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Dritan Hasa

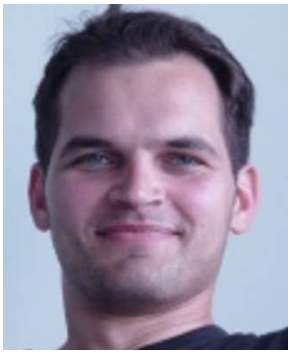
Mechanochemical synthesis of functional (pharmaceutical) solids

Mechanochemistry - the use of mechanical force to induce and/or sustain chemical transformations has recently been highlighted by IUPAC as "one of the ten most important chemistry innovations that will change the world". Although such discipline is relatively new with a significant growth of interest observed particularly over the last three decades, several independent studies have demonstrated mechanochemistry to be effective and often superior to other approaches for the discovery of new solid forms. The propensity of a specific molecule to give different polymorphs and/or form multicomponent crystals can be assessed mechanochemically by changes in the exact conditions of the reaction, including neat grinding (NG), variable temperature grinding (VATEG), liquid-assisted grinding (LAG), variable amount LAG (VALAG), ion liquid-assisted grinding (ILAG) and polymer-assisted grinding (POLAG). This presentation has particular focus on the several mechanochemical developments available in pharmaceutical materials science, and relates the outcomes both to the operational conditions and to the chemical characteristics of the reactants. Some relevant examples already available in literature will be mentioned, and the most recent result in our laboratory will be also presented.

Claudia Crestini

Lignin Valorisation: Advances and Challenges

Abundant polyphenolic non-fossil-based, but renewable resources continue to have problems in benefitting from the growing trends of sustainability in general and substitution of non-sustainable 'traditional' active ingredients in every-day consumer products in particular. Especially lignin, despite enormous research efforts , still suffers from its intrinsic diversities and variabilities ranging from differences stemming from natural origins to issues emerging during industrially feasible isolations. Concerted efforts lead to improved understanding of lignins structure, ever improved processes allowing isolation of lignins with less impurities or directly fractionating lignins into homogeneous components. As a direct consequence, now it is possible to directly trigger the rational design of chemical functionalization/valorisation strategies. Novel lignins and or newly refined lignins thus need to be tested in eventually extended fields of application or re-tested within more focused fields of application. Functionalisation of novel industrially isolated lignins has the objective to change or improve their inherent characteristics and performances for making them suitable sustainable materials for specific downstream applications, or for dedicated downstream processing. These modifications require control of lignin multifunctionality and are often run using simple and simplest chemistries or sustainable enzyme-based processes. Development of lignin based nanomaterials constitutes the frontier in lignin valorization yielding smart products ranging from controlled active delivery devices to high performance nanofibers.



Albano Cossaro

Molecules on surfaces: probing the ultra-fast charge dynamics

In organic electronics, a prototype of electronic device is in general designed as a sequence of thin organic films supported by a metallic electrode. The electronic properties of the interfaces of such a system largely determine the efficiency of the device in terms of the electronic transport. For thin films constituted by small organic molecules, the study of the molecule/substrate and the molecule/molecule interaction schemes becomes therefore a key issue for the development of new organic-based devices. In particular, the evidence of ultra-fast charge delocalization at the interfaces may be related to charge transport in the system under working conditions. Ultra-fast delocalization refers to charge delocalization in the 0.1-100 fs temporal range and is usually promoted by well-defined bonding scheme between molecules or between molecules and electrodes. The resonant photoemission spectroscopy (RESPES) technique is a powerful tool for probing ultra-fast charge dynamics. In this lecture, a brief introduction to the scientific topic of the electronic properties and to the established photoemission (XPS) and absorption (NEXAFS) techniques will be given. The RESPES technique and the related core-hole clock method for the evaluation of the delocalization time will be then introduced and some recent results we obtained at the Elettra Synchrotron in Trieste will be presented as examples.

Federico Polo

Coupling electrochemistry and plasmonic to develop biosensing platform for cancer diagnostics

Early-stage cancer detection is essential to allow implementing effective and personalized therapeutic strategies. The onset of cancer is signaled by one or more biomarkers in the biofluids, such as proteins, cell-free DNA, miRNA, and cancer cells themselves. Circulating protein biomarkers are the most investigated and still provide a benchmark in clinical analyses, thus playing a pivotal role in the clinical practice.[1]

A major concern when detecting cancer biomarkers stems from their availability in biofluids, which often shows very low concentrations. Therefore, new analytical tools capable of precisely, rapidly and reproducibly detect them are highly sought. Modern biosensing platforms rely on an improved ELISA (enzyme-linked immunosorbent assay) test where a receptor (e.g. antibody) is tethered to an active surface and capture the analyte cancer biomarker. Then a second receptor, usually carrying a label (e.g. enzyme, fluorophore, etc.) is added in a second stage leading to the formation of the "immunosandwich" and serves to detect the analyte.

In this respect, electrochemical biosensing platforms offer several advantages, such as high sensitivity, low detection limits, robustness, ease of miniaturization and high throughput. However, developing reproducible platform architectures requires some efforts. Surface plasmon resonance (SPR) technology enabled the precise characterization of important parameters, which a fully functional immunosandwich platform rely on, such as surface coverage of capturing receptors, thermodynamics of binding event (association and dissociation constants) between receptors and analyte. On the other hand, electrogenerated chemiluminescence (ECL), the light emission caused by annihilation of electrogenerated radicals, offers the best detection methodology in terms of sensitivity and instrumental design. Therefore, with the aim of developing electrochemical

biosensing platforms to detect the breast cancer protein biomarker HER2,[2] we investigated the possibility to couple plasmonic and electrochemistry.

In this presentation we describe our first attempt to integrate SPR, cyclic voltammetry and ECL responses to survey the interfacial adsorption and energy transfer processes involved in ECL on a plasmonic substrate. Coincidentally, our findings provided unprecedented information about the interfacial processes occurring on the electrode: in fact, the energy transfer between the ECL process and the plasmon revealed that the optically excited plasmon reduced the ECL intensity in the far-field by about 40% due to a lower plasmon mediated luminescence process.[3] Hence, the combination of SPR and ECL is highly advantageous to study electrochemical processes and to develop new nanostructured architectures, which will enable the detection of cancer biomarkers while simultaneously providing information about the thermodynamics of the binding process.

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[2] Agnolon, V.; Contato, A.; Meneghello, A.; Tagliabue, E.; Toffoli, G.; Gion, M.; Polo, F.; Fabricio, A. S. C. ELISA assay employing epitope-specific monoclonal antibodies to quantify circulating HER2 with potential application in monitoring cancer patients undergoing therapy with trastuzumab. *Sci. Rep.* **2020**, *10*, 3016.

[3] Dinel, M.-P.; Tartaggia, S.; Wallace, G. Q.; Boudreau, D.; Masson, J.-F.; Polo, F. Fundamentals of real-time surface plasmon resonance-electrogenerated chemiluminescence. *Angew. Chem. Int. Ed.* **2019**, *58*, 18202-18206.