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Attosecond photoelectron spectroscopy

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We combined an innovative actively-stabilized attosecond interferometer with a magnetic-bottle time-of-flight spectrometer equipped with a liquid microjet [1] to perform attosecond experiments with in the gas and liquid phases. We determined the relative photoionization delays between photoelectrons associated with the two spin-orbit states ($^2P_{3/2}$ and $^2P_{1/2}$) of Xe^+ and Kr^+ by using the RABBIT technique (Reconstruction of Attosecond Beating By Interference of Two-photon transitions, [2]). The measurements reveal surprisingly large delays up to 100 attoseconds in the case of Xe and a much smaller delay in the case of Kr.

RABBIT experiments have also been performed in water vapor. A global-fit approach has been developed to extract the relative photoionization delays between the $1b_1$, $3a_1$ and $1b_2$ orbitals from the overlapping photoelectron spectra. This constitutes the first attempt of measuring the attosecond photoionization dynamics of a polyatomic molecule. Finally, we are performing RABBIT experiments using the liquid-water microjet, in an effort to extend attosecond spectroscopy to the liquid phase. The results of these experiments will be compared to the results from water in the gas phase. We expect that these measurements will allow us to characterize the effect of solvation on the attosecond dynamics of photoionization.

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Submm wave spectroscopy in the range 72 to 100 GHz of meta- and ortho-D-phenol: Probing tunneling switching dynamics

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A particularly intriguing recent development is the theoretical prediction of tunneling switching in meta- and ortho-D-phenol (C_6H_4DOH) as opposed to phenol (C_6H_5OH) [1] where only tunneling dominates the dynamics. For meta and ortho-D-phenol at low energy, tunneling is completely suppressed due to isotopic substitution, which introduces an asymmetry in the effective potential. It effectively localizes the molecular wavefunction at either the *syn* or the *anti* structure of meta- and ortho-D-phenol. At higher torsional states of meta and ortho-D-phenol, tunneling becomes dominant, thus switching the dynamics to a delocalized quantum wavefunction. For that reason we have measured and investigated the rotational spectra of meta- and ortho-D-phenol in the range 72 to 100 GHz and their rotationally resolved THz and IR spectra in the range 200 to 1000 cm^{-1}[2]. Here we shall discuss in detail the submm wave spectra of meta- and ortho-D-phenol measured so far without detailed analysis for excited states [3]. We were able to assign and analyse the ground state rotational spectra of the *syn* and *anti* isomers of meta- and ortho-D-phenol up to *J=35*. Assignments of the rotational transitions of the excited torsional states based on the analysed rovibrational transitions [2] shall be discussed as well. Work supported by ETH, SNF and ERC.

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Control of chemical reactivity through spatial separation of molecular conformations

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Many molecules have multiple conformations (rotational isomers), which can exhibit different reactivities, opening up perspectives to manipulate chemical reactions by selecting specific molecular conformations [1]. However, a detailed understanding of the role of conformations in gas-phase chemical reactions still has to be established. In a recent experiment we studied the reactive collisions between conformationally selected 3-aminophenol and a Coulomb crystal of laser-cooled Ca^+ ions [2,3]. This reaction was chosen as a model system. 3-Aminophenol exhibits two different conformations (*cis* and *trans*) with different permanent dipole moments. Their interaction with external inhomogeneous electric fields enables the two conformers to be spatially separated in a molecular beam passing through an electrostatic deflector [4]. Coulomb-crystals of spatially localized Ca^+ ions stored in an ion trap [5] provide a suitable stationary target for the conformer-selected molecular beams enabling the study of conformer-specific reactive collisions with extremely high sensitivities down to the level of single reaction events.
By tilting the molecular beam machine mechanically with respect to the ion trap, conformationally pure components of the molecular beam have been overlapped with the ion trap. The progress of the reaction was monitored by imaging the laser-induced fluorescence of unreacted ions. The observed rate constant for cis-3-aminophenol is a factor of 2 larger than the one measured for the trans-3-aminophenol. These results agree well with the results from adiabatic capture theory calculations [6], indicating that the dynamics of the Ca^+ - *cis/trans*-3-aminophenol reaction are mainly controlled by conformer-specific differences in the long-range ion molecule interaction potential.
In a new experiment, we want to study short-range reactive effects in an ion-molecule reaction. We are investigating the reaction of conformationally selected methyl vinyl ketone (MVK) with CO^+ ions and the reaction between MVK and MVK^+. These are Diels-Alder like cycloaddition reactions that should show significant differences in the dynamics for different conformations. To analyze the products of this reaction, we designed a new time of flight mass spectrometer that will be coupled to the ion trap. On the poster we present a summary of the Ca^+ - Aminophenol experiment as well as first results and simulations regarding the new experiment.

