



# Article Influence of High Energy Ball Milling and Dispersant on Capacitive Properties of Fe<sub>2</sub>O<sub>3</sub>—Carbon Nanotube Composites

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Abstract: This investigation is motivated by increasing interest in ferrimagnetic materials and composites, which exhibit electrical capacitance. It addresses the need for the development of magnetic materials with enhanced capacitive properties and low electrical resistance.  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-multiwalled carbon nanotube (MWCNT) composites are developed by colloidal processing and studied for energy storage in negative electrodes of supercapacitors. High energy ball milling (HEBM) of ferrimagnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles results in enhanced capacitive properties. The effect of HEBM on particle morphology is analyzed. Gallocyanine is used as a co-dispersant for  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and MWCNTs. The polyaromatic structure and catechol ligand of gallocyanine facilitated its adsorption on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and MWCNTs, respectively, and facilitated their electrostatic dispersion and mixing. The adsorption mechanisms are discussed. The highest capacitance of 1.53 F·cm<sup>-2</sup> is achieved in 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte for composites, containing  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, which is high energy ball milled and co-dispersed with MWCNTs using gallocyanine. HEBM and colloidal processing strategies allow high capacitance at low electrical resistance, which facilitates efficient charge–discharge. Obtained composites are promising for fabrication of multifunctional devices based on mutual interaction of ferrimagnetic and capacitive properties.

**Keywords:** iron oxide; carbon nanotube; supercapacitor; milling; dispersant; nanoparticle; electrode; composite

# 1. Introduction

Many recent investigations have focused on the design and optimization of processing techniques for the fabrication of advanced composites [1–4]. Significant interest has been generated in the development of colloidal techniques [5–8]. The design of electrostatic self-assembly methods resulted in the fabrication of novel nanocomposites with high performance [9–12]. Advanced nanocomposites have been developed, combining functional properties of inorganic materials, polymers and carbon nanotubes [13–16]. A technological problem in the development of such composites by colloidal techniques is related to dispersion of carbon nanotubes, and their efficient co-dispersion and mixing with other materials. Various techniques have been reported for the dispersion of carbon nanotubes [13,17–19]. However, their co-dispersion with metal oxide nanoparticles presents difficulties due to the lack of efficient co-dispersants. Therefore, there is a need for the development of co-dispersant molecules, which must be adsorbed on both materials and facilitate their mixing on the nanometric scale. It is challenging to co-disperse carbon nanotubes with nanoparticles of magnetic oxides, which are prone to agglomeration due to van der Waals and magnetic forces.

Another challenge is related to the development of advanced techniques for fabrication of nanoparticles. High energy ball milling (HEBM) is a promising technique for sustainable production of different nanoparticles, such as metals, alloys and oxides [20–22]. Particle shape and properties can be modified by HEBM [23]. Aluminum nanoparticles with



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**Copyright:** © 2022 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/). enhanced reactivity were prepared by this method [24]. Moreover, Al-Ni mixed powders with enhanced reactivity were fabricated [25].

HEBM is under development for the mechanochemical synthesis of materials [26-28]. This technique offers advantages of waste-free eco-friendly processing [26]. Mechanochemical alloying is one of the promising applications of HEBM [29,30]. The use of HEBM allowed the fabrication of advanced composites with uniform dispersion of ceramic particles in a metal alloy matrix [31]. Such composites exhibited advanced mechanical properties [31]. Mg alloys showed significant enhancement of H-storage properties after HEBM [32]. This resulted from reduction in grain size and improved distribution of a catalyst material [32]. HEBM allowed modification of microstructure and properties of magnetic materials and facilitated the fabrication of advanced alloys with hard magnetic properties [33]. HEBM is a promising technique for the fabrication of particles for energy storage applications in supercapacitors and batteries [34–36]. The reduction in particle size allowed an improved rate performance of  $Li_4Ti_5O_{12}$  electrodes [34]. HEBM treatment of graphite created abundant oxygen functional groups on the particle surface [37] and supercapacitor devices with an enlarged voltage window and high capacitance were obtained. However, the effect of HEBM on Ni(OH)<sub>2</sub> battery electrode material performance is not well understood. The structure changes in Ni(OH)<sub>2</sub> electrodes showed deterioration of their electrochemical performance [38]. Such controversial and diverging results generate a need for further investigation of HEBM for fabrication of active materials for energy storage devices.

