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Evaluation of the PhD thesis of Dawid Pakulski

to receive the PhD of

Adam Mickiewicz University in Poznań and Universite de Strasbourg

Specialty: Chemistry/Physical Chemistry"

" Graphene based materials and their potential applications"

The topic developed in the manuscript focuses on synthesis of functionalized two-dimensional materials (graphene and GO) by using approaches that may enable their mass production and their comprehensive physico-chemical characterization, with particular properties of heavy metal and dyes adsorption for environmental applications or for the synthesis of hybrid POM-graphene hybrids for energy storage applications. This provides great flexibility for the generation of a variety of architectures and functional objects ranging from complex molecular mixtures, coordination or dynamic organized surfaces. These strategies are easily accessible and lead to studies of great scientific value in several areas of chemistry. Several dynamic systems have been imagined from a wide range of devices with interesting properties!

The manuscript is divided in 3 main chapters, each having three parts: state of the art, results and discussions and experimental part:

1. Synthesis of graphene oxide-branched polyethyleneimine hybrid material (BPEI-GO) for removal heavy metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}) from aqueous solution.
2. Preparation of graphene oxide-aminosilica mesoporous composite (SiO2NH2-GO) for fast and efficient sequester organic cationic dyes (MB-methylene blue, MV-methylene violet, RhB-Rhodamine B).
3. Structural and electrical properties of electrochemically exfoliated graphene modified with surfactant encapsulated polyoxomolybdate POM (Mo_{132}-DTAB-EEG) for advanced electrode for supercapacitors application.

The first chapter focus the development of the BPEI-GO composites prepared *via* covalent grafting of graphene oxide with the branched polyethyleneimine polymer BPEI, containing

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amine moieties that can be used for the functionalization of GO through the ring-opening reaction of epoxy groups. The physico-chemical characterization has been performed by using Raman spectroscopy, Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS). Then the amine 2D GO materials were used in adsorption processes of heavy metal cations Pb^{2+}, Cd^{2+}, Cu^{2+} from aqueous solutions and flame atomic absorption spectrometry (FAAS) has been used to quantify the adsorption experiments. They revealed that the BPEI-GO system presents a higher adsorption for heavy metal ions ((Cu^{2+} - 1096 mg g^{-1}, Cd^{2+} - 2051 mg g^{-1}, Pb^{2+} - 3390 mg g^{-1}) with respect to other carbonaceous materials and there is a possibility of effective regeneration of BPEI-GO adsorbents in the presence of acid solutions (0.1 M EDTA and/or 0.1 M HNO_3).

The second topic of this PhD work is dedicated to the investigation of GO /aminosilica nanoparticle (SiO_2NH_2) composites and their adsorption properties with respect to selected cationic dyes for environmental applications. Similarly, to previously class of GO-BPEI composites, the synthesis of 2D covalently functionalized architectures was performed via condensation reaction on epoxy groups of GO with amino moieties. The SiO_2NH_2-GO composite presents high absorbtion values for organic dyes (RhB - 358 mg g^{-1}, MB - 300 mg g^{-1}, MV - 178 mg g^{-1}). It was shown that there is a possibility of effective regeneration of adsorbents in the presence of 0.1 M HCl, which is necessary in the practical use of sorption material on a larger scale.

Finally, in the last part of the manuscript, the electrochemical exfoliation for the production of graphene (EEG) in liquid media is presented as an approach for the large scale and fast production of graphene by using supramolecular surfactant encapsulated cluster (SEC) for EEG. The main goal of this work concerns exploiting the electrical properties of modified graphene with Keplerate-type polyoxometalate surfactant encapsulated cluster (Mo_{132}-DTAB) by non-covalent interactions for potential application as supercapacitors that combine the POM redox properties and high electrical conductivity of graphene. Highly negative charged polyoxometalates- POMs are inorganic compounds with nanometric dimensions having interesting catalytic, photochemical and electrical properties. Their ability to adsorb alkali metal ions (including Na^+, Li^+), makes them promising platforms for advanced electrical materials. The physicochemical characterization by using HR-TEM - high-resolution transmission electron microscopy, XRD - X-ray diffraction, XPS) confirmed the formation of stable Mo_{132}-

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DTAB-EEG materials having interesting electrical properties and may find potential application in the production of supercapacitors. This result encourages future pursuits in designing electronic devices containing organic species with very good conductive properties.

For each chapter, Dawid proposed further characterization techniques that could complete the results and proposed new lines of research arising from the results obtained in his thesis.

As a general conclusion on the PhD manuscript, one can notice the high interest of the systems investigated and characterized through a large spectrum of analytical methods, that were appropriately and successfully used. Also, the manuscript is of high quality of format and layout.

At the same time, due to the high quality of experimental results included in the doctoral dissertation, reliable and systematic implementation, innovative solutions that will certainly impact on the development of the studied field, I recommend for its distinction.

Therefore, I strongly recommend Dawid Pakulski to receive the doctorate degree of Adam Mickiewicz University in Poznań and Universite de Strasbourg

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