed well the increased semiconductivity after the composite formation, reflecting promising applications of this nanocomposite for semiconductor devices [27]. In addition to that, the FTIR of Ppy is mentioned in Figure 1 (blue curve). The 1545 and 1463 cm⁻¹ bands are for C=C for the Ppy ring. Moreover, the C-N band is at 1317 and 1112 cm⁻¹. The other bands for the Ppy appear well through the figure.

The X-ray diffraction (XRD) analysis of the POABT material (Figure 1b) showed the formation of five distinct peaks in the region from 23.3° to 29.2°. This high degree of crystallinity indicates a well-ordered structure in the material.

In addition to the POABT peaks, the XRD pattern of the Fe_2S_3 - Fe_2O_3 /POABT composite shows additional peaks related to the presence of Fe_2O_3 and Fe_2S_3 materials. The peaks at 12°, 17.3°, 26.5°, and 39.1° for Fe(OH)₃ correspond to growth directions at (110), (200), (320), and (211), and are indicative of the crystallinity of iron hydroxide. These peaks match well with JCPDS card no. 34-1266 [28]. The presence of Fe₂O₃ was also confirmed through the peaks located in the range from 30.9 to 75.4°, which correspond to growth directions at (110), (024), (200), (018), (214), (300), (218), (1010), and (220), while Fe₂S₃ is present at 30.6°, 43.6°, and 54.7° for the growth directions (110), (114), and (107), respectively (JCPDS 29-0725) [29,30].



Figure 1. The chemical estimation of Ppy, POABT, and Fe_2S_3 - Fe_2O_3 /POABT nanocomposite using (a) FTIR and (b) XRD. (c) XPS survey, (d) Fe, (e) O, and (f) S elements XPS analyses for Fe_2S_3 - Fe_2O_3 /POABT nanocomposite.

The crystalline size (D) of the fabricated composite was estimated to be 117 nm using the Scherrer equation (Equation (1)) [31]. Here, β and λ represent the full-width half maximum and wavelength, respectively, and were used to estimate the particle size. Moreover, the Scherrer constant was 0.94.

$$D = 0.94\lambda/\cos\theta \tag{1}$$

According to Figure 2 (blue curve), the Ppy materials exhibited a semicrystalline behavior, as evidenced by the presence of two peaks at 24.5° and 26.7°. This suggests that the crystals in the Ppy materials were well-ordered, which contributes to the conductive behavior of Ppy.



Figure 2. (a) SEM of POABT and (b) TEM and (c,d) SEM of Fe₂S₃-Fe₂O₃/POABT nanocomposite and (e,f) Ppy under various magnifications.

The XPS analysis of the Fe₂S₃-Fe₂O₃/POABT nanocomposite in Figure 1c provides insights into the chemical composition of the material. The presence of Fe, O, and S elements confirms the presence of inorganic components, while the presence of S, C, and N elements confirms the presence of the POABT polymer. The peaks observed at 164, 285, and 400 eV correspond to the characteristic energy levels of the polymer structure, indicating its presence in the nanocomposite. The O elements were detected at 532 eV, as shown in Figure 1e, and the S elements were detected at 163 and 164 eV, related to the S2p3/2 and S2p1/2, respectively, for the S^{2–} [32] (Figure 1f). In Figure 1d, the Fe2p peaks at 711 and 724 eV confirm the formation of Fe₂O₃, while the presence of peaks at 710 eV confirms the formation of Fe₂S₃ in the nanocomposite [33].

The topography and morphology of the synthesized POABT and Fe_2S_3 - Fe_2O_3 /POABT nanocomposite were demonstrated through SEM analysis. Figure 2a illustrates the porous ball shape of POABT from the SEM analysis. This porous ball has a diameter of 500 nm, and the great porous surface motivates the additional composite.

