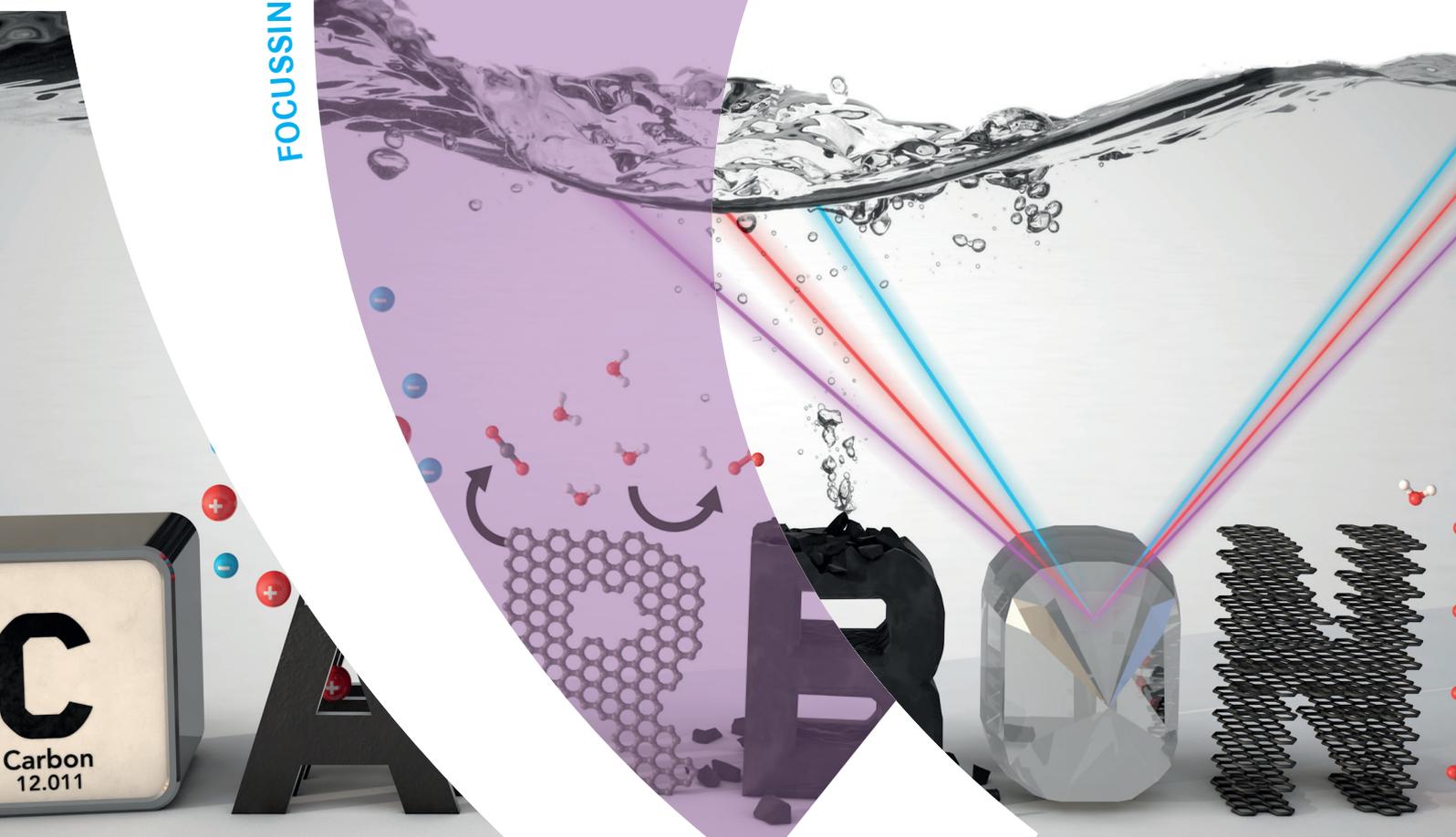


FOUSSING ENERGY REALIZING VISIONS



# CARBON NANOMATERIALS IN AQUEOUS ENVIRONMENT: FROM CHARACTERIZATION TO APPLICATIONS

February 21 – 23, 2018  
Book of Abstracts

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# Welcome

Dear Colleagues,

Welcome to the Workshop on "Carbon Nanomaterials in Aqueous Environment: From Characterization to Applications" taking place at the Helmholtz-Zentrum Berlin, bringing together researchers from different fields who shares common interests.

In aqueous environment, carbon nanomaterials interact with water and ions in many ways. A large variety of carbon nanomaterials, including nanoparticles (nanodiamonds, carbon dots) and 2D materials (carbon nitride, graphene, MXene, . . . ), have recently been proposed for applications in energy conversion and storage, water remediation and filtration, or nanomedicine among others. For all these applications, complex interactions with aqueous environment are involved, which remain poorly investigated yet.

In this interdisciplinary workshop, various aspects involving carbon-liquid interface will be discussed. New methods enabling *in situ/operando* characterization of nanomaterials in liquid, in particular using synchrotron sources such as BESSY II, will be highlighted. Several applications where carbon-water interactions are essential will also be presented. Theoretical studies are also very valuable to the understanding of these interactions and will be briefly addressed. The topic of this workshop is quite broad and it is certainly not foreseen that an exhaustive view of the field will be provided. However I hope that relevant examples of studies performed on carbon materials will stimulate fruitful discussions.

I hope you will enjoy this workshop and wish you a good time in Berlin.



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Tristan Petit

on behalf of the organizers:  
Tristan Petit (scientific),  
Sandra Fischer (local)

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# 1 Programme

| Wednesday, February 21 <sup>st</sup> , 2018                                     |   |
|---|---|
| 17:00   | Registration and Refreshments   |
| <b>Carbon Materials for Energy Applications</b> ( <i>Chair: Tristan Petit</i> ) |   |
| 18:00   | <b>Yury Gogotsi</b> ( <i>Drexel University, USA</i> )<br>Confinement of Ions in Carbon-Based Materials for Energy Storage                                     |
| 18:45   | <b>Dirk Guldi</b> ( <i>Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany</i> )<br>Versatile Carbon Nanodots in Electron Donor-Acceptor Architectures |
| 19:30   | Welcome Reception   |

| Thursday, February 22 <sup>nd</sup> , 2018                                       |   |
|--|---|
| 08:30  | Registration  |
| 09:00  | <b>Opening</b> <ul style="list-style-type: none"> <li>• Welcome by the Helmholtz-Zentrum Berlin (Bernd Rech)</li> <li>• Welcome by the Volkswagen Foundation (Oliver Grewe)</li> <li>• Welcome and Workshop Presentation (Tristan Petit)</li> </ul> |
| <b>X-ray Spectroscopies and X-ray Scattering</b> ( <i>Chair: Tristan Petit</i> ) |   |
| 9:30   | <b>Juan Velasco-Velez</b> ( <i>Fritz Haber Institute, Germany</i> )<br>Graphene as Transparent Electrode for Electrochemistry and X-ray Spectroscopy Applications in Liquid Environment   |
| 10:00  | <b>Masanari Nagasaka</b> ( <i>Institute for Molecular Science, Japan</i> )<br>Interactions of Organic Molecules with Water in Aqueous Solutions Studied by Soft X-ray Absorption Spectroscopy   |
| 10:30  | <b>Mirjam Zobel</b> ( <i>Bayreuth Universität, Germany</i> )<br>Solvent Restructuring around Colloidal Nanoparticles as seen by High-Energy X-rays  |
| 11:00  | Coffee Break  |

| <b>Thursday, February 22<sup>nd</sup>, 2018 (continued)</b>                |   |
|--|---|
| <b>Vibrational Spectroscopies</b> (Chair: Jean-Charles Arnault)            |   |
| 11:30  | <b>Tristan Petit</b> (Helmholtz-Zentrum Berlin, Germany)<br>Towards Operando Spectroscopy at Nanocarbon-Water Interface   |
| 12:00  | <b>Mailis Lounasvuori</b> (Helmholtz-Zentrum Berlin, Germany)<br>Acid Deprotonation Driven by Cation Migration at Biased Graphene Nanoflake Electrodes  |
| 12:30  | <b>Ljiljana Puskar</b> (Helmholtz-Zentrum Berlin, Germany)<br>IRIS Beamline for Nanodiamonds & Nafion Polymer Membranes Doped with Nanodiamonds   |
| 13:00  | Group Picture   |
| 13:15-15:00  | Lunch Break and <b>Poster Session</b>   |
| <b>Electrochemical Energy Storage and Conversion</b> (Chair: Yury Gogotsi) |   |
| 15:00  | <b>Martin Oschatz</b> (Max Planck Institute of Colloids and Interfaces, Germany)<br>Understanding the Role of Nanocarbon-Water Interfaces in Electrochemical Energy Storage and Heterogeneous Catalysis |
| 15:30  | <b>Ameer Al-Temimy</b> (Helmholtz-Zentrum Berlin, Germany)<br>Electronic Structure of Intercalated MXene: Towards Next Generation Supercapacitor  |
| 15:45  | <b>Roland Netz</b> (Freie Universität Berlin, Germany)<br>Interfacial Model for the Capacitance and Electrokinetics of Charged Carbon Surfaces  |
| 16:15  | <b>Giorgia Greco</b> (Helmholtz-Zentrum Berlin, Germany)<br>Pyrolytic Graphite Electrodes Intercalated by AlCl <sub>4</sub> Anions Probed by X-ray Tomography and Small Angle X-ray Scattering          |
| 16:45  | End of the day  |
| 18:30  | Meeting at Dorint Hotel for Workshop's dinner   |
| 19:30  | Workshop's Dinner (Invitation Only)   |

