

Mini-workshop on photocatalysis



- 9** Welcome and opening remarks (*M. Cerruti*, McGill University)
- 9:05 – 9:45** Photo-induced reactions in aquatic systems: application of TiO₂-based photocatalysts to simulate environmental processes and to water remediation (*P. Calza*, U. Torino)
- 9:45 – 10:05** Environmental transformations of emerging contaminants through the use of heterogeneous photocatalysis: application to the case of anticancer drugs. (*M. Sarro*, U. Torino)
- 10:05-10:20** Coffee break
- 10:20 – 11:00** Electron Paramagnetic Resonance Technique and its applications in catalysis and photocatalysis (*M.C. Paganini*, U. Torino)
- 11:00-11:40** Solar Water Splitting using Group-III Nitride Nanowire Arrays (*Z. Mi*, McGill University)
- 11:40 – 12:00** High Efficiency Photochemical Water Splitting using III-Nitride Nanowire Arrays Under UV and Visible light (*M.G.Kibria*, McGill University)

All are welcome! No registration needed. Just send an email to marta.cerruti@mcgill.ca if interested.

Abstracts

Photo-induced reactions in aquatic systems: application of TiO₂-based photocatalysts to simulate environmental processes and to water remediation

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Heterogeneous photocatalysis is indeed a widely used method not only to achieve the decontamination of aquatic systems, but also useful to simulate the abiotic transformation of pollutants occurring in the euphotic zone and leading to potentially harmful transformation products. With this in mind, this talk will focus on the fate of emerging contaminants, i.e. pharmaceuticals, as widespread pollutants of surface water, groundwater and drinking water. The study of their degradation processes becomes important in understanding their toxic effects in the aquatic environment and, in particular, on human beings. Initially, laboratory experiments were performed to artificially produce degradation compounds similar to those formed in oxido/reductive pathways by adopting a photocatalytic process as a model-system and, afterwards, to identify them in real samples, beside parent compounds. This approach was successfully used and permitted to identify several TPs, alongside the parent compounds, in water samples. Acute toxicity related to these EPs and to their transformation products was evaluated, too. In the second part, it will be presented some efforts to try to improve the photocatalytic efficiency, finalized to obtain water remediation, by preparing hybrid materials.

Environmental transformations of emerging contaminants through the use of heterogeneous photocatalysis: application to the case of anticancer drugs.

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Heterogeneous photocatalysis can be applied to the study of environmental transformations of emerging contaminants, whose concentration in the environment is of the order of $\mu\text{g/l}$ or ng/l , and which are potentially hazardous to human health and to the ecosystem. In particular, we report the study of some anticancer drugs: doxorubicin, methotrexate, mitomycin C and cyclophosphamide. We evaluated both the kinetics of disappearance of the molecule and the formation of degradation products. These unknown compounds were characterized through HPLC-HRMS using an LTQ-Orbitrap as analyser. In addition, we assessed the potential toxicity of these compounds and of their transformation products by employing an acute toxicity assay based on the use of *Vibrio fischeri* bacteria. Both pharmaceuticals and their transformation products were then search out in river water.

Electron Paramagnetic Resonance Technique and its applications in catalysis and photocatalysis

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Electron spin resonance (ESR) or Electron paramagnetic resonance (EPR) spectroscopy is an experimental technique for detecting and characterizing chemical systems bearing one or more unpaired electrons. The application of the technique, the background of which is similar to the more diffused nuclear magnetic resonance (NMR) spectroscopy, therefore concerns (i) organic and inorganic free radicals, (ii) trapped radicals in various matrices, including irradiated solids (radiation chemistry), frozen inert matrices and solid surfaces, (iii) transition metal ion compounds in classical inorganic systems or in biological systems, (iv) excited paramagnetic states (triplets) and several other systems of relevant scientific interest. ESR or EPR is a powerful tool for investigating paramagnetic entities in the domains of chemistry, physics and biology. The limitation of the technique is evident from the previous definition, in that all diamagnetic systems, which represent the majority of the substances, are excluded from EPR investigations. However, this limitation is also an advantage since, for instance, reactive paramagnetic intermediates present in complex media or paramagnetic centers belonging to a complex chemical system (e.g. a paramagnetic ion in a protein) can be studied without any spectroscopic interference.

The use of EPR in catalysis and photocatalysis is starting to be popular. EPR is basically an experimental research technique, extremely useful for structural investigations of various systems, rather than being a routine analytical technique. Nevertheless some applications of the technique having an analytical character have been proposed in the recent past such as spin trapping and spin label technique, radiation dosimetry and dating.

