Final report

M-ERA.NET: Hybrid Materials for Low Cost Volatile Organic Compound Sensor System

OTKA NKFIH NN 110676

1 September 2013 – 30 August 2016

Introduction

The objective of this OTKA NKFIH project was to provide the Hungarian implementation background for the „*M-ERA.NET: Hybrid Materials for Low Cost Volatile Organic Compound Sensor System*" project. This project was the joint effort of an international consortium consisting of the National Taiwan University (coordinator), the Finnish SME Nanordic Oy, the Spanish company Ingenieros Asesores, S.A. and the University of Szeged, Hungary. The goal of the M-ERA.NET consortium was to develop a low-cost sensor for detecting volatile organic compounds. The operating principle of the sensor was the change of optical properties of a polymer nanocomposite upon volatile organic compound (VOC) adsorption. The specific role of the University of Szeged in the consortium was the synthesis and development of various nanoparticles to be utilized in such nanocomposites by the Taiwanese partner.

Networking results

The VOCSENSOR consortium has fulfilled its main purpose in creating a real collaborative network between the partners. The three networking highlights of the project were the invited participation of the project partners at the reception organized by the Taiwanese Minister of Foreign Affairs to celebrate the 102th National Day in Taipei (2013), the invited talk given by the VOCSENSOR coordinator Prof. Wei-Fang Su at the 6th International Workshop on Advances in Nanoscience (Szeged, 2014) and the recognition of the VOCSENSOR project as a highly successful M-ERA.NET venture at the M-ERA.NET international evaluation event (Warsaw, 2015).

The core partnership formed in this project between the National Taiwan University and the University of Szeged resulted in a joint M-ERA.NET 2 pre-proposal in 2016. This pre-proposal ("CLEARPV") was evaluated positively by all financing organizations, therefore, we are now invited to submit the full proposal by the beginning of November 2016.

Research highlights

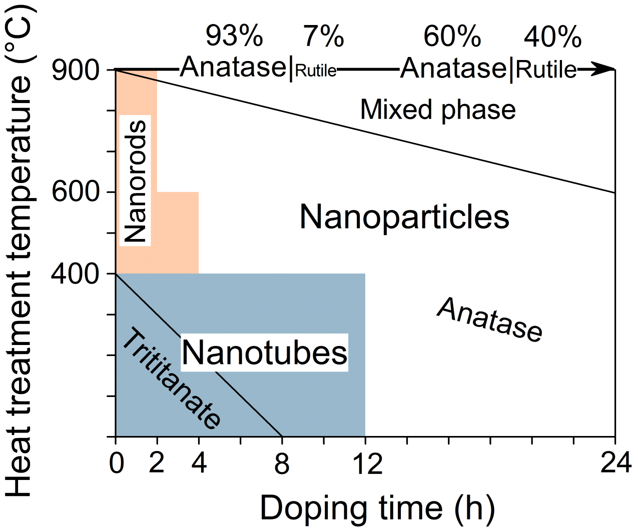
Our results were continuously published in scientific journals, so we refer to these publications for all experimental details and literature reviews. The section below provides a short overview of the most important Szeged achievements.

Nanoparticle synthesis

Titanate nanowire synthesis and functionalization

Gold decorated titanate nanowires and nanotubes were investigated by XPS, XRD and HRTEM. XPS and UV-Vis diffuse reflectance results suggested that a certain part of gold underwent an ion exchange process. Higher gold loadings lead to the formation of nanosized-dispersed particles complexed to oxygen vacancies, with a diameter distribution of 1.5-10 nm. Gold additives catalyzed the transformation of the tube structure to anatase. Gold, however, stabilized the wire-like structure up to 873 K.[1]

Hydrothermally synthesized protonated titanate nanotubes were doped by nitrogen using ammonia gas as dopant. Thermal decomposition of urea served as ammonia source offering a low-temperature synthesis route for obtaining a potential visible-light photocatalyst. Nitrogen doping could be achieved at as low as 200 °C. The doped samples were calcined at different temperatures and changes in morphology and crystalline phase were studied by transmission and scanning electron microscopy, selected area electron diffraction, energy dispersive X-ray spectroscopy and X-ray diffraction. Nitrogen content and calcination temperature were found to affect the size and shape of the particles as well as their crystalline phase to a great extent. H-form trititanate was showed to transform to rutile TiO_2 through the anatase phase in parallel with the collapse of the nanotube morphology and the production of first rod-like then finally round nitrogen-doped nanoparticles. A phase map (see below) was constructed from the data to facilitate the rational design of N-doped trititanate nanotube based nanostructures.[2]