The goal of this investigation was fabrication and testing of  $Fe_2O_3$ -carbon nanotube composite electrodes for supercapacitors. The approach was based on synergy of two methods, colloidal processing and HEBM. An important finding was that gallocyanine is a promising co-dispersant which adsorbs on  $Fe_2O_3$  and carbon nanotubes and allows for their efficient co-dispersion and mixing. We analyzed the influence of HEBM on morphology of  $Fe_2O_3$  particles. Electrochemical testing results revealed benefits of HEBM and colloidal processing in the presence of gallocyanine, which facilitated the fabrication of the  $Fe_2O_3$ -carbon nanotube composite electrodes with enhanced capacitance.

## 2. Materials and Methods

Multiwalled carbon nanotubes (MWCNTs, OD 13 nm, ID 4 nm, length 1–2  $\mu$ m, Bayer, Leverkusen, Germany), Ni foams (thickness 1.6 mm, 95% porosity, Vale, Mississauga, Canada), Fe<sub>2</sub>O<sub>3</sub> nanopowder (size < 50 nm), Na<sub>2</sub>SO<sub>4</sub>, poly(vinyl butyral) (PVB), gallocyanine (MilliporeSigma, Oakville, Canada) were used. The mass ratio Fe<sub>2</sub>O<sub>3</sub>:MWCNT:PVB was 80:20:3 in composites 1–3. The composite electrodes were prepared by impregnation of Ni foam current collectors with mixed Fe<sub>2</sub>O<sub>3</sub> and MWCNT slurries in ethanol, containing dissolved PVB. The slurries were ultrasonicated for 30 min before impregnation of the current collectors. As-received Fe<sub>2</sub>O<sub>3</sub> powder was used for the preparation of composite 1, whereas high energy ball milled  $Fe_2O_3$  was utilized for composites 2 and 3. Composite 2 was prepared without gallocyanine, whereas gallocyanine was used for preparation of composite 3 using a preliminary co-dispersion procedure, described below. High energy ball milling was performed using a Mixer Mill MM 500 Nano (Retsch GmbH, Haan, Germany) at a frequency of 15 Hz. Milling time was 30 min. A preliminary co-dispersion and mixing procedure was used for the preparation of composite 3. In this preliminary procedure, the ball milled Fe<sub>2</sub>O<sub>3</sub> powder was mixed with MWCNTs in ethanol, containing dissolved gallocyanine. The mass ratio of gallocyanine:  $Fe_2O_3$  was 0.15. After ultrasonication for 30 min, filtering for removal of non-adsorbed gallocyanine and drying, the obtained mixture was used for preparation of a slurry in ethanol, containing PVB for impregnation of the current collectors. The impregnated electrodes were dried in air at 60  $^{\circ}$ C and pressed to 30% of original thickness. The total mass of impregnated material after drying (mass loading) was  $40 \text{ mg} \cdot \text{cm}^{-2}$ .

Electron microscopy investigations were performed using a JSM-7000F, (JEOL, Tokyo, Japan) scanning electron microscope (SEM) and Talos 200 (Thermo Fisher Scientific, Waltham, MA, USA) transmission electron microscope (TEM). X-ray diffraction (XRD) analysis

(diffractometer Bruker D8, Bruker, Billerica, MA, USA) was performed at the rate of 0.01 degrees per second using Cu-K $\alpha$  radiation. Fourier transform infrared spectroscopy (FTIR) studies were performed using a Bruker Vertex 70 spectrometer (Bruker, Billerica, MA, USA). The IR spectra were registered between 400 and 4000 cm<sup>-1</sup> as a result of the average of 3 scans with a resolution of 0.5 cm<sup>-1</sup>. Zeta potential measurements were performed by a mass transfer method [39].

The capacitive behavior of the electrodes was analyzed in aqueous 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte using a PARSTAT 2273 (Ametek, Berwyn, PA, USA) potentiostat for cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). A BioLogic VMP 300 potentiostat (Biologic, Willow Hill, IL, USA) was used for galvanostatic charge–discharge (GCD) investigations. A 3-electrode electrochemical cell was used, which contained a working electrode, counter-electrode (Pt mesh) and a reference electrode (SCE, saturated calomel electrode). Gravimetric (C<sub>m</sub>,  $F \cdot g^{-1}$ ) and areal (C<sub>S</sub>,  $F \cdot cm^{-2}$ ) capacitances were calculated from the CV, EIS and GCD data as was described in previous investigations [40,41].

