Research Plan Defense 2017

Graphene-based materials for energy storage devices

Jaime Sánchez Sánchez

Electrochemical Processes Unit, IMDEA Energy Institute, Móstoles (Madrid) Spain.

Supervised by: Dra. Rebeca Marcilla
Dr. Afshin Pendashteh

Tutor UAM: Pilar Ocon

Outline

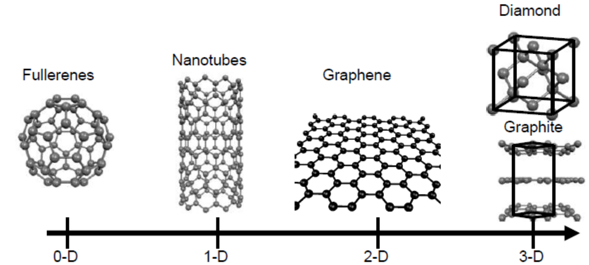
1. Introduction
   - What is Graphene?
   - Graphene in Energy Storage
2. Objectives and motivation of the research plan
3. Methodology
   - Synthesis of Graphene Oxide (Modified Hummer's route)
   - Synthesis method of the hybrid materials
   - Characterization techniques
4. Experimental Results
   - Synthesis & Structural Characterization
   - Electrochemical Behaviors
   - Asymmetric Aqueous Batteries
5. Future Work

What is Graphene?

Introduction

- **Graphene can be described as a single atomic layer of GRAPHITE packed into a 2D structure**

- **Andre Geim & K. Novoselov isolated a single layer (2004)**



Nobel Prize in Physic (2010)

Amaia Zurutuza et al., Nature Nanotechnology. Vol. 9. October 2014

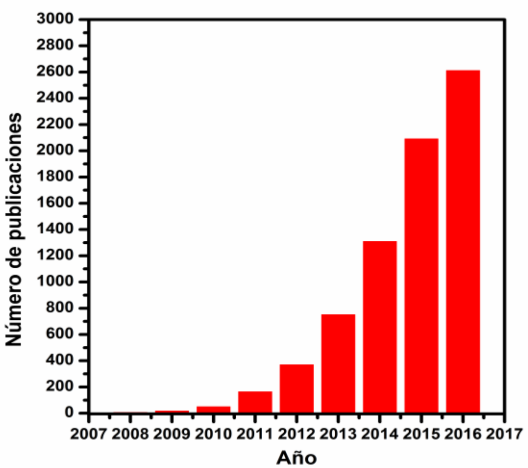


Figure 1. Published documents per year according to Scopus with "Graphene" and "Supercapacitor" as searching keywords

