

CO₂ Capture by Amino-functionalized Graphene Oxide

Marina González-Barriuso^{a,b,*}, Carmen Pesquera^b, Fernando González^b, Ángel Yedra^a and Carmen Blanco^b

^aFundación Centro Tecnológico de Componentes. C / Isabel Torres, No. 1, in the Scientific and Technological Park of Cantabria, Santander 39011 Cantabria, Spain.

^bInorganic Chemistry Group. Dpt. of Chemistry and Process & Resource Engineering. University of Cantabria-, Av. de los Castros s/n, Santander 39005 Cantabria, Spain.
mgonzalez@centrotecnologicocct.com

Human activity is increasing CO₂ atmospheric concentration contributing to global warming. In this situation CO₂ reversible capture and storage, what it is known as carbon capture and conversion (CCC), can be part of the solution. In this context, searching for a suitable material for this application is necessary. The present study was carried out to investigate the CO₂ adsorption of amino-functionalized graphene oxide on its surface. Amino-functionalized graphene oxide samples were prepared by different methods with two kind of molecules: 3-aminopropyltrimethoxysilane (APTMS) and polyethylenimine (PEI). A characterization study of the prepared samples was done with thermal analysis, thermogravimetry (TG) and differential scanning calorimetry (DSC), and X-ray photoelectron spectroscopy (XPS). To evaluate the CO₂ adsorption of the samples CO₂ adsorption isotherms were done. These isotherms correspond with a type I and shows an improvement in CO₂ chemisorption regarding graphene oxide.

1. Introduction

Fossil fuels are a significant contribution in climate change and global warming, due to CO₂ emissions. On the other hand, they are versatile energy sources. A balance between their drawbacks and benefits is needed. In the latest years, plenty of works have been developed aimed at the solution of this problem (Najafabadi, 2015). In addition, there is a problem in some industrial applications where gas separation is needed, such as hydrogen production via steam reforming methane followed by water-gas shift (WGS) where the resulting gas is a mixture of CO₂ and H₂. Carbon capture and conversion (CCC) approach can be efficiently used for CO₂ separations in this kind of industrial complication where a mixed gas stream: H₂/CO₂, CH₄/CO₂ or N₂/CO₂.

Basic amine groups inside the structure of a nanoporous support can create a composite material with preference in slightly basic CO₂ adsorption. There are studies related to carbon capture on adsorbent solids as chemisorbents (Fernández et al., 2010) and amine-functionalization of nanoporous materials (Chen et al., 2014), specifically silicic nanoporous materials (Sanz et al., 2015; Ahmed et al., 2016; González-Barriuso et al., 2016). In this context, graphene and its derivatives are shown as the ideal materials for this kind of applications. The main reason for this is its 2D structure, high specific surface, and the ability to modify its surface to give them the adequate selectivity. Graphene doping with nitrogen can show a selective CO₂ adsorption and a potential industrial application. Amine functionalization of graphene and carbon nanotubes with different molecules and its applications has been reported (Bhowmik et al., 2016). In this paper graphene oxide is functionalized with amine groups, from polyethylenimine (PEI) and 3-aminopropyltrimethoxysilane (APTMS). Also, its carbon dioxide capture capacity is evaluated. The incorporation of these amine groups (-NH₂-, -NH-) has been already studied on other porous or big surface materials, like silicic materials (MCM-41, SBA-15, silica gel...) related to its CO₂ chemisorption capability. This chemisorption is a reversible reaction between CO₂ molecules and the amine groups of the amino-functionalized graphene oxide surface for the formation of carbamates (Sanz et al., 2015; Ahmed et al., 2016; Sánchez-Vicente et al., 2015). This and the intrinsic characteristics of graphene oxide makes this graphene oxide functionalized with amine a possible adsorbent in carbon capture. The main novelty of this work is to use a graphene derivative as a CO₂ adsorbent.