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Rydberg Spectroscopy of Zeeman-Decelerated Beams of Metastable Helium Molecules

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Having three and four electrons, respectively, He^+_2 and He_2 represent systems for which highly accurate ab-initio calculations might become feasible in the near future [1]. With the goal of performing accurate measurements of the rovibrational energy-level structure of He^+_2 by Rydberg spectroscopy of He_2 and multichannel-quantum-defect-theory extrapolation techniques [2], we have produced samples of helium molecules in the $a\ ^3\Sigma^+_u$ state in supersonic beams with velocities tunable down to 100 m/s by combining a cryogenic supersonic-beam source with a multistage Zeeman decelerator [3]. The molecules are formed at an initial velocity of 500 m/s by striking a discharge in the pulsed expansion of helium gas from a reservoir kept at a cryogenic temperature of 10 K. Using rotationally-resolved pulsed-field-ionization zero-kinetic-energy photoelectron spectroscopy, we have probed the rotational-state distribution of the molecules produced in the discharge and found vibrational levels up to $v'' = 2$ and rotational levels up to $N'' = 21$ to be populated. The molecular beam is coupled to a multistage Zeeman decelerator that employs pulsed inhomogeneous magnetic fields to further reduce the beam velocity. By measuring the quantum-state distribution of the decelerated sample using photoionization spectroscopy (see figure) we did not observe any rotational or vibrational state-selectivity of the deceleration process, but found that one of the three spin-rotation components of the $He_2\ a\ ^3\Sigma^+_u$ rotational levels is eliminated [4].

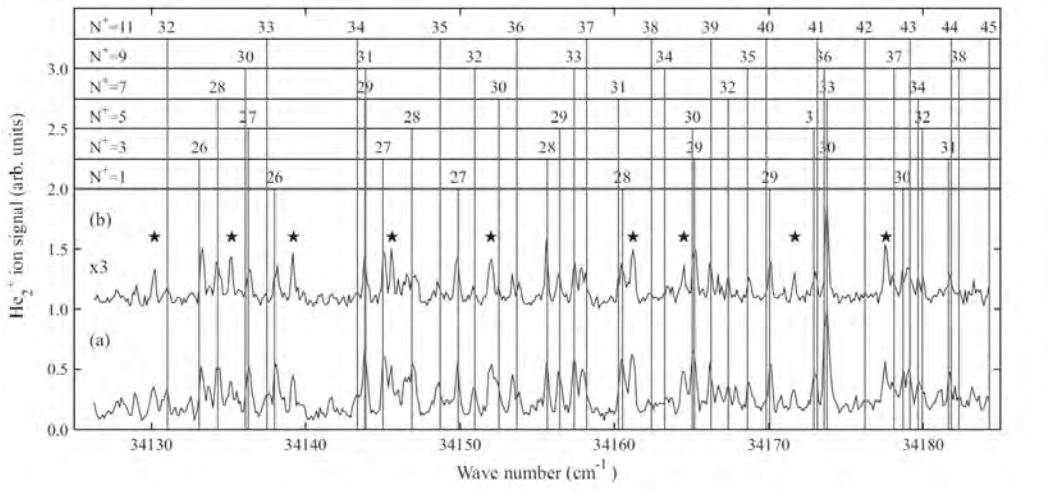

Fig. Photoionization spectra (with assignment bars) of He_2 in the vicinity of the ionization threshold from the $a\ ^3\Sigma^+_u$ state recorded for (a) an undecelerated beam and (b) a beam decelerated to a final velocity of 135 m/s.