Zero valent iron nanoparticles in environmental applications

For evaluation of oxidative degradation of industrial azo dye Rosso Zetanyl B-NG (RZ B-NG), three clay supported nanoscale zero-valent iron materials were synthesized: bentonite, kaolin and native clay-supported nanoscale zero-valent iron (B-nZVI, K-nZVI and NC-nZVI). All clays used as a support material not only dispersed and stabilized nanoscale zero valent iron (nZVI) but also improved the adsorption and degradation of dye as they consequently improved heterogeneous Fenton oxidation. Under the optimal conditions, for the used nanomaterial concentrations of 112, 168 and 224 mg/L for B-nZVI, NC-nZVI and K-nZVI, the decolourization efficiencies achieved were 92.7, 92.1 and 91.6% and appropriate TOC removals were 57.8, 57.2 and 50.7% in the same order. The best catalytic performance was exhibited when B-nZVI was used. These results correlate with the specific surface area and mesoporous structure of the synthesized materials. They contributed to Fenton reaction enhancement by generating effective reaction sites for potential adsorption and subsequent oxidative degradation of the azo dye. Based on these results, all clay supported nanomaterials have proved to be superior heterogeneous Fenton-like catalysts for removing azo dyes from wastewater.[3]

Based on the success of nZVI-clay composites in organic pollutant removal, we investigated the possibility of using supported nanoscale zero-valent iron with bentonite and kaolinite for immobilization of As, Pb and Zn in contaminated sediment from the Nadela river basin (Serbia). Assessment of the sediment quality based on the pseudo-total metal content (As, Pb and Zn) according to the corresponding Serbian standards shows its severe contamination, such that it requires disposal in special reservoirs and, if possible, remediation. A microwaveassisted sequential extraction procedure was employed to assess potential metal mobility and risk to the aquatic environment. According to these results, As showed lower risk to the environment than Pb and Zn, which both represent higher risk to the environment. The contaminated sediment, irrespective of the different speciation of the treated metals, was subjected to the same treatment. Semi-dynamic leaching test, based on leachability index and effective diffusion coefficients, was conducted for As-, Pb- and Zn-contaminated sediments in order to assess the long-term leaching behaviour. In order to simulate "worst case" leaching conditions, the test was modified using acetic and humic acid solution as leachants instead of deionized water. A diffusion-based model was used to elucidate the controlling leaching mechanisms; in the majority of samples, the controlling leaching mechanism appeared to be diffusion. Three different single-step leaching tests were applied to evaluate the extraction potential of examined metals. Generally, the test results indicated that the treated sediment is safe for disposal and could even be considered for "controlled utilization".[4]

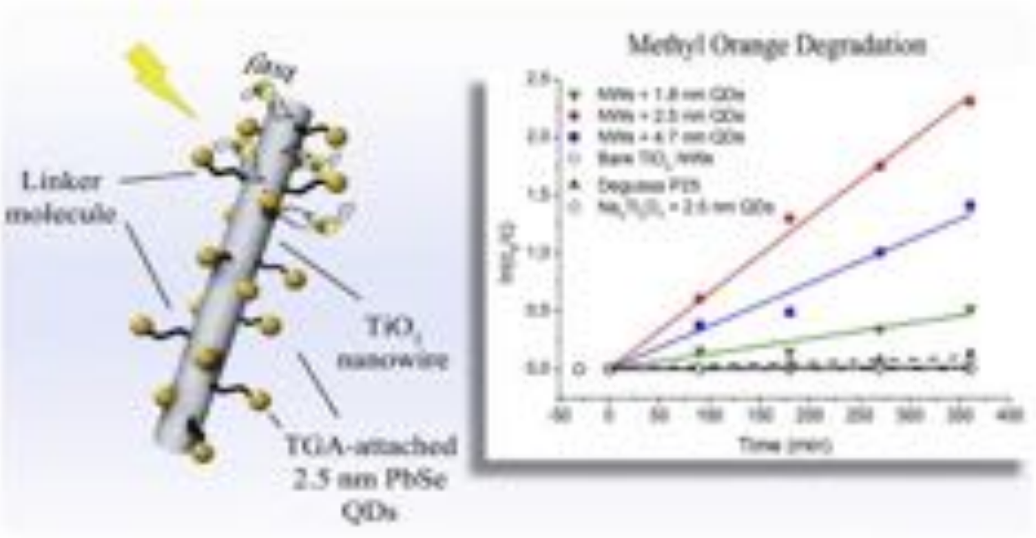
Carbon nanotubes in sensing and in polymer composite development

Carbon paste electrodes (graphite/paraffin oil) bulk-modified with multiwalled carbon nanotubes (MWCNT) and chemically oxidized MWCNT (O-MWCNT) were used as sensors for the hydrodynamic chronoamperometric determination of hydrogen peroxide (H_2O_2). Experimental parameters, such as the type and pH of the supporting electrolyte or the working potential(s) applied were investigated in the batch arrangement.[5]