| Friday, February 23 <sup>rd</sup> , 2018  |  |
|---|--|
| <b>Solar Fuels</b> (Chair: Martin Oschatz)                                      |  |
| 09:00   | <b>Anke Krüger</b> (Würzburg Universität, Germany)<br>Surface Functionalized Nanodiamond for Energy Storage and Catalysis  |
| 09:30   | <b>Sneha Choudhury</b> (Helmholtz-Zentrum Berlin, Germany)<br>X-Ray Spectroscopic Investigations of the Band Structure Manipulation in Diamond Based Photocatalysts              |
| 09:45   | <b>Demetra Achilleos</b> (Cambridge University, UK)<br>Carbon Nanodots for Solar-Induced H <sub>2</sub> generation   |
| 10:15   | <b>Jian Ren</b> (Helmholtz-Zentrum Berlin, Germany)<br>Probing the Electronic Structure of Atomically-Thin Carbon Nitride Nanosheets Photocatalysts by Soft X-ray Spectroscopies |
| 10:30   | Coffee Break   |
| <b>Biomedical and Nanofluidics Applications</b> (Chair: Anke Krüger)            |  |
| 11:00   | <b>Raz Jelinek</b> (Ben Gurion University, Israel)<br>Sensing Applications using Carbon Dots in Water: Fluorescence Quenching, Enhancement, and in between                       |
| 11:30   | <b>Jean-Charles Arnault</b> (CEA-LIST, France)<br>Nanodiamond as Radiosensitizer: Chemical and Physical Investigations   |
| 12:00   | <b>Hyung Gyu Park</b> (ETH Zürich, Switzerland)<br>Mass Transport through Low-Dimensional Carbon Nanomaterials   |
| 12:30   | Lunch Break  |
| <b>Time-Resolved Spectroscopy and Electron Dynamics</b> (Chair: Iain Wilkinson) |  |
| 13:30   | <b>Robert Godin</b> (Imperial College, UK)<br>Time-Resolved Spectroscopic Investigation of Excited State Dynamics  |
| 14:00   | <b>Annika Bande</b> (Helmholtz-Zentrum Berlin, Germany)<br>Graphene Oxide Quantum Dots in <i>Bits</i> - not only in <i>Pieces</i>  |
| 14:30   | <b>Christoph Merschjann</b> (Helmholtz-Zentrum Berlin, Germany)<br>Evidence for Low-Dimensional Charge Transport in Carbon Nitride Polymers                                      |
| 15:00   | <b>Franziska Buchner</b> (Helmholtz-Zentrum Berlin, Germany)<br>Transient Absorption Spectroscopy of Nanodiamonds in Water: Direct Observation of Solvated Electrons             |
| 15:15   | Closing Remarks ( <i>Tristan Petit</i> ) and Coffee Break  |
| 16:00   | <b>BESSY II Tour for participants / Feedback Round with Advisors</b>   |
| 17:00   | End of Workshop  |

## **2 Abstracts of the Oral Presentations**

## **Confinement of Ions in Carbon-Based Materials for Energy Storage**

Yury Gogotsi\*

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Chemical (batteries) and capacitive (electrochemical capacitors or supercapacitors) energy storage plays an increasingly important role as we are moving towards the electrical economy. This lecture will discuss the role of ion confinement in carbon and carbon-based (2D carbides) nanomaterials in electrical energy storage applications. The main message is that the success in increasing both, the energy stored by the device and its power, can be achieved by combining the right carbon or carbide with a proper aqueous electrolyte. There is no perfect electrode material and no electrolyte to suit every performance goal. However, a large variety of nanostructured carbon-based materials are available nowadays. The exciting world of carbon materials includes 0-, 1-, 2- and 3D structures. Zero- and one-dimensional nanoparticles, such as onion-like carbon and nanotubes, can provide a high power due to fast ion sorption/desorption on their outer surfaces. 2D graphene has been receiving an increasing attention due to its higher charge-discharge rates compared to porous carbons and high volumetric energy density. Three-dimensional porous activated, carbide-derived and templated carbon networks, having a high surface area and porosity in the subnanometer or a few-nanometers range, can provide high energy density if the pore size is matched with the electrolyte ion size. While aqueous electrolytes, such as sodium sulfate, are the safest and least expensive, they have a limited voltage window. Non-flammable highly concentrated aqueous electrolytes are attracting an increasing attention due to safe operation in a wide temperature range and a larger voltage window resulting in a higher energy density compared to conventional electrolytes. The use of transition metal carbides (MXenes) with aqueous solutions confined between hydrophilic 2D layers allows the storage of energy using surface redox reactions of transition metal. Moreover, this can be achieved at very high rates, the same or higher than in double-layer capacitors utilizing pure carbon electrodes. A combination of carbon and carbide electrodes in an asymmetric devices is another way to widen the voltage window and increase the energy density. The mechanisms of charge storage and ion transport in confinement, as well as properties of materials affecting the electrochemical behavior in aqueous electrolytes will be discussed.

## **Versatile Carbon Nanodots in Electron Donor-Acceptor Architectures**

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The versatility of carbon-based nanomaterials in terms of structural and electronic properties renders them broadly applicable electroactive components for future energy devices. Throughout the past decades, the fundamental basis has been laid for understanding and tailoring the charge-transfer characteristics of carbon nanomaterials ranging from fullerenes and carbon nanotubes to graphene, as well as chemically modified derivatives. Fullerenes are essential for understanding unidirectional charge-transport and -transfer phenomena at the molecular level, whereas with carbon nanotubes and graphene, efficient intrinsic bidirectional transport and transfer are realized. Such a plethora of nanomaterials fosters the idea of developing functional all-carbon-based devices. In this presentation, we survey the role of carbon nanodots (CND) in energy-conversion schemes. In particular, we highlight charge-transfer processes on the molecular scale in covalently linked and non-covalently assembled electron donor-acceptor architectures, in which CNDs function as either electron donors or acceptors.

## Graphene as Transparent Electrode for Electrochemistry and X-Ray Spectroscopy Applications in Liquid Environment

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Graphene has become a major topic of research because of its unique electronic and chemical properties.<sup>1–3</sup> Desirable properties of graphene include high mechanical strength, good thermal and electrical conductivity and chemical stability in aggressive media making graphene an ideal candidate as electrode for chemical energy conversion related processes. However, graphene is not active and required its functionalization with other materials to make it electrochemically active, which demands to uncover the electronic structure that the electrode undergoes during reaction conditions in order to design more efficient and stable catalysts. X-ray spectroscopy is a powerful technique that allows unequivocal identification of the target element in an element specific manner. However, these spectroscopy techniques (especially in the soft X-ray regime) are hardly compatible with liquid environments. We have overcome this issue recently by developing a new electrochemical setup based in a graphene membrane, which is transparent to the photoelectrons generated close to the solid liquid interface but still leak tight to the liquids enabling X-ray spectroscopy in situ, i.e during electrochemical reactions.<sup>4</sup> Graphene is produced through chemical vapour deposition (CVD), which produces polycrystalline sheets of variable quality, determined by the density of grain boundaries, point defects and chemical contamination. Subsequently, graphene was transferred to different substrates behaving high stability under aqueous environment<sup>5</sup> and under high electrochemical potentials.<sup>6</sup> This approach opens the possibility for studies of virtually any solid-liquid interface, which was not possible with techniques such as X-ray absorption in fluorescence mode used until now. In this talk we will describe the development of this methodology including the different challenges that we faced at different fabrication stages. Finally, we will illustrate the operation of this setup including our actual results in electroplating<sup>4</sup> and in the oxygen evolution reaction (OER) which are within the most relevant topics in electrochemistry.

(1) A. K. Geim, K. S. Novoselov (2007), Nat. Mat., 6, 183–191.

(2) A. H. Castro Neto et al (2009) Mod. Phys. 81, 109162.

(3) A. K. Geim, Science (2009), 324, 1530-1534.

(4) Velasco-Velez, J. J. et al (2015), Angew. Chem. Int. Ed., 54(48), 14554-14558.

(5) Velasco-Velez, J. J. et al (2014), J. Phys. Chem. C. 118(44), 25456-25459.

(6) Velasco-Velez, J. J. et al (2013), JES 160(9), C445-C450.

## Interactions of Organic Molecules with Water in Aqueous Solutions Studied by Soft X-Ray Absorption Spectroscopy

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Soft X-ray absorption spectroscopy (XAS) is an effective method to study interactions of organic molecules with water in aqueous solutions because organic molecules are measured in C and N K-edges and solvent water is separately observed in O K-edge. However, the thickness of a liquid layer should be smaller than 1  $\mu\text{m}$  to measure XAS of aqueous solutions in transmission mode because soft X-rays below 1 keV are strongly absorbed by solvent water. Recently, we have successfully developed a liquid flow cell for XAS in transmission mode, in which the liquid thickness is controllable from 20 nm to 2000 nm, and studied local structures of several aqueous solutions.<sup>1</sup> In this talk, we will explain details of a liquid flow cell that is developed at soft X-ray beamline BL3U at UVSOR-III Synchrotron. For the application of XAS, we have studied the interaction of pyridine with water in aqueous solution by using XAS in C, N, and O K-edges.<sup>2</sup> By comparing the energy shifts of XAS peaks with quantum chemical inner-shell calculations, we have found that small pyridine clusters exist in the HB network of bulk water even in dilute pyridine solution. Phase transition of aqueous triethylamine (TEA) solution is studied by XAS at different temperatures. Aqueous TEA solution shows a lower critical solution temperature (LCST), in which two liquids are mixed at lower temperature and splits into two phases above 19 °C. Local structures of liquid-liquid interfaces above LCST have also studied by spatially-resolved XAS in C and O K-edges with the spatial resolution of 140 nm, which are measured by scanning transmission X-ray microscope (STXM) at soft X-ray beamline BL4U.<sup>3</sup> Finally, we discuss in situ XAS measurements of catalytic<sup>4</sup> and electrochemical reactions<sup>5</sup> in aqueous solutions for the future applications in energy conversion and storage.

(1) M. Nagasaka, H. Yuzawa, N. Kosugi, *J. Electron Spectrosc. Relat. Phenom.* 2015, 200, 293-310.

(2) M. Nagasaka, H. Yuzawa, N. Kosugi, submitted to *Z. Phys. Chem.*

(3) T. Ohigashi, M. Nagasaka, T. Horigome, N. Kosugi, S. M. Rosendahl, A. P. Hitchcock, *AIP Conf. Proc.* 2016, 1741, 050002.

(4) H. Yuzawa, M. Nagasaka, N. Kosugi, *J. Phys. Chem. C* 2015, 119, 7738-7745.

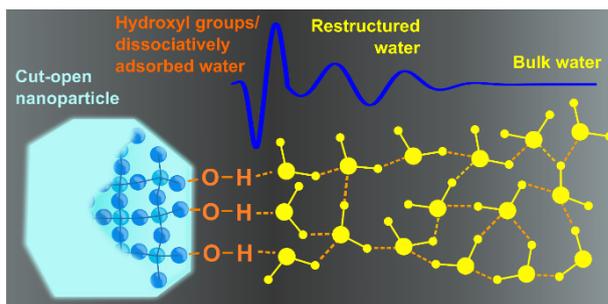
(5) M. Nagasaka, H. Yuzawa, T. Horigome, A. P. Hitchcock, N. Kosugi, *J. Phys. Chem. C* 2013, 117, 16343-16348.