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Probing a Conformational Change of a Photoswitchable Allosteric Protein with Ultrafast IR Spectroscopy

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By covalently linking an azobenzene photoswitch across the binding groove of a PDZ domain, a conformational transition can be initiated by a laser pulse (Fig. 1). This transition mimics the conformational change of the unmodified domain upon ligand binding (Fig. 2). We have studied this light induced transition by ultrafast IR spectroscopy. Following the changes in the amide I band from picoseconds to microseconds after the excitation of the photoswitch (Fig. 3), gives information about the overall changes in the backbone structure of the protein [1]. More site-specific information can be gained by inserting IR labels at different positions in the protein.

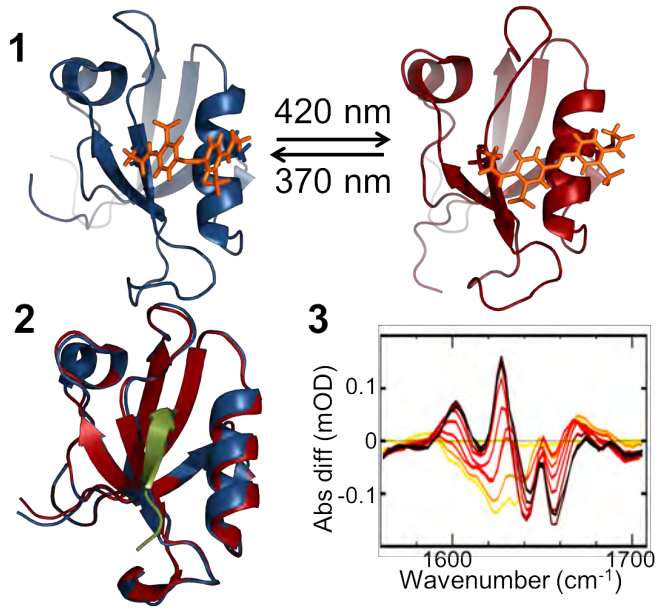

Figure 1) NMR structures with the photoswitch in *cis* (left, PDB 2M0Z) and in *trans* (right, PDB 2M10)
2) Overlay of the unmodified apo (blue, PDB 3LNX) and holo structures (red with green ligand, PDB 3LNY)
3) Development of the amide I band from 10 ps to 10 µs by decade (from yellow to black).

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Light-induced charge transfer in the cytochrome bc_1 at high quantum yield

Adrien Chauvet[1], Andre Al Haddad[1], Wei-Chun Kao[2], Frank van mourik[1], Majed Chergui[1] *

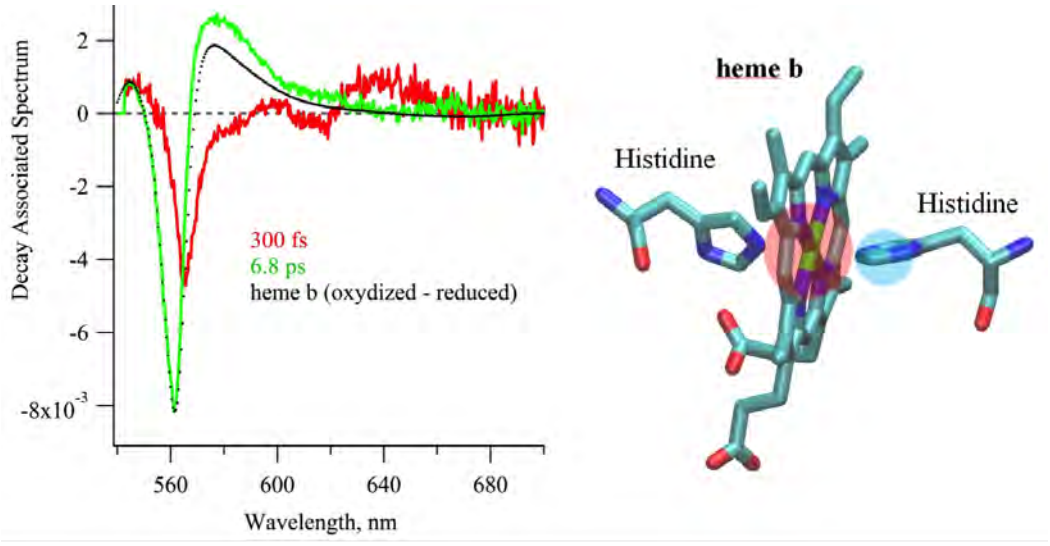
[1]EPFL Lausanne, [2]University of Fribourg