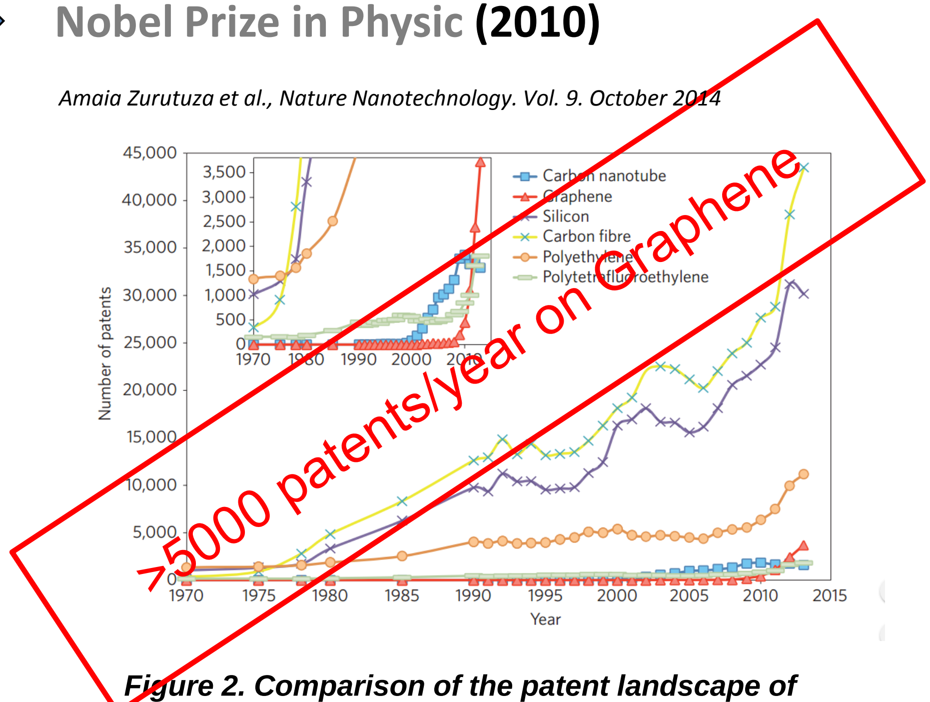


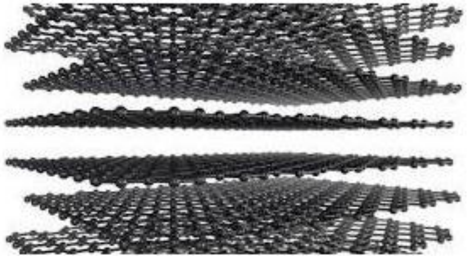
Figure 2. Comparison of the patent landscape of different materials.

Among the many affected areas of materials science, the actual graphene fever has influenced particularly the world of electrochemical energy storage devices:

- **High electrical conductivity (high rate capability)**
- **Relatively Large Specific Surface Area**

However,Graphene-based materials (rGO, GO, Graphene..) exhibit unsatisfactory values in capacitance/capacity due to inevitable restacking of graphene nanosheets.

- **Low capacitances/capacity values**



EUROPEAN UNION STRUCTURAL FUNDS

La Suma de Todos
Comunidad de Madrid
www.madrid.org

MAD2D

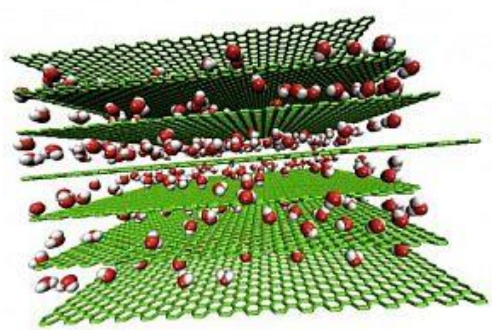
instituto imdea energía

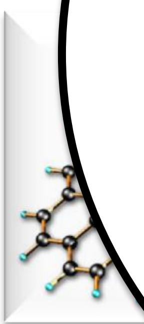
Objectives and motivation

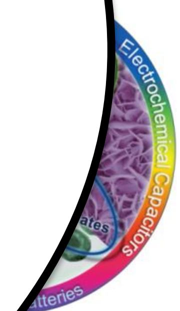
Objectives

Graphene-Metal Oxide Hybrid materials

- High capacity arises from their Faradaic reactions
- High cycle life due to metal oxides can suppress the re-stacking of graphene nanosheets.
- Synergistic Effects







○ **Carbona**
○ **No chemical**
○ **High conductivity**
○ **Low charge storage capa**

e, Mn…)
Limited cycle life
conductivity
rge storage capacity

* Figure Source: D. Lou et al., *Angew. Chem. Int. Ed*. **2014**, 53, 1488-1504.

