Hybrid Layer-by-Layer composites based on conducting polyelectrolyte and Fe₃O₄ nanostructures grafted on graphene for supercapacitors application

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Using the Layer-by-Layer process, we developed a new and original ternary hybrid material based on magnetite iron oxide raspberry nanostructures, 250–300 nm in size, synthesized directly on Few Layer Graphene (Fe₃O₄@FLG) alternated with conducting poly(3,4-ethylenedioxy thiophene):poly(styrene sulfonate) (PEDOT:PSS) as electrode material for supercapacitors. Magnetite based nanostructures were used as electroactive materials. Graphene and PEDOT:PSS ensured the electric conductivity. PEDOT:PSS plays also the role of binder conferring a cohesion to the hybrid material. Using spin-coating, the step-by-step buildup leads to very regular and well controlled film properties such as the film thickness and the content in iron oxide. The electrochemical properties of the so obtained hybrid material were investigated in 0.5 M Na₂SO₃ aqueous electrolyte by cyclic voltammetry, electrochemical impedance spectroscopy and chronopotentiometry. In contradiction with reported poor capacitance and poor cycling stability of iron oxide based supercapacitor, hybrid Fe₃O₄@FLG/PEDOT:PSS multilayers provide a high specific capacitance (153 F g⁻¹ at 0.1 A g⁻¹) and a high structural and cycling stability (114% retention after 3500 cycles). This hybrid developed system opens the route for even higher specific capacitance using other types of metal oxides.

1. Introduction

Nowadays, increasing demands for energy promotes the research in sustainable and efficient energy storage systems. Supercapacitors (SCs), also known as electrochemical supercapacitors or ultracapacitors, are rechargeable electrochemical energy storage devices. During the last decades, these devices have received a considerable attention due to their properties: high capacitance reaching thousands of farads, high power density, long cycling stability, low cost and fast charge and discharge rate.¹ SCs can be classified in two categories according to the charge-discharge mechanism: (i) electrical double layer capacitors (EDLCs), where the capacitive process is based on the charge separation at the interface between the electrodes and the electrolyte (non-faradaic process) and (ii) pseudocapacitors, which involve a fast and reversible Faradaic redox reaction (Faradaic process).^{2, 3} In order to provide an increase of the capacitance, it is important to have materials with a large specific area leading to an improved contact between the electrode and the electrolyte.⁴ Carbon nanostructured materials like activated carbon, carbon nanotubes or graphene have been extensively studied as SCs electrode materials for EDLC systems.⁵⁻¹¹ Easily obtained from graphitic materials,¹²⁻¹⁴ graphene (and FLG - Few Layer Graphene) has great advantages due to its 2-dimensional structure: high surface area, excellent electrical conductivity and mechanical and morphological

properties.¹⁵ However, single layer graphene is easily restacking, limiting its application in high power density devices. In the case of pseudocapacitors, two kinds of materials are commonly used: transition metal oxides or conductive polymers (CP). The Faradaic process is based on redox reactions of the metal oxide or on the reversible electrochemical doping-dedoping process of CP. The capacitance provided by the devices depends highly on the electrode materials used. High power and energy densities could be achieved by combining EDLC and pseudo capacitance materials. Thus, hybrid materials based on carbon materials, metal oxide and/or CP are more and more studied.¹⁶ Metal-oxide RuO₂ in combination with carbon nanotubes is the most promising material reported in the literature with a very high capacitance (953 F g⁻¹).¹⁷ However, RuO₂ has several limitations: high price, toxicity and scarcity. Other metal oxides are investigated such as MnO₂,^{18, 19} SnO₂,²⁰ or Fe₃O₄.²¹⁻²⁴ Non-toxic, environmental friendly, earth abundant and cheap, iron oxide combined with carbon materials is a promising composite system. Concerning CP/carbon hybrid materials, they can store charges not only in the electrical double layer (EDL) but also through the rapid faradaic charge transfer showing much higher capacitance than carbon electrodes.²⁵ Different CPs were combined with graphene or carbon nanotubes such as polyaniline,²⁶⁻²⁸ polypyrrole,^{29, 30} or polythiophene derivatives, poly(3,4-ethylenedioxy thiophene): poly(styrene sulfonate)

(PEDOT:PSS).^{31, 32} The obtained properties depend on the elaboration process.

