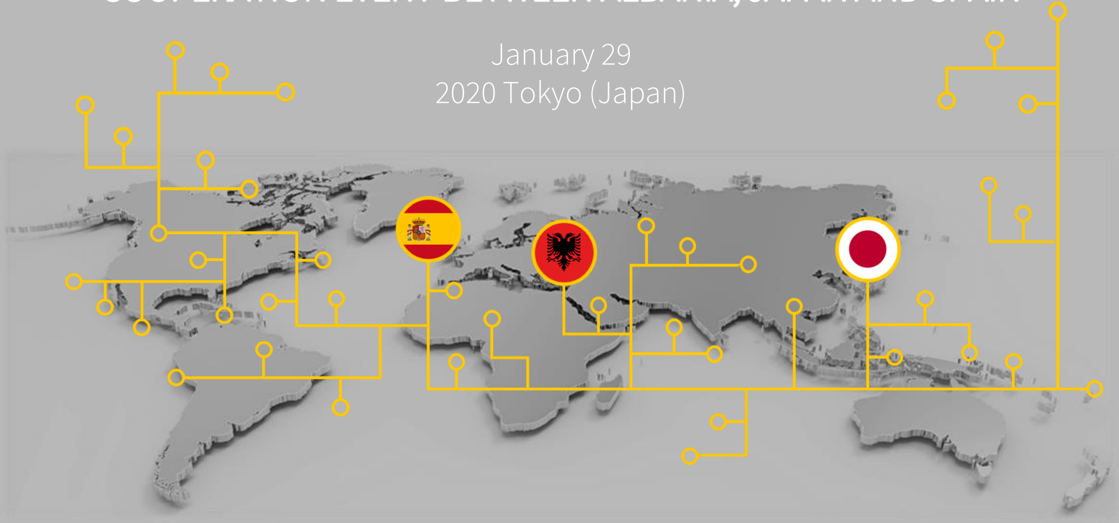
NANOTECHNOLOGIES FOR 21st CENTURY

COOPERATION EVENT BETWEEN ALBANIA, JAPAN AND SPAIN

January 29
2020 Tokyo (Japan)



The Albanian government has established an earthquake relief fund. All those who would like to contribute to the fund can send their donations through the following bank accounts: https://e-albania.al/donate/

Organizing Committee of this meeting appreciate very much any contribution for this issue!

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The main objective of this nano-workshop will be to enhance the cooperation between three countries, Albania, Japan and Spain in the field of Nanoscience and Nanotechnologies and their applications in crucial areas such as life sciences, information technologies or energy among others. This century nanotechnologies are going to play a key role in the development of cutting edge diagnostics devices for citizens health, environment monitoring, offering innovative technologies and materials with interest for energy harvesting, telecommunication in addition to other industries. While Spain and Japan are in the vanguard of nanotechnology developments in Europe and Asia, Albania a small European country is willing to join future activities in this area and pushing cooperation with leading countries.

This event is a clear example of the need of cooperation in this multidisciplinary technology area with the idea to foster the exchange of ideas and establish new cooperation and exchange programs between the three countries.

ORGANISERS

Index alphabetical order

SPEAKERS

Nanobiodevices, Quantum Technology, and AI for Future Healthcare

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We have devolved nanobiodevices, quantum technology, and AI for biomedical applications and healthcare [1-6], including single cancer cell diagnosis for cancer metastasis, circulating tumour cell (CTC) detection by microfluidic devices, nanopillar devices for ultrafast analysis of genomic DNA and microRNA, nanopore devices for single DNA sequencing, nanowire devices for exosome analysis, single-molecular epigenetic analysis, AI-powered nano-IoT sensors, quantum switching *intra vital* imaging of iPS cells and stem cells, and quantum technology-based cancer theranostics.

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Sample-in-answer-out paper platforms for diagnostic applications

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This presentation will shortly introduce some examples of paper-based analytical devices developed in our group, with special focus on simplified user operation and signal detection. Approaches presented include fluorimetric protein detection in tear fluid [1], colorimetric protein detection in urine [2], bioluminescence readout-based antibody detection in whole blood [3] and colorimetric detection of serum potassium [4]. The most user-friendly devices require nothing more than the application of an untreated sample and the simplest ways of reading out an assay result are in the form of interpreting the length of a colored bar similar to an analogue thermometer, or text or symbols directly displayed on the paper substrate itself.