US 20100178531 A1 PATENT

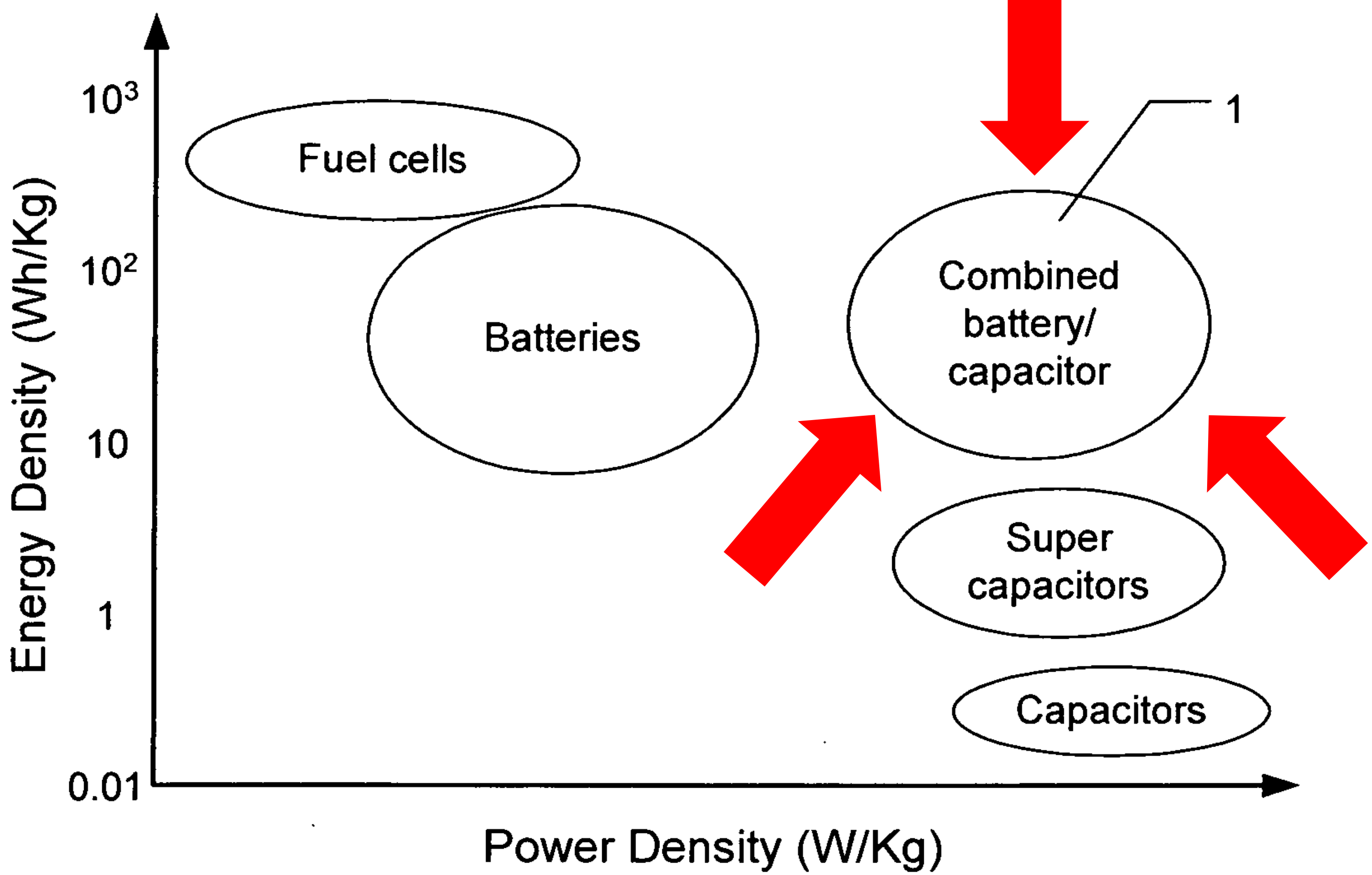
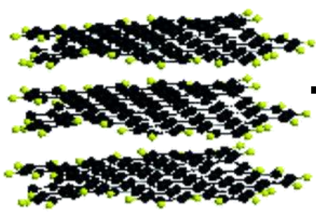


Figure 3. Ragone Plot of the main electrochemical devices

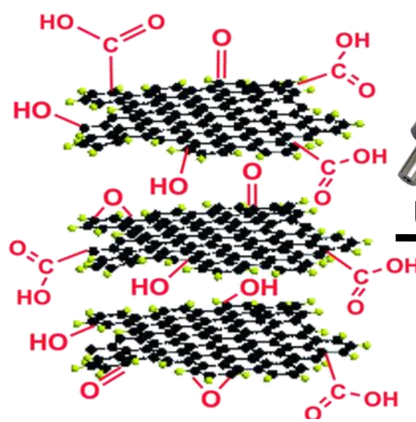
2. METHODOLOGY

Synthesis of Graphene Oxide (Modified Hummer's route)