## Solvent Restructuring around Colloidal Nanoparticles as Seen by High-Energy X-Rays

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Pair distribution function (PDF) measurements have originally been used to study the structure of bulk liquids and glasses.<sup>1</sup> Almost forgotten since, the method experienced a revival with increasing interest in nanoparticles and in-situ studies of chemical reactions, where common X-ray diffraction fails.<sup>2</sup> Owing to the tremendous improvements in flux at high X-ray energies and detector technologies at synchrotron radiation facilities, highly diluted nanoparticle dispersions (< 1 wt%) can be studied by PDF nowadays alike. In such high-energy X-ray scattering experiments combined with PDF analysis we showed that even restructured solvation shells around colloidal nanoparticles in dispersions can be detected.<sup>2,3</sup> The solvent molecules reorient around the nanoparticles over 3 to 5 molecular layers compared to their short-range order in the corresponding bulk solvent. The feasibility to assess solvation shells in water, alcohols and alkanes will be demonstrated on a wide range of nanoparticles including various metal oxides.<sup>3</sup> Alcohol molecules reorient perpendicular to the particle surface and hereby create a sinusoidal oscillation of the solvent electron density profile in the corresponding PDF. The rearrangement reaches out as far as 2 nm into the bulk liquid and decays exponentially. In case of water, we could resolve a more complex behaviour involving one or two closely adsorbed layers at the surface, as well as a more loosely bound hydration shell, see figure below.



- (1) Zachariasen, W. H., J. Chem. Phys. 3 (1935), 158.
- (2) Borkiewicz, O. J., et al, Phys. Chem. Chem. Phys. (2013) 15, 8466.
- (3) M. Zobel, R. B. Neder, S. A. J. Kimber, Science (2015)347, 6219, 292 .
- (4) M. Zobel, Acta Cryst.(2016) A72, 621 .

## Towards Operando Spectroscopy at Nanocarbon-Water Interface

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Carbon-water interaction plays a central role in many applications involving nanocarbons for energy storage and conversion, biomedical or sensing applications for example. However, the influence of aqueous environment on electronic and chemical structures of nanocarbons remains poorly understood so far.

Core-level X-ray spectroscopies, such as X-ray absorption (XA), X-ray Emission (XE) and X-ray Photoemission (XP) spectroscopies are powerful methods to probe the electronic structure of materials because it is element-specific and highly sensitive to chemical environment. Nevertheless, these methods are difficult to apply to nanocarbons in liquid. Indeed, soft X-ray (200-1000 eV) are required to probe K-edges of light elements such as carbon, oxygen and nitrogen, and L-edges of transition metals, which imply that measurements have to be performed under vacuum. Several technical methods, involving microjet and flow cells, have been developed to apply X-ray spectroscopies to liquid samples.

Vibrational spectroscopies, such as Raman and infrared spectroscopies, are on the other hand highly sensitive to chemical structure of nanocarbons and does not require vacuum conditions. Direct application in water is however also complicated because of the strong absorption of water molecules in the infrared region. They can also be applied in aqueous environment, for example using Attenuated Total Reflectance FTIR.

In our group, we are implementing X-ray and infrared spectroscopies to nanocarbons in aqueous environment. First examples with nanodiamonds, carbon dots, carbon nitrides and titanium carbides will be presented. Furthermore, perspectives to apply these methods to follow *in operando* electro- and photochemical processes at the surface of nanocarbons will also be discussed.

## Acid Deprotonation Driven by Cation Migration at Biased Graphene Nanoflake Electrodes

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Graphene nanoflakes (GNF) with average diameter of 30 nm and edge-terminated with carboxylic acid (COOH) functionalities have recently been synthesised.<sup>1</sup> The small size of the flakes and the high concentration of the acidic edge groups lead to different bonding environments, such as armchair and zigzag edge, as well as varying degrees of electrostatic and hydrogen-bonding interactions between groups. Consequently, deprotonation of GNF has been observed to occur over a wide pH range.<sup>2</sup>

It is well-known that the pKa of an acid depends on local environment and can change as a function of solution composition, surface immobilization and identity of neighboring species. Protonation states of electrode-immobilized species are also found to vary as a function of applied potential. However, results from different studies are contradictory, with some finding that negative potentials induce protonation while others report the opposite (<sup>3</sup> and references therein). Here we show how in situ infra-red spectroelectrochemistry can be used to observe potential-induced changes in the protonation state of a graphene electrode carboxylic acid edge groups.<sup>3</sup> The influence of solution pH, electrolyte concentration and identity of ions were explored. Deprotonation at negative applied potential resulted from a decrease in the apparent pKa of acidic functional groups in response to a local change in ion activity close to the electrode. We find additionally that the pKa of solution species are similarly affected by the potential-induced changes in ion activity at the electrode interface. Deprotonation of the surface acids is suppressed at low ionic strength and in the presence of solution species with a higher pKa.

(1) Rosillo-Lopez, M., Lee, T.J., Bella, M., Hart, M., and Salzmann, C.G., Formation and chemistry of carboxylic anhydrides at the graphene edge. *RSC Advances* 2015, 5, 104198-104202.

(2) Lounasvuori, M.M., Rosillo-Lopez, M., Salzmann, C.G., Caruana, D.J., and Holt, K.B., Electrochemical characterisation of graphene nanoflakes with functionalised edges. *Faraday Discussions* 2014, 172, 293-310.

(3) Lounasvuori, M. M. and Holt, K. B., Acid deprotonation driven by cation migration at biased graphene nanoflake electrodes. *Chem. Commun.* 2017, 53, 2351-2354.

## IRIS Beamline for Nanodiamonds & Nafion Polymer Membranes Doped with Nanodiamonds

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The capabilities of infrared radiation from synchrotron sources such as the IRIS beamline at HZB will be presented.<sup>1</sup> FTIR in conjunction with microscopes for example enables precise spatial chemical imaging of sample structures otherwise too small to be detected using conventional instrumentation. The benefit of this technique with respect to nanodiamonds inside biological cells/tissues will be highlighted. In addition, the study of the effects of nanodiamonds inside the proton exchange membrane (PEM) films, which play a significant and demanding role in the operation of fuel cells, will be presented. The performance of PEMs is found to degrade during the more challenging operation conditions at higher temperatures and lower humidity.<sup>2</sup> PEM containing inorganic nanoparticles have been reported to induce significant changes inside the pores and channels and influence the physical and proton transport properties of these membranes.<sup>3</sup> The influence of nanodiamonds of different surface functionalities on the water retention capability and structure inside Nafion films (most commonly used PEM) undergoing temperature induced dehydration will be reported here. The investigation was performed with FTIR in mid- and far-infrared regions using synchrotron light source at the IRIS beamline. Nanodiamonds with tunable reactive surface structures strongly influence the organisation of water surrounding them<sup>4</sup> which could influence the proton conductivity of the Nafion layer.

(1) Puskar, L., Schade, U., The IRIS THz/Infrared beamline at BESSY II., *Journal of Large Scale Research Facilities* 2016, 2, A-95.

(2) Puskar, L., Ritter, E., Schade, U., Yandrasits, M., Hamrock, S.J., Schaberg, M., Aziz, E.F., Infrared dynamics study of thermally treated perfluoroimide acid proton exchange membranes, *Phys. Chem. Chem. Phys.* 2017, 19, 626635.

(3) Safranova, EYu., Yaroslavtsev, AB, Prospects of Practical Application of Hybrid Membranes, *Petroleum Chemistry* 2016, 56, 4, 281-293.

(4) Petit, T., Puskar, L., et al, Unusual Water Hydrogen Bond Network around Hydrogenated Nanodiamonds, *J. Phys. Chem. C* 2017, 121, 9, 51855194.

## Understanding the Role of Nanocarbon-Water Interfaces in Electrochemical Energy Storage and Heterogeneous Catalysis

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Profound understanding of interaction phenomena at carbon-water interfaces is crucial for designing carbonaceous catalytic compounds and energy storage materials. Carbon-based materials can cover a wide range of adsorption strength with water. While classical  $sp^2$ -dominated carbon nanomaterials have a rather hydrophobic surface, recent findings have also revealed the presence of ultrahydrophilic carbon-based materials by controlled doping with heteroatoms (most often nitrogen).<sup>1,2</sup>

New attempts for the synthesis of such carbonaceous materials with well-defined nitrogen-rich structure motives and strong hydrophilicity due to highly polarizing surface properties by using pre-organized organic precursors will be presented. Different templating approaches to control the porosity in parallel to the surface atomic composition will be shown as well.<sup>2</sup>

The importance of precise control over the strength of carbon-water interaction will be presented on two examples. Firstly, salt-templated carbon materials with various surface functionalities have been applied as catalytic supports for gold nanoparticles and used as catalysts for the oxidation of glucose to gluconic acid in aqueous solution.<sup>3</sup> Secondly, the importance of water-carbon interaction plays an important role in electric-double-layer capacitors with aqueous electrolytes.<sup>4</sup>

Finally, some significant examples for water vapor adsorption measurements, which are known to be a very useful technique for the characterization of the surface atomic construction of carbon nanomaterials but also for the evaluation of pore connectivity and structures of water carbon-interfaces, will be presented.<sup>1,5</sup>

(1) G.-P. Hao, G. Mondin, Z. Zheng, T. Biemelt, S. Klosz, R. Schubel, A. Eychmüller, S. Kaskel, Unusual Ultra-Hydrophilic, Porous Carbon Cuboids for Atmospheric-Water Capture. *Angew. Chem. Int. Ed.* 2015, 54, 19411945.

(2) N. Fechner, N. P. Zussblatt, R. Rothe, R. Schlögl, M.-G. Willinger, B. F. Chmelka, M. Antonietti, Eutectic Syntheses of Graphitic Carbon with High Pyrazinic Nitrogen Content. *Adv. Mater.* 2016, 28, 12871294.

(3) S. M. G. Lama, J. Schmidt, A. Malik, R. Walczak, D. Varón Silva, A. Vlkol, M. Oschatz, Modification of salt-templated carbon surface chemistry for efficient oxidation of glucose with supported gold catalysts. Submitted.

(4) M. Oschatz, S. Boukhalfa, W. Nickel, J. P. Hofmann, C. Fischer, G. Yushin, S. Kaskel, Carbide-derived carbon aerogels with tunable pore structure as versatile electrode material in high power supercapacitors. *Carbon*, 2017, 113, 283291.

(5) L. F. Velasco, R. Guillet-Nicolas, G. Dobos, M. Thommes, P. Lodewyckx, Towards a better understanding of water adsorption hysteresis in activated carbons by scanning isotherms. *Carbon* 2016, 96, 753758.

