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Reference

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43. From Cellulose (and Other Biopolymers) to Functional Sensors

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Abstract: The wide availability and biocompatibility of natural polysaccharides, such as cellulose and alginate, have enabled their inclusion in diverse applications, such as drug delivery, tissue engineering, or environmental remediation. In addition to those, the rich chemical functionality of these polymers has also enabled the development of traditional and wearable sensors that can not only play an essential role as a non-invasive tool to monitor multiple analytes in real time, but also provide information complementary to that potentially obtained by more complex (and invasive) systems. In addition, and while materials have the potential to diversify the substrates available for the development of biosensors, their application is still limited by several fundamental challenges that affect not only the fabrication procedures, but also the performance of the devices. Aiming to address these shortcomings, our group has explored several routes to use and modify these biopolymers and apply them towards biosensing applications. Specifically, this presentation will describe the possibility to perform the thermal treatment of cellulose at either low (leading to the formation of redox-active fluorescent molecules) or high temperatures (carbonization). In addition, the presentation will also describe approaches towards the fabrication of complementary electrochemical, optical, and chemiluminescent biosensors based on these biopolymers.

44. Evidence of Hexavalent Chromium Formation and Plant Uptake in Agricultural Soils after Simulated Fires

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Abstract: Controlled fires are widely used in many common agricultural practices to remove the vegetation residues and manage weeds and pests. High temperatures occurring during fire events can cause significant changes in soil physico-chemical properties and element biogeochemistry. Therefore, also potentially toxic elements (PTEs) can change their speciation and hence their bioavailability. In particular, chromium (Cr), depending on the soil redox conditions and the content and type of organic matter (OM), can modify its oxidation state thus forming highly mobile and toxic hexavalent species (Cr(VI)). In the present study, the effect of laboratory-simulated fires on the distribution, speciation, and plant uptake of Cr in highly polluted agricultural soils was investigated. Three thermal treatments (up to 300 °C, 400 °C, and 500 °C) were performed by means of a muffle furnace to simulate a fire event of medium severity. The soil chemical and mineralogical

characteristics were assessed before and after each thermal treatment, as well as the Cr fractionation and speciation. The latter were assessed through an integrated approach based on conventional analyses (determination of total Cr, total Cr(VI), and exchangeable Cr(VI), DTPA extraction, BCR sequential extractions), and X-ray based techniques, including synchrotron X-ray absorption spectroscopy (XAS). Heating treatments strongly altered the soil chemical characteristics, especially the OM content and Cr fractionation and availability. After heating, a partial oxidation of Cr(III) to Cr(VI) was observed, and from 21% to 88% of the total Cr(VI) was in the exchangeable form. A combination of bulk and micro X-ray absorption near edge spectroscopy (XANES) analyses allowed the identification of different Cr species in the polluted soil samples before and after the thermal treatments, showing an increase of chromite (FeCr_2O_4), Cr(III)goethite, and CaCrO_4 with increasing temperature, and a decrease of Cr-OM complexes. The formation of Crgoethite and chromite caused a relative immobilization of Cr, while CaCrO_4 , being slightly soluble, could represent a potential risk for the environment with negative consequences for plants and human health. Indeed, rhizotest experiments with durum wheat plants confirmed an increased Cr accumulation in plant tissues. Cr concentration in roots increase from $34 \text{ mg kg}^{-1} \text{ DW}$, in the unheated soil, to 467 and $825 \text{ mg kg}^{-1} \text{ DW}$ in 300°C and 500°C -heated soil, respectively. Cr was also detected in shoots of plants grown on 300°C and 500°C -heated soils, at concentrations of 26 and $51 \text{ mg kg}^{-1} \text{ DW}$, respectively. The Cr accumulation in plants appeared to be related to the exchangeable Cr(VI) amount in soil. The overall results suggest that Cr was preferentially taken up by the plants as Cr(VI), as also supported by micro X-ray fluorescence analyses. Further experiments are needed to investigate Cr speciation inside the plant and Cr-uptake mechanisms underlying its plant acquisition.

45. Morphology Control of PEDOT: PSS Polyelectrolyte by Hard-Cation-Soft-Anion Ionic Liquids: Microscopic Observation by Molecular Dynamics Simulation

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Abstract: Water-processable mixtures of positively charged poly-3,4-ethylenedioxythiophene (PEDOT) and negatively charged polystyrenesulfonate (PSS) have received great attention as a flexible, stretchable, conformable, lightweight, transparent, and low-cost organic (semi)conductor and electrochemical transistor, which can be used for applications, such as organic LED, solar cell, thermoelectric generator, self-powered implantable sensor and actuator, and artificial skin. They form 10–30-nm granular domains, where conducting but hydrophobic PEDOT-rich regions are surrounded by hydrophilic but insulating PSS-rich regions, hindering the formation of large conducting PEDOT domains. This makes PEDOT:PSS water-soluble, thermally stable, and environmentally benign, but poor in terms of conductivity. Adding polar organic solvents, acids, or organic/inorganic salts to the PEDOT:PSS solution enhanced the conductivity by 2–3 orders of magnitude. Recently, a remarkable 5000-fold improvement of conductivity was achieved by mixing proper ionic liquids (ILs) in a PEDOT:PSS solution of deionized water and polar organic solvents. In a series of free energy calculations [1–5] using density functional theory and molecular dynamics simulations based on the classic “hard soft acid (cation) base (anion)” principle, we have demonstrated the following: (1) ion exchange between $\text{PEDOT}^+:\text{PSS}^-$ and $\text{A}^+:\text{X}^-$ ILs would help PEDOT^+ to decouple from PSS^- and to grow into large-scale conducting domains of π -stacked PEDOT^+ decorated by IL anions X^- ; (2) the most spontaneous decoupling between hydrophobic/soft PEDOT^+ and hydrophilic/hard PSS^- would be induced by strong interaction with hydrophobic/soft anions X^- and hydrophilic/hard cations A^+ , respectively; and (3) the most efficient IL anions X^- remaining in the PEDOT domain after the ion exchange would sustain the highest number