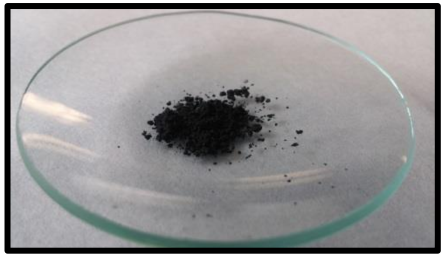


Graphite

Pre-oxidization and Oxidization

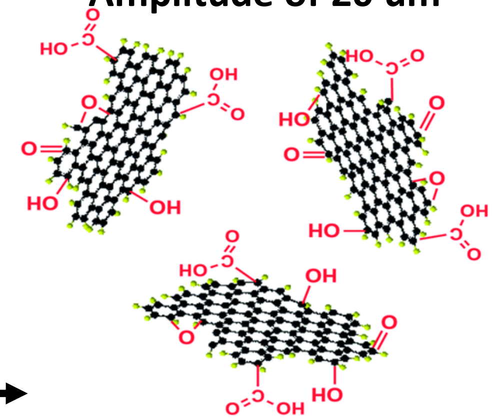


Graphite Oxide

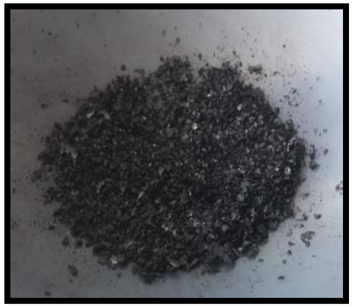


Ultrasonication

2 – 10 min 24 kHz
Amplitude of 20 um



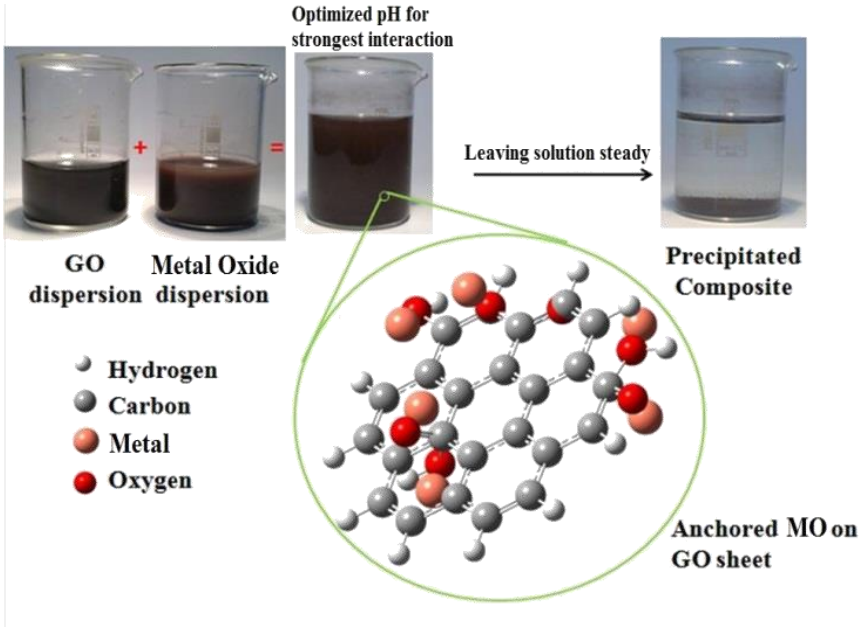
Graphene Oxide



1,5 g GO
Yield ≈ 75%

Synthesis of the hybrid materials

Methodology



Electrostatic Coagulation

Hydrothermal method ✚ **Thermal treatment**

Variables:

- Hydrothermal reaction time.
- Hydrothermal temperature.
- Ratio oxide/carbon.

Characterization techniques

Methodology

1. Structural and morphological characterization:

- X-ray diffraction (XRD)
- Raman Spectroscopy
- Thermal gravimetric analysis (TGA)
- N_2 adsorption/desorption isotherms
- Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) analysis methods
- X-ray photoelectron spectroscopy (XPS)
- Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)
- …

2. Electrochemical Characterizaction:

- Cyclic Voltammetry (CV)
- Galvanostatic Charge-Discharge (GCD)
- Electrochemical Impedance Spectroscopy (EIS) measurements