Multiwalled carbon nanotubes were synthesized by Chemical Vapor Deposition over an Fe-Co/alumina catalyst. Nanotubes were then oxidized and grafted with polyvinyl alcohol (PVA). The obtained nanostructure was characterized by Raman spectroscopy, XRD, FTIR, EDX, SEM, TEM and TGA methods. FTIR confirmed the presence of the characteristic peaks of the anticipated ester group. The formation of polymer nanocomposites based on polyvinyl alcohol and multiwalled carbon nanotubes was confirmed by SEM and TEM. High resolution electron micrographs revealed that the primary binding sites for PVA grafting are the sidewall defects of the nanotubes. The novelty of this work is the use of the Fischer esterification reaction for creating the permanent link between the nanotubes and the PVA matrix.[6][7]

Synthesis of photoresponsive nanoparticles

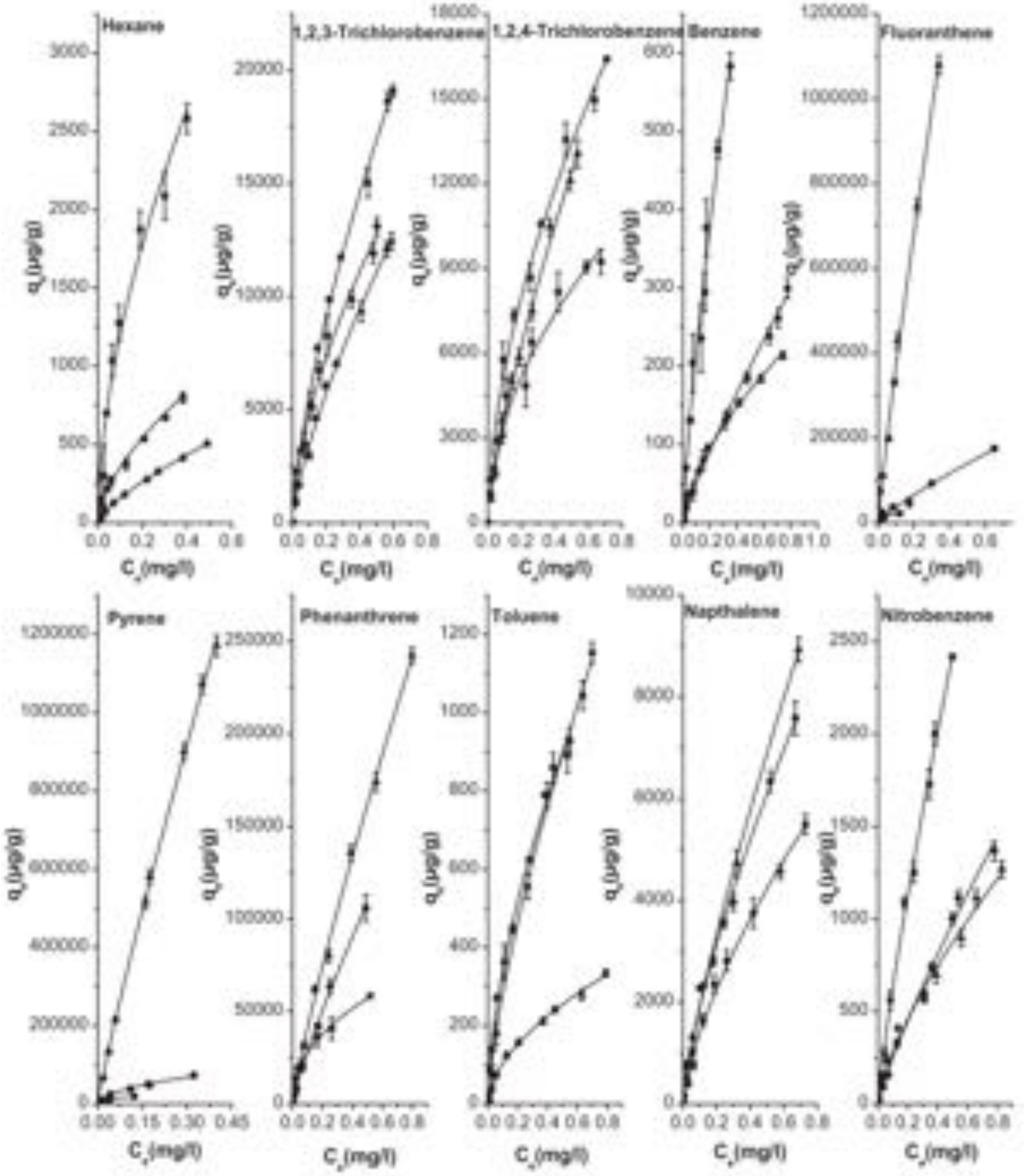
We used differently sized PbSe quantum dots as photosensitizers for anatase TiO_2 nanowires under visible light illumination. After the organometallic synthesis of PbSe quantum dots with three different average diameters (1.8, 2.5 and 4.7 nm), the nanocrystals were attached to the surface of nanowires with thioglycolic acid as a linker molecule. These quantum dot decorated nanowires were used as photocatalyst in the methyl orange degradation model reaction with promising results. The best performance achieved was 90% degradation of the initial concentration of methyl orange in six hours over 2.5 nm PbSe quantum dot sensitized nanowires using a 40 W quartz UV lamp equipped with a 400 nm cut-off filter.[8]