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Preparation and Characterization of Hydroxide of Alkaline Earth Metals Nanoparticle Dispersions for Cultural Heritage Application

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Nanomaterials have been applied in the construction and maintenance of the world cultural heritage with the aim of improving the consolidation and protection treatments of damaged stone. These nanomaterials include important advantages that could solve many problems found in the traditional interventions. The most commonly used inorganic consolidants are the products based on hydroxide nanoparticles due to their compatibility with a large part of the built and sculptural heritage. In this work, a rapid "bottom-up" procedure of the preparation of alcoholic dispersions of calcium hydroxide and strontium hydroxide has been realized. The particles of calcium hydroxide have an average diameter of 360 nm, PdI (Poly dispersion Index) is equal to 0.188 (mono-disperse) and the colloidal particles show a good kinetic stability (600 nm) with a zeta potential of +37mV. The particles of strontium hydroxide show an average diameter of 180nm, PdI is 0.260 and zeta

potential of +14mV. The first studies concerning the use of the Triton X100 as an additive during preparation of strontium hydroxide, under the same experimental conditions, shown that the average particle size changes little (206nm), while the PdI (0.204) and zeta potential of the colloid increases significantly (+49mV). Both hydroxides shown a fast carbonation into air; due to the particle size obtained for these colloids (180~360nm), they can be used for rapid absorption through capillarity of macro-pores of calcareous materials[1-4]. This procedure, moreover, leads to easily reproducible experimental conditions and makes the procedure itself scalable. The characterization is performed by powder X-Ray diffraction and dynamic light scattering. The kinetic stability of nanoparticle dispersions has been determined by UV-VIS spectrophotometric studies at 600 nm.

The authors acknowledge the financial support from CNR (Italy) – MOES - AKKSHI (Albania) Bilateral Agreement Program.

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Magneterehological Properties of a Mixture of Carbonyl Iron Powders Suspended in Ionic Liquid

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Properties of a magnetorheological (MR) fluid synthesized by dispersing a mixture of two carbonyl iron powders (CIP) in an ionic liquid have been investigated. At first, mixtures of CM (d_{50} = 7 μm) and HQ (d_{50} = 1.1 μm) CIP powders, prepared at the same solid weight fraction but at various weight fractions of large particles, were dispersed in the ionic liquid (N,N-Diethyl-N-methyl-N-(2-methoxyethyl) ammonium tetrafluoroborate), which is stable even at high temperature. Then, the magnetic clusters of the synthesized MR fluids were observed by using an optical microscope, whereas the magnetorheological properties were investigated by using a bi-cylindrical viscometer. Each apparatus was equipped with a magnetic field generator to create a uniform magnetic field. After finding the most suitable mixing ratio of powders, a new batch of MR fluid was synthesized. Finally, the properties of the MR fluid with or without addition of surfactant were compared. The experimental results showed that the MR fluid with 60 wt% fraction of large particles exhibited the highest MR response [1].

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Electrochemical application of boron-doped diamond electrodes

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Boron-doped diamond (BDD) electrodes are very attractive material, because of their wide potential window, low background current, chemical inertness, and mechanical durability.[1] In these years, we have reported several examples for electrochemical sensor applications such as detection of influenza virus,[2a] free chlorine,[2b] microsensing system for in vivo real time detection of local drug kinetics[2c], and so on. Furthermore, some of them are developing into practical use. Applications for electrochemical organic synthesis including CO2 reduction[3] are also being developed. For example, we investigated the electrochemical reduction of CO_2 to HCOOH in a flow cell using BDD electrodes. The faradaic efficiency (FE) for the production of HCOOH was as high as 94.7%. Furthermore, the selectivity for the production of HCOOH was more than 99%.

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TiO_2 Photocatalysis and Diamond Electrode

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Chemical conversion of light energy is an ideal technology, and the tremendous amount of research of semiconductor photoelectrochemistry, photocatalysis, and electrochemistry has been carried out over the last half century. I will explain the present situation of photocatalysis.

The realization of the Sustainable Development Goals (SDGs) through carbon recycling technology is also an urgent issue to be addressed because of the environmental problems on a global scale. In the present talk, I will explain and introduce the recent progress, and our main target of CO_2 reduction using diamond electrodes.

Hybrid Nanomaterials for Energy Storage

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Energy storage is one of the key pieces to fix the upcoming but complex sustainable energy puzzle. Batteries and supercapacitors are two of the strongest technologies contributing to practical electrochemical energy storage but have complementary strengths and weaknesses concerning energy / power density or cyclability. In our group we are actively developing new hybrid materials and hybrid devices aiming to fill the gap between batteries and supercapacitors in terms of mechanisms and properties. Our recent work on nanocomposites based on nanocarbons and inorganic clusters will be used as a representative example of the materials – related work in this area and we will present also our own approaches to the development of new hybrid devices made with different nanocarbon electrodes.