3. EXPERIMENTAL RESULTS

Synthesis and characterization

Results

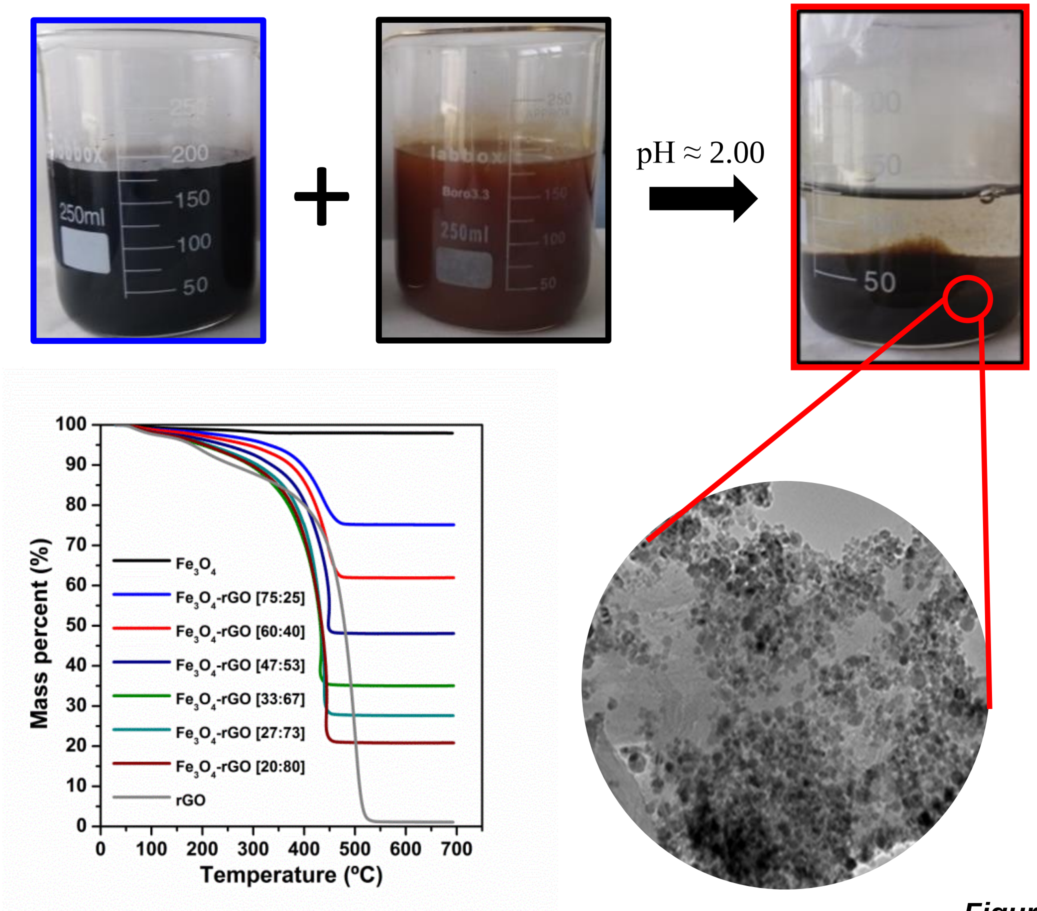


Figure 4. Synthesis scheme and TGA curves of the Fe_3O_4-rGO nanocomposites

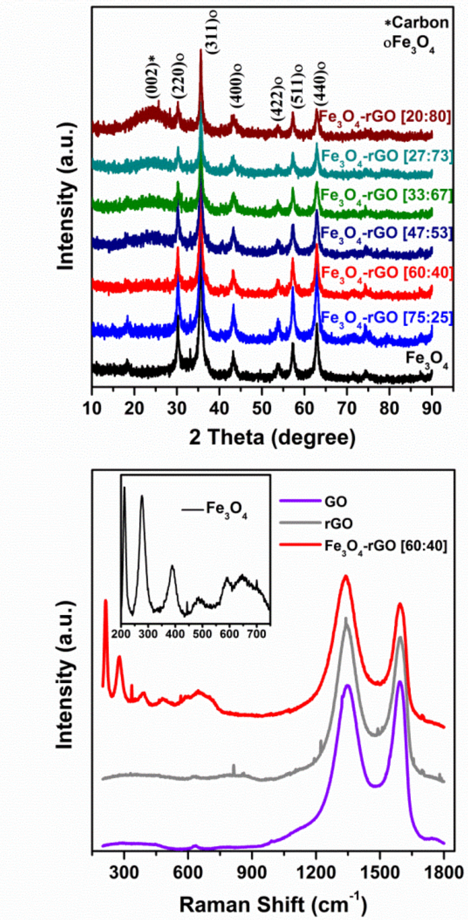
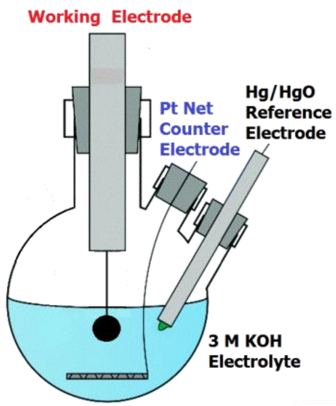