VOC interaction with nanoparticles

We investigated the adsorption of four groups of organic compounds (OCs): (1) nitroaromatics, (2) nonpolar aliphatics, (3) monoaromatics and (4) polycyclic aromatic hydrocarbons (PAHs) on multiwalled carbon nanotubes (MWCNTs). In order to investigate the influence which oxygen containing functional groups exert on the adsorption process, three MWCNTs were used: the pristine (original, as-received) MWCNTs (OMWCNT) and two MWCNTs functionally modified by acid treatment of OMWCNT during 3 h and 6 h (FMWCNT3h, FMWCNT6h). All adsorption isotherms well fitted with the Freundlich model. The nonlinearity of the isotherms ranged from 0.418 to 0.897. The results show that K_d values for PAHs increased with increasing specific surface areas (SSAs) The adsorption affinities of the larger molecular size OCs (PAHs) were higher than those of the smaller size OCs (benzene, toluene and hexane) which is probably due to their large contact area with the surface of the adsorbent. Adsorption of OCs on MWCNTs was mainly controlled by hydrophobic interactions, except for the nitroaromatic compound, as shown by the increasing adsorption affinities with the compound's hydrophobicity. KOW-normalized adsorption coefficients (Kd/KOW) for all the investigated compounds on all the MWCNTs followed the order:

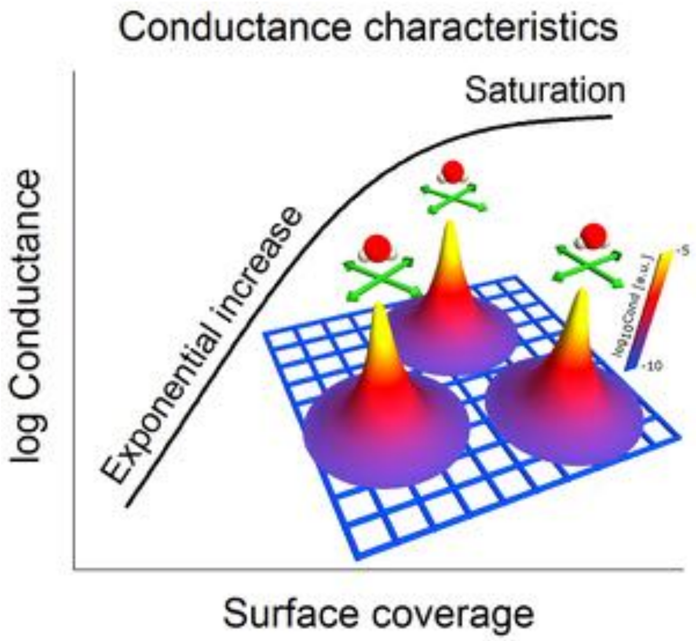
nonpolar aliphatic < monoaromatics < PAHs < nitroaromatic, implying that p–p interactions enhanced the adsorption of aromatics on the MWCNTs. It can be concluded that the strong adsorptive interactions between the MWCNTs and nitroaromatics was due to the p–p electron-donor–acceptor (EDA) interaction between nitroaromatic molecules (electron acceptors) and the highly polarisable graphene sheets (electron donors) of the carbon nanotubes.[9]