The Layer-by-Layer (LbL) process is one of the most promising methods to build-up nanoscale structures by alternated deposition of oppositely charged materials.³³ In general, film thickness increases linearly with the number of deposition steps, presenting a stratified structure. Composition and thickness of the films can thus be controlled to tune the properties of the material. Allowing the incorporation of an unprecedented range of functional building blocks, LbL process enables the design of a large variety of films for several areas of applications.^{34,35} Recently, nanoscale supercapacitor electrodes were developed.³⁶ Using graphene oxide in combination with CP or magnetite, high capacitance (between 49 and 151 F g⁻¹) were obtained for film thicknesses between 36 – 350 nm.^{37, 38} Low ionic and electronic resistance are obtained due to a good access of electrolyte ions inside LbL thin films.

One of the challenges in SCs is to develop a system with a good structural and cycling stability while preserving a high specific capacitance. In the last years, ternary hybrid materials were reported in the literature to address this challenge. Graphene decorated by metal oxide were wrapped with CP by dipping and dry processes using PEDOT:PSS³⁹ or by electropolymerization using PANI.^{40,41} The synergy of metal oxide, graphene and CP allows enhancing the electrochemical performances such as cycle stability, specific capacitance thanks to the contribution of the different physical and electrochemical properties of the individual constituents.

In this study, a ternary hybrid material was developed based on raspberry Fe₃O₄ nanostructures, graphene and PEDOT:PSS named (Fe₃O₄@FLG/PEDOT:PSS)_n, using the LbL process (Fig. 1). We present a new way to realize such an architecture based on the synthesis of iron oxide nanostructures directly on Few Layer Graphene (Fe₃O₄@FLG) by a polyol mediated solvothermal technique and on the alternate deposition of these structures with PEDOT:PSS in an LbL manner.

Fig. 1 Schematic representation of the studied hybrid LbL architecture: (bPEI/PEDOT:PSS)₂(Fe₃O₄@FLG/PEDOT:PSS)_n, i.e. (Fe₃O₄@FLG/ PEDOT:PSS)_n. After the deposition of (bPEI/PEDOT:PSS)₂ precursor multilayer film, alternated depositions of Fe₃O₄@FLG, Fe₃O₄ raspberry nanostructures grafted on Few Layer Graphene, and PEDOT:PSS were performed by spin-coating on a gold electrode.

Easily implemented, this new method leads to very regular and well controlled film properties providing a high structural stability with an excellent and reproducible control of the amount of Fe₃O₄ incorporated. The electrochemical performance and stability of Fe₃O₄@FLG/PEDOT:PSS architectures were evaluated and compared to a system composed of the separated constituents, i.e. Fe₃O₄/FLG/PEDOT:PSS.

2. Experimental section

2.1 Materials.

Branched poly(ethylene imine) (bPEI; P3143; Mw ~25,000), Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS; 483095; 1.3 wt% dispersion in water), sodium sulfite (Na₂SO₃; 31454), succinic acid (398055) and Triton X-100 (X100) were purchased from Sigma-Aldrich. Hexahydrate iron(III) chloride (FeCl₃·6H₂O; 12497), urea (36428) and ethylene glycol (A11591) were purchased from Alfa Aesar. Gold foil (0.25×50×50 mm³; 99,99%) were purchased from Mateck GmbH. Ethanol absolute and toluene were purchased from Carlos Erba. 18.2 MΩ deionized water (TOC < 1 ppb), supplied by a Q20 Millipore or Ultra Analytique (Helga/Veolia) systems were used for suspension and solution preparation.

2.2 Few Layers Graphene (FLG).

3 g of expanded graphite (Le Carbone Lorraine - SAFRAN) in 900 mL of toluene and 9 g of triton X-100 were sonicated with a probe twice during 30 min with a break of 15 min between the two sonications. After 15 min of decantation, 300 mL of the supernatant was filtered and the graphene was washed with EtOH. The same procedure was repeated 3 times. The collected graphene was dried at 120°C for 12 h. FLG with a number of layers comprised between 5 and 30 was typically obtained.

2.3 Synthesis of raspberry nanostructures in suspension (Fe₃O₄) and grafted on graphene (Fe₃O₄@FLG).

Iron oxide raspberry nanostructures have been synthesized following a procedure described elsewhere.⁴² In a typical synthesis of raspberry nanostructures (Fe₃O₄), Iron (III) chloride hexahydrate (6 mmol), succinic acid (2 mmol) and urea (60 mmol) were completely dissolved in ethylene glycol (60 mL) by vigorous mechanical stirring during 6h and sonicated for 1h. The solution was sealed in a Teflon lined stainless steel autoclave (120 mL capacity), slowly heated at 200°C at 2°C min⁻¹ and kept at this temperature for 6h. The autoclave was cooled down to room temperature afterwards by water circulation for 1h. The sediments were separated by decantation and washed 3 times with ethanol and 3 times with deionized water to eliminate organic and inorganic impurities. Finally, the precipitate was frozen and dried to remove water giving rise to a brown powder. For the synthesis of Fe₃O₄@FLG, 120 mg of FLG was dispersed in 30 mL of ethylene glycol by sonication probe (3 times). The prepared solution was added to 30 mL of Iron (III) chloride hexahydrate solution to follow the same procedure as described before. After synthesis and washing steps, the precipitate was frozen and dried to remove water giving rise to a dark powder. Pressure and temperature during synthesis have been followed by a homemade pressure and temperature acquisition into the autoclave.