## Electronic Structure of Intercalated MXene: Towards next Generation Supercapacitor

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MXenes are a new class of 2D materials consisting of transition metals carbides and nitrides that demonstrated extraordinary features for electrochemical energy storage.<sup>1</sup> However, the electronic structure and the mechanism leading to energy storage are largely unexplored so far.<sup>2</sup> In this work, we have investigated MXene ( $\text{Ti}_3\text{C}_2$ ) in water using soft X-ray absorption spectroscopy (XAS) at the O K-edge and Ti L-edge before and after urea intercalation. The samples were characterized not only as dried state in vacuum but also in aqueous dispersion solution using a flow cell system. Pure urea was compared as reference. For liquid samples, total fluorescence yield measurements have been performed whereas total electron fluorescence measurements were done for dry samples.

The impact of intercalation of urea molecules between the MXene planes as well as the effect of aqueous dispersion on their electronic structure will be discussed. In addition, correlation with the electrochemical properties of MXene-based supercapacitor, will be investigated.

This study provides new insights toward the understanding of MXene modification after urea intercalation. It demonstrates that XAS performed directly in aqueous media is a powerful method for the characterization of energy-related materials and future experiments related to in operando characterization of MXene-based supercapacitors will also be mentioned.

(1) Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y. 25th Anniversary Article: MXenes: A New Family of Two-Dimensional Materials. *Adv. Mater.* 2014, 26, 9921005.

(2) Lukatskaya, M. R.; Bak, S.-M.; Yu, X.; Yang, X.-Q.; Barsoum, M. W.; Gogotsi, Y. Probing the Mechanism of High Capacitance in 2D Titanium Carbide Using In Situ X-Ray Absorption Spectroscopy. *Adv. Energy Mater.* 2015, 5, 1500589.

## Interfacial Model for the Capacitance and Electrokinetics of Charged Carbon Surfaces

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A charged surface and its counterions constitute a nanometer-scale capacitor, the capacitance of which depends sensitively on the properties of the interfacial layer. When a lateral electric field or pressure gradient is applied, the double layer gives rise to electrokinetic transport phenomena. We construct an analytical model to account for the influence of a sub-nanometer-thick aqueous interfacial layer on the differential capacitance and the electro-osmotic mobility of carbon-electrolyte interfaces. We calculate the differential capacitance and the electro-osmotic mobility as a function of the surface charge density and the salt concentration, both with and without steric interactions between the ions. We compare the results from our theoretical model with experimental data on a variety of systems. Our theory yields a power-law dependence of the electro-osmotic flow velocity on the surface charge density for high surface charges, reproducing the experimental data.<sup>1</sup> We examine different types of hydrodynamic boundary conditions, a finite-viscosity layer explains the experimental data better than the usual hydrodynamic slip boundary condition. Our analytical model allows us to extract the properties of the subnanometer-wide interfacial layer by fitting to macroscopic experimental data. Although at present, complete experimental surveys of electrostatic and electrokinetic properties on a single surface type are lacking, recent electrokinetic experiments using carbon and boron-nitride nanotubes<sup>2</sup> provide an exciting new area for the future application of our theoretical framework.

(1) Y. Uematsu, R. R. Netz, D. J. Bonthuis, *Chem. Phys. Lett.* 670, 11-15 (2017).

(2) E. Secchi, S. Marbach, A. Niguès, D. Stein, A. Siria, and L. Bocquet, *Nature* 537, 210 (2016).

## Pyrolytic Graphite Electrodes Intercalated by $\text{AlCl}_4$ Anions Probed by X-ray Tomography and Small Angle X-ray Scattering

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Due to the cost and limited resources of lithium, the use of Li-ion batteries for large scale applications is nowadays under discussion.<sup>1,2</sup> Other metallic materials such as aluminum<sup>3–6</sup> and which are more abundant than lithium<sup>7</sup> have been considered as suitable candidates for electrochemical storage devices. Aluminum based secondary batteries could be a viable alternative to the present Li-ion technology because of their high volumetric capacity ( $8040 \text{ mAh}\cdot\text{cm}^3$  for Al vs.  $2046 \text{ mAh}\cdot\text{cm}^3$  for Li).<sup>7</sup> Additionally, the low cost aluminum makes these devices appealing for large-scale electrical energy storage.

We report the structural characterization by a combination of x-ray tomography and SAXS (Small Angle X-ray Scattering) related to electrochemical performances of aluminum tetrachloride ( $\text{AlCl}_3$ ) electrolyte in an aluminum/graphite battery. A special battery cell was designed that allowed in-operando studies of the graphite intercalation compound (GIC) formation. Thanks to this modified cell different phase formation upon charging and discharging has been observed. Moreover an irreversible process has been also detected.

(1) D. Larcher, J.-M. Tarascon, *Nat. Chem.* 2014, 7, 19.

(2) J.-M. Tarascon, *Nat. Chem.* 2010, 2, 510.

(3) M.-C. Lin, M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B.-J. Hwang, H. Dai, *Nature* 2015, 520, 324.

(4) H. Sun, W. Wang, Z. Yu, Y. Yuan, S. Wang, S. Jiao, *Chem. Commun.* 2015, 51, 11892.

(5) E. I. Shkolnikov, A. Z. Zhuk, M. S. Vlaskin, *Renew. Sustain. Energy Rev.* 2011, 15, 4611.

(6) Q. Li, N. J. Bjerrum, *J. Power Sources* 2002, 110, 1.

(7) U.S. Geological Survey, *U.S. Geol. Surv. Miner. Commod. Summ.* 2015, 196

## Surface functionalized nanodiamond for energy storage and catalysis

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Carbon nanomaterials have recently attained much interest due to their useful physical and chemical properties. Among them, nanoscale diamond as a representative of non-graphitic carbon materials stands out for its unique electronic and chemical characteristics.<sup>1</sup> These are beneficial for a variety of applications in the field of biomedicine, composite materials and energy storage.<sup>2</sup>

The efficient storage and supply of energy from renewable resources is a worldwide challenge and requires efficient and fast energy storage devices. Technologies such as lithium ion and other battery systems are already widespread. Carbon materials, and among them synthetic nanoscale diamond and related materials, are a promising class of materials for energy storage, e.g. in batteries and supercapacitors. Another important area of research is the generation of solar fuels using benign and readily available catalysts for the transformation e.g. of carbon dioxide into useful chemicals and building blocks.

Here we report on the production, characterization of surface functionalized nanodiamond and related materials such as bucky diamond of different origin. The resulting nanodiamond derivatives can be used as additives in supercapacitor materials, as heterogenized organocatalysts as well as for the photocatalytic generation of solar fuels. Challenges such as the stable surface modification and the agglomeration of nanoparticles will be addressed.

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- (1) A. Krueger, D. Lang, Functionality is Key: Recent Progress in the Surface Functionalization of Nanodiamond, *Adv. Funct. Mater.* 2012, 22, 890-906.
- (2) J-C. Arnault (Ed.), *Nanodiamonds*, Elsevier, London 2017, ISBN: 9780323430296.

## X-Ray Spectroscopic Investigations of the Band Structure Manipulation in Diamond Based Photocatalysts

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Diamonds are promising candidates for highly energetic photocatalytic reactions<sup>1</sup> owing to their negative electron affinity when terminated with H on the surface.<sup>2</sup> However, due to a large band gap of 5.5 eV, deep UV illumination is necessary for the photoexcitation process thus making it challenging and highly inefficient. To eliminate the need for deep UV radiation, the band structure of diamond must be manipulated in a way that it enables the absorption of photons of lower energy either through defect based transitions as in the case of B doped diamonds or through functionalization with a visible light active complex, in this case transition metal complexes with appropriately matched HOMO LUMO levels to facilitate charge transfer processes from the complex to the diamond. In this presentation, both the above mentioned approaches for band structure manipulation will be discussed with respect to X-ray spectroscopy investigations. Soft X-ray absorption and emission spectroscopy at the C K edge was performed to investigate the change in mid-gap acceptor levels in boron doped diamond with a change in morphology. Additionally, the band structure of Ru functionalized nanodiamonds was studied experimentally and theoretical XAS calculations on the Ruthenium complexes were used to interpret the experimental data and to obtain a better understanding of the possible optical transitions in the system.

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(1) Zhu, D.; Zhang, L.; Ruther, R.; Hamers, R. *Nature Materials* 2013, 12, 836-841

(2) Takeuchi, D.; Kato, H.; Ri, G.; Yamada, T.; Vinod, P.; Hwang, D.; Nebel, C.; Okushi, H.; Yamasaki, S. *Applied Physics Letters* 2005, 86, 152103

## Carbon Nanodots for Solar-Induced H<sub>2</sub> generation

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Photocatalysis is considered an excellent approach for mitigating simultaneously both the energy and environmental concerns that our society is facing. This is because it facilitates the storage of the abundant solar energy in high energy density fuels, such as H<sub>2</sub> (120 MJ/kg), in non-toxic, benign aqueous media. To achieve this at an economically viable level, the synthesis of new light-harvesters and catalysts of low cost and toxicity but still of good performance is of high demand. Carbon dots (CDs) are considered ideal candidates as photosensitizers for this purpose since they fulfil all these requirements. In particular, CDs are (1) inexpensive and non-toxic, (2) easy to synthesize and modify their surface chemistry, (3) chemically and photochemically robust, (4) show good water solubility and (5) controlled photocatalytic properties upon pre-designed synthesis.<sup>1,2</sup> Our group focuses on the synthesis of carbonaceous nanomaterials from naturally abundant, inexpensive, organic precursors via bottom-up synthetic approaches, upon pyrolysis at optimum conditions.<sup>3–6</sup> When combined with noble-metal free molecular catalysts and/or redox enzymes in aqueous-based photocatalytic systems, these CDs serve as the sole photosensitizers leading to high photocatalytic activities. More specifically, either a Ni-bis- (diphosphine) catalyst or hydrogenase have been used as catalysts for this purpose resulting in substantially high H<sub>2</sub> evolution capacities, turn-over numbers and specific activities.<sup>3–6</sup> To understand the parameters that enable good light harvesting capabilities for the newly synthesized CDs, all materials underwent detailed structural, spectroscopic and optical characterization prior photocatalytic testing. More specifically, transmission electron microscopy, atomic force microscopy, X-ray diffraction, Raman spectroscopy, nuclear magnetic resonance, fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, UV/vis spectroscopy, zeta potential measurements and elemental analysis are among the techniques that have been employed for this purpose.