Solar Water Splitting using Group-III Nitride Nanowire Arrays

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Since the discovery of photoelectrochemical water splitting on crystalline TiO₂ by Fujishima and Honda, solar water splitting has gained worldwide acceptance as one of the key sustainable technologies to provide environmentally friendly solution to the worldwide energy crisis. In order to translate this technology from R&D to the commercial world, there is a need to find an efficient, stable and recyclable photocatalyst material for solar water splitting. Therefore, significant research effort has been made in this area over the last four decades. Recently, metal nitrides (i.e., GaN, InGaN) have attracted considerable attention, as they possess all the requirements (i.e., band gap, band alignment and corrosion resistant) for water splitting. We have recently shown that one-dimensional (1D) GaN and InGaN nanowires possess suitable band alignment and potential for overall pure water splitting under UV, blue and green light (up to ~560 nm) irradiation, the longest wavelength ever reported [1]. We have further developed multi-band InGaN/GaN nanowire heterostructures that can lead to highly stable, efficient hydrogen production from pure water splitting [2]. The estimated absorbed photon conversion efficiency is ~13% at ~440-450 nm wavelength. It is also observed that the efficiency is directly related to the band bending in the near-surface region, which can significantly affect charge carrier transport to the photocatalyst-water interface. By tuning the surface charge properties through controlled dopant incorporation, we have demonstrated that the quantum efficiency of spontaneous water splitting can be drastically enhanced [3]. Such InGaN/GaN nanowire arrays grown directly on low cost, large area Si substrates can also function as highly stable photoanode/photocathode in acidic solution. Relatively high incident photon-to-current-conversion efficiency (upto ~ 27%) is measured using InGaN/GaN core-shell double-band photoelectrode under ultraviolet and visible light irradiation. Detailed structural characterization on such nanowire arrays further confirms that there is virtually no degradation after an extended period of photoelectrochemical reaction. This work provides a promising approach for achieving scalable and stable production of solar fuels by using non-oxide nanoscale photocatalyst wafers.

References:

- [1] D.Wang, *et al. Nano Lett.* **11**, 2353 (2011).
- [2] M. Kibria *et al. ACS Nano* **7**, 7886-7893 (2013).
- [3] M. Kibria *et al. Nature Comm.* **5**, 3825, (2014).
- [4] B. AlOtaibi *et al. Nanotechnology*, **24**, 175401 (2013).
- [5] AlOtaibi *et al. Nano Lett.*, **13**, 4356-4361 (2013).

High Efficiency Photochemical Water Splitting using III-Nitride Nanowire Arrays Under UV and Visible light

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Solar energy is the ultimate solution that can provide carbon-neutral and sustainable energy to mitigate current and future global energy appetite. Mimicking the natural photosynthesis process, solar energy can be stored in the form of chemical energy through solar-water splitting. One of the main challenges in artificial photosynthesis is the production of stable H₂ and O₂ from water splitting in a way which is much efficient than that of green plants. Therefore, high efficiency and stable water splitting under has been of great challenge over the last four decades. Recently, metal nitrides (i.e., GaN, InGaN) have attracted considerable attention, as they possess the thermodynamic and kinetic potential requirements for water splitting. We have recently shown that one-dimensional (1D) GaN nanowires offer significantly improved photocatalytic activity over commonly used GaN nanoparticles for overall water splitting [1]. To further enhance the photocatalytic activity, surface band bending and therefore carrier transport properties of nanowires can be engineered by controlled dopant incorporation. Our studies revealed that high efficiency and stable photochemical overall pure water splitting can be achieved under UV and visible light (>400 nm) irradiation by engineering the charge properties at the nonpolar surfaces of GaN and InGaN nanowire arrays with controlled p-type dopant incorporation. By tuning the band bending on the nonpolar surfaces of one-dimensional GaN nanowires, we have demonstrated an internal quantum efficiency (IQE) of ~51%, the highest value ever reported for overall water splitting under any broadband ultraviolet (UV) light irradiation [2]. Furthermore, in order to efficiently capture the solar spectrum, we have designed a triple-band InGaN/GaN nanowire photocatalysts, which leads to efficient and stable water splitting under UV, blue, and green light irradiation, the longest wavelength ever reported [3]. At ~440-450 nm, the IQE is estimated to be ~13%, the highest value reported in visible spectrum. Furthermore, our recent research shows that by optimizing the surface charge properties through p-type Mg dopants, the IQE can reach ~69% for InGaN nanowires under visible light. This wafer-level approach of water splitting offers recyclable and environmentally benign photocatalyst for solar-powered artificial photosynthesis for the production of hydrogen and other solar fuels.

References:

- [1] D. Wang, *et al.* *Nano Lett.* **11**, 2353 (2011).
- [2] Md Kibria *et al.* *Nature Comm.* **5**, 3825, (2014).
- [3] Md Kibria *et al.* *ACS Nano* **7**, 7886-7893 (2013).