Paper Received: 27 March 2018; Revised: 7 July 2018; Accepted: 5 November 2018

Please cite this article as: Gonzalez-Barriuso M., Pesquera C., Gonzalez F., Yedra A., Blanco C., 2019, CO₂ Capture by Amino-functionalized Graphene Oxide, Chemical Engineering Transactions, 75, 637-642 DOI:10.3303/CET1975107

2. Experimental

Graphene oxide (av-GOx-70, from Avanzare Technologies), ethanol (96%, from Panreac), 3-aminopropyltrimethoxysilane (APTMS, from Aldrich), polyethylenimine (branched PEI Mw=800g/mol and branched PEI Mw=60,000g/mol, both from Aldrich) and trimethylamine (from Aldrich) were all use as received.

2.1 Graphene oxide amino-functionalization

Synthesis of GO-APTMS. A suspension of 0.200g of graphene oxide (GO) in 40ml of ethanol and 2ml of water was prepared. Then, the suspension was sonicated for 20minutes by ultrasound by means of a Sonopuls HD 3200 with a maximum piezoelectric power of 200W (using a MS73 tip and 25% amplitude of power). Subsequently, 200 μ L of APTMS were added. The reaction takes place under stirring at room temperature for 3h. Finally, the mixture was filtered and washed with distilled water. The resulting solid was dried at 60°C (Hosseinabadi-Farahani, et al. 2015). This sample was named GO-APTMS1. This process was repeated to prepare a second sample, GO-APTMS2, where 600 μ L of APTMS were used.

Synthesis of GO-PEI. Initially, a solution of 1.500g low molecular weight PEI in 100ml ethanol via bath sonication was prepared. After, to create a basic media, 300 μ L of trimethylamine were added to the mixture. A suspension of 0.150g of graphene oxide in 100ml of water was prepared. This suspension was sonicated for 20minutes by ultrasound by means of a Sonopuls HD 3200 with a maximum piezoelectric power of 200W (using a MS73 tip and 50% amplitude of power). Then, both solutions were mixed together and heated to reflux in continuous stirring for five days. Finally, the mixture was filtered and washed with distilled water and ethanol. The resulting solid was dried at 60°C. This sample was named GO-PEI1.

This process was repeated to prepare a second sample, GO-PEI2, where a high molecular weight PEI was used and the PEI solution was 0.750g PEI in 100ml ethanol.

2.2 Characterization techniques

The characterization of the amino-functionalized graphene oxide has been carried out by the following techniques:

Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed. It was used a thermogravimetric TG-DSC Setaram equipment with a working temperature range from room temperature up to 1500°C. The working conditions for the analysis in this work were a temperature range between 20 to 1000°C, under air atmosphere. Also, a heat velocity of 10°C/min and an air flux of 50cm³/min.

Mass spectrometry was conducted using a ThermoStar GSD 301T mass spectrometer connected in series to the thermogravimetric TG-DSC Setaram. Its normal working pressure is between 1·10⁻⁶ to 5·10⁻⁶mbar.

X-ray photoelectron spectroscopy (XPS) was carried by a SPECS, with a Phoibos 100 hemispherical electronic energy analyzer and with a monochromatic Mg K α (1253.6eV) X-ray source under a pressure of 10⁻⁷Pa in the analysis chamber during the measurements. In deconvolutions, each individual component is considered as a convolution of a Gaussian function and a Lorentzian one in 80:20 proportion. XPS is used to analyze the surface chemistry of the materials.

The CO₂ adsorption isotherms were obtained by an automatic ASAP-2000 systems from Micromeritics, volumetric gas adsorption–equipment at room temperature and CO₂ pressures between 0 to 1atm. Prior to measurements, samples were outgassed at 110°C and 10⁻⁴ mbar for 6h.

3. Results and discussion

3.1 Thermal analysis: DSC, TG and mass spectrometry

The thermal analysis gives us information about the incorporation of the amine compounds in the graphene oxide. Figure 1(left) shows TG and DSC of the graphene oxide sample, it was performed in air atmosphere at 10°C/minute. The TG shows a first step with a 9.74% of weight lost with a DSC soft endothermic signal around 100°C. This could be assigned to the adsorbed water molecules on the graphene oxide. The water signal (mass 18), in the mass spectrophotometer couple to the thermobalance, (Figure 1, right) prove it.

