PhD in Ingegneria Chimica

Research Title: Elucidating the active sites and mechanism of reaction of CO_2 reduction photo/electrocatalysts by modelling and advanced characterization techniques

Funded by	DISAT (CRT) - Progetto Europeo H2020 - ECCO - N.Russo

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Context of the research activity	Greenhouse Gases (GHG) emissions (of which ~ 65% is constituted by CO_2) is one of the most challenging environmental issues to face in the 21st century. Besides, current EU energy system is 80% based on fossil fuels use that cause 80% of EU GHG emissions, and about 53% of energy consumed in EU is imported from outside countries. Carbon Capture and Utilization (CCU) is one of the major technologies that could be addressed worldwide to mitigate CO_2 emissions. Among different processes, the photo/electrocatalytic reduction of CO_2 is an attractive solution that can be exploited as an efficient route to convert CO_2 into chemical or fuels by using the most abundant renewable energy source (*i.e.* sunlight) and water as source of protons (H^+) and electrons (e^-), in the so-called "artificial photosynthesis" process. In this way, CO_2 can be used as a feedstock in a circular economy perspective, so transforming a waste into useful and value-added products, to tackle both GHG emissions and energetic problems related to the dependence on fossil fuels. Nowadays, the development of highly active materials for this reaction, which do not contain precious metals (*i.e.* Pt, Au) and are prepared with scalable techniques, is a challenge for the practical

	implementation of this technology. The other major challenges are to obtain a high selectivity (preferable for a liquid fuel, which have a higher energy density) with a high catalyst stability. The nature of the photo/electrocatalyst material plays a major role on both selectivity and productivity of the process toward a specific desired product. The chemical and physical properties of the catalysts (e.g. active surface area, particle size, morphology, bulk and superficial composition and crystalline structure) can be tuned optimizing the synthesis methods. However, since the photo/electrocatalyst is modified under the electroreduction conditions, it is very difficult to understand the actual catalytic active phase that is formed, which could be responsible for a higher selectivity toward a specific product of interest, like methanol. In-situ and operando (under actual operative conditions) characterization studies of photo/catalyst materials are emerging in different fields of photocatalysis and electrochemistry, but there are already few techniques that have been employed to study photo/electrocatalysts for the CO_2 electroreduction reaction (CO_2RR) under operative conditions. Thus, few studies in literature have focussed on the correlation between the physical-chemical properties of CO_2RR photo/electrocatalysts and their photo/catalytic activity and selectivity, which will be the focus of this PhD research.

Objectives	The objectives of this PhD are: - To study novel nanostructured photo/electrocatalyst materials for the conversion of CO_2 to higher-added value products, *i.e.* methanol or others. - To correlate physical-chemical properties of the photo/electrocatalyst (obtained by different characterizations techniques including spectroscopic and microscopic methods) with their catalytic performance and selectivity. The expected outcomes of the studies that will be performed are: - To investigate new photo/electrocatalysts for the CO_2 conversion to methanol (or other added value products) based on earth abundant materials. - To assess the role of each catalyst component on the CO_2RR activity and selectivity to tune novel photo/catalysts formulations. - Pioneering use of advanced in-situ and operando photo/electrochemical techniques (e.g. TEM, Raman and IR Spectroscopy) to elucidate structural & physical-chemical

	properties of the catalyst under real CO_2 photo/electroreduction conditions and elucidate their mechanisms of reaction. - Identify structural or chemical-physical changes in the photo/electrocatalyst leading to its eventual deactivation to develop strategies to enhance its stability. Different characterization techniques available at Polito-DISAT (FESEM, XRD, XPS), and soon at the "Dipartimento di Eccellenza" (TEM, FIB-FESEM, Raman) will be exploited for the chemical-physical characterization of the prepared catalysts in powder form and deposited on transparent conductive substrates. A photo/electrochemical test-bench at DISAT, recently acquired in the framework of the regional project *CO_2 Circle Lab* between Polito and IIT@Polito, will be used for the macroscopic electrochemical activity tests. Products analysis will be performed by using analytical instruments, e.g. HPLC, GC-MSD with head-space, micro-GC, among others.
Skills and competencies for the development of the activity	- Knowledge of industrial chemistry, chemical engineering, chemistry, physics engineering and /or materials engineering are required. - Know-how and willing to learn electrochemical characterization techniques, electrocatalyst preparation methods and TEM microscopic analyses is very important. - Good knowledge of common practices and previous experience in chemical laboratories are desirable. - Ability in setting priorities, working in a multicultural and multidisciplinary team, plaining the work and respecting deadlines are important.