After the Fe_2S_3 - Fe_2O_3 /POABT nanocomposite's formation, the morphology was changed very well (Figure 2b,d), in which a double-ball shape was formed with a length of 180 nm; the smaller size of the composite compared to POABT indicates that the addition of Fe_2S_3 - Fe_2O_3 to the POABT structure increased the morphological sites of the composite, which in turn increased the active sites available for charge storage. The porous structure of POABT and the double-ball shape of the composite are expected to enhance the performance of the SC. In addition to that, a highly wrinkled porous Ppy is illustrated well in Figure 2e,f. This great morphology explains the great surface area of these materials and the charge stored on the active sites.

The TEM (Figure 2c) illustrates the composite's formation through a 2D image, in which the coating of the polymer (grey color) on the Fe_2S_3 - Fe_2O_3 (dark color) appears. These great contacts confirm the composite formation well.

SC Electrochemical Study

An electrochemical assessment was conducted using a CHI608E power station, focusing on the utilization of an SC constructed from the Fe_2S_3 - Fe_2O_3 /POABT nanocomposite. To create a binding agent, Nafion, a binder, was mixed in an ethanol solution of 0.75 mL. The influence of Ppy was explored—1:3 percent in relation to the composite constituents. The resulting paste was applied onto a Au electrode and allowed to dry. Following this, Whatman paper was inserted to serve as a separator, and the plates were sealed using a sealing tip. The choice of electrolyte was 1.0 M NaOH due to its significant ion mobility, owing to the presence of OH⁻ anions. This combination of experimental elements constituted the setup for the electrochemical analysis, enabling the evaluation of the supercapacitor's performance and behavior [34–37].

Figure 3a,b graphically illustrate the charging behavior of the Fe_2S_3 - Fe_2O_3 /POABT SC, both in its pristine state and with the inclusion of Ppy nanomaterial. The presented outcomes distinctly signify that the introduction of Ppy brought about a substantial improvement in the charging performance of the SC. Specifically, at a current density of 0.2 A/g, the charge time extended from 23 to 123 s upon the incorporation of Ppy into the paste.

This enhancement can be attributed to the distinctive role of Ppy in enabling efficient charge storage through its interconnected chains, as well as the presence of OH⁻ ions that confer a negative charge and bolster the conductivity of the polymer materials. The calculation of specific capacitance (CS) was achieved by employing Equation (2) [38], based on the data depicted in Figure 3c,d for both the paste devoid of Ppy and the paste enriched with Ppy.

The outcomes reveal a pronounced elevation in C_S values in the presence of Ppy, underscoring an amplified capacity for charge storage. Particularly noteworthy is the observed C_S of 44 F/g for the supercapacitor without Ppy, compared to a significantly increased value of 161 F/g for the supercapacitor infused with Ppy, at the given current density of 0.2 A/g. This comprehensive evaluation emphasizes the marked impact of Ppy on enhancing the charge storage potential of the supercapacitor, thereby presenting a compelling case for its favorable incorporation.

$$C_s = 4I.\Delta t / \Delta V.m \tag{2}$$

In a similar manner, the calculation of energy density (E) was performed utilizing Equation (3), which hinges on the square of the maximum voltage (V_{max}^2) subtracted from the square of the minimum voltage (V_{max}^2) . Remarkably, the inclusion of Ppy yielded a notable surge in the energy density, reaching a substantial 30 W.h.kg⁻¹. This achievement is in stark contrast to the energy density value of 8.18 W.h.kg⁻¹ observed in the absence of Ppy materials.

$$E = 0.5C_{\rm s.} \left(V_{max}^2 - V_{min}^2 \right) / 3.6 \tag{3}$$



Figure 3. The effect of Ppy, (**a**,**c**) without, and (**b**,**d**) with Ppy, on the charging behavior and C_S values, respectively, for the Fe₂S₃-Fe₂O₃/POABT SC at a current density 0.2 to 0.8 A/g using 1.0 M NaOH electrolyte.