The second step takes place around 220°C and the mass lost is 21.92%. This suggest that is caused by the oxygenated groups lost (hydroxyl, carboxyl) from de graphene oxide (Song et al., 2017). The exothermic DSC signal, due to a dehydroxylation and decarboxylation, and the water (mass 18) and CO₂ (mass 44) signals prove it (Figure 1, right). The third TG step, with a 39.07% mass lost above 450°C, belong to the complete oxidation of the graphene structure. A fourth step, at an upper temperature (above 770°C), belong to the graphitic material oxidation, 14.88% mass lost, that in the GO exfoliation process was not exfoliated. In both steps the DSC signal point out an exothermic peak that belong to the carbon material combustion and is associated with the 44 mass signal of the mass spectrophotometer (Figure 1, right,).

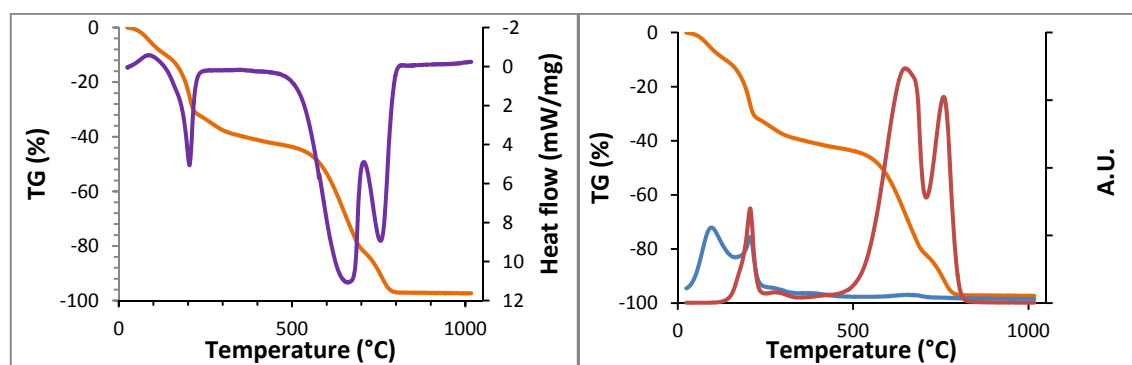


Figure 1. Left, Thermogravimetric analysis (orange) and DSC (purple). Right, mass tracing by mass spectrometry of H_2O (18, blue), and CO_2 (44, red) of graphene oxide (GO) sample.

Figure 2 shows the TG curves of the samples after functionalization. In Figure 2-right, could be observed a decrease in the second stage belonging to the GO carboxyl- hydroxyl groups and an increase in the mass lost between 230–450°C. This increased belong to the amino-functionalized groups decomposition/oxidation on the graphene oxide surface. In Figure 2- left, the 18 and 44 mass signals could be seen by mass spectrometry. This water and CO_2 came from the amine group decomposition/oxidation. It could be appreciated that these APTMS functionalized materials shown 11-16% of residue after the oxidation at 1000°C higher than the initial GO, which correspond with the SiO_2 residue from the APTMS molecules (aminosilanes).

In the TG curves of PEI functionalized materials (Figure 2-right), could be seen the same decrease in the mass lost belonging to the GO carboxyl-hydroxyl groups and an increase in the mass lost between 230–450°C because of the PEI functionalization. Also, the increases of the water and CO_2 signals in this temperature range could be observed by mass spectrometry. The residue percentage at 1000°C for these samples is almost negligible because of the PEI functionalization.