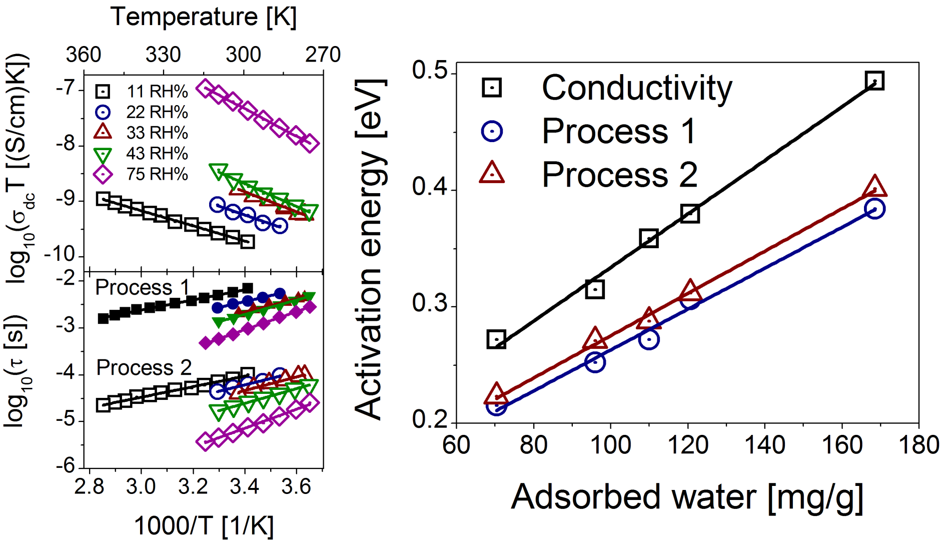
Interface phenomena and sensing

Humidity response of nanowires

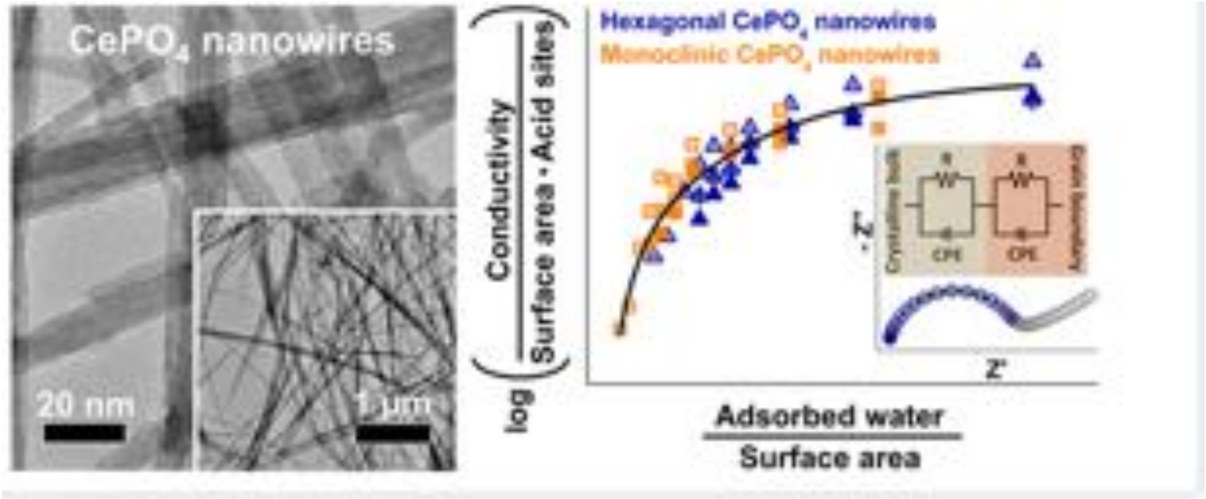
The variation of conductance during sorption in a variety of different materials exhibits a similar response. However, the detailed understanding of the surface conduction during adsorption still has to be achieved. A simple theoretical framework was developed, in which we were able to model adsorption-induced conductance changes and obtain the well-known shape of the characteristics. Our model calculations revealed that the unexpected similarity of the response is the consequence of the dynamic nature of adsorption processes in real systems.[10]



The temperature dependence of dielectric processes in humid titanate nanowires was investigated via broadband dielectric spectroscopy under quasi-isosteric conditions in the temperature range of 150-350 K. It was found that the dynamic parameters obtained from low-temperature measurements couldn't describe the dielectric behavior of the system above 273 K, implying changes in the dynamics of the corresponding dielectric processes. The calculated activation energies and pre-exponential factors counter intuitively increase linearly with the amount of adsorbed water, while compensation effect was also found to apply to all contributions in the TiONW spectra.[11]