2.4 Characterizations

Fe₃O₄ nanostructures and Fe₃O₄@FLG nanocomposites were characterized by X-Ray diffraction (XRD) using a Bruker D8

Advance equipped with a monochromatic copper radiation source, ($K\alpha = 0.154056$) and a Sol-X detector. High purity silicon powder ($a = 0.543082$ nm) was systematically used as an internal standard to reset the zero 2θ to calculate with accuracy the lattice parameters of Fe_3O_4 . Profile matching refinements were performed through the Fullprof program using Le Bail's method with the modified Thompson-Cox-Hasting (TCH) pseudo-Voigt profile function. Size and morphology of Fe_3O_4 and Fe_3O_4 @FLG have been characterized by scanning electron microscopy (SEM) on a JEOL 6700F with a 2 nm point resolution. Thermogravimetric analyses (TGA) were performed from 20°C to 900°C under air flow with a heating rate of 5°C min^{-1} by using a Texas Instruments SDT Q600. The specific surface areas were determined with a Micromeritics sorptometer (Tristar). The samples were outgassed at 250°C under vacuum for 12h in order to desorb moisture or adsorbed species from its surface. The measurements were carried out using N_2 as adsorbent at its liquid temperature. The quantification of iron oxide present in the deposited architecture was performed using inductively coupled plasma optical emission spectroscopy (ICP-OES, VARIAN 720-ES). The hybrid coating was first immersed in HNO_3 solution (69%) to dissolve iron oxide nanostructures. The solution was further analysed by ICP-OES at the characteristic wavelengths of iron (*i.e.* $\lambda=238.204$, 259.94 and 258.588 nm).

2.5 Buildup of hybrid LbL by spin-coating.

The LbL buildup was performed using WS-650-23NPP Spin Coater (Laurell Technologies, North Wales, USA). Before to be used as substrates, $15 \times 15 \text{ mm}^2$ gold electrodes were cleaned with water, ethanol dried and activated for 30 min by UV-Ozone. The whole surface of the gold electrode was covered by spin-coating using the following conditions for the deposition and the washing steps: 40 s at 2500 rpm, with an initial acceleration of 500 rpm s^{-1} . Silicium wafer ($1.5 \times 1.5 \text{ cm}^2$; BT electronics, France) were used for ellipsometry measurement and SEM images. Several dispersions were used: bPEI at 1 mg mL^{-1} in $\text{H}_2\text{O}:\text{EtOH}$ (1:1), PEDOT:PSS at 0.13 wt % obtained by diluting the commercial solution in $\text{H}_2\text{O}:\text{EtOH}$ (1:1), Fe_3O_4 @FLG at 5 mg mL^{-1} in EtOH, FLG at 0.15 mg mL^{-1} in EtOH and $\text{Fe}_{3-x}\text{O}_4$ at 5 mg mL^{-1} in water. A precursor multilayer was always deposited on the substrates to allow a good anchoring of the hybrid architecture. $100 \mu\text{L}$ of bPEI solution was deposited followed by a washing step with $120 \mu\text{L}$ of water. After bPEI deposition, $120 \mu\text{L}$ of PEDOT:PSS was deposited followed by the same washing step. The whole procedure was repeated twice to obtain the precursor multilayer, named (bPEI/PEDOT:PSS)₂. After the deposition of the precursor multilayer, (bPEI-PEDOT:PSS)₂(Fe_3O_4 @FLG/PEDOT:PSS)_{*n*} architectures with $n = 8, 10, 15, 20, 30, 60, 120$ were obtained by using the following procedure *n* times. $45 \mu\text{L}$ of Fe_3O_4 @FLG was deposited followed by $80 \mu\text{L}$ of EtOH (washing step). $80 \mu\text{L}$ of PEDOT:PSS was deposited twice followed by the same washing step. (bPEI-PEDOT:PSS)₂(FLG/ Fe_3O_4 /PEDOT:PSS)₁₅ was obtained using the following procedure 15 times. $45 \mu\text{L}$ of FLG

was deposited 6 times followed by a washing step with $80 \mu\text{L}$ of EtOH and $200 \mu\text{L}$ of water. $120 \mu\text{L}$ of $\text{Fe}_{3-x}\text{O}_4$ was deposited followed by $80 \mu\text{L}$ of PEDOT:PSS twice followed by the same washing step. (bPEI-PEDOT:PSS)₂(FLG/ Fe_3O_4)₁₅ architecture was obtained by using the following procedure 15 times. $45 \mu\text{L}$ of FLG was deposited 6 times followed by EtOH and water washing step. $120 \mu\text{L}$ of $\text{Fe}_{3-x}\text{O}_4$ was deposited followed by the same washing step. For the sake of clarity, the architecture will be named without mentioning the precursor multilayer.