(1) Yu, H.; et al, T. Adv. Mater. 2016, 28, 9454.

(2) Wang, R.; Lu, K.-Q.; Tang, Z.-R.; Xu, Y.-J. J. Mater. Chem. A 2017, 5, 3717.

(3) Martindale, B. C. M.; Hutton, G. A. M.; Caputo, C. A.; Reisner, E. JACS 2015, 137, 6018.

(4) Hutton, G. A. M.; Reuillard, B.; Martindale, B. C. M.; Caputo, C. A.; Lockwood, C. W. J.; Butt, J. N.; Reisner, E. JACS 2016, 138, 16722.

(5) Hutton, G. A. M.; Martindale, B. C. M.; Reisner, E. Chem. Soc. Rev. 2017, 46, 6111.

(6) Martindale, B. C. M.; Hutton, G. A. M.; Caputo, C. A.; Prantl, S.; Godin, R.; Durrant, J. R.; Reisner, E. Angew. Chem. Int. Ed. 2017, 56, 6459.

## Probing the Electronic Structure of Atomically-Thin Carbon Nitride Nanosheets Photocatalysts by Soft X-ray Spectroscopies

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Polymeric carbon nitride (PCN) is a promising earth-abundant 2D material for solar energy conversion.<sup>1</sup> Optical, electronic, mechanical and chemical properties of PCN materials can be manipulated by changing the size, composition, dimension and shape of their reactive (nano)domains. Exfoliation is a promising strategy to enhance PCN photocatalytic performance via preparation of ultrathin carbon nitride nanosheets. Recently, a facile continuous thermal treatment strategy was presented to prepare atomically-thin carbon nitride nanosheets and endow them with strong hydrophilicity and Lewis basicity to dramatically enhance the photocatalytic hydrogen generation performance.<sup>2</sup> In this work, the electronic structures and surface chemistry of the oxygen- and amino group decorated atomically-thin PCN nanosheets, as determined from infrared, soft X-ray absorption and ultraviolet photoemission spectroscopies, will be detailed. A special attention will be given to determine the structure-performance relationship of PCN photocatalysts by comparing the photocatalytic activity of these different materials with their electronic and surface chemical properties. These soft X-ray absorption spectroscopy measurements were performed at the BESSY II synchrotron in Berlin. Synchrotron radiation-based soft X-ray spectroscopies have become powerful techniques to investigate the electronic structure of 2D materials.

(1) F. K. Kessler, Y. Zheng and D. Schwarz et al. *Nat Rev Mater* 2, 17030 (2017).

(2) N. Meng, J. Ren and Y. Huang et al. *Energy Environ. Sci.* (2018),

DOI:10.1039/C7EE03592F

## Sensing Applications using Carbon Dots in Water: Fluorescence Quenching, Enhancement, and in between

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Carbon dots (Cdots) are unique carbonaceous nanoparticles exhibiting tunable, multicolor fluorescence. Unlike inorganic nanoparticles (i.e. quantum dots) in which the fluorescence emission depends on particle size, the fluorescence colors of Cdots have been linked to their surface properties – the molecular nature, abundance, and reactions of surface–displayed functional units. This feature has made Cdots a powerful sensing platform for diverse analytes which interact and modulate the surface properties of the particles. In this presentation I discuss several experiments in which we exploited Cdot surface modifications for sensing varied biological and chemical analytes in water. In particular, Cdot designs will be presented in which the signal mechanisms are based upon either quenching of Cdots' fluorescence, enhancement, or combined "on–off–on" fluorescence sensing routes.

(1) Sagarika Bhattacharya, Rhitajit Sarkar, Sukhendu Nandi, Angel Porgador, Raz Jelinek, In vitro reactive oxygen species (ROS) sensing by a carbon-dot-ascorbic acid hydrogel, *Analytical Chemistry*, 2017, 89, 830-836.

(2) S., Chakraborty, B., Sarkar, R., Porgador, A., Jelinek, R. Nitric oxide sensing through azo-dye formation on carbon dots, Bhattacharya, *ACS Sensors*, 2017, 2017, 2, 1215-1224.

(3) Susanta Kumar Bhunia, Susmita Dolai, Hongchen Sun, Raz Jelinek, "On/off/on" hydrogen-peroxide sensor with hemoglobin-functionalized carbon dots, *submitted for publication*.

## Nanodiamond as Radiosensitizer: Chemical and Physical Investigations

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Since the last ten years, nanodiamonds (NDs) have attracted raising interests from research groups and companies. Their tunable size from 100 nm down to 3 nm, their low cytotoxicity and genotoxicity, their versatile surface chemistry and their ability to host color centers (NV, SiV) are essential assets for the development of bioapplications.<sup>1-3</sup> Recently, we reported on the behavior of plasma hydrogenated NDs (H-NDs) to produce reactive oxygen species (ROS) in radioresistant human cancer cells under gamma irradiation. This radiosensitive behavior was in vitro demonstrated, turning these cancer cells into senescence state which corresponds to an irreversible ageing state.<sup>4</sup>

This talk will focus on the intrinsic properties of detonation H-NDs, from the surface chemistry to the colloidal behavior in water suspensions. Indeed, the surface chemistry is strongly governing the colloidal properties of NDs. The stability of H-NDs in water was reported with H-NDs exhibiting a positive zeta potential.<sup>5</sup> Two hydrogenation methods (plasma or annealing) will be compared in terms of hydrogen grafted or incorporated into NDs via isotope studies (<sup>3</sup>H).<sup>6</sup> The physical and chemical mechanisms involved in the production of radicals were investigated by illuminating aqueous colloids of NDs under X-rays and gamma-rays for NDs behaving different surface chemistries. An overproduction of hydroxyl radicals and solvated electrons versus water radiolysis was measured for H-NDs using the 7-OH-coumarin as a fluorescent probe.<sup>7</sup> The origin of the radical overproduction will be discussed taking into account the interactions between H-NDs and water molecules. These results well evidence that NDs can act as active nanoparticles under illumination.

- (1) O. A. Shenderova, G. E. McGuire, *Biointerphases* 10 (2015) 030802.
- (2) K. Turcheniuk and V. N. Mochalin, *Nanotechnology* 28 (2017) 252001.
- (3) Y. Y. Hui, L. J. Su, O. Y. Chen, Y. T. Chen, T. M. Liu, H. C. Chang, *Scientific Reports* 4 (2014) 5574.
- (4) R. Grall, H. A. Girard, L. Saad, T. Petit, C. Gesset, M. Combis-Schlumberger, V. Paget, J. Delic, J. C. Arnault, S. Chevillard, *Biomaterials* 61 (2015) 290-298.
- (5) T. Petit, H. A. Girard, A. Trouvé, I. Batonneau-Gener, P. Bergonzo, J. C. Arnault, *Nanoscale* 5 (2013) 8958.
- (6) H.A. Girard, A. El Kharbachi, S. Garcia-Argote, T. Petit, P. Bergonzo, B. Rousseau, J.C. Arnault, *Chem. Comm.* 50 (2014) 29162918.
- (7) M. Kurzypp, H. A. Girard, Y. Cheref, E. Brun, C. Sicard-Roselli, S. Saada, J. C. Arnault, *Chem. Commun.*, 53 (2017) 1237.

## Mass Transport through Low-Dimensional Carbon Nanomaterials

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Membrane technology poses great potential towards process intensification for sustainable industrialization. Nanotechnology could play a substantial role in this effort through direct engineering of pores of a membrane; for example, proper nanoarchitecture of pores can help endow selectivity and permeance by design. In this talk, I will discuss carbon-based architectures and pertaining mass transport properties. Mass transport through partial hydrophobic nanocapillaries offered by carbon nanotubes and graphene is unique in terms of transport efficiency and selectivity, thereby offering practically novel opportunities for various membrane processes for separation. It is, hence, crucial to understand these transport phenomena and construct platforms in order to realize envisaged applications. This talk will present a brief overview of theoretical and experimental efforts to predict and measure the transport properties under the graphitic nanoconfinement, our construction story of the graphitic membranes offering continuous and discontinuous confinements, observation of ultrahigh permeation, and investigation of their separation properties. Finally, technological importance will be discussed.

(1) Holt J. K., Park H. G. et al., Fast mass transport through sub-2-nanometer carbon nanotubes. *Science* 2006, 312 (5776), 1034-1037.

(2) Celebi K., Buchheim J., Park H. G. et al., Ultimate permeation across atomically thin porous graphene. *Science* 2014, 344 (6181), 289-291.

## Time-Resolved Spectroscopic Investigation of Excited State Dynamics in Carbon-Based Photocatalysts

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Carbon nitrides are attracting significant research interest for photocatalysis because of their high activity combined with good stability and facile synthesis. However, there still remains significant gaps in our knowledge of the photophysical properties of these organic polymeric materials. Using time-resolved absorption and photoluminescence spectroscopies to monitor excited state dynamics, we have investigated the photophysical processes of a series of carbon nitride photocatalyst materials on timescales ranging from femtoseconds to seconds.<sup>1</sup> Both absorption and photoluminescence intensities decay according to power laws, indicative of charge trapping-detrapping processes, yet over the timescales studied the transient absorption signal decays by only 2 orders of magnitudes compared to over 8 orders of magnitude decrease in PL. Emission is still observed on the millisecond timescale, assigned to thermal excitation of trapped carriers back up to the conduction/valence bands and formation of the high energy emissive state. To account for these observations, we develop a simple, quantitative model for the charge carrier dynamics in carbon nitrides that includes consideration of carrier relaxation into an exponential tail of trap states extending over 1 eV into the bandgap. We determined the energetics of trapped carriers as a function of carrier density and time after photoexcitation, and found that loss in driving force for charge transfer reactions on the order of 1.5 eV, negatively impacting photocatalysis. Comparing a series of carbon nitride materials, the yield of these unreactive trapped electrons is seen to correlate inversely with H<sub>2</sub> evolution rates, consistent with the presence of deep energetic traps that play a key role in controlling photoactivity. Preliminary studies of carbon nitrides with different chemical terminations suggest that these play a role in determining the density of trap states and the reactivity of long-lived photogenerated electrons.<sup>2</sup> Our interests in high-efficiency photocatalytic systems that are completely devoid of noble and toxic metals have also lead us to investigate carbon dots. These nanoparticles are easily prepared by carbonisation of appropriate precursors, but in contrast to carbon nitrides, carbon quantum dots are colloidally stable in aqueous media, enabling homogeneous photocatalysis. Our TAS studies give us a glimpse of the relevant timescales for charge transfer between the carbon quantum dots and sacrificial electron donor or H<sub>2</sub>-evolving molecular catalysts, and offers insights into promising optimisation routes.<sup>3</sup>

(1) Godin, R.; Wang, Y.; Zwiijnenburg, M. A.; Tang, J.; Durrant, J. R., *JACS* 2017, 139, 5216

- (2) Kasap, H.; Caputo, C. A.; Martindale, B. C.; Godin, R.; Lau, V. W.; Lotsch, B. V.; Durrant, J. R.; Reisner, E., *JACS*, 2016, 138,9183
- (3) Martindale, B. C. M.; Hutton, G. A. M.; Caputo, C. A.; Prantl, S.; Godin, R.; Durrant, J. R.; Reisner, E., *ACIE*, 2017, 56, 6459

## Graphene Oxide Quantum Dots in *Bits* - not only in *Pieces*

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The quest for efficient and sustainable solar fuel catalysts has brought grapheneoxide quantum (GQDs) dots into the focus of scientists that are capable of undergoing efficient charge transfer upon light-absorption. Such QDs are formed from truncated and eventually stacked layers of graphene sheets with a random distribution of oxygen functionalization on the surface. To present the GQDs are being characterized in little pieces: here an infrared spectrum of a GQD with a certain mass, there XAS spectra of one with a certain nitrogen content, and eventually UV/vis spectra of a last one with an certain shape. Numerous of such *pieces* of information are needed to gain a full picture. Only a few experimentalists are capable of putting together all these little *pieces*.