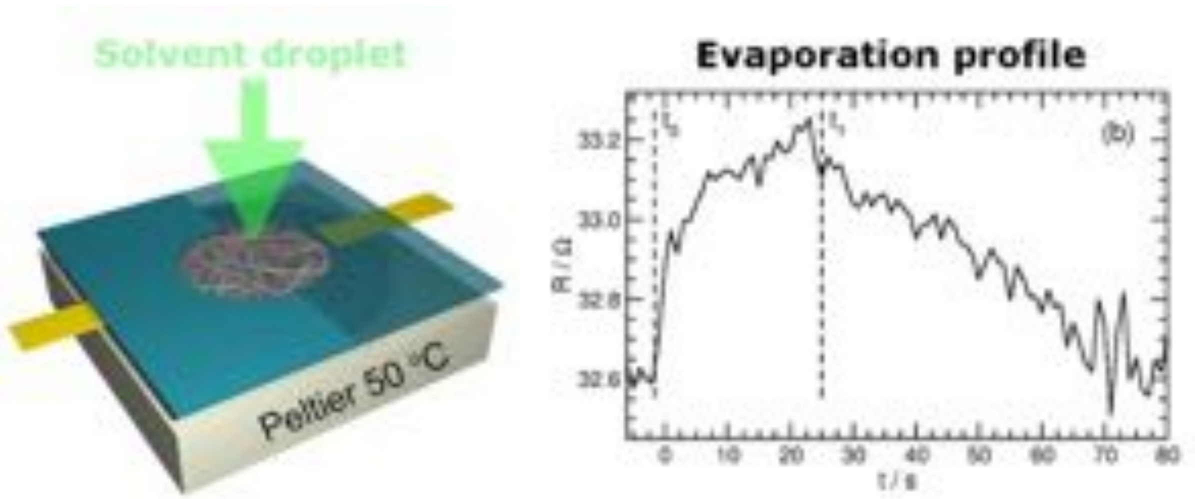


Cerium phosphate nanowires with monoclinic and hexagonal crystal structures were synthesized via the hydrothermal and ambient temperature precipitation routes, and their structural and surface properties were examined by using high-resolution transmission electron microscopy, X-ray diffractometry, nitrogen and water sorption, temperature- programmed ammonia desorption, and potentiometric titration techniques. The relative humidity (RH)-dependent charge- transport processes of hexagonal and monoclinic nanowires were investigated by means of impedance spectroscopy and transient ionic current measurement techniques to gain insight into their atomistic level mechanism. Although considerable differences in RH-dependent conductivity were first found, the distinct characteristics collapsed into a master curve when specific surface area and acidity were taken into account, implying structure-independent proton conduction mechanism in both types of nanowires.[12]