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Device applications of graphene prepared by chemical vapor deposition transparent antennas and chemical sensors

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Graphene has attracted attention owing to its unique properties and possibilities for numerous practical device applications. Chemical vapor deposition (CVD) growth is a promising way to synthesize high-quality and large-area graphene sheets. We demonstrated CVD growth of single-crystal monolayer graphene on Ir(111)/sapphire substrates, and the reuse of the same substrates in multiple CVD growth [1]. We also demonstrated several device applications of the CVD graphene sheets including optically transparent dipole antennas operating at 20 GHz [2], luminescent graphene [3] and free residual chlorine sensor based on graphene field effect transistors.

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CSIC nanotechnologies for market applications

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The Spanish National Research Council (CSIC) is the largest public research institution in Spain and the third in Europe. In the last decade CSIC has designed and implemented a series of actions in order to take advantage of the knowledge generated in nanotechnology by mean of an appropriate transfer to both the Spanish and the international industry [1]. Continuing with this initiate, CSIC has recently patented a simple procedure to isolate highly crystalline graphene for electronic devices applications, a flexible graphene- based transistor for measuring full-band electrophysiological signals for medical devices applications, and a novel hybrid nanomaterial very active in the degradation of organic pollutions that shows magnetic properties which allow its recovery from the media for environmental applications.

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The use of conducting composite polymers of PANI and PPY in different electrochemical devices

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In this research we have studied the d.c. conductivity, σ, of zeolite/polyaniline (PANI) and zeolite/polypyrrole (PPy) blends of various concentrations in zeolite and the application of these compounds in the construction of various electrochemical devices. Our studies show that PANI/Zeolite and PPY/Zeolite at certain ratios (w/w) exhibits very good conductivity as well as a slow thermal aging. We have used such properties in the construction of an electrochemical cell of a Pt particles layer on a conducting polyaniline/zeolite and PPy/zeolite blend. Our results show that these sensors are stable in aqueous electrolyte solutions of low pH value at temperatures up to 45°C with response time in seconds. The ability of zeolite to accommodate and neutralize a great number of cations with all three mechanisms, adsorption, intercalation, and cation exchange reaction, combined with the high conductivity and stability of HCl—protonated polyaniline, which interposes into its laminar structure and the good contact between zeolite surface and polyaniline, make the polyaniline/zeolite composites very suitable for use as a cathode electrode in dry electrical primary coin cells. Our results show that when Polyvinylalcohol (PVA) gel was used as the electrolyte and a Mg foil as the anode, the e.m.f. values of the cells ranged from 1.62 to 1.94 V, their specific energies from 4.34 to 8.88 Wh/kg and their energy densities from 3.10 to 6.34 mWh/cm3 for cathodes containing 10–50 w% zeolite. Moreover, surface examination of the different samples, was performed by EDS analysis, scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques

Nanobiosensors for diagnostics applications: paper-based platforms

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Both paper and nanopaper-based biosensors are emerging as a new class of devices with the objective to fulfil the “World Health Organization” requisites to be ASSURED: affordable, sensitive, specific, user-friendly, rapid and robust, equipment free and deliverable to end-users. How to design simple paper-based biosensor architectures? How to tune their analytical performance upon demand? How one can ‘marriage’ nanomaterials such as metallic nanoparticles, quantum dots and even graphene with paper and what is the benefit? How we can make these devices more robust, sensitive and with multiplexing capabilities? Can we bring these low cost and efficient devices to places with low resources, extreme conditions or even at our homes? Which are the perspectives to link these simple platforms and detection technologies with mobile phone communication? I will try to give responses to these questions through various interesting applications related to protein, DNA and even contaminants detection all of extreme importance for diagnostics, environment control, safety and security.

From atomically-precise graphene nanoarchitectonics to applications

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In this talk, I will describe the recent advances in the on-surface synthesis field. Then, I will discuss our recent results to synthetize atomically precise 2D nanoporous graphene [1], 1D graphene nanoribbons and their chemical functionalization and how to organize them into superlattices[2,3].

At the end of the day, this talk will demonstrate the full path to synthetize a semiconducting graphene material with a bandgap similar to that of silicon, its atomic-scale characterization, and its implementation in an electronic device. Further potential applications include in nanoelectronics, photonics and highly selective molecular filtration and sensing systems.