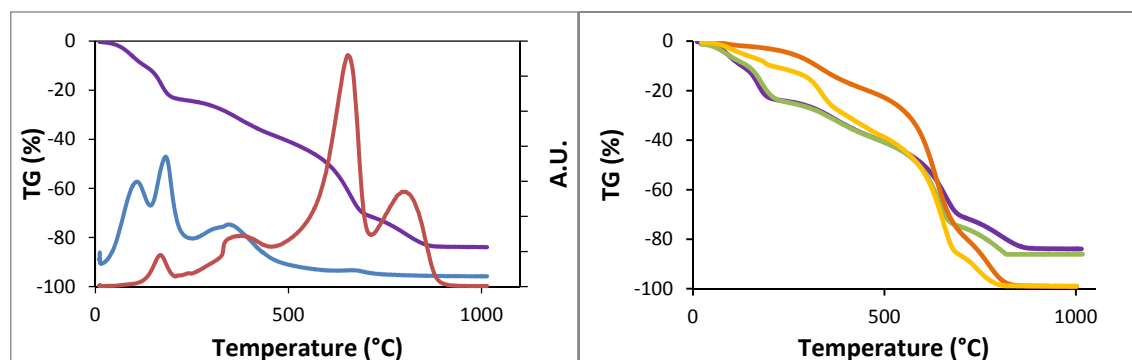


Figure 2. Left, Tg, and mass tracing of H_2O (blue) and CO_2 (red) of GO-APTMS1 sample. Right, Tg of amino-functionalized samples. GO-APTMS1 (purple), GO-APTMS2 (green), GO-PEI1 (orange), GO-PEI2 (yellow).

3.2 X-ray photoelectron spectroscopy (XPS)

XPS analysis provides elemental and chemical state information about surfaces. The elemental analysis of all samples is represented in Table 1. Carbon (C 1s) and oxygen (O 1s) peaks are recorded in the XPS spectrum of graphene oxide (GO) sample. Also, small sulfur and chlorine contributions are recorded in the XPS spectrum. These small contributions came from the material preparation process and disappear in the functionalized samples. In the functionalized samples appear an additional nitrogen (N 1s) peak. It appears for those functionalized with PEI and those with APTMS. Silicon (Si 2s and Si 2p) peaks are shown in functionalized samples with APTMS. These results indicate that PEI and APTMS are grafted onto the GO surface. An increase in C/O atomic ratios (Table 1) in samples functionalized indicated that GO sample was reduced during the functionalization process. This increase is smaller in APTMS functionalized samples because of the Si-O groups incorporation.

Table 1: Elemental samples composition (atomic %)

Samples	Carbon	Oxygen	Nitrogen	Silicon	C/O ratio
GO	77.2	20.1	-	-	3.84
GO-APTMS1	72.6	14.9	5.8	6.7	4.87
GO-APTMS2	74.0	14.1	5.5	6.3	5.25
GO-PEI1	84.7	8.9	6.4	-	9.52
GO-PEI2	79.6	7.5	11.9	-	10.61

Figure 3 shows the C1s XPS spectra of GO and GO-APTMS1 samples. The C1s spectrum of GO, Figure 3-left, was deconvoluted in three elementary peaks, 284.4eV corresponding to sp^2C , 286.4eV to C-O, and 288.1eV to O=C=O groups (Shao et al., 2009; Paredes et al., 2008). The C1s spectrum of GO –APTMS1, Figure 3-right, shows a peak displacement and a widening of the 286.5eV signal belonging to C-O and C-N groups (Ramanathan et al., 2005). This overlap of the peaks indicates, clearly, that the functionalization of GO is mainly achieved via reaction with oxygen groups to form C-N bond.