The capacitance was obtained from CV data using the following equation:

$$C = \frac{\Delta Q}{\Delta U} = \frac{\left|\int_{0}^{t(Umax)} Idt\right| + \left|\int_{t(Umax)}^{0} Idt\right|}{2Umax}$$
(1)

where  $\Delta Q$  is charge, I—current, t—time and  $\Delta U$ —the potential range. GCD data were used for the calculation of capacitance by the following equation:

$$C = I\Delta t / \Delta U.$$
 (2)

The complex capacitance  $C^*(\omega) = C'(\omega) - iC''(\omega)$  was calculated at different frequencies ( $\omega$ ) from the complex impedance  $Z^*(\omega) = Z'(\omega) + iZ''(\omega)$  data:

$$C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2},$$
(3)

$$C''(\omega) = \frac{Z'(\omega)}{\omega |Z(\omega)|^2}.$$
(4)

 $C_S$  and  $C_m$  obtained from CV and GCD data in a potential window of 0–0.9 V represented integral capacitances. EIS data obtained in an open circuit potential at voltage amplitude of 5 mV provided differential capacitances. The EIS spectra were acquired in the frequency range of 10 Hz–1 kHz.

#### 3. Results

Figure 1 shows the X-ray diffraction pattern of as-received Fe<sub>2</sub>O<sub>3</sub> powder. The diffraction pattern shows peaks of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phase. Labeled peaks in Figure 1 correspond to JCPDS file 025-1402 of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

Figure 2 shows TEM images of as-received and HEBM nanoparticles at different magnifications. The particle size of as-received  $Fe_2O_3$  powder was typically below 50 nm, is agreement with the information provided by the powder manufacturer. However, TEM observations revealed a small number of larger spherical particles with a particle size of 200–250 nm (Figure 2A). Such particles were not observed after HEBM (Figure 2B). Therefore, HEBM eliminated such relatively large particles. The TEM images at a higher magnification (Figure 2C,D) did not show a significant difference in the size of nanoparticles before and after HEBM. It is in this regard that HEBM over 90 h resulted in a similar size of  $Fe_2O_3$  nanoparticles [42]. However, TEM analysis of HEBM nanoparticles showed significant particle grinding, which resulted in a rough particle surface (Figure 3).



**Figure 1.** X-ray diffraction pattern of as received  $Fe_2O_3$  powder ( $\blacklozenge$ —peaks corresponding to JCPDS file 025-1402 of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phase).



**Figure 2.** TEM images (**A**–**D**) at different magnifications for Fe<sub>2</sub>O<sub>3</sub> nanoparticles: (**A**,**C**) before and (**B**,**D**) after HEBM. Arrow shows large particle in as-received Fe<sub>2</sub>O<sub>3</sub>.



**Figure 3.** (**A**,**B**) High magnification TEM images of Fe<sub>2</sub>O<sub>3</sub> nanoparticles after HEBM, which show increased surface roughness of the particles.

It is known that  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phase (maghemite) is a ferrimagnetic material with relatively high spontaneous magnetization [43,44]. The fabrication of stable suspensions of such nanoparticles for colloidal processing presents difficulties due to van der Waals and magnetic interactions, which promote particle aggregation and sedimentation. Another problem is related to poor electronic conductivity of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, which is detrimental for applications of this material in supercapacitors.

In this investigation, gallocyanine was used as a dispersion agent for  $Fe_2O_3$ . A sedimentation test of as-received  $Fe_2O_3$  powder in ethanol showed fast precipitation. The addition of gallocyanine with mass ratio gallocyanine:  $Fe_2O_3 = 0.15$  resulted in colloidal stability for 2 days for as-received  $Fe_2O_3$  and more than 10 days for HEBM  $Fe_2O_3$ . It was hypothesized that gallocyanine adsorbed on  $Fe_3O_4$  particles and provided electrostatic stabilization. Figure 4A shows the chemical structure of gallocyanine. It contains a catechol ligand, which can facilitate gallocyanine adsorption on inorganic surfaces (Figure 4B).



**Figure 4.** (**A**) Chemical structure of gallocyanine, (**B**) adsorption of gallocyanine on Fe<sub>2</sub>O<sub>3</sub> particle involving catecholate-type complexation of Fe atom on the particle surface.