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Utilization of photocatalytic reactions for biological applications

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Photo-functional materials are useful in a variety of applications, such as devices converting light energy into electrical energy, optical sensor and filter etc. In our group, we develop photo-functional materials that convert light energy into chemical reaction energy which achieves decomposition of environmental pollutants and harmful microorganisms, and also production of valuable chemicals (solar chemicals) converting from common resources. By using the technologies based on photo-functional materials, we recently focus on developing environment maintenance and resource utilization technologies for living in space environment. Our group is promoting both basic and applied research that integrates knowledge of chemistry and biology using the photo-functional materials that can utilize light energy that is inexhaustible in the earth and space.

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Mass production of 2D nanocarbons

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Exfoliation of graphite through oxidation is a promising technique to produce two-dimensional nanocarbons on a large scale. We have achieved a 500 g scale production of graphene oxide in laboratory, and now the scale is increasing to 10 kg. The large-scale production was achieved by the mechanistic study of the oxidation process using in situ analyses, such as XRD and XANES analyses. Our optimized graphene oxide production processes enabled the control of the size, oxidation degree, and functional group distributions on graphene. We also developed a method for the non-destructive oxidation of graphite using the specially designed electrolyte. It is confirmed that the choice of solvents and electrochemical conditions enabled excellent control over the functionalization degree and type of functional groups on graphene.

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Nanoendoscopy AFM: a window into the cell

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Innovative research in cell biology strongly depends on the capacity to study cell structures in their own physiological environment. Current available techniques have failed to internally measure the cell with sub-nanometer resolution in physiological conditions without breaking or taking it apart. Thus, new research strategies require redesigning and developing new laboratory equipment, improving existing techniques and implementing new methods that allow us to perform disruptive studies in cell biology and medicine. Here, we present a novel nanoendoscopy technique based on the atomic force microscope to measure cells internal structures, in their own physiological environment without compromising their integrity or disassembling them, obtaining images that reflect the precise cell's structures and functions

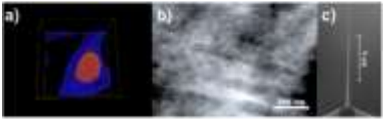

Figure 1. a) HeLa cell 3D-map performed with an AFM. b) Image of the internal side of the apical cytoplasmic membrane of a HeLa cell. c) Example of a needle like structure used to penetrate and internally measure cells, fabricated by FIB milling

Bridging in cascade Science and Industry (Calibri 11 Bold)

Juan Antonio Ruiz Fuentes (Calibri 9)
Nadetech Innovations (Calibri 8)
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The presentation will introduce the activity of Nadetech, running from their initial solutions to the position and messages nowadays. There will be several examples supporting and illustrating the title, ‘Bridging in cascade Science and Industry’.

Nano/microfluidic platforms for biosensing applications

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Fabricating large-scale bioplasmonic materials at high-throughput is important for the development of bio/chemical sensors and high resolution nanomaterial based bioimaging tools. However, techniques specific to large-scale synthesis of biocompatible nanoplasmonic materials have found limited acceptance in industry due to their time-consuming and complex fabrication procedures. Here, by exploiting properties of reactive ions in a SF_6 plasma environment, we assemble nanoplasmonic substrates containing mushroom-like structures with SiO_2 (insulator) stems and metal caps of gold (45-60 nm in total height, ~20 nm in width), evenly distributed with ~10 nm spacing on a glass slide. We demonstrate that our developed gold nanomushroom (Au NM) substrate is biocompatible and sensitive for localized surface plasmon resonance (LSPR) based biosensing applications, achieving a limit of detection of 66 zM for small molecules [1]. In addition, this platform is exploited to monitor mitosis of fibroblasts for 7 days [2], E. coli biofilm formation and drug screening [3], and DNA polymerase activity in real-time [4].

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Highly active photocatalyst based on TiO2 nanomaterials