2.6 Electrochemical Measurement.

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic chronopotentiometric measurements were performed using a Bio-logic potentiostat SP300 (Bio-Logic SAS, Claix, France). All the measurements were performed using a three-electrode cell with separated electrode compartments under N_2 in $0.5 \text{ M Na}_2\text{SO}_3$ aqueous solution. The working electrode was a gold plate ($15 \times 15 \text{ mm}^2$) cut from gold foil ($0.25 \times 50 \times 50 \text{ mm}^3$), coated with the hybrid multilayers, the reference electrode and counter electrode were Mercury Sulfate (MSE) and platinum wire (Pt), respectively. The potentials in the paper are reported in MSE scale ($0.00 \text{ V RHE} = -0.68 \text{ V / MSE}$). CV curves were recorded from -1.3 V to -0.4 V at the following scan rates 1, 2, 5, 10, 20, 50, 100, 200 and 500 mV s^{-1} . The specific capacity from CV was calculated by the integration of the curve and dividing the charge by the potential interval range and the mass of the active material. EIS measurement were performed in a frequency range from 200 KHz to 0.1 Hz (6 frequency points per decade), with a 6 mV potential amplitude. The galvanostatic charge-discharge curves were measured at various current densities 0.1, 0.25, 0.5, 1 and 1.75 A g^{-1} with switch potentials of -1.3 V to -0.4 V . The cycling life test was performed over 1600 cycles for all the systems at 1 A g^{-1} . The specific capacitance measured by chronopotentiometry was calculated from the current density per mass of active material according to the equation as follow:

$$C_{sp} = \frac{I \times \Delta t}{\Delta E \times m}$$

where C_{sp} (F g^{-1}) is the specific capacitance of the electrode, I (A) the constant discharging current, Δt (s) the discharging time, ΔE (V) potential range during the discharge process and m the mass of active materials deposited on the electrode. The current density was calculated according to the mass of active materials iron oxide. All electrochemical experiments were carried out at room temperature.

3 Results and discussion

3.1 Synthesis of iron oxide nanostructures on graphene

Two kinds of iron oxide raspberry nanostructures were synthesized, one in suspension (Fe_3O_4) and the other one directly grafted on the FLG (Fe_3O_4 @FLG) by the same polyol mediated solvothermal process. The morphology of these materials was characterized by scanning electron microscopy (SEM). When synthesized alone, well dispersed and monodisperse in size iron

oxide nanostructures with a raspberry shape are obtained with an average diameter of 297 ± 15 nm (Fig. 2a). They consist in original orientated aggregates of Fe_3O_4 nanocrystals with a mean size of 25 nm.⁴² Synthesized in the presence of FLG (Fig. 2b), well separated layers of graphene totally covered with iron oxide raspberry nanostructures are obtained, named $\text{Fe}_3\text{O}_4@\text{FLG}$ (Fig. 2c and 2d). Anchored Fe_3O_4 nanostructures present similar morphology and diameter 246 ± 9 nm than the ones synthesized alone.

Fig. 2 Typical SEM images of (a) Fe_3O_4 iron oxide raspberry nanostructures, (b) few layer graphene FLG and (c, d) $\text{Fe}_3\text{O}_4@\text{FLG}$ nanocomposites, iron oxide raspberry nanostructure grafted on few layer graphene.