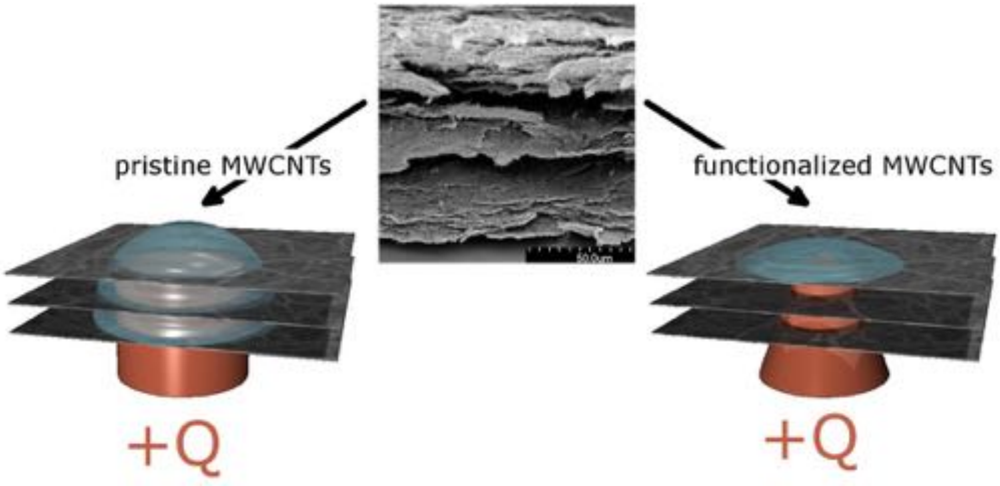


Interaction of MWCNT buckypaper and sessile water droplets

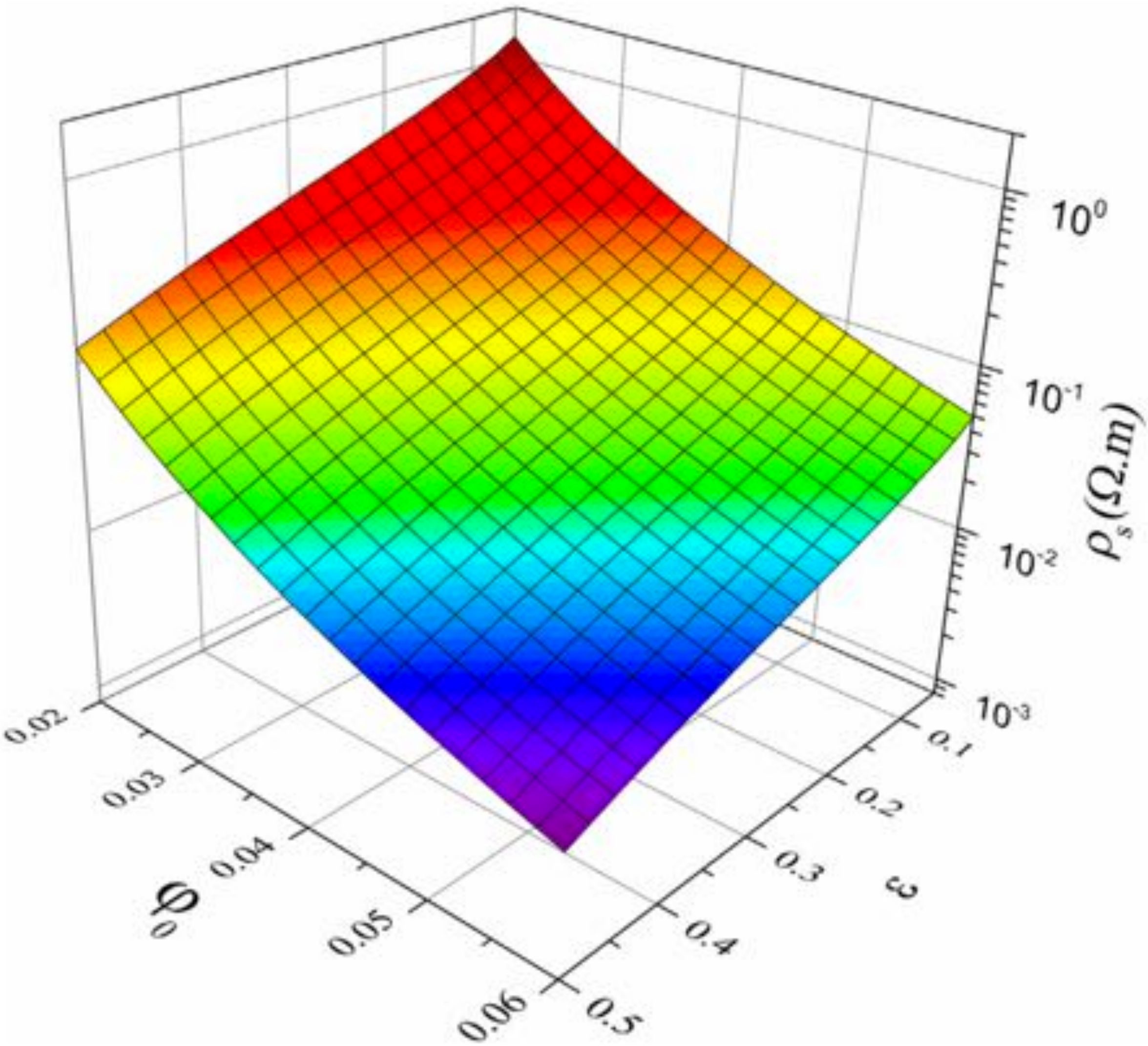
Buckypaper is a mesoporous, self-supporting, electrically conducting mat of multiwall carbon nanotubes prepared by filtering a nanotube suspension through a submicron pore diameter membrane and drying the filter cake. Multiple phenomena take place simultaneously when a liquid droplet contacts the buckypaper surface: wetting, spreading, adsorption, capillary filling, evaporation from the surface, evaporation from the pores, infiltration of nanotube–nanotube junctions, gravity induced convective flow, etc. The electrical resistance of the buckypaper as a function of time exhibits a maximum curve during these processes. The fine details of the shape of this curve are slightly different for every solvent. We refer to this characteristic function as the evaporation profile of the studied liquid. In this paper we combine simultaneous electrical resistivity measurement, weight measurement and visible image processing methods to reveal the basic properties of the evaporation profile. A good correlation between the changes in buckypaper mass and electrical resistance was found and the distribution of the liquid penetrating the buckypaper matrix followed specific patterns and was correlated with the shape of the measured evaporation profile. Results are compared with fluid dynamic simulations. The evaporation profile emerges as a reproducible and inexpensive qualitative analytical tool for liquid identification. Alternatively, recording the evaporation profile of a chosen test liquid could become a feasible characterization method for mesoporous materials.[13]



The heat transfer coefficient between a single water droplet and a multiwall carbon nanotube film (buckypaper) was measured for pristine and for carboxy functionalized nanotubes by infrared thermography. The value for non-functionalized nanotubes (438 Wm^2 K^{-1}) was more than twice as large as that for functionalized ones (204 $Wm^2 K^{-1}$) even though the water to nanotube affinity is larger in the latter case as indicated by contact angle measurement. This apparent contradiction can be explained by the hydrophilic surface pinning of the droplet and the vertically periodic layered structure of the buckypaper.[14]