Figure 5. (a) XRD of Fe_3O_4-rGO nanocomposites; (b) Raman spectroscopy of GO, rGO and Fe_3O_4-rGO. Inset shows Raman spectrum of pure Fe_3O_4.

EUROPEAN UNION
STRUCTURAL FUNDS
La Suma de Todos
Comunidad de Madrid
www.madrid.org
MAD2D
instituto imdea energía

Electrochemical behaviour 3-electrode configuration

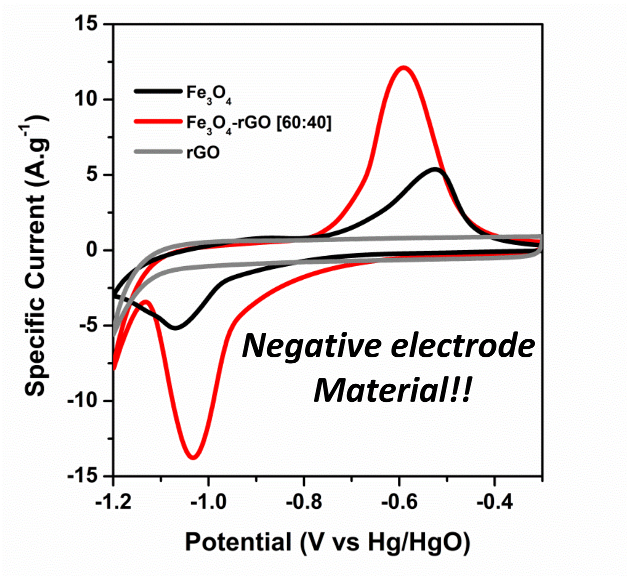
Results



Electrode composition:
70% rGO-Fe_3O_4,
20% Carbon Black
10% PTFE

$Fe^{III} + 2e^{-} + 3H_2O \rightarrow 2Fe^{II} + 2OH^{-}$

Mass loading: 5-10 mg/cm²



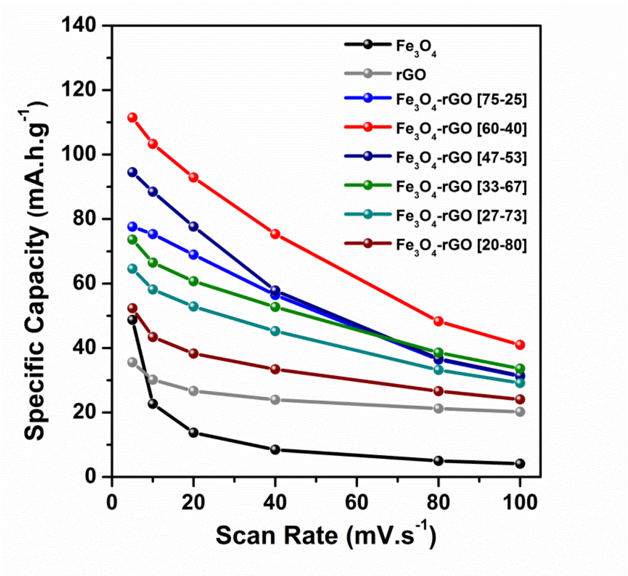
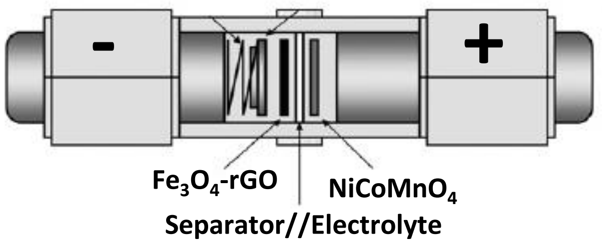
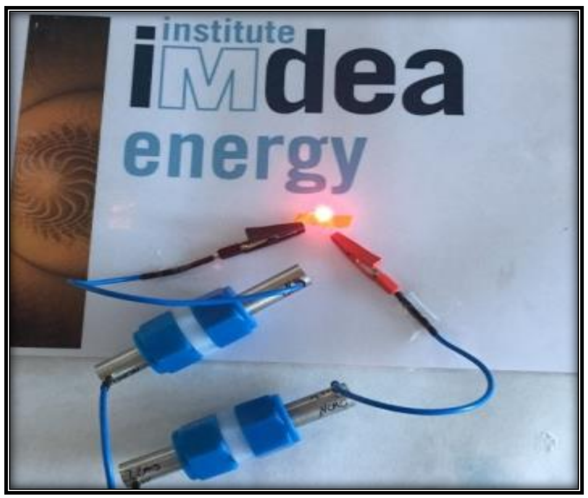


