Università degli Studi di Torino
Dipartimento di Chimica

chimica

Commissione Ricerca

DAYS #6

Chemistry of TiO_2: Quo Vadis

Venerdì 20 Giugno 2014, ore 9, aula Analitica

Introduzione: C. Minero e M. Chiesa

9:00-9:15 - **Excess electrons in TiO2: something old, something new, something blue....**
Mario Chiesa, Stefano Livraghi, Maria Cristina Paganini, Sara Maurelli, Elio Giamello
(10 min di discussione)

9:25-9:40 - **(Non-photo-) Catalytic activity of stoichiometric and non-stoichiometric TiO_2.**
Lorenzo Mino, Elena Groppo; Caterina Balzan e Giuseppe Spoto
(10 min di discussione).

9:50-10:05 - **Energy without light from TiO_2: graphene hybrids as anodic materials for lithium ion batteries**
Marco Minella, *Claudio Minero*
(*10 min discussione*)

10:15-10:30 - **Any need to establish TiO_2 nanoparticle standards? The Torino response TiO2: toxic or safe?**
Ivana Fenoglio, Gianmario Martra, Valter Maurino, Giuseppe Spoto
(*10 min discussione*)

10:40-10:50 - **Commissione Spoke**

10:50-11.15 - **Coffee break (discussion)**

11:15-11:30 - **3D structuration: a strategy to improve TiO_2 performance**
Fabrizio Sordello, Claudio Minero
(10 min discussione)

11:40-11:55 - **TiO_2 - Nano vs micro: which is the best?**
Sara Morandi, Pinuccia Cerrato
(10 min di discussione).

12:05-12:20 - **TiO2: toxic or safe?**
Ivana Fenoglio
(*10 min discussione*)

12.30 - Termine dei lavori

Excess electrons in TiO_2: something old, something new, something blue....

Mario Chiesa, Stefano Livraghi, Maria Cristina Paganini, Sara Maurelli, Elio Giamello

Titanium dioxide (TiO2), is among other semiconducting oxides, one of the most studied systems and can be considered as a model substrate to investigate phenomena concerned with excess charge generation and transport. Key to the applications of this oxide in different areas are in fact excess electrons associated with intra band gap defective states, induced by reductive treatments or n-type doping with aliovalent elements (e.g. Nb or F). The nature and importance of these states will be discussed with emphasis on excess electron localization-delocalization phenomena.

Catalytic activity of stoichiometric and non-stoichiometric TiO_2.

Lorenzo Mino, Elena Groppo; Caterina Balzan e Giuseppe Spoto

TiO2 enjoys extraordinary popularity due to its photo-activity. On the contrary the examples of applications as a catalyst for not photo-activated processes are limited in number. The reasons are obviously related to the structural and electronic properties of the solid itself, which are for instance responsible for the lack of enhanced surface acidity or basicity. Based on these premises we were quite surprise discovering the ability of the stoichiometric (fully oxidized) solid to oligomerize acetylene (and derivatives), especially since the reaction products are colored, strongly anchored to the surface and possibly consist of polycyclic aromatic hydrocarbons, *i.e.* potential precursors for larger graphenic-like surface structures. The possibility that these surface species produced *in situ* can modulate the TiO_2 photo-catalytic properties deserves further investigation. Along with these, we will also illustrate the activities on the catalytic properties of non-stoichiometric (reduced) TiO_2 toward oligomerization of unsaturated hydrocarbons, an industrial field currently dominated by the Ziegler-Natta type catalysts.

Energy without light from TiO_2: graphene hybrids as anodic materials for lithium ion batteries

Marco Minella, Claudio Minero

The development of new energy storage systems with high capacity, cheaper, safe and with low environmental impact will be a key point of a winning energetic strategy, especially in a context where the non continuous and renewable energy sources will furnish a significant fraction of the whole energetic request. In this context the development of new materials for the electrodes of lithium batteries is a hot area of research.

The attention on TiO_2 as anode material for Li-ion batteries has recently increased due to its low cost, low environmental impact and intrinsic safety, combined to interesting electrochemical performance. However, its use for high power applications, e.g. in electric vehicles, is hampered by the poor ionic and electronic conductivity. To overcome this problem, TiO_2 powders can be synthesized with a conductive coating.

In this talk we focus on the development of a simple way to prepare TiO_2 /graphene hybrids by using commercial TiO_2 anatase as raw material. Graphene oxide (GO) was adsorbed on nanoscale TiO_2 anatase powder and reduced to Reduced Graphene Oxide (r-GO) in order to restore the electrical conductivity and obtain the desired high conductive composite. Different loading of GO and several reduction strategies have been tested and the electrochemical performances of the synthesized hybrids evaluated together with their structural-morphological properties. In particular, we measured

the specific capacity at different charge/discharge rates, assessing the cycling performances in lab-scale Li-based cells and identify the best synthetic methods.

The synthesized materials showed interesting and encouraging electrodic performances. We observed an increment of the specific capacity of the anodic hybrid materials in comparison with the pristine TiO_2 and a marked dependence of the electrochemical features not only from the overall carbon loading, but also from the reductive procedure adopted.