Catecholate molecules are gaining attention for surface modification and dispersion of different materials. One of the greatest drivers of catecholate dispersant development is investigation of strong mussel adsorption on different surfaces, which is based on bidentate bonding of catechol ligands of mussel adhesive proteins [45–47]. Recent studies of monoaromatic charged molecules from the catechol family led to the development of advanced dispersants [48]. Caffeic acid, tiron, dopamine and other cationic and anionic catecholates were used for dispersion of ZrO<sub>2</sub>, TiO<sub>2</sub>, MnO<sub>2</sub>, ZnO and other metal oxides in ethanol [48,49]. Adsorption of caffeic acid on positively charged MnO<sub>2</sub> particles in

ethanol resulted in charge reversal [50]. Therefore, it was not surprising that gallocyanine adsorbed on  $Fe_2O_3$  and facilitated particle dispersion. The gallocyanine adsorption on  $Fe_2O_3$  nanoparticles was confirmed by FTIR studies (Figure 5).



**Figure 5.** FTIR spectra of (a) as-received Fe<sub>2</sub>O<sub>3</sub>, (b) gallocyanine, (c) Fe<sub>2</sub>O<sub>3</sub>, containing adsorbed gallocyanine.

The FTIR spectrum of as-received Fe<sub>2</sub>O<sub>3</sub> showed absorption at 1404 cm<sup>-1</sup>, which can result from vibrations of adsorbed CO<sub>2</sub> [51]. The spectrum of gallocyanine showed absorption at 1722 cm<sup>-1</sup> related to C=O stretch [52]. Absorptions at 1591 and 1555 cm<sup>-1</sup> are related to C=C-C stretch [18,19]. Absorptions at 1385, 1312 and 1119 cm<sup>-1</sup> are related to C–O, C–N–C and C–O–C stretches, respectively [18,52]. The spectrum of Fe<sub>2</sub>O<sub>3</sub> dispersed using gallocyanine showed similar peaks and confirmed gallocyanine adsorption on Fe<sub>2</sub>O<sub>3</sub> particles. The spectra of pure Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> dispersed using gallocyanine (Supplementary Information, Figure S1) showed broad absorptions at 550 cm<sup>-1</sup> related to Fe–O stretching [53].

The larger size of gallocyanine, compared to the size of monoaromatic catecholates, such as caffeic acid, tiron and dopamine, is beneficial for dispersion of Fe<sub>2</sub>O<sub>3</sub>. Figure 4 indicates that gallocyanine is a cationic molecule. Therefore, gallocyanine was used as a cationic dispersant for Fe<sub>2</sub>O<sub>3</sub>. Electrophoretic experiments in an electric field of 30 V cm<sup>-1</sup> for Fe<sub>2</sub>O<sub>3</sub> suspensions, containing gallocyanine, confirmed that Fe<sub>2</sub>O<sub>3</sub> particles were positively charged, as they moved toward the cathode under the influence of the electric field and deposited electrophoretically on the cathode surface. Zeta potential of Fe<sub>2</sub>O<sub>3</sub> particles was found to be +8.2 mV. Figure 4 indicates that gallocyanine is a polyaromatic molecule. It was found that gallocyanine allowed for efficient dispersion of MWCNTs in ethanol. The adsorption mechanism involved  $\pi$ - $\pi$  interactions of polyaromatic gallocyanine were unstable and showed rapid precipitation. In contrast, the MWCNT suspension containing gallocyanine showed colloidal stability for more than 2 weeks. Therefore, the adsorbed gallocyanine provided electrostatic dispersion of MWCNTs and electrostatic co-dispersion of Fe<sub>2</sub>O<sub>3</sub> and MWCNTs in mixed suspensions.

Figure 6 shows SEM images of composites 1–3 impregnated into Ni foam current collectors. Composite 1 contained mainly nanoparticles of  $Fe_2O_3$  and a small number (about 1%) of spherical particles with a typical size of 200–250 nm in agreement with the results of TEM studies (Figure 6). HEBM resulted in crashing and elimination of such

particles. The SEM images of composites 2 and 3 showed only nanoparticles of  $Fe_2O_3$ , which were mixed with MWCNTs (Figure 6B,C). The porosity of the electrode materials was beneficial for electrolyte access to the active material.



**Figure 6.** SEM images of (**A**) composite 1, (**B**) composite 2 and (**C**) composite 3 impregnated into Ni foam current collectors. Arrows show large particles in composite 1. Composite 1 was prepared using as-received  $Fe_2O_3$ . HEBM was used for preparation of composites 2 and 3. Composite 2 was prepared without dispersants, composite 3 was prepared using gallocyanine as a co-dispersant.