The Cytochrome (Cyt) bc_1 complex is a key element of the respiratory chain. It oxidizes ubiquinol while reducing cytochrome c in order to create an electrochemical potential across the membrane. It is therefore the driving force of ATP synthesis and other ion transport. As a dimer, it is comprised of pair of heme c_1 and two pairs of b-hemes (b_h and b_l) that are similar in structure to the low-spin, 6-coordinated cytochrome c and b_5 respectively. The ferrous (Fe^{2+}) centers of the later hemes are known to photo-dissociate with their methionine or histidine ligand after excitation by a short laser pulse (~50 fs). This “instantaneous” cleavage is then followed by the ligand recombination within 5-7 ps.

To our knowledge, this is the first ultrafast analysis of the Cyt bc_1.We report the following:

- The heme c_1 in Cyt bc_1 shows similar ultrafast behavior than that of the Cyt c.
- Unexpectedly, under the same conditions, we monitored for the b-hemes transient signals that resembles that of an ultrafast oxidation of the corresponding hemes.
- This photo-oxidation occurs with an unexpected and unprecedented high quantum yield of at least 0.5 while exciting in the visible range.
- The nearby histidine residue most probably serves as electron acceptor, and we report a charge recombination time of 6.8 ps.

Such unique behavior shines light on the still intriguing electron-coupled-proton transfer mechanism of the complex, and open the doors to future studies on bio-inspired novel energy sources in which light-induced charge separation plays an essential role.



Orientation and excited-state dynamics of DNA probes at liquid/water interfaces

Giuseppe Leonardo Licari[1], Sandra Mosquera Vazquez[1], Eric Vauthey[1] *

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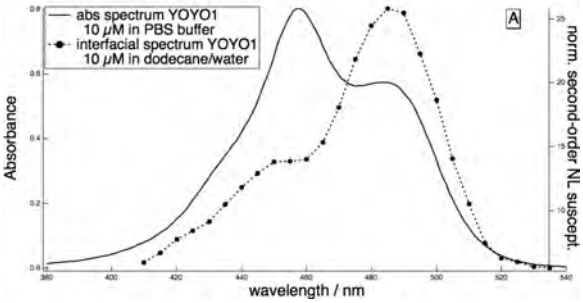
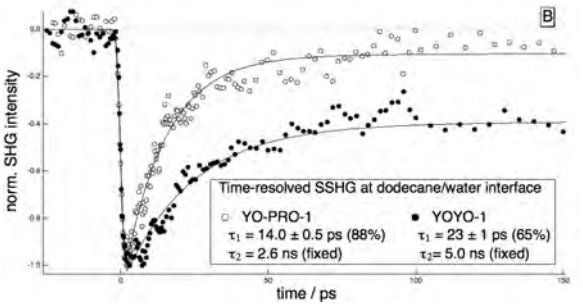
Cyanine dyes belonging to the YO-PRO-1 family represent a well-established monomeric and homodimeric class of DNA binders that can detect nucleic acids in a very low concentration range.[1,2] Previous investigations of the excited-state dynamics of these dyes in solution have revealed an ultrafast nonradiative deactivation associated with large amplitude motion with time constants of the order of 3-4 ps.[3]
We will present our study of the photophysics of these dyes at liquid/water interfaces using static and time-resolved surface second harmonic generation, this technique being well known for its interfacial selectivity. [4]
Substantially different behaviors were observed upon going from bulk phase to interface: anisotropic orientation with the transition dipole moment lying almost parallel to interfacial plane, strong decrease of H-dimer formation (Fig. A) and a slowing down of the excited-state decay by a factor of 4 to 8 (Fig. B). The origin of the differences will be discussed and the effect of DNA addition in the aqueous phase will also be presented.