Any need to establish TiO_2 nanoparticle standards? The Torino response

Ivana Fenoglio, Gianmario Martra, Valter Maurino, Giuseppe Spoto

The awareness of emerging needs and challenges in strategic sectors for mankind, like energy production and use, sustainable development, healthcare practices and systems, is attracting/increasing a new or renewed interest towards the possibility to use TiO_2, and in particular nano-TiO_2 based systems, to attain real, effective and efficient innovations. These inputs are resulting in a flourish of both fundamental and technological studies devoted to titania, with a consequent increase in reports dealing with new functional behaviours and/or improved performances, with respect to what was previously known. However, it can be difficult to attain an objective and comprehensive evaluation of the impact of the proposed novelties, because of the wide heterogeneity of:

i) types of TiO_2-based NPs developed, each of them often exhibiting a rich dimensional and morphological variety,

ii) surface and/or interfacial molecular states,

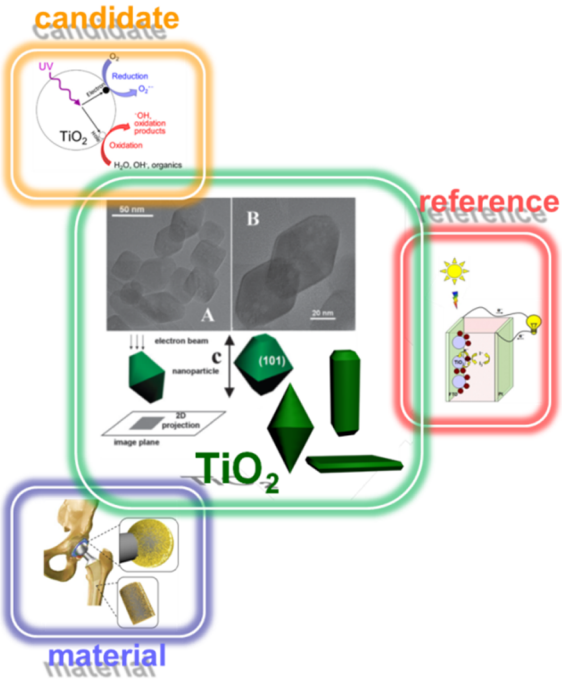
iii) assembly/aggregation states of the NPs to form nanostructured and nano-enabled systems,

iv) measurement conditions of the functional performances of these systems.

In such a scenario, recent achievements reported in the literature on the possibility of preparing TiO_2 NPs with defined shapes and surfaces acted as the seed of the basic concepts in the SETNanometro project (www.setnanometro.eu):

1) pursue the preparation of sets of TiO_2 NPs, each highly defined and homogeneous in bulk structure, shape, size, surface structure, to be used as such and/or in highly controlled and reproducible aggregated or assembled forms on proper supports

2) carry out an extensive and comprehensive metrological research devoted to the characterisation and production of standardised nanomaterials and nano-enabled systems to be considered as candidate Certified Reference Materials in the three technological fields depicted in the Figure.



3D structuration: a strategy to improve TiO_2 performances

Fabrizio Sordello, Claudio Minero

3D structuration is a way to increase the efficiency of solar cells, photoelectrodes and photocatalysts and can be successfully applied to TiO_2, which can be synthesized in the form of inverse opals, macroporous structures with ordered arrangement of the pores. In that form TiO_2 is characterized by an improved light absorption, and also by larger specific surface areas and faster substrate mass transfer. TiO_2 inverse opals have higher photocatalytic activity towards the degradation of pollutants with respect to disordered porous structures or TiO_2 nanoparticles. The photoelectrochemical study of these materials confirmed the increased light absorption and also proved that the porosity is available for reactions in solution. The hydrogen production on Pt loaded TiO_2 inverse opals is also increased, demonstrating that this optimization strategy, owing to a better exploitation of the incident light, can be conveniently used in every photocatalytic reaction.

TiO_2 - Nano vs micro: which is the best?

Sara Morandi, Pinuccia Cerrato

It is well known that TiO_2 is the most promising photocatalysts for many different purposes, among which the abatement of both outdoor and indoor pollutants (such as NOx and volatile organic compounds - VOCs) are of great interest. In particular, the best performances have been obtained up-to-now by nano-sized materials, such as the commercial Aeroxide® P25 powder. However, as far as the impact of nanoparticles on human body is concerned, some health indications are incoming and (few) specific restrictions have been recently published.

Taking into account the health concerns, the attention of our group, in collaboration with the group of prof. Claudia Bianchi (UniMI), is focussed on the study of micrometric TiO_2 powders, mainly of commercial nature and normally employed as pigments. The UniMI group proved the good photocatalytic performances of micro-sized TiO_2 towards the abatement of the above mentioned pollutants, either in gas or in liquid phase. Our role is aimed at investigating structural, morphological and surface features of the various TiO_2-based materials, in order to (i) correlate them with the photodegradation results and (ii) move some steps towards the improvement of the photocatalytic performances.

TiO2: toxic or safe?

Ivana Fenoglio

TiO_2 has been used commercially since the early 1900s in numerous industrial applications. The current worldwide production of this material is around 5 million tonnes leading the exposure of workers, consumers and environment possible. TiO_2 has been considered for decades a safe and biocompatible material. However, in the last years, a growing number of evidences show that, in the nano-form, TiO_2 may elicit adverse effects in humans. The international debate on the risk related to the exposure to this material, the current knowledge of the molecular mechanisms of toxicity, and the role of chemistry in developing strategies to make it safer will be here summarized. An overview of the of the past and current research on this topic in our group and on the future trends will be given.