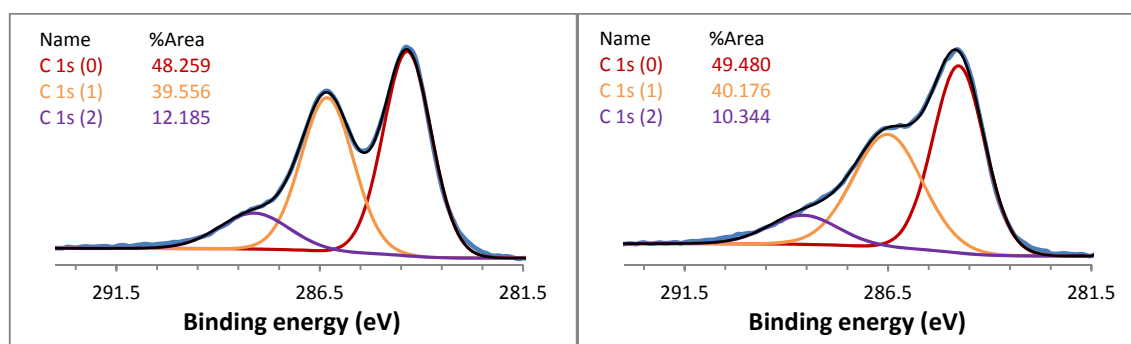


Figure 3. Left C 1s decomposed spectrum of GO. Right, C 1s decomposed spectrum of GO-APTMS1 sample.

Figure 4 shows the N 1s XPS spectra of GO-PEI2 and GO-APTMS1 samples. In Figure 4-left, correspondence with GO-PEI2 sample, it can be observed that N 1s was deconvoluted in two peaks with binding energies located at 400.02 and 401.1eV. These two peaks are attributed to the C-N bond presence which are assigned to -CO-NH and -CH₂-NH₂, respectively (Shen et al., 20017). In Figure 4-right, correspondence with GO-APTMS1 sample, it can be observed that N 1s was deconvoluted in three peaks. The third binding energy located at higher values than 402.2eV can be associated with quaternary nitrogen. Probably, due to the amine groups protonation by the ethanol that was used in the synthesis as solvent (Rocha et al, 2017). Also, by the elemental analysis, Table 1, can be observed that in the APTMS and PEI samples nitrogen had been incorporated. All these facts clearly indicate that the amino-functionalization process in the GO sample has been successful.

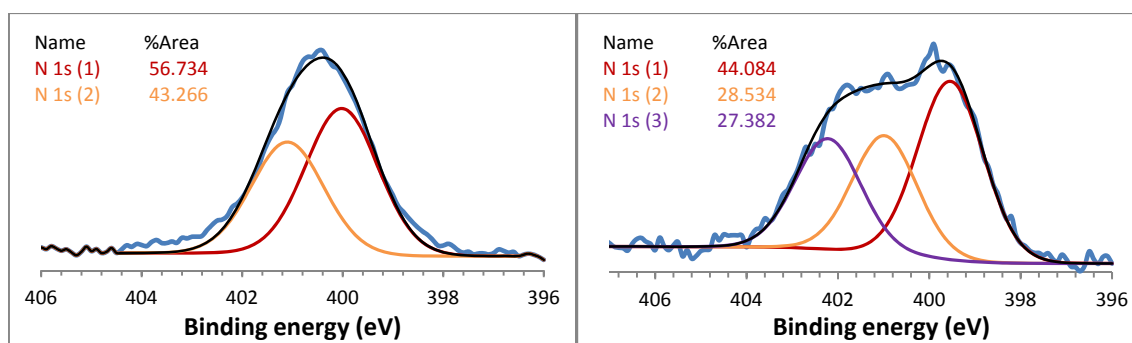


Figure 4. Left, N 1s decomposed spectrum of GO-PEI2. Right, N 1s decomposed spectrum of GO-APTMS1.

CO₂ adsorption characterization

CO₂ adsorption isotherms at 25°C were obtained in order to determine the CO₂ adsorption properties of these samples. The CO₂ adsorption isotherms of samples (Figure 5) correspond to type I according to IUPAC. The

CO₂ adsorption capacities calculated from them is showed in Table 2, reach values of 55.30 cm³·g⁻¹(STP) at 25°C and 1atm for the GO-PEI2 sample. APTMS functionalized samples reach values of 38.68 cm³·g⁻¹(STP) at 25°C and 1atm. The adsorption capacities can be attributed to the amine functional groups present in the samples. The reaction of CO₂ with an amine adsorbent consists in two steps: 1) a zwitterion is formed between the amine group and the CO₂, 2) another amine group reacts and leaves with a positive charge to form a carbamate. Under dry conditions 2mol of amine is required to capture 1mol of CO₂ (Bhowmik et al., 2016), as indicated in the following reaction:



Table 3 shows the amine groups quantity in each sample in mmol/g and the CO₂ capture capacity of each sample in mmol/g and mg/g. These data are deducted from the CO₂ adsorption isotherms at 1atm. The last column shows the CO₂ capture efficiency of the incorporate amine groups in the functionalized materials. The efficiency is higher in the APTMS functionalized samples, up to 82%, versus the PEI functionalized samples. This could be cause by the difficult access of the CO₂ molecules to the amine groups, steric restrictions, because of the branched PEI structure. In the PEI functionalized samples the most efficient CO₂ capture sample is the one functionalized by high molecular weight PEI. This better access to the amine groups by the CO₂ molecules could be due to the more open structure of the higher molecular weight PEI.

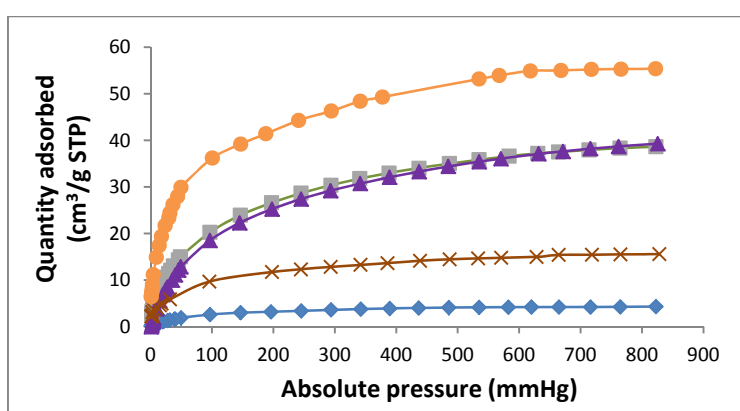


Figure 5. CO₂ adsorption isotherms of GO (◆), GO-APTMS1 (■), GO-APTMS2 (▲), GO-PEI1(X) and GO-PEI2(●) samples.

Table 2: CO₂ capture capacity of the samples studied.

Samples	CO ₂ capture (cm ³ /g, ±0.05)	
	at 1atm	at 0.1atm
GO	4.19	2.51
GO-APTMS1	38.34	17.64
GO-APTMS2	38.68	15.70
GO-PEI1	15.52	8.15
GO-PEI2	55.30	33.08

Table 3: Elemental CO₂ adsorption characteristics of the samples studied.

Samples	Amine loading (mmol N/g)	Capacity (ISOT) (mmol N/g)	Capacity (ISOT) mg CO ₂ /g	Amine efficiency (CO ₂ /2N)
GO-APTMS1	4.21	1.71	75.24	0.82
GO-APTMS2	4.02	1.73	76.12	0.86
GO-PEI1	5.13	0.69	30.36	0.28
GO-PEI2	9.58	2.47	108.68	0.52

4. Conclusions

Polyethylenimine (PEI) and 3-aminopropyltrimethoxysilane (APTMS) incorporation on the graphene oxide surface results in amino-functionalized materials able to capture CO₂. The thermogravimetric analysis (TG) and the X-ray photoelectron spectroscopy (XPS) indicate a change of nature in the materials. This change is due to the amine-functionalization of the graphene oxide surface.

CO₂ adsorption isotherms of the amino-functionalized samples show an improvement in CO₂ chemisorption regarding GO sample. The high molecular weight PEI incorporation increases the CO₂ capture capacity more than when the low molecular weight PEI is used. The efficiency in the amine groups activity is higher in the APTMS functionalized materials. The CO₂ accessibility in branched PEI functionalized materials is more difficult because of steric restrictions. These steric restrictions are less significant in the high molecular branched PEI sample, due to the more open structure.