The electrochemical performance of the composite electrodes was tested in 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. Figure 7A–C show CVs for composites 1–3.



**Figure 7.** (A–C) CVs for (A) composite 1, (B) composite 2 and (C) composite 3 at scan rates of (a) 5, (b) 10, (c) 20 mV·s<sup>-1</sup>, (D) capacitance versus scan rate for (a) composite 1, (b) composite 2, (c) composite 3.

The CVs for composites 1–3 showed pseudocapacitive behavior of the electrodes. Composite 2 showed improved shape of CVs, which were nearly of rectangular shape. Composite 3 showed enlarged CV area, which indicated higher capacitance. The capacitances calculated from the CV data were 0.59  $\text{F} \cdot \text{cm}^{-2}$  (14.75  $\text{F} \cdot \text{g}^{-1}$ ), 0.88  $\text{F} \cdot \text{cm}^{-2}$  (22.0  $\text{F} \cdot \text{g}^{-1}$ ) and  $1.53 \text{ F} \cdot \text{cm}^{-2}$  (38.25 F·g<sup>-1</sup>) at a scan rate of 2 mV·s<sup>-1</sup>. The higher capacitance of composite 2 compared to composite 1 can be attributed to effect of HEBM, such as crushing of large particles and increase in surface roughness of nanoparticles. It should be noted that capacitance increase cannot be correlated with surface area. Previous investigations did not show correlations between surface area and capacitance of different pseudocapacitive oxides [54–57]. Composite 3 showed the highest capacitance due to the beneficial effect of HEBM and enhanced mixing of Fe<sub>2</sub>O<sub>3</sub> and MWCNT, which was achieved using gallocyanine as a co-dispersant for colloidal processing. The observed capacitances were mainly attributed to pseudocapacitive properties of Fe<sub>2</sub>O<sub>3</sub> due to low capacitance of MWCNTs and low (20%) content of MWCNTs in the composites. In our approach, MWCNTs were used as conductive additives, which improved electronic conductivity of the composites. We found that the mass ratio of conductive MWCNTs must be 20% of the total mass of Fe<sub>2</sub>O<sub>3</sub> and MWCNTs in order to achieve low impedance and high capacitance. Further increase in the MWCNT content in the composite resulted in reduced capacitance.

Figure 8 shows electrochemical impedance spectroscopy testing results. Composites 1–3 showed a relatively low real part of impedance, which indicated low electrode resistance. Composites 2 and 3 showed higher capacitance, compared to composite 1 at low frequencies, in agreement with CV data. However, composite 2 showed higher capacitance, compared to composite 3. The capacitances obtained from the impedance data were lower than capacitances derived from CVs. The difference may have resulted from different measurement conditions. The AC capacitance represents a differential capacitance measured at voltage amplitude of 5 mV. The differential capacitance depends on electrode potential. In contrast, the capacitance calculated from the CV data represents an integral capacitance, measured in a voltage window of 0.8V.



**Figure 8.** (A) Nyquist plot of  $Z^*$ , (B,C) frequency dependences of (B)  $C_s'$  and (C)  $C_s''$  for (a) composite 1, (b) composite 2 and (c) composite 3.

Figure 9A–C shows GCD data for composites 1–3 at different current densities. The charge–discharge curves had a nearly triangular shape. The charge–discharge time increased with decreasing current density. Composite 3 showed longer discharge times, compared to composites 1 and 2 at fixed current densities. The capacitances of 0.65, 1.09 and 1.26  $F \cdot cm^{-2}$  were obtained at a current density of 3 mA cm<sup>-2</sup> for composites 1, 2 and 3, respectively. The capacitances decreased with increasing current density (Figure 9D).



**Figure 9.** (A–C) GCD data for (A) composite 1, (B) composite 2 and (C) composite 3 at current densities of (a) 3, (b) 5, (c) 7 and (d) 10 mA.cm<sup>-2</sup> and (D) capacitance versus current density for (a) composite 1, (b) composite 2 and (c) composite 3.