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Photoelectric conversion based on light induced proton pumps and proton-coupled electron transfer reactions

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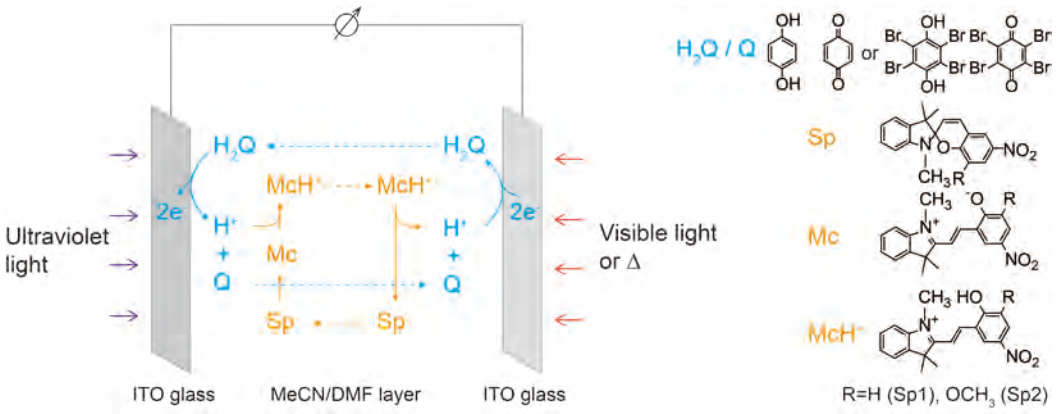
Making efficient use of solar energy is one of the biggest challenges of our time. We introduce here new ways of doing photoelectric conversion with the help of photoswitchable spiropyrans (Sp), compounds that can convert reversibly between two structures (Sp and Mc) with different pKas. In the first approach, protons are carried by UV activated Sp from the UV side of the membrane to the opposite side, where Mc is converted back to Sp form. This is the first example of a light-induced proton pump in a liquid membrane conceptually similar to the biological light-triggered proton pumps across a cell membrane. The electric cell is completed with two Ag/AgCl electrodes in HCl solutions separated by the Sp doped membrane. This system is able to produce a light driven proton flux across the polymer membrane, thus converting light to electrical energy with an efficiency of ~ 0.12%. An open-circuit voltage of ~ 210 mV and a membrane gradient of ~ 3.6 ΔpH units have been achieved. UV and VIS can result in flux with opposite directions. Therefore, in addition to direct current, alternating illumination with UV and visible light (VIS) on the membrane can generate alternating currents. In the second approach, the Ag/AgCl electrodes were replaced with proton-coupled electron transfer (PCET) redox pairs (Quinone/Hydroquinone). The redox potential of the PCET redox pair is dependent on local pH conditions, which can be controlled with spiropyrans and light.

Although the efficiencies are not yet high, these are new principles for photoelectric conversion and potentially valuable to solar energy utlization.



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Long-lived Charged Carriers in Oligothiophene Nanowires

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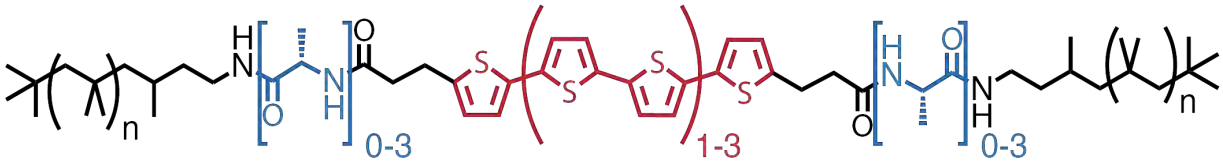
Organic nanowires are not only of interest in chemical sensing, photovoltaic device or future nanoelectronic circuitry, but may also provide insights into the fundamental processes of charge generation and transport in organic semiconductors under nanoscopic confinement. The optoelectronic properties of nanowires depend on the molecular structure of the included chromophores, the supramolecular π–π interactions between adjacent molecules and their defined aggregation into nanowires. Here, we demonstrate how a simple substitution of oligothiophene cores with polymer-oligopeptide conjugates results in nanowires with defined lateral dimensions that comprises a single stack of tightly π–π stacked chromophores at their core. The internal packing of the chromophores was beneficial for the formation of radical cations at unprecedently high densities of 10^{19} cm^{-3} and with surprisingly long lifetime of several days. The origin of their formation and their stability was investigated by electron spin resonance, in situ visible-NIR absorption measurement under illumination and transient absorption spectroscopy. Our results, thus, provide an example of a universal organic nanowire model system that successfully links molecular design, well-defined supramolecular structure formation, charge carrier generation, and finally macroscopic charge transport.