Acknowledgements

This work was supported by "Help Industrial Doctorate" granted by the University of Cantabria in its 2014 call associated with the project N° 51.DI03.648 and it is gratefully acknowledged

References

- Ahmed S., Ramli A., Yusup S., 2016, CO₂ adsorption study on primary, secondary and tertiary amine functionalized Si-MCM-41, *International Journal of Greenhouse Gas Control*, 51, 230-238.
- Bhowmik K., Chakravarty A., Bysakh S., De G., 2016, γ -Alumina nanorod/reduced graphene oxide as support for poly(ethylenimine) to capture carbon dioxide from flue gas, *Energy Technology*, 4, 1409–1419.
- Chen C., Kim J., Ahn W., 2014, CO₂ capture by amine-functionalized nanoporous materials: A review, *Korean Journal of Chemical Engineering*, 31, 1919-1934.
- Fernández J., González F., Pesquera M.C., Blanco C., Renedo M.J., 2010, Study of the CO₂/sorbent interaction in sorbents prepared with mesoporous supports and calcium compounds, *Industrial and Engineering Chemistry Research*, 49, 2986–2991.
- González-Barruso M., Gómez L., Pesquera C., Perdígón A., González F., Yedra A., Blanco C., 2016, CO₂ capture at low temperature by nanoporous silica modified with amine groups, *Chemical Engineering Transactions*, 47, 181-186.
- Hosseiniabadi-Farahani Z., Mahmoodi N.M., Hosseini-Monfared H., 2015, Preparation of surface functionalized graphene oxide nanosheet and its multicomponent dye removal ability from wastewater, *Fibers and Polymers*, 16, 1035-1047.
- Najafabadi A.T., 2015, Emerging applications of graphene and its derivatives in carbon capture and conversion: current status and future prospects, *Renewable & Sustainable Energy Reviews*, 41, 1515-1545.
- Paredes J.I., Villar-Rodil S., Martínez-Alonso A., Tascón J.M.D., 2008, Graphene oxide dispersions in organic solvents, *Langmuir*, 24, 10560–10564.
- Ramanathan T., Fisher F.T., Ruoff R.S., Brinson L.C., 2005, Amino-functionalized carbon nanotubes for binding to polymers and biological systems, *Chemistry of Materials*, 17, 1290-1295.
- Rocha R.P., Soares O.S.G.P., Gonçalves A.G., Órfao J.J.M., Pereira M.F.R., Figueiredo J.L., 2017, Different methodologies for synthesis of nitrogen doped carbon nanotubes and their use in catalytic wet air oxidation, *Applied Catalysis: A, General*, 548, 62-70.
- Sánchez-Vicente Y., Stevens L.A., Pando C., Torralvo M.J., Snape C.E., Drage T.C., 2015, Cabañas A., A new sustainable route in supercritical CO₂ to functionalize silica SBA-15 with 3-aminopropyltrimethoxysilane as material for carbon capture, *Chemical Engineering Journal*, 264, 886-898.
- Sanz R., Calleja G., Arencibia A., Sanz P.E.S., 2015, CO₂ capture with pore-expanded MCM-41 silica modified with amino groups by double functionalization, *Microporous and Mesoporous Materials*, 209, 165-171.
- Shao L., Bai Y.P., Huang X., Gao Z.F., Meng L.H., Huang Y.D., 2009, Multi-walled carbon nanotubes (MWCNTs) functionalized with amino groups by reacting with supercritical ammonia fluids, *Materials Chemistry Physics*, 116, 323-326.
- Shen J.F., Huang W.S., Wu L.P., Hu Y.Z., Ye M.X., 2007, Thermo-physical properties of epoxy nanocomposites reinforced with amino-functionalized multi-walled carbon nanotubes, *Composites Part A: Applied Science Manufacturing*, 38, 1331-1336.
- Song Y., Cao L., Yu J., Zhang S., Chen S., Jiang Y., 2017, Amino-functionalized graphene oxide blend with monoethanolamine for efficient carbon dioxide capture, *Journal of Alloys Compounds*, 70, 245-253.