Figure 6. (a) CV curves of the rGO, Fe_3O_4 and Fe_3O_4-rGO [60:40] samples at a scan rate of 5 $mV.s^{-1}$; (b) Rate capability of the samples at various scan rates

Asymmetric Aqueous Batteries

Results





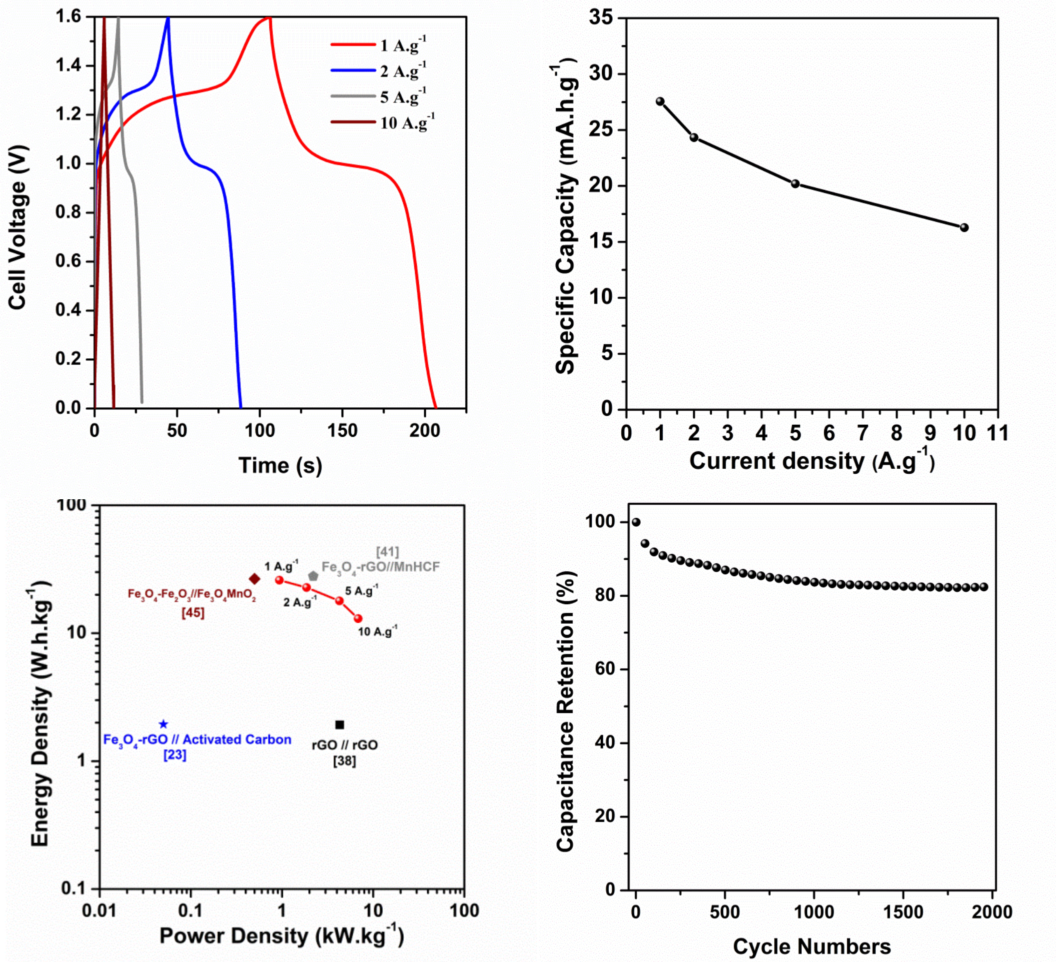


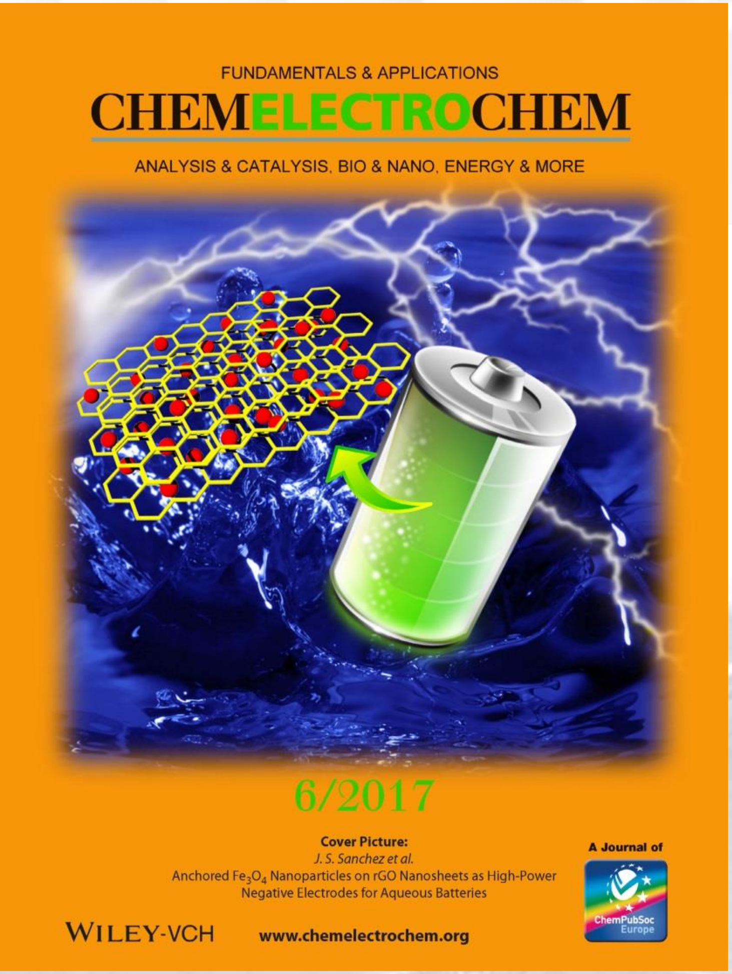
Figure 7. Electrochemical performance of Fe_3O_4-rGO NSs// $NiCoMnO_4$ aqueous battery: (a) GCPL curves in two-electrode configuration (b) Rate capability (c) Ragone Plot (d) Cyclability.

EUROPEAN UNION
STRUCTURAL FUNDS

La Suma de Todos
Comunidad de Madrid
www.madrid.org

MAD2D

instituto imdea energía



ChemElectroChem 10.1002/celc.201700048

ARTICLE WILEY-VCH

Anchored Fe_3O_4 Nanoparticles on rGO Nanosheets as High-Power Negative Electrodes for Aqueous Batteries

Jaime S. Sanchez[a], Afshin Pendashteh[a]*, Jesus Palma[a], Marc Anderson[a],[b] and Rebeca Marcilla[a]*

Future work

- Our contribution could be the Synthesis of different Novel Graphene-Composites and research their application in Energy Storage Devices (e.g. Supercapacitors, batteries or supercapacitor-battery hybrid devices).
- Explore Hydrothermally decoration of different porous Metal Oxides and Mixed Transition Metal Oxides on rGO.
- Investigation of ORR Electrocatalytic Activity of the different Composites synthesized.

Thank you so much for your attention

MAD2D

EUROPEAN UNION
STRUCTURAL FUNDS

La Suma de Todos
Comunidad de Madrid
www.madrid.org

MAT2015-64167-C2-1-R
MAD2D-CM Program (S2013/MIT-3007)