With quantum mechanical calculations we add several more bits of information to the available *pieces*, which also facilitates interpreting results. We have chosen a number of GQD model structures with up to 100 atoms and a composition as the GQDs being investigated experimentally in the Petit group. We systematically study various functionalization pattern, i.e. the number of functional groups, their placement, and their combination. For all structures theoretical UV/Vis, X-Ray and IR spectra are calculated and the comparison of *bits and pieces* revealed that those structures who have a non-extensive  $\pi$  electron system bear the highest potential for catalytic activity. For nitrogen-doped GQDs that are still unavailable for the experimentalists, we even predict a desirable structure for the water-splitting reaction. To really proof the catalytic potential we finally plan electron dynamics calculations for the first steps of the reduction reaction, which is the fast electron transfer from the GQD to an adjacent water molecule.

## Evidence for Low-Dimensional Charge Transport in Carbon Nitride Polymers

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Carbon nitride (CN) polymers have gained much interest in recent years due to their potential application as both dark- and photocatalysts for various renewable-energy tasks, including water-splitting and CO<sub>2</sub> reduction, and others.<sup>1,2</sup> Given their layered, van-der-Waals bound structure, these materials resemble graphite, and are hence often called graphitic carbon nitrides (g-C<sub>3</sub>N<sub>4</sub>).<sup>1</sup> The main technical advantage of CNs is the abundance of their constituents C, N, and H and the absence of precious metals. However, compared to metal-based catalysts, the activity of CN materials is still rather low, a fact that has been largely attributed to their low conductivity.<sup>1</sup> Recently, we found evidence that this low conductivity is due to polaronic hopping motions of photoexcited electrons and holes, which predominantly move vertical to the graphitic planes of the material.<sup>3</sup> Backed-up by very recent transient-spectroscopy studies, we will discuss the validity of such a low-dimensional transport scenario, and its consequences for applications in catalysis as well as in organic electronics in general.

(1) F. K. Kessler, Y. Zheng, D. Schwarz, C. Merschjann, W. Schnick, X. Wang, M. J. Bojdys, Functional carbon nitride materials design strategies for electrochemical devices. *Nat. Rev. Mater.* 2017, 2, 17030.

(2) A. Indra, A. Acharjya, P. W. Menezes, C. Merschjann, D. Hollmann, M. Schwarze, M. Aktas, A. Friedrich, S. Lochbrunner, A. Thomas, M. Driess, Boosting Visible-Light-Driven Photocatalytic Hydrogen Evolution with an Integrated Nickel Phosphide-Carbon Nitride System. *Angew. Chem. Int. Ed.* 2017, 56, 16531657.

(3) C. Merschjann, S. Tschierlei, T. Tyborski, K. Kailasam, S. Orthmann, D. Hollmann, Th. Schedel-Niedrig, A. Thomas, S. Lochbrunner, Complementing Graphenes: 1D Interplanar Charge Transport in Polymeric Graphitic Carbon Nitrides. *Adv. Mater.* 2015, 27, 79937999.

## Transient Absorption Spectroscopy of Nanodiamonds in Water: Direct Observation of Solvated Electrons

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Due to their unique physical properties, diamonds are promising materials for a large variety of applications. In 2014, Hamers and co-workers have shown that a hydrogen-terminated boron-doped diamond film emits solvated electrons upon UV light excitation.<sup>1</sup> The solvated electrons were used to reduce nitrogen (N<sub>2</sub>) to form ammonia (NH<sub>3</sub>)<sup>2</sup> and to reduce carbon dioxide (CO<sub>2</sub>) to form carbon monoxide (CO).<sup>3</sup> This result has opened a new field of applications for diamond materials: solar fuels production. However, the CO<sub>2</sub> reduction mechanism is still a matter of discussion.

We have now applied ultrafast transient absorption spectroscopy to nanodiamonds (NDs) with different surface terminations and characterized the dynamics of solvated electron emission in water. Aqueous dispersions of NDs have been excited by a deep UV pulse (225 nm) and the change in the absorption spectrum was probed by a white light pulse (500-750 nm). Applying this method, the high energy part of the solvated electron absorption spectrum is directly probed.

With this technique, NDs with different surface terminations were studied including -H, -OH and -COOH. They all show a very long-lived transient signal exceeding the probe range (2 ns) which is most probably due to solvated electrons. In the presentation, I will discuss to what extent the dynamics of the solvated electrons depend on the surface termination of the NDs.

This work has received funding from the European Union's Horizon 2020 Program under Grant Agreement number 665085 (DIACAT).

(1) R. J. Hamers, J. A. Bandy, D. Zhu and L. Zhang, Photoemission from diamond films and substrates into water: dynamics of solvated electrons and implications for diamond photoelectrochemistry. *Faraday Discussions* 2014, 172, 397411.

(2) D. Zhu, L. Zhang, R. E. Ruther, R. J. Hamers, Photo-illuminated diamond as a solid-state source of solvated electrons in water for nitrogen reduction. *Nature Materials* 2013, 12, 836-841.

(3) L. Zhang, D. Zhu, G. M. Nathanson, R. J. Hamers, Selective Photoelectrochemical Reduction of Aqueous CO<sub>2</sub> to CO by Solvated Electrons. *Angewandte Chemie-International Edition* 2014, 53(37), 97469750.

### **3 Abstracts of the Poster Presentations**

## Interactions of Nanodiamonds and Surfactants in Aqueous Suspensions

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Chemically complex surface of nanodiamonds (NDs) makes this material very promising for many applications in biomedicine as drug carriers, fluorescent markers, adsorbents. Surface functionalization can make NDs more stable, biocompatible or provide their hydrophobic/hydrophilic properties. The advances of these applications are determined by interactions of NDs with cells. As it is known the cell membrane consists of a bilayer made of surfactants. Aside from that, addition of surfactants allows to increase the stability of suspensions of nanodiamonds. That is why the study of interactions between nanodiamonds and surrounding molecules including surfactants is very crucial.

In this study the interactions of detonation nanodiamonds (DNDs) with the ionic surfactants in aqueous suspensions were investigated by means of Raman and fluorescence spectroscopy. Aqueous suspensions of sodium octanoate with DNDs having different surface functionalization hydrophobic (DND-H) and hydrophilic (DND-COOH) - were objects of researches. It was found that nanoparticles and surrounding molecules influence on each other.

The following effects were observed: 1) DNDs with hydrophobic surface weaken the hydrogen bonds in suspensions more strongly in comparison with hydrophilic surface, 2) DNDs influence on the micelle formation of sodium octanoate, 3) water molecules and surfactants influence on the fluorescence of DNDs. The mechanisms of the observed interactions between hydrophobic/hydrophilic DNDs and the surrounding molecules are proposed.

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## Transient Absorption Spectroscopy of Ru-functionalised Nanodiamonds in Water

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Due to their unique physical properties, diamonds are promising materials for a large variety of applications. It has been shown that a hydrogen-terminated boron-doped diamond film emits solvated electrons upon UV light excitation and carbon dioxide (CO<sub>2</sub>) was reduced to carbon monoxide (CO).<sup>1</sup> In the DIACAT project,<sup>2</sup> we aim at exploiting this reaction by using nanodiamonds as a catalyst for solar fuels production. Hence, charge transfer dynamics may be crucial, i.e. how the positive charge in the ND is compensated after solvated electron emission. Ru-functionaliation might be the key to exploit nanodiamonds.

We have now applied ultrafast transient absorption spectroscopy to Ru-functionalised nanodiamonds (NDs) where the Ru-complex is attached to the ND via different linkers. Aqueous dispersions of NDs have been excited by a deep UV pulse (225 nm) and the change in the absorption spectrum was probed by a white light pulse (500–750 nm). Applying this method, the high energy part of the solvated electron absorption spectrum is directly probed. Possibilities of charge transfer between NDs and Ru complexes were also evidenced and will be discussed in this poster.

This work has received funding from the European Unions Horizon 2020 Program under Grant Agreement number 665085 (DIACAT).

(1) R. J. Hamers, J. A. Bandy, D. Zhu and L. Zhang, Photoemission from diamond films and substrates into water: dynamics of solvated electrons and implications for diamond photoelectrochemistry. *Faraday Discussions* 2014, 172, 397411.

(2) [www.diacat.eu](http://www.diacat.eu)

## Electrochemical Oxidation of ND-Cu<sub>2</sub>O Electrodes Probed by Operando X-ray Absorption Spectroscopy

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In the face of current energy problems, effective utilization of solar energy by converting them to chemical fuels is a potentially sustainable and attractive solution. For practical applications, the process of photosynthesis occurring in nature may be mimicked to develop photoelectrochemical processes such as water splitting<sup>1</sup> and CO<sub>2</sub> reduction<sup>2,3</sup> that could convert the abundant solar energy to sustainable chemical fuels such as hydrogen and alcohols/hydrocarbons respectively. These processes can be realized in a photoelectrochemical (PEC) cell where photogenerated electrons and holes in a semiconductor electrode further catalyze the electrochemical reactions when driven into solution by means of an electric field at the semiconductor/liquid junction. In literature, different Cu<sub>2</sub>O based hybrid electrodes and photocatalyst systems have been investigated for CO<sub>2</sub> reduction.<sup>4,5</sup> However, since diamonds are highly promising candidates for catalyzing highly energetic reactions such as N<sub>2</sub><sup>1</sup> and CO<sub>2</sub><sup>7</sup> reduction owing to their negative electron affinity,<sup>8</sup> combining nanodiamonds with Cu<sub>2</sub>O may be a good strategy for the development of a promising hybrid photocatalyst.