Charge-transfer dissociation at organic donor-acceptor interfaces probed with time-resolved electroabsorption

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Organic solar cells offer a panel of donor-acceptor candidates and geometrical structures, with power conversion efficiencies reaching over 10%. Typically, a polymer or a small molecule is used as electron donor in combination with fullerenes, which are widely used as electron acceptors. The molecular arrangement and therefore the interfaces between the donor and acceptor moieties are of great interest as they directly influence charge separation and transport.

Therefore, dynamics of charge separation at donor-acceptor interfaces and transport to the electrodes are key processes to be monitored in third-generation photovoltaics. Ultrafast optical spectroscopy techniques, such as time-resolved electroabsorption due to the Stark effect and transient absorption, are two complementary techniques enabling the tracking of the photogenerated charge carrier dynamics, with and without applied electric field, respectively.

Herein, we report on the first steps of charge separation and extraction in Cy3P:C60 planar heterojunction solar cells[1], as well as on pBTTT:PCBM bulk heterojunction blends. Field dependent charge separation will be addressed, as well as transport in the separate materials.

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Particle size and shape dependence of the ionic diffusivity in $LiMnPO_4$ cathode for lithium ion batteries

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Advanced lithium ion batteries require higher safety, lower cost, longer durability and lower toxicity to apply larger applications [1].
$LiMnPO_4$ can be an alternative cathode material due to its stable structure, low material cost, lower toxicity, high theoretical capacity (170 mAh/g), high operating voltage (4.1 V vs. Li) and good capacity retention. However, it suffers from poor electronic and ionic conductivity[2]. Its poor ionic conductivity can be overcome by employing nano-particles in order to shorten Li-ion path lengths[3]. Enhancement in electron transport is achieved by carbon coated nanocomposite cathode material [4]. Most high-performing $LiMnPO_4$ materials were so far achieved by adding a large amount of carbon (15 – 30 wt%) in order to increase the electronic conductivity [5,6]. Recently,we reported $_4$ reached 97 % of theoretical capacity with 10 wt% of carbon additive in total in the electrodes [7]. We investigated further to study the favorable direction for lithium ions in different shapes of nano-$LiMnPO_4$ and the desired composite structure to improve the electrochemical properties.
Since olivine $LiMnPO_4$ materials have one preferred direction of lithium ion diffusion in the lattice, we synthesized various shapes and sizes of nano-$LiMnPO_4$ (Fig. 1). Chemically exfoliated graphene from graphite flake was applied to nano-$LiMnPO_4$, forming a thin coating on the surface of the active material (Fig. 2).

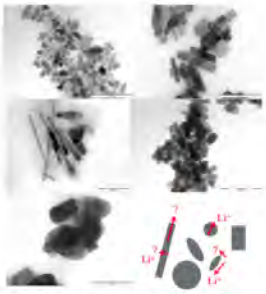

Fig. 1. TEM images show the various shapes and sizes of $LiMnPO_4$ nanoparticles.

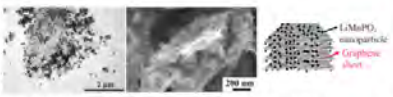

Fig. 2. TEM (left), SEM (middle) images and a schematic (right) of $LiMnPO_4$ and graphene composite.

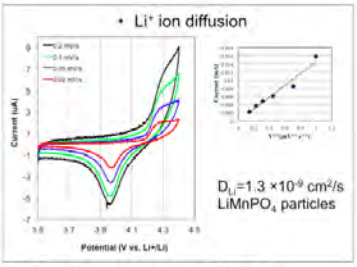

Fig. 3. Cyclic voltammograms (left) and the relationship between square roots of sweeping rates ($v^{1/2}$) and anodic current peaks (right) of $LiMnPO_4$ cathode.

Several processes of making nanocomposites have been investigated to understand the kinetics of diffusivity in $LiMnPO_4$ cathode.

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