BET analyses reveal a surface area of $24 \text{ m}^2 \text{ g}^{-1}$ for $\text{Fe}_3\text{O}_4@\text{FLG}$ and $21 \text{ m}^2 \text{ g}^{-1}$ for Fe_3O_4 nanostructures. These similar values show that the formation of nanostructures either in solution or at the graphene surface do not affect the porous structure. Furthermore, the presence of graphene does not modulate the specific surface area, which agrees with its high covering by iron oxide nanostructures. N_2 isotherm adsorption and desorption of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{FLG}$ are represented in Fig. S1 in ESI. Fe_3O_4 N_2 isotherm has type II shape (according IUPAC classification) indicating nonporous structure (or macroporous taking into account the space between the nanocrystals Fe_3O_4 in the raspberry structure). In the case of $\text{Fe}_3\text{O}_4@\text{FLG}$, N_2 isotherm showed a type IV shape with a hysteresis typical for mesoporous materials. Thermogravimetric analyses allow determining the amount of Fe_3O_4 nanostructures in $\text{Fe}_3\text{O}_4@\text{FLG}$. The major weight losses occurred in the range of $450\text{--}700^\circ\text{C}$, corresponding to the release of CO and CO_2 . The reduced weight may correspond to the oxidation of graphene nanosheets. Assuming that the final residues are $\text{Fe}_{3-x}\text{O}_4$ nanostructures, they represent around 75% of the material (Fig. S2 in ESI). Powder X-ray diffraction (pXRD) pattern of $\text{Fe}_3\text{O}_4@\text{FLG}$ showed reflection peaks at 18.2° , 30.1° , 35.4° , 43.1° , 55.1° , 57.0° , 62.6° and 74.1° corresponding to the miller index (111), (220), (311), (400), (004), (511), (440) and (533) respectively. They are attributed to a spinel structure of iron oxide. The calculated lattice parameter, $8.39(7) \text{ \AA}$, is very close to that of the stoichiometric magnetite phase ($8.396 \text{ \AA}$, JCPDS card n°00-019-0629).⁴³ These

nanostructures consist of oriented aggregates of iron oxide nanocrystals (nanocrystals with common crystallographic orientations directly combined together to form larger ones) which ensure a very low oxidation state of Fe_3O_4 nanocrystals. Two additional peaks were also observed at 26.5° and 54.9° corresponding to the (002) and (004) reflections of the hexagonal crystalline structure of the graphite.^{44, 45}

Fig. 3 pXRD patterns of Fe_3O_4 raspberry nanostructures and $\text{Fe}_3\text{O}_4@\text{FLG}$ nanocomposites.

3.2 Buildup of LbL hybrid architectures

Dipping or spraying processes are usually used to build up LbL assemblies mainly based on electrostatic interactions between the building blocks. For neutral or less charged species, spin-coating is an alternative method. Moreover, it allows a rapid and homogeneous deposition of ultrathin films with a small amount of used material. We thus choose the spin coating to build up the hybrid architectures. A precursor multilayer film based on the alternate deposition of bPEI and PEDOT:PSS, $(\text{bPEI}/\text{PEDOT:PSS})_2$, was always deposited on the electrode surface as an anchoring layer. Branched polycation bPEI allows obtaining a highly positively charged surface and PEDOT:PSS plays the role of CP. Even if not conductive, Tang *et al.* reports that bPEI does not interfere with the electrochemical properties of the multilayer films.⁴⁶ To obtain a thin film deposition with full electrochemical accessibility throughout the precursor bilayer, a low concentration of bPEI (1 mg mL^{-1}) was used. Negatively charged PEDOT:PSS interacts electrostatically with bPEI providing conductive layers essential in energy storage application. A $(\text{bPEI}/\text{PEDOT:PSS})_2$ multilayer film has a dry thickness, measured by ellipsometry, of $28 \pm 1 \text{ nm}$ with a very good homogeneity (Fig. S3 in ESI). For the sake of clarity, the precursor multilayer will not be mentioned in the following of the paper.

The $(\text{Fe}_3\text{O}_4@\text{FLG})_{15}$ architecture was first studied. The successive depositions of $\text{Fe}_3\text{O}_4@\text{FLG}$ nanocomposites on the precursor multilayer film lead to an unstable coating in 0.5 M Na_2SO_3 electrolyte solution, used for the electrochemical characterization. In order to overcome this problem, PEDOT:PSS was deposited after each $\text{Fe}_{3-x}\text{O}_4@\text{FLG}$ layer leading to $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS})_n$ architectures with $n = 8, 10, 15, 20, 30, 60$ and 120 bilayers. Acting as a binder material between each $\text{Fe}_3\text{O}_4@\text{FLG}$ layer, PEDOT:PSS should also participate in the charge storage process by the contribution of the electrical double layer and the rapid faradaic charge transfer. SEM images allow characterizing the surface and evaluating the thickness of the obtained hybrid architecture. For $n = 15$ bilayers, $\text{Fe}_3\text{O}_4@\text{FLG}$ nanocomposites are homogeneously distributed on the surface of the electrode and inside the layers (Fig. 4a-b). Whatever the number of bilayers deposited, Fe_3O_4 raspberry nanostructures have a good dispersion and size homogeneity inside the layers (Fig. S4 and Fig. S5 in ESI). In composition mode, iron oxide nanostructures are distinctly observed in contrast with the other materials present (Fig. S6 in ESI). Determined by using SEM cross-sections (Fig. S5 in ESI), the thickness of $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS})_n$ architectures increases linearly from 9 to 72 μm with $n = 15$ to 120 bilayers (Fig. 4c).