The electrochemical measurements performed on the Cu<sub>2</sub>O electrode give information about the different potentials at which a change in oxidation state of Cu can be observed. However, till date there has been no report on the direct observation of the change in oxidation states under in-operando conditions. Here we report an in-operando soft X-ray absorption spectroscopy study of electrochemically deposited Cu<sub>2</sub>O on a nanodiamond film. Change of the Cu oxidation state was followed by monitoring the Cu L edge in operando by applying a bias of  $-1,2V$  and  $+0,5V$  v/s Ag/AgCl during measurements in KHCO<sub>3</sub> electrolyte. Possible origin for the change of Cu oxidation state will be discussed. This study opens new perspectives for the in operando characterization of Cu-based electrocatalysts.

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- (1) Michael G. Walter, Emily L. Warren, James R. McKone, Shannon W. Boettcher, Qixi Mi, Elizabeth A. Santori, Nathan S. Lewis *Chem. Rev.*, 2010, 110 (11), pp 64466473
- (2) Cokoja, M., Bruckmeier, C., Rieger, B., Herrmann, W. A. , Khn, F. E. *Angew. Chem. Int. Ed.*, 2011, 50: 85108537.
- (3) Somnath C. Roy, Oomman K. Varghese, Maggie Paulose, Craig A. Grimes *ACS Nano*, 2010, 4 (3), pp 12591278
- (4) Xiaoqiang An, Kimfung Li, and Junwang Tang *ChemSusChem*, 2014, 7, 1086 1093
- (5) Ji-Chao Wang, Lin Zhang, Wen-Xue Fang, Juan Ren, Yong-Yu Li, Hong-Chang Yao, Jian-She Wang, Zhong-Jun Li *ACS Appl. Mater. Interfaces*, 2015, 7 (16), pp 86318639
- (6) Zhu, D., Zhang, L., Ruther, R., Hamers, R. *Nature Materials* 2013, 12, 836-841
- (7) Zhang, L., Zhu, D., Nathanson, G. M. and Hamers, R. J. *Angew. Chem. Int. Ed.*, 2014, 53: 97469750.
- (8) Takeuchi, D., Kato, H., Ri, G., Yamada, T., Vinod, P., Hwang, D., Nebel, C., Okushi, H., Yamasaki, S. *Applied Physics Letters* 2005, 86, 152103

## Theoretical Characterization of Nitrogen-Doped Graphene Oxide Quantum Dots

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Nitrogen-doped graphene oxide quantum dots (NGO-QDs) are known to be capable of catalyzing water splitting reactions under irradiation with light in the visible range.<sup>1</sup> The structure of NGO-QDs depends on the specific synthesis process used.<sup>2</sup> Since this results in a somewhat randomized functionalization pattern, it is not known yet what structural features cause the photocatalytic properties. Similar to the approach used for GO-QDs,<sup>3</sup> we use a two step procedure to calculate the properties of a large set of model structures. The first step is the validation of the model system by comparison of the theoretically and experimentally obtained IR, UV, and X-ray spectra. We expand this method to NGO-QDs since the addition of nitrogen is expected to lower the electron-hole recombination rate, thereby increasing hydrogen and oxygen production.<sup>1</sup> In order for the NGO-QD to induce the necessary oxidation and reduction reactions, it has to have an appropriate band gap and a low electron-hole recombination rate. The second feature is not known yet, but can be investigated with electron dynamics calculations of the charge transfer reactions that occur during photocatalysis, which is the second step in the procedure.

So far, all of the model systems have an appropriate band gap for catalyzing water splitting reactions and several show high intensity peaks in the visible range, which makes them good candidates for running further charge transfer calculations. However, experimental validation of the model systems has not been done yet, due to the lack of a suitable sample.

(1) T.F. Yeh , C.Y. Teng, S.J. Chen, H. Teng *Adv. Mater.* (2014)

(2) D.R. Dreyer, S. Park, Bielawski, *Ruoff Chem. Soc. Rev.*, 39, 228 (2010)

(3) F. Weber, J. Ren, T. Petit, A. Bande (work in preparation)

## Effect of Surface Chemistry on Optical, Chemical and Electronic Properties of Blue Luminescent Carbon Dots

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Due to their unique physical properties, particularly their electronic and luminescent properties, carbon dots (CDs) are expected to be suitable for a wide range of applications in bioimaging, electro-optical and photonic materials or energy harvesting among others.<sup>1</sup> Tuning the surface chemistry provides an efficient approach to modulate the fluorescence and distinct electronic properties of CDs.<sup>2</sup> Nevertheless, the role of surface chemistry on the electronic structure of CDs remains poorly understood.

In this poster, we will compare the electronic and chemical structures of three CDs functionalized with different groups, combining experimental and theoretical approaches. First, the electronic structure of CDs was characterized by soft X-ray absorption (XA) and X-ray emission (XE) spectroscopies at the BESSY II synchrotron radiation source, probing unoccupied and occupied electronic states, respectively. The interpretation of XA spectra was discussed based on theoretical calculations. Subsequently, the chemical structure of the CDs was characterized by ATR-FTIR. Since the interface between CDs and water is believed to play a central role in the chemical reactivity and the optical properties in aqueous environments, the CDswater interface was probed by in-situ attenuated total reflection Fourier transform infrared (ATR-FTIR). We previously demonstrated that monitoring the OH vibrations of water molecules during exposure to humid air was a powerful method to probe hydrogen bond environment around carbon nanomaterials.<sup>3</sup> For CDs, clear surface-dependent water adsorption profiles are observed and discussed. Finally, the optical properties of these CDs were characterized by UV/Vis absorption and photoluminescence measurements.

Our results suggest that the surface chemistry of the CDs significantly affects their electronic structures and optical properties. Moreover, these findings will contribute to an improved understanding of the structureactivity relationship of CDs and other carbon nanomaterials with surface modifications.

- (1) LeCroy, GE. et al. Functionalized carbon nanoparticles: Syntheses and applications in optical bioimaging and energy conversion. *Coord. Chem. Rev.* 320-321, 2016.
- (2) Zhu, S. et al. Investigating the surface state of graphene quantum dots. *Nanoscale* 7, 2015.
- (3) Petit, T. et al. Unusual water hydrogen bond network around hydrogenated nanodiamonds. *J. Phys. Chem. C* 121, 2017.

## Photoinduced Early-Time Charge Separation Dynamics in Carbon Nitrides Studied by XUV Photoelectron Spectroscopy

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Carbon nitride is a promising target polymer material for photocatalytic solar energy conversions that attracts research interest because of its high stability and facile synthesis. Despite the worldwide enthusiasm in the preparation and application of carbon nitrides, the photophysical processes, in particular the separation dynamics of photogenerated charges, remain unclear.

Herein, we perform a pump-probe ultrafast XUV photoelectron spectroscopic study on the melamine-derived polymeric carbon nitrides. We follow on a femtosecond time scale the early-time electron dynamics of the charge carriers induced by a short light pulse of 400 nm wavelength.

The transient XUV photoemission signal reveals the contribution of a number of short-lived intermediate states in the process of charge separation. The experimental data are analyzed in terms of a model that assumes the presence of two excited states and their sequential population. The results indicate that the charge separation is completed within 1 ps after the photoexcitation event.

## Graphene functionalized by ultra-thin anchor layers towards biosensor application

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The functionalization of single layer graphene and with specifically binding receptor molecules enables the facile fabrication of biosensors. The linkage between graphene and the receptor can be easily achieved by covalently bound molecules. We present the deposition of ultra-thin layers of such linker molecules on large area CVD-grown graphene by the electrochemical reduction of aryl diazonium salts containing amino, maleimide and thiol groups.<sup>1</sup> The successful deposition of the functional groups and the change of the graphene structure were detected by infrared-spectroscopic ellipsometry, Raman backscattering, and electrochemical quartz crystal microbalance (E-QCM) measurements. The homogeneity of the electrochemical functionalization was shown by infrared atomic force microscopy.<sup>2</sup> For the thiol functionalization a symmetrical disulfide was deposited and cleaved to achieve an ultra-thin thiol layer.<sup>3</sup> Furthermore, the reactivity of these functional groups was tested by specific wet-chemical modification with small molecules. Finally, the functionalized and modified graphene was transferred from copper to different substrates including glass, silicon and flexible PTFE tape.

(1) F. Rösicke, M. A. Gluba, K. Hinrichs, G. Sun, N. H. Nickel, J. Rappich, Quantifying the electrochemical maleimidation of large area graphene. *Electrochem. commun.* 2015, 57, 52-55

(2) F. Rösicke, M. A. Gluba, T. Shaykhtudinov, G. Sun, C. Kratz, J. Rappich, K. Hinrichs, N. H. Nickel, Functionalization of any substrate using covalently modified large area CVD graphene. *Chem. Commun.*, 2017, 53, 9308-9311

(3) Z. Peng, A. H. Holm, L. T. Nielsen, S. U. Pedersen, K. Daasbjerg, Covalent Sidewall Functionalization of Carbon Nanotubes by a "Formation-Degradation" Approach. *Chem. Mater.* 2008, 20, 6068-6075

## Pyrolytic Graphite Electrodes Intercalated by $\text{AlCl}_4$ Anions Probed by X-ray Tomography and Small Angle X-ray Scattering

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Due to the cost and limited resources of lithium, the use of Li-ion batteries for large scale applications is nowadays under discussion.<sup>1,2</sup> Other metallic materials such as aluminum<sup>3–6</sup> and which are more abundant than lithium<sup>7</sup> have been considered as suitable candidates for electrochemical storage devices. Aluminum based secondary batteries could be a viable alternative to the present Li-ion technology because of their high volumetric capacity (8040 mAh cm<sup>3</sup> for Al vs. 2046 mAh cm<sup>3</sup> for Li).<sup>7</sup> Additionally, the low cost aluminum makes these devices appealing for large-scale electrical energy storage.