Cyclic voltammetry testing was carried out on the Fe₂S₃-Fe₂O₃/POABT SC, both with/without Ppy material addition, within the paste. This experimental procedure is illustrated in Figure 4a,b, respectively. When the scan rate was altered within the range of 50 to 300 mV.s^{-1} , the plates' capacity exhibited an upward trend. This capacity enhancement was reflected in the resultant increase in the generated current. The presence of Ppy in the paste resulted in a significant enhancement in the current density [39]. This enhancement is evident in the heightened oxidation and reduction peak values, indicative of enhanced charge transfer due to Ppy's presence. This phenomenon underscores the efficient charge storage capability of Ppy nanoparticles within the paste. The electrochemical function of Ppy is interconnected with its initial role, which involves enhancing the homogeneity of the supercapacitor paste. This enhanced homogeneity simplifies the even distribution of the paste across the plates, ultimately aiding in its electrochemical performance. Moreover, the presence of OH⁻ groups from the electrolyte increases the semiconductor nature of the paste [40], which in turn increases its ability to store charges [41,42], In addition to the great ability of Fe₂S₃ and Fe₂O₃ to perform charge storage related to their semiconductive nature. The findings indicate a noteworthy enhancement in charge storage capacity and overall performance of the Fe₂S₃-Fe₂O₃/POABT supercapacitor with the incorporation of Ppy into the paste. This addition of Ppy material substantially boosted the supercapacitor's ability to store and manage electrical charges, underscoring its potential for improved energy storage applications.



Figure 4. CV of the fabricated Fe₂S₃-Fe₂O₃/POABT SC from 1.0 M NaOH solution (**a**) without and (**b**) with Ppy.

Figure 5a,b depict Nyquist plots of the Fe₂S₃-Fe₂O₃/POABT supercapacitor, both in the absence/presence of Ppy materials. These plots provide insight into the real (Z') and imaginary (Z'') impedance values, which are instrumental in assessing the charge transfer capabilities within the paste [43,44]. The charge transfer resistance (Rct) and solution resistance (Rs) of the supercapacitor were estimated using Randle's cell model [45,46], which is characterized by a semicircular shape. The analysis revealed that the Rs value remained consistent at 5.7 Ω , regardless of the presence or absence of Ppy material. However, the Rct value displayed variation upon the introduction of Ppy, manifesting as Rct values of 1.1 Ω and 2.1 Ω with and without Ppy material, respectively. This alteration signifies the influence of Ppy on the charge transfer dynamics of the supercapacitor.

Moreover, the power density (P) is expressed using Equation (4) [13] and illustrated in Figure 5e,f through a Ragone plot, elucidating the connection between stored energy and the duration of energy transfer. Notably, the influence of Ppy became markedly evident, leading to a substantial enhancement in power density. Prior to the inclusion of Ppy, the power density registered at 820 (W/kg), whereas after Ppy integration, it reached an impressive 880 (W/kg).

$$P = 3600 \text{ E}/\Delta t \tag{4}$$

Based on the information extracted from Figure 5b,c, an assessment of the supercapacitor's longevity was conducted, tracking charge behavior in relation to the number of cycles. Notably, the study demonstrates that the supercapacitor showcased comparable stability whether Ppy was present or absent. However, the incorporation of Ppy nanomaterial into the paste yielded a discernible enhancement in stability.

Figure 5d portrays the retention coefficient, which signifies the percentage of capacitance sustained following a specified number of cycles. Analysis revealed that after 500 cycles, the retention coefficient stood at around 80% without Ppy nanomaterial and 81% in its presence. This indicates that the integration of Ppy nanomaterials into the paste led to a slightly improved preservation of capacitance over time. This observation potentially implies the enhanced stability of the supercapacitor. The amalgamation of sophisticated technical and mechanical attributes inherent to the selected materials, alongside their reproducibility, confers a marked advantage to the engineered device.



Figure 5. The (**a**) Nyquist plot, (**b**,**c**) the stability, (**d**) the retention coefficient, and (**e**,**f**) Ragone plot of the Fe_2S_3 - Fe_2O_3 /POABT SC from 1.0 M NaOH solution with/without Ppy nanomaterials.

3. Experimental Section

3.1. Materials

 $K_2S_2O_8$, ferric nitrate (Fe(NO₃)₃), HCl, and NaOH were obtained from Piochem Co., Cairo, Egypt. *O*-amino benzenethiol was supplied from Darmstadt, Germany, Merck Co., while Nafion was supplied from USA, Sigma Aldrich Co. (St. Louis, MO, USA).