Fig. 4 Characterization of $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS})_n$ architectures. (a) Top and (b) cross-sectional of SEM views of 15 $\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS}$ bilayers. (c) Evolution of the thickness, determined by SEM, as a function of the number of deposited $\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS}$ bilayers. (d) Amount of Fe_3O_4 , determined by ICP-AES measurements, as a function of the number of deposited $\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS}$ bilayers.

Inductively coupled plasma (ICP-AES) analyses were performed to evaluate the quantity of iron oxide included in the architecture. The amount of Fe_3O_4 increases linearly as a function of the number of bilayers deposited from 0.21 to 5.1 mg with $n = 8$ to 120 bilayers (Fig. 4d). A good control of distribution and the quantity of iron oxide nanostructures is achieved inside the film. The LbL approach is highly reproducible and versatile for this kind of hybrid assemblies. For comparison, separated building blocks, FLG, ungrafted Fe_3O_4 nanostructures and PEDOT:PSS, were also used to build in a LbL manner $(\text{FLG}/\text{Fe}_3\text{O}_4/\text{PEDOT:PSS})_{15}$ hybrid architecture, using diluted suspension of FLG to avoid restacking. This way of building the

film is not only increasing the buildup time but also gives a heterogeneous coating with non-coated areas and aggregated nanostructures (Fig. S7 in ESI). The average thickness cannot be evaluated precisely in this case. For comparison, the following electrochemical characterizations will be done on both hybrid architecture: based on the grafted $\text{Fe}_3\text{O}_4@\text{FLG}$ alternated with PEDOT:PSS and based on the separated building blocks.

3.3 Electrochemical Properties of LbL hybrid architectures

The electrochemical properties $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS})_n$ were evaluated at different number of layers in 0.5 M Na_2SO_3 aqueous electrolyte using a gold electrode as a substrate. According to Wang *et al.*, Na_2SO_3 electrolyte solution allows measuring the capacitive current from both EDLC and pseudocapacitance, involving successive reduction of the specifically adsorbed sulfite anions on iron oxide.⁴⁷ CVs of $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT})_n$, with different numbers of bilayers, were first performed with a potential range between -1.3 and -0.4 V (vs MSE) at different scan rates from 1 to 500 mV s^{-1} . An increase of the capacitance is obtained with the number of bilayers. The shape of the CV curves shows the contribution of the two SC mechanisms. Related to the electrical double layer, rectangular voltammograms are obtained at scan rates lower than 100 mV s^{-1} (Fig. 5a, Fig. S8 and S9 in ESI). At higher scan rates, cathodic and anodic peaks both at -0.75 V (vs MSE) appears clearly corresponding to the following reversible reaction:

These redox peaks indicate a pseudocapacitive mechanism (Fig. 5a, Fig. S8 and S9 in ESI).^{48, 49} A loss of the pseudocapacitive contribution is observed for 60 and 120 bilayers at high scan rates (Fig. S8f-g in ESI). Increase in the number of layers results in an increase of its intrinsic electrical resistance. Thus, charging of the layer requires longer time or slower charging rate. If charging rate is constant (Fig. 5), for thicker samples lower contribution of slower capacitance component can be expected. Comparing to double-layer capacitance, pseudocapacitance phenomena provides relatively slow component contribution into the overall capacity. Thus, one observes less and less significant contribution of pseudocapacitance as thickness layer increases. Reported per mass of active material (*i.e.* iron oxide), the gravimetric capacitance of the system was studied as a function of the number of bilayers at different scan rates (Fig. 5b and Fig. S10 in ESI). A maximum value of 116 F g^{-1} at 1 mV s^{-1} is obtained for 15 bilayers. By increasing the number of bilayers, the gravimetric capacitance decreases to 46 F g^{-1} for 120 bilayers. For more than 30 deposited bilayers, *i.e.* thickness higher than 17 μm , the performance of $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT})_n$ system decreases. This behaviour can be attributed to the densification of the films which prevents the penetration of the electrolyte ions into the film. This phenomenon was previously reported in the literature in the case of ultrathin films with thickness lower than 500 nm.^{38, 50} On the contrary, the areal capacitance, referred to the geometric surface area of the electrode, increases linearly from 7 to 40 mF cm^{-2} for 30 bilayers with a slower increase until

120 bilayers at 85 mF cm^{-2} (Fig. 5c). Since, the coated surface area for all samples was similar, the linear increase of areal capacitance with the number of layers is due to an increase of the amount of electrochemically active material per cm^2 .