We report the structural characterization by a combination of x-ray tomography and SAXS (Small Angle X-ray Scattering) related to electrochemical performances of aluminum tetrachloride ( $\text{AlCl}_3$ ) electrolyte in an aluminum/graphite battery. A special battery cell was designed that allowed in-operando studies of the graphite intercalation compound (GIC) formation. Thanks to this modified cell different phase formation upon charging and discharging has been observed. Moreover an irreversible process has been also detected.

(1) D. Larcher, J.-M. Tarascon, *Nat. Chem.* 2014, 7, 19.

(2) J.-M. Tarascon, *Nat. Chem.* 2010, 2, 510.

(3) M.-C. Lin, M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B.-J. Hwang, H. Dai, *Nature* 2015, 520, 324.

(4) H. Sun, W. Wang, Z. Yu, Y. Yuan, S. Wang, S. Jiao, *Chem. Commun.* 2015, 51, 11892.

(5) E. I. Shkolnikov, A. Z. Zhuk, M. S. Vlaskin, *Renew. Sustain. Energy Rev.* 2011, 15, 4611.

(6) Q. Li, N. J. Bjerrum, *J. Power Sources* 2002, 110, 1.

(7) U.S. Geological Survey, *U.S. Geol. Surv. Miner. Commod. Summ.* 2015, 196

## A high performances aluminum/graphite battery

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Modern society is in urgent need of sustainable and efficient energy storage devices. The renewable energy production is characterized by an intermittent power output, and requires for large scale applications an improvement on the capability of energy storage (currently less than 1% of the electrical energy production can be stored).<sup>1</sup> The development of low cost and environmentally friendly electrochemical storage systems characterized by high performance is of fundamental importance for a sustainable energy economy. The currently most mature battery technology is the lithium ion battery, considered one of the most appealing candidates as power source for electric vehicle applications. However, the large scale application of lithium ion batteries is nowadays under discussion due to the limited amount of lithium resources.<sup>2</sup> Several other metallic anodic materials such as sodium,<sup>3</sup> potassium,<sup>4</sup> calcium,<sup>5</sup> magnesium<sup>6</sup> and aluminum,<sup>7,8</sup> characterized by a higher abundance with respect to lithium, have been considered as suitable candidates for electrochemical storage devices in replacement of lithium systems. In particular aluminum, the most abundant metallic element in the earth's crust, is considered a promising candidate for application in stationary electrochemical storage systems. The light weight of aluminum and its ability to exchange three electrons during the electrochemical process ( $Al^{3+} + 3e^- \leftrightarrow Al$ ) grant both, a high gravimetric and volumetric capacity density of 2.98 Ah g<sup>-1</sup> and 8.04 Ah cm<sup>-3</sup>, respectively, the latter value being four times as high compared to a lithium metallic anode. Additionally, the aluminum can be handled in open air leading to enormous advantages in the cell fabrication and an extreme improvement of the safety level of electrochemical storage systems employing this electrode material.

In our work we propose the use of advanced graphite cathode material for the application in aluminum batteries. Electrochemical tests have been performed employing 1-ethyl-3-methylimidazolium chloride (EMImCl) ionic liquid and AlCl<sub>3</sub> in a molar ratio of EMImCl:AlCl<sub>3</sub> 1:1.5 as the electrolyte. The suitability of the electrolyte medium against aluminum metal has been evaluated by means of impedance spectroscopy

as well as of cyclic voltammetry, revealing the reversibility of the electrochemical process of stripping and deposition of the aluminum in the employed cell configuration.

- (1) Z. Yang et al., *Chem. Rev.*, 111, 35773613 (2011).
- (2) J.-M. Tarascon, *Nat. Chem.*, 2, 510 (2010).
- (3) N. Yabuuchi, K. Kubota, M. Dahbi, and S. Komaba, *Chem. Rev.*, 114, 1163611682 (2014).
- (4) X. Ren and Y. Wu, *J. Am. Chem. Soc.*, 135, 29232926 (2013).
- (5) A. Ponrouch, C. Frontera, F. Bardé, and M. R. Palacín, *Nat. Mater.*, 15 (2015).
- (6) D. Aurbach et al., *Nature*, 407, 1316 (2000).
- (7) M.-C. Lin et al., *Nature*, 520, Pages: 324328 (2015)
- (8) G. A. Elia, et al. *Adv. Mater.* (2016). doi:10.1002/adma.201601357

## Attractive Structural Features of the Nanocarbons for Energy Storage and Conversion Devices

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In modern electrochemical energy conversion/storage devices (e.g., supercapacitors, lithium-ion batteries, gas storage and water desalination devices, etc.) the structural features of used nanocarbon play a key role and thus, the relevant electronic and porosity properties of nanocarbon determine the performance of the systems.<sup>1-4</sup> Depending on the synthesis route and conditions chosen, the nanocarbons have different physico-chemical properties such as surface area, porosity, electronic and ionic conductivity, hydrophilicity and electrocatalytic activity.<sup>3-5</sup> Despite the efforts made so far, there is still a strong need for better understanding of processes related to the mass transport properties of electrolyte ions inside of the porous electrode materials driven by their morphology.<sup>6,7</sup>

For characterization, the x-ray microcomputed tomography ( $\mu$ CT), small-angle neutron scattering (SANS), and small-angle x-ray scattering (SAXS) techniques were applied. The detailed structural information will be used for further optimization and development of the supercapacitors based on nanoporous carbon.<sup>8,9</sup> A key structural features of RP-20 nanocarbon will be the subjects of a presentation.

- (1) A. Laheäär, A. Jänes, E. Lust, *Electrochim. Acta*, 56 (25), (2011) 9048.
- (2) C.C. Rochester, G. Pruessner, A.A. Kornyshev, *Electrochim. Acta* 174 (2015) 978.
- (3) D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, et al., *Nat. Nanotechnol.* 5 (9) (2010) 651-654.
- (4) J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, *Science* 328 (5977) (2010) 480-483.
- (5) C. Prehal, C. Koczwara, N. Jäckel, A. Schreiber, M. Burian, H. Amenitsch, M. A. Hartmann, V. Presser and O. Paris, *Nature Energy*, 2, 16215 (2017).
- (6) S. Renault, V. Alina Mihali, K. Edström, D. Brandell, *Electrochem. Comm.*, Volume 45, (2014) 52.
- (7) A. Poullikkas, *Renewable and Sustainable Energy Reviews*, 27 (2013) 778.
- (8) E. Härk, N. Kardjilov, A. Hilger, A. Petzold, S. Risse, I. Vaas, G. Goerigk, C. Jafta, M. Ballauff, E. Lust, *ECS Trans.* 77 (2017) 1133.
- (9) E. Härk, A. Petzold, G. Goerigk, M. Ballauff, U. Keiderling, R. Palm, I. Vaas, E. Lust, The effect of a binder on porosity of the nanoporous RP-20 carbon. A combined study by small angle X-ray and neutron scattering, *Electrochimica Acta* (submitted).

## X-ray Absorption Spectroscopy of TiO<sub>2</sub> Nanoparticles in Water using a Holey Membrane-based Flow Cell

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Measuring the electronic structure of photocatalytic nanoparticles directly in aqueous solution is highly relevant since their applications generally necessitate aqueous environment. Soft X-ray absorption spectroscopy (XAS) is highly sensitive to the chemical environment, however XAS measurement in aqueous environment remains challenging, especially in the water window (below 535 eV), required to probe the core level of light elements (C, N, O) and the Ti L edge. The characterization of TiO<sub>2</sub>- and carbon-based photocatalysts close to real conditions therefore requires the development of new methods for applications of XAS in liquid in this energy region. We introduce here a new approach to measure fluorescence yield XAS (FY-XAS) of nanoparticles in water using a holey membrane flow cell.<sup>1</sup> To isolate the aqueous dispersion from the vacuum, silicon nitride membranes with small holes (750 nm) are used instead of solid membranes to ensure enhanced X-ray transmission, especially in the water window. The small size of the holes ensure good vacuum conditions due to liquid surface tension. This method was applied to anatase TiO<sub>2</sub> nanoparticles aqueous dispersions with two different sizes.

XAS of TiO<sub>2</sub> nanoparticles at the titanium L edge and at the oxygen K edge were successfully measured with a holey membrane-based flow cell at the synchrotron BESSY II. Modifications of the XA spectra, probably induced by hydration, were observed for dispersed samples compared to solid references. In addition, formation of an amorphous ice layer at the liquid water-vacuum interface in the holey area was evidenced and will be discussed.

The use of holey membrane enables new perspectives for the characterization of nanoparticles in liquid with XAS in the water window. We believe that these methods will facilitate the in situ characterization of new photocatalytic nanomaterials with XAS in the soft X-ray region and can contribute to the development of more efficient photocatalysts.

(1) Petit, T.; Ren, J.; Choudhury, S.; Golnak, R.; Lalithambika, S.; Tesch, M.; Xiao, J.; Aziz, E., "X-Ray Absorption Spectroscopy of TiO<sub>2</sub> Nanoparticles in Water Using a Holey Membrane-Based Flow Cell", *Adv. Mater. Interfaces* 2017, 4 (23), 1700755.

## Writing and Publishing Research with SciFlow

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Collaborative scientific writing is an important part of the research workflow.<sup>1</sup> Based on the pain-points researchers experience when collaborating on a paper,<sup>2</sup> we introduced SciFlow, an online platform for collaborative writing and publishing. By conducting interviews with researchers throughout the development,<sup>3</sup> we identified key focus areas for SciFlow to provide benefits to a scholarly writer.

1. All authors must be able to access the latest version of the document
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Additionally to our original observations on frustrations throughout the publication workflow, we share the frustration with many researchers and institutions when it comes to the current status quo of accessibility of research.<sup>4</sup> While funders are doing their part in improving the accessibility of research (i.e. Open Access), SciFlow wants to do their part in making research more accessible, while still supporting researchers in publishing in traditional formats. Specifically some of the next focus areas will be to

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- Providing journal search within SciFlow to easily discover alternative journals for publication Researchers can access SciFlow on our website<sup>5</sup> for free.

(1) Yore, L. D.; Hand, B. M.; Florence, M. K. Scientists Views of Science, Models of Writing, and Science Writing Practices. *Journal of Research in Science Teaching* 2004, 41 (4), 338.

(2) Eichler, F.; Reinhardt, W. [Simplifying the Scientific Writing and Review Process with Sci- Flow]. *Future Internet* 2010, 2 (4), 645.

(3) Hypothesis-Driven Entrepreneurship: The Lean Startup.

(4) Project DEAL <https://www.projekt-deal.de/about-deal/>.

(5) SciFlow GmbH. [SciFlow for Researchers] <https://www.sciflow.net/en/researcher>.

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