3.2. POABT and Fe₂S₃-Fe₂O₃/POABT Nanocomposite

POABT was synthesized via oxidative polymerization ($K_2S_2O_8$ is an oxidant), with (0.6 M) HCl serving as a solvent and acid medium. The OABT monomer (0.12 M) was dissolved well in this acid using vigorous stirring, until it became clear. Under the sudden addition of the oxidant, the polymerization process was performed, and a dark greenishblue color was formed. The Fe₂S₃-Fe₂O₃/POABT nanocomposite was synthesized using a similar approach, but with the use of Fe(NO₃)₃ as the oxidant at a concentration of 0.15 M. The polymerization process was carried out, resulting in the incorporation of the Fe₂S₃-Fe₂O₃ material within the POABT polymer. Then, centrifuging, cleaning, washing, and drying (60 °C) steps were performed; then, the produced polymer composite powder was applied for the fabrication of the pseudocapacitor device.

3.3. SC Fabrication

To fabricate the SC, the Fe₂S₃-Fe₂O₃/POABT nanocomposite was first formed into a paste and applied onto the Au-plated electrodes of the capacitor. The paste consisted of 0.04 g of this fabricated composite and traces of graphite (0.005 g), along with (100 μ L) Nafion and (750 μ L) ethanol as additives. The two electrodes were then separated using Whatman paper that had been saturated with a 1.0 M NaOH solution. The performance of the two symmetric electrodes SC was studied through electrochemical measurements, including the potential–time and potential–current relations, which were used to calculate the capacitance. The measurements were conducted using a power station (CHI608E). To complete the testing, impedance was also demonstrated, and reproducibility was assessed under the charge repeating curves. All of these tests were performed both with and without the addition of polypyrrole (Ppy) material, allowing for an evaluation of the impact of Ppy on the performance of the SC.

3.4. Characterization

To perform elemental and crystalline structure characterization of the Fe₂S₃-Fe₂O₃/POABT nanocomposite, X-ray diffraction (XRD) was carried out (1.54Å) using an X'Pert Pro apparatus from Holland. To confirm the chemical structure and obtain additional information, a Jasco instrument (model 340), an FTIR device, was used. The 2D and 3D morphological behaviors of this composite were confirmed using TEM (JEM-2100, Massachusetts, USA) and SEM (ZEISS, Oberkochen, Germany), correspondingly.

4. Conclusions

The oxidation of *O*-amino benzenethiol was performed using $Fe(NO_3)_3$, leading to the formation of a highly uniform and novel Fe_2S_3 - Fe_2O_3 /POABT nanocomposite that was formed in one step. At the same time, highly wrinkled porous polypyrrole and POABT with a porous ball-like structure were prepared under the oxidation of pyrrole using $K_2S_2O_8$. The 2D and 3D morphologies of these materials were analyzed using SEM and TEM analyses. Using XRD and FTIR analyses, the crystalline and chemical compositions were confirmed well. The Fe_2S_3 - Fe_2O_3 /POABT nanocomposite pseudocapacitor was fabricated and tested with/without the incorporation of Ppy inside the paste.

The introduction of Ppy brought about substantial enhancements in C_S, signifying a notable improvement in charge storage capacity. For instance, at 0.2 A/g, the C_S values were distinctly elevated: 44 F/g without Ppy and 161 F/g with Ppy. Correspondingly, the computation also demonstrated an upward trend due to Ppy integration. The energy density escalated to 30 W.h.kg⁻¹, a remarkable increase compared to the 8.18 W.h.kg⁻¹ recorded without Ppy incorporation. The underlying mechanism responsible for these observations is likely the improved charge transfer facilitated by Ppy. This inference aligns with the Nyquist plot, showcasing R_{ct} values of 1.1 Ω and 2.1 Ω with and without Ppy, respectively. Given the advantageous combination of cost-effectiveness and technical superiority, this capacitor exhibits considerable potential for widespread commercial applications.

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