Fig. 5 Cyclic voltammetry of $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS})_n$ recorded at a scan rate of 1 mV s^{-1} for different numbers of bilayers: (a) Voltammograms, (b) gravimetric capacitances, referred to the mass of deposited active material and (c) areal capacitances, referred to the geometric surface area of the electrode.

In comparison to $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT})_{15}$ architectures at the same number of deposition steps in iron oxide, the shape of the voltammograms appears less rectangular at high scan rates in the case of the separated building blocks, *i.e.* $(\text{FLG}/\text{Fe}_3\text{O}_4/\text{PEDOT:PSS})_{15}$ (Fig. 6a-b). It demonstrates a lower contribution from the double layer capacitance attributed to graphene. Fig. 6c shows the gravimetric capacitance as a function of the scan rate for both systems. A higher gravimetric capacitance is obtained for $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT})_{15}$ with 116 F g^{-1} compared to 78 F g^{-1} for the separated building blocks system. A better electrochemical performance, *i.e.* gravimetric capacitance, is obtained when Fe_3O_4 nanostructures are grafted on FLG compared to those ungrafted. It can be argued that the anchoring of iron oxide nanostructures on graphene leads to a more efficient separation between different layers of FLG and prevents their restacking in solution (Fig. 2c-d). The strong interactions between nanostructures and FLG may be ascribed to the nucleation and then growth of nanostructures on defects and/or steps in graphene sheets. In contrast to separated Fe_3O_4 and FLG architecture (Fig. S7 in ESI), the entire electrode was coated (Fig. 4a-b, Fig. S4 and Fig. S5 in ESI) and a good dispersion of Fe_3O_4 nanostructures is obtained inside the film by using grafted $\text{Fe}_3\text{O}_4@\text{FLG}$. This allows a better access of an electrolyte to active sites. In the case of separated Fe_3O_4 and FLG architecture, the electrode is partially covered presenting uncoated areas and aggregates (Fig. S7c-d). Due to FLG restacking in solution, a less efficient separation between the different layers of FLG is obtained on the coated areas affecting the accessibility of active sites. Poorer electrochemical performance were thus obtained for $(\text{FLG}/\text{Fe}_3\text{O}_4/\text{PEDOT:PSS})_{15}$ architecture in comparison with $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT})_{15}$ architectures.

Fig. 6 Voltammograms obtained for (a) $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS})_{15}$ (b) $(\text{FLG}/\text{Fe}_3\text{O}_4/\text{PEDOT:PSS})_{15}$ at different scan rates: (blue) 50 mV s^{-1} , (green) 20 mV s^{-1} , (orange) 10 mV s^{-1} , (cyan) 5 mV s^{-1} , (black) 2 mV s^{-1} and (red dashed) 1 mV s^{-1} . (c) Gravimetric capacitance (F g^{-1}) as a function of the scan rate for (red) $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS})_{15}$ and (black) $(\text{FLG}/\text{Fe}_3\text{O}_4/\text{PEDOT:PSS})_{15}$.

Finally, $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT})_{15}$ architectures were characterized by EIS in open circuit conditions before and after 1000 galvanostatic cycles (Fig. 7). Using a conventional approach to model electrochemical capacitors, the data were fitted by a simple circuit model where the capacitors are replaced by a constant phase element (CPE).⁵¹ Two parallel capacity circuits (C_1 and R_2C_2) can be attributed to the double layer capacitance and pseudo-capacitance, respectively, where R_2 is related to the charge transfer resistance of involved faradaic processes.

Fig. 7. Nyquist plots of EIS spectra of $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT})_{15}$ measured in $0.5 \text{ M Na}_2\text{SO}_3$ at open circuit potential (A) before and (B) after 1000 galvanostatic cycles. Insert is the zoomed area of high frequencies.

In the case of $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT})_{15}$, the phase shift constants a_1 and a_2 of corresponding CPEs are close to 1, the value for an ideal capacitor (Table S1 in ESI). The deviation from ideal capacitor behaviour is commonly attributed to the inhomogeneous distribution of local surface capacity, inhomogeneous layer thickness or contribution from non-capacitive components, like mass-transport induced Warburg

impedance. Thus, this result confirms the structural homogeneity of $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT})_{15}$ architecture and indicates the absence of significant mass transport limitations. Moreover, the results are similar before and after 1000 galvanostatic cycles showing the stability of the system. For thicker coatings (higher number of deposited bilayers), the deviation from ideal capacitor behaviour was systematically stronger (Table S1 in ESI), confirming that for these deposits the ionic transport limitations play an important role. The cycling stability of $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT})_{15}$ and $(\text{FLG}/\text{Fe}_3\text{O}_4/\text{PEDOT:PSS})_{15}$ hybrid architectures were tested over 1600 cycles using continuous charge-discharge cycles at a constant discharge current density of 1 A g^{-1} (Fig. 8a). The capacitance retention, *i.e.* the ratio of the gravimetric capacitance of the final and initial cycle, of the $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT})_{15}$ system increases slowly for the first 500 cycles and remains stable at 114% till 1600 cycles. The capacitance retention was performed until 3500 cycles for different number of bilayers (Fig. S11 in ESI) where almost the same stability is observed.