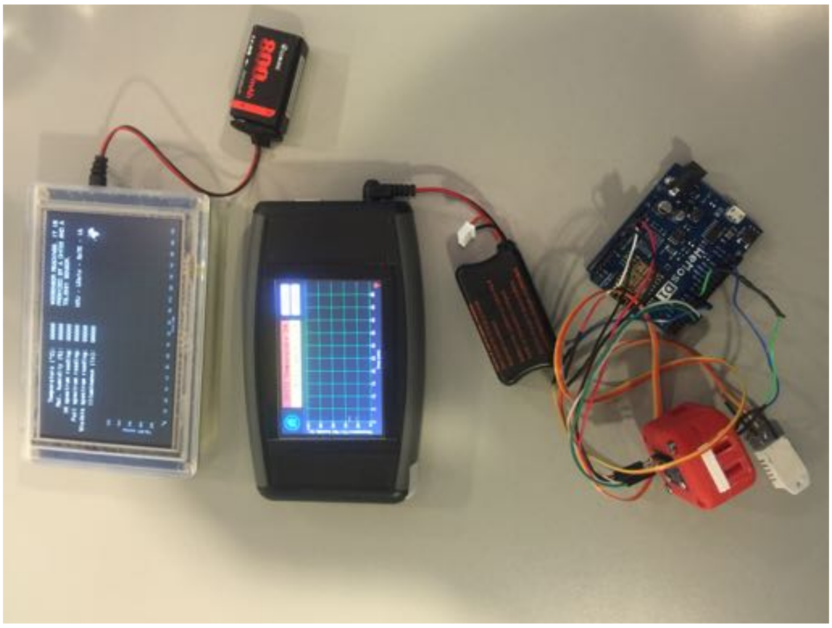
Although individual carbon nanotubes possess remarkable electrical properties, the electrical resistance of pristine buckypaper (BP) is usually too high for practical applications. However, the electrical resistivity of BP can be attenuated by applying modest compressive stresses. We developed an analytical model for predicting the electrical resistivity of BP under defined level of compressive strain. The predictive piezoresistive model of BP was developed by formulating a direct relationship with the structural parameters, physical and electrical properties of CNTs. The basis of the piezoresistive model relied upon the geometrical probability approach in combination with classical Hertzian contact mechanics and constriction resistance techniques. A comparison has been made between the theoretical and experimental results of electrical resistivity of BPs with varying densities. A reasonably good quantitative agreement was obtained between the theory and experiments. The main source of error was caused by the uncertainty in the measurement of the initial BP thickness. Through theoretical modeling, the initial volume fraction of CNTs was found to be one of the key parameters that modulated the piezoresistive behavior of BP. The figure below summarizes the findings of our model: the theoretical electrical resistivity of buckypaper is shown as a function of initial CNT volume fraction (φ_0) and compressive strain (ε_0).[15]

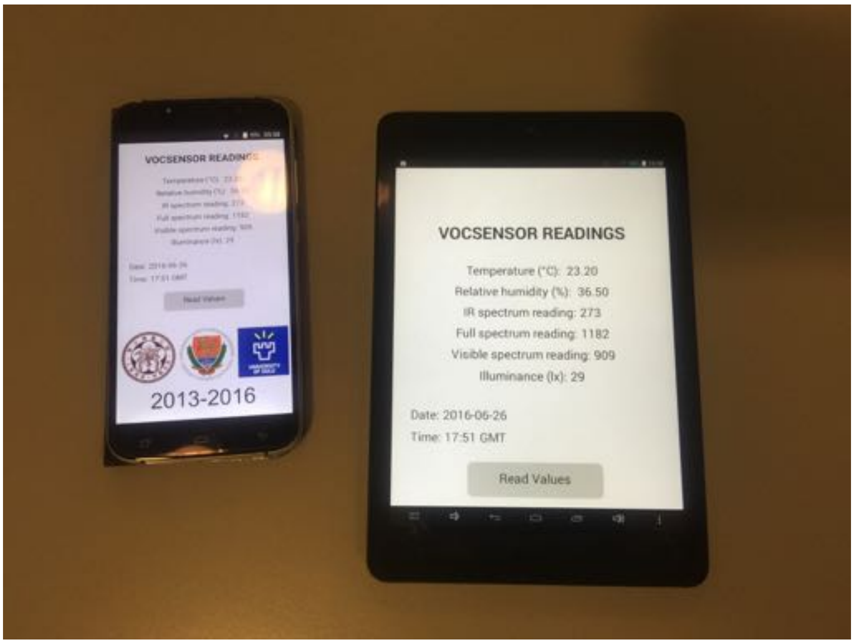

10^0
10^-1
10^-2
10^-3
ρ_s (Ω.m)
0.02
0.03
0.04
0.05
0.06
Φ_0
0.1
0.2
0.3
0.4
0.5
ε

Final results

Consortium level

The VOCSENSOR consortium created several prototypes and proof-of-concept type demonstrators. The final prototype unit (see below) was presented at the June 2016 evaluation meeting (Oulu, Finland). This system consists of a purpose built optical spectrometer containing the nanocomposite polymer film (red box), an interface and a microcontroller. Touchscreen and web-based server-client type interfaces were also developed and demonstrated on mobile devices.





VOCSENSOR READINGS

Temperature (°C): 23.20
Relative humidity (%): 36.50
IR spectrum reading: 273
Full spectrum reading: 1182
Visible spectrum reading: 909
Illuminance (lx): 29

Date: 2016-06-26
Time: 17:51 GMT

University of Szeged level

Our group participated actively in the M-ERA.NET consortium during the whole duration of the project. The most important strengths of the Szeged group were the fundamental scientficic observations made about (i) nanoparticle synthesis, (ii) adsorption of organic compounds and (iii) the interaction between vapors/liquids and nanoporous networks. Our materials were tested extensively within the consortium as additives to the polymer sensing matrix. The main weakness of the Szeged contribution was the moderate performance of the sensors created with these additives. Nevertheless, the scientific results outlined above have resulted in 31 peer-reviewed papers published in international journals with impact factors. The cumulative impact factor of these papers is close to 120. Therefore, we believe that our contribution to the M-ERA.NET objectives was overall successful.

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