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Titanium dioxide (TiO2) is a representative material for photocatalysis, and its form of nanoparticle as well as their composite to thin film are very attractive products to the environmental and energy issues. One of the world-spread application of photocatalysis is self-cleaning exterior such as tile and glass on the building and house. The outdoor applications, on which the photocatalysis was irradiated by sunlight including ultraviolet wavelength, were quite well utilized. Turning to the interior application and the highly efficient photocatalysis, the visible-light active photocatalysts are highly required. Chen et al. reported the black TiO2 in 20111). Oxygen vacancies were induced in TiO2 nanoparticles, and therefore their color changed from the pristine white to black. Two factors of keeping nano-sized structure and inducing oxygen vacancy only around sub-surface of TiO2 nanoparticles enhanced the oxidation of organics in water and the hydrogen evolution by reducing water with the use of a sacrificial reagent. In this study, we demonstrate the solution plasma processing (SPP) to treat the starting TiO2 nanoparticles instead of the hydrogenation process by Chen et al., in which the photocatalysts were treated in hydrogen atmosphere of 2 MPa at 200°C for 5 days. Not only the replacement of manufacturing process but the novel photocatalysts were investigated using of SPP and adapting some starting TiO2 materials such as anatase, rutile and their mixtures. TiO2 nanoparticles (Anatase: ST-01 from Ishihara Sangyo, Rutile: MT150A from Tayca, Mixture: P25 from Aerosil) were dispersed in KCl aqueous solution. After 3 hours treatment, the photocatalytic performance of plasma-treated samples was evaluated by the complete decomposition of acetaldehyde under fluorescent lamp with 8,000 lx. Final product of gaseous acetaldehyde decomposed by photocatalytic reaction is carbon dioxide (CO2), and the stoichiometric ration between acetaldehyde and CO2 is 1:2. As a result, TiO2 treated by the SPP for 3 h showed a high gaseous photocatalytic performance (91.1%) for acetaldehyde degradation to CO2 compared with the activity of untreated TiO2 (51%). The SPP-treated TiO2 was also more active than nitrogen-doped TiO2 driven by visible light (66%). The SPP technique could be used to enhance the activity of readily available feedstocks with a short processing time2). These results demonstrate the potential of this method for modifying narrow-band gap metal oxides, metal sulfides, and polymer composite-based catalyst materials. The modifications of these materials are not limited to acetaldehyde degradation and could be used in a wide range of VOC pollutant removal applications.

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Carbon-based sensors for industrial applications

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Carbon based electrochemical sensors and biosensors are developed for different applications. i)The surface of GCE is modified with Hg film for determination of HM. The modification is done in different ways: by electrodeposition of Hg and by mechanically coating with modifying solution Hg:Naffion; ii) Modification of Carbon Paste is widely experimented based on the excellent advantages relating with simplicity of the biosensor construction and low cost. Home made sensor (CPE), modified with pure enzyme, plant tissue and/or Au-Np are used for determination of phenolic compounds. The performance of the biosensor is improved in the case of two modifiers are used in the same sensor. (iii) Different types of screen-printed sensors are experimented. Voltametric determination of amino acids is performed using a system of two printed electrodes (working and reference electrode). Pt wire is used as counter electrode. The system of three printed electrodes (working, reference and counter electrodes), are experimented to determine HM in sea water using ASV; Determination of histamine in food samples is performed using printed carbon electrodes modified with rhenium (IV) oxide. Counter and reference are classical ones. Modification of carbon based electrodes at all scientifically improve the analytical performance of the biosensor (selectivity and sensitivity).

Salient gas and photosensorial properties of new ternary and quaternary nano and micro mixed valence crystalline compounds

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The compounds In_5Ch_5X (Ch = S, Se; X = Cl, Br) represent mixed valence solids with indium occurring simultaneously in three different oxidation states: In^+, In^{3+} and In^{2+}. Despite the similar ionic formulation ($In_5Ch_5X = In^+ 2In^{3+} (In_2)^{4+} 5Ch^{2-} X^-$), they crystallise in two structure types (In_5Ch_5Cl-type: monoclinic, $P2_1/m$; In_5Ch_5Br-type: orthorhombic, $Pmn2_1$)[1]. The mixed valence character and their structural characteristics offer substitution possibilities on the cationic and anionic sites. The quaternary derivative of In_5Ch_5Cl, obtained by mutual substitution of one indium species by thallium, $TlIn_4S_5Cl$, synthesized in form of nanowires shows salient the resistivity sensitivity toward gaseous NO_2 and NH_3 in air [2]. Its resistivity can decrease by more than two orders of magnitude due to the adsorption of the NO_2 molecules. The *I*-*U* measurements on the individual micro needle-shaped crystals, of the ternary and quaternary mixed valence compounds revealed significant light sensitivities. Within the potential range 0–3 V and maximal LED illumination intensity, current jumps of two orders of magnitude are observed for white light (4100 K; 200 lm), followed by the blue light (460 nm; 976 mW) [3]. The mutual structural substitution of selenium by sulphur and bromine by chlorine, led to pronounced differences in the photo chromatic sensorial properties. These differences increased with the applied potential increase. The increase of selenium content in In_5Ch_5Cl (Ch = S, Se) shifts the optical band gap toward the higher wavelengths. The introduction of Thallium in the structure shows the opposite effect. These properties are supposed to be particularly important for future nanodevice applications.

Key words: Mixed valence, ternary and quaternary compounds, needle shape crystals, gas sensitivity, photo chromatic sensitivity.

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