Areal capacitance is an important characteristic of electrodes with high active mass loading [40]. Table 1 compares areal capacitance of the composite 3 electrode with literature data on areal capacitance of Fe<sub>2</sub>O<sub>3</sub> electrodes, containing conductive additives. It is seen that previous investigations of negative electrodes based on Fe<sub>2</sub>O<sub>3</sub> in Na<sub>2</sub>SO<sub>4</sub> electrolyte were mainly focused on testing of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which is an antiferromagnetic material. In contrast,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is a ferrimagnetic material, which showed relatively high capacitance (Table 1). Despite the difficulties related to colloidal processing of ferrimagnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles, we achieved higher capacitance of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-based composites. This resulted from the effect of HEBM and the use of gallocyanine as a co-dispersant.

The combination of ferrimagnetic and capacitive properties in a single material is very promising, because reduction of Fe<sup>3+</sup> ions results in changing of their magnetic moments. Therefore, interesting effects can potentially be observed in such materials due to the influence of the charging process on magnetization or the influence of magnetic field on the charging process. Pseudocapacitive ferrimagnetics or ferromagnetics represent an important alternative to magnetically ordered ferroelectrics [58], which exhibit interesting magnetoelectric effects. It is in this regard that capacitance of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is significantly higher than that of magnetically ordered ferroelectrics [58]. Moreover, magnetically ordered ferroelectrics exhibit antiferromagnetic or weak ferri/ferromagnetic properties. In contrast,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is a ferrimagnetic material, which has a high magnetization. Therefore, this material, which exhibits advanced capacitive and magnetic properties, is promising for potential applications in multifunctional devices based on mutual interactions of magnetic and capacitive properties.

Material	Mass Loading	Voltage Window	Cs	Reference
	mg·cm <sup>−2</sup>	V	mF cm <sup>-2</sup>	
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /graphene	1.0	-1.0-0.0	286	[59]
		vs. SCE	at 2 mV $\cdot$ s $^{-1}$	
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /carbon	2.4	-1.0-0.0	862	[60]
		vs. SCE	at $1 \text{ mA} \cdot \text{cm}^{-2}$	
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /carbon	1.1	-1.0-0.0	430.8	[61]
nanoarray		vs. Ag/AgCl	at 1 mA·cm <sup>−2</sup>	
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /carbon	N/A	-0.8-0.0	340	[62]
		vs. Ag/AgCl	at 1 mA·cm <sup>−2</sup>	
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /carbon	40	-0.8-0.0	1530	this work
· · · · ·		vs. SCE	at 2 mV $\cdot$ s $^{-1}$	

**Table 1.** Capacitance of Fe<sub>2</sub>O<sub>3</sub>-based composites containing conductive carbon additives in Na<sub>2</sub>SO<sub>4</sub> electrolyte in negative potential range.

## 4. Conclusions

Composites of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and MWCNTs with active mass loading of 40 mg·cm<sup>-2</sup> were prepared by colloidal processing for energy storage in negative electrodes of supercapacitors. The composites combined advanced ferrimagnetic properties with high capacitance. The high capacitance was achieved at a low electrical resistance, which is beneficial for efficient charge–discharge. HEBM exerted influence on powder morphology and facilitated the fabrication of composites with enhanced capacitance. Gallocyanine allowed efficient co-dispersion of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and MWCNTs. The catechol group of this dispersant facilitated its adsorption on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, whereas the polyaromatic structure allowed adsorption on MWC-NTs. The electrostatic co-dispersion allowed for efficient mixing of individual components of the composite material. The highest capacitance of 1.53 F·cm<sup>-2</sup> was achieved in Na<sub>2</sub>SO<sub>4</sub> electrolyte for composites, containing  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, which was high energy ball milled and co-dispersed with MWCNTs using gallocyanine. Obtained composites are promising for fabrication of multifunctional devices based on mutual interaction of ferrimagnetic and capacitive properties.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/jcs6060177/s1, Figure S1: FTIR spectra of (a) as-received Fe<sub>2</sub>O<sub>3</sub>, (b) gallocyanine, (c) Fe<sub>2</sub>O<sub>3</sub>, containing adsorbed gallocyanine.

**Author Contributions:** Conceptualization, C.Z. and I.Z.; methodology, C.Z.; software, C.Z.; validation, C.Z. and I.Z.; formal analysis, C.Z.; investigation, C.Z.; resources, I.Z.; data curation, C.Z.; writing—original draft preparation, C.Z. and I.Z.; writing—review and editing, C.Z. and I.Z.; visualization, C.Z. and I.Z.; supervision, I.Z.; project administration, I.Z.; funding acquisition, I.Z. All authors have read and agreed to the published version of the manuscript.

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