Fig. 8 (a) Cycling stability over 1600 cycles of (red) $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS})_{15}$ and (black) $(\text{FLG}/\text{Fe}_3\text{O}_4/\text{PEDOT:PSS})_{15}$. (b) Galvanostatic charge and discharge curves at various current densities of $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS})_{15}$ architecture.

This increase can be attributed to the activation of iron oxide nanostructures. Fe_3O_4 nanostructures can be partially oxidized during the electrode preparation, leading to a decrease in their capacitance.^{43,52} On the contrary for the separated building block system, a significant decrease of the capacitance retention is observed during the first 100 cycles with a loss of 20% (Fig. 8a). Then, the decrease continues slowly to reach 65% of retention till 1600 cycles showing a relatively poorer cycle stability. The heterogeneity of the architecture (Fig. S7c-d in ESI) could explain the poor retention of the system. The aggregates could favor the (i) loss of the conductivity of polymers films and (ii) restacking of graphene layers during the cycling. The better electrochemical properties of $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT})_{15}$ can also be observed by EIS where similar values are obtained before and after 1000 cycles (Table S1 in ESI). In the case of $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS})_{15}$, an asymmetrical behaviour of galvanostatic charge-discharge curve appears at low current density (Fig. 8b). Previous studies associated this shape to the pseudocapacitance of Fe_3O_4 based on its slow redox reaction.^{38,53} The specific capacitances of $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS})_{15}$ can be calculated from the corresponding charge-discharge curves. At current density of 1 A g^{-1} , the specific capacitance is of 46 F g^{-1} . At very low current density (0.1 A g^{-1}), it increases to 153 F g^{-1} (Fig S12 in ESI). This is a relatively high value in comparison with other values reported on similar materials

(Table S2 in ESI). Indeed, the different studies on carbon and Fe_3O_4 based materials obtained specific capacitances between 117.2 F g^{-1} and 220 F g^{-1} .^{36, 48,52, 53} Other types of oxide, like $\text{MnCo}_2\text{O}_{4.5}$,⁵⁶ V_2O_5 ,⁵⁷ Co_3O_4 ,⁵⁸ were reported in the literature with higher capacitance. We are planning to extend our method of hybrid materials synthesis to these oxides.

Conclusions

We have carried out an extensive study of hybrid LbL materials/film/nanostructure based on conducting PEDOT:PSS polyelectrolyte and Fe_3O_4 nanostructures grafted on FLG. Using spin-coating, a good control and reproducibility of the distribution and quantity of iron oxide immobilized on the surface of the electrode is obtained. The study of the electrochemical performances reveals the contribution of two mechanisms: the double electrical layers and the pseudocapacitive corresponding to the slower reversible reactions of $\text{Fe}(\text{II}) \leftrightarrow \text{Fe}(\text{III})$. The electrochemical properties were investigated as a function of the number of deposited bilayers, with a maximum gravimetric capacitance (116 F g^{-1} at 1 mV s^{-1}) in the case of 15 bilayers. The $(\text{Fe}_3\text{O}_4@\text{FLG}/\text{PEDOT:PSS})$ hybrid coating has a good stability after 1600 cycles with capacitance retention of 114%. This system leads to specific capacitance calculated at 153 F g^{-1} at current density of 0.1 A g^{-1} . Reported capacitance and short-term stability are relatively high for iron oxide based materials compared with literature data. The approach of hybrid LbL with active nanostructures anchored on the carbon materials combining with conductive polymers is an easy and friendly method of functionalization. This allows fabricating electrode in a reproducible and versatile manner. It is a promising way to develop new electrodes for supercapacitor application.

Acknowledgements

E. P. was supported by a post-doctoral fellowship from Labex "Nanostructures in interactions with their environment" (Labex NIE, CONV/2012/01/CIRFC n°22). The authors thank O. Gerber for fruitful collaboration. The authors gratefully acknowledge financial support from Labex NIE and from International Center for Frontier Research in Chemistry (icFRC).

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Electronic Supplementary Information (ESI) available: XXX See DOI: 10.1039/b000000x/

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