Prof. Ariel Kushmaro- Research topics related to nanotechnology:

#### 1. Functional Free-Standing Graphene Honeycomb Films

Fabricating free-standing, three-dimensional (3D) ordered porous graphene structure can service a wide range of functional materials such as environmentally friendly materials for antibacterial medical applications and efficient solar harvesting devices. A scalable solution process able strategy is developed to create such free-standing hierarchical porous structures composed have functionalized graphene sheets via an "on water spreading" method. The freestanding film shows a large area uniform honeycomb structure and can be transferred onto any substrate of interest. The graphene-based free-standing honeycomb films exhibit superior broad spectrum antibacterial activity as confirmed using green fluorescent protein labeled Pseudomonas aeruginosa PAO1 and Escherichia coli as model pathogens. Functional nanoparticles such as titanium dioxide (TiO2) nanoparticles can be easily introduced into conductive graphene-based scaffolds by premixing. The formed composite honeycomb film electrode shows a fast, stable, and completely reversible photocurrent response accompanying each switch-on and switch-off event. The graphene-based honeycomb scaffold enhances the light-harvesting efficiency and improves the photoelectric conversion behavior; the photocurrent of the composite fi lm is about two times as high as that of the pure TiO2 film electrode. Such composite porous films combining remarkably good electrochemical performance of graphene, а large electrode/electrolyte contact area, and excellent stability during the photo-conversion process hold promise for further applications in water treatment and solar energy conversion.

Yin S. Goldovsky, Y.; Herzberg, M.; Liu, L.; Sun, H.; Zhang, Y.; Meng, F.; Cao, X.; Sun, D. D.; Chen, H.; Kushmaro, A.; Chen, X.\* 2013. "Functional Free-stansding Graphene Honeycomb Films" Adv. Funct. Mater. 2013, 23 (23): 2972-2978. I

# 2. Hybrid multi-walled carbon nanotubes-alginatepolysulfone beads for adsorption of bisphenol-A from aqueous solution

In recent years, the potential application of carbon nanotubes (CNTs) as sorbent materials in wastewater treatment has garnered tremendous attention. Concerns that CNTs may be toxic to living organism, however, necessitate that the containment of CNTs to prevent their release into the environment in order to realize their practical application in wastewater treatment. In this study, we immobilized multi-walled carbon nanotubes (MWCNTs) within macro-calcium alginate beads. The composite beads were coated with an additional polysulfone (Psf) layer both to provide an external barrier to MWCNTs release into the effluent and also to improve the mechanical integrity of the beads. The hybrid beads were tested for their capacity to remove the bio-refractory endocrine disruptor compound bisphenol-A (BPA) using batch and packed bead column experiments. Maximum BPA removal was achieved at 22% MWCNTs, which was the dispersion limit of MWCNTs in our study. The adsorption of BPA followed Langmuir isotherm model with good correlation. The maximum adsorption capacity of the composite beads of dosage 4 g L–1 as obtained using the Langmuir model was 24.69 mg g–1. Addition of the Psf layer, together with MWCNTs, improved the bead compression performance by up to twelvefold at 40% compressive extension. This study showed that the hybrid alginate-Psf bead

may serve as compartment for encapsulation of MWCNTs for removal of BPA. Improved compression performance introduced by addition of Psf layer could protect hybrid beads used, for example, in reactors subjected to extreme conditions such as high flow rates.

M. R. Hartono, R. S. Marks, X. Chen & A. Kushmaro\*. 2014. Hybrid multi-walled carbon nanotubes-alginatepolysulfone beads for adsorption of bisphenol-A from aqueous solution. Desalination and Water Treatment (DOI:10.1080/19443994.2014.896291).

#### 3. Metal-enhanced bioluminescence: An approach for monitoring biological luminescent processes

Bacteria, which are capable of generating specific bioluminescence signatures upon metabolic changes general toxicity", have been studied from both glass and silvered glass microwell bottoms, where the silvered microwells have been modified with surface deposited silver island films SiFs". The presence of the SiFs plasmon amplifies the near-field bioluminescence signatures, 50 nm from the surface, enabling amplified detection of the reporter bioluminescence indicating sample toxicity. Using our approach a greater than fivefold enhancement in far-field bioluminescence occurs with much greater enhancements in the near field predicted.

E. Eltzov, D. Prilutsky, A. Kushmaro, R.S. Marks, C.D. Geddes. 2009. Metal-Enhanced Bioluminescence: A New Approach for Monitoring Biological Luminescent Processes. Appl. Phys. Lett. 94, 083901.

# 4. Increased Sensitivity of Bioactive Molecule Discovery: Bioassays and Detection Using Metal-Enhanced Bioluminescence

Bioluminescent signal enhancement via proximity to deposited silver nanoparticles for bioactive compound discovery employs a whole cell bioreporter harboring a plasmidborne fusion of a specific promoter incorporated with a bioluminescent reporter gene. The silver deposition process was first optimized to provide optimal nanoparticle size in the reaction time dependence with fluorescein. The use of silver deposition enabled the doubling of the bioluminescent signal for the bacterial bioreporter when compared to a nonsilvered screening microtiter plate surface (a control sample). This recording is carried out in the less optimal but necessary far-field distance. SEM micrographs provided a visualization of the proximity of the bioreporter to the silver nanoparticles. The electromagnetic field distributions around the nanoparticles were simulated using Finite Difference Time Domain, further suggesting a re-excitation of non-chemically excited bioluminescence in addition to metal-enhanced bioluminescence. The possibility of an antiseptic silver effect caused by such a close proximity may be eliminated by the dynamic growth curves of the bioreporter strains as seen using viability staining. As a highly attractive biotechnology tool, this silver deposition technique, coupled with whole cell sensing, enables increased bioluminescence sensitivity, making it especially useful for cases in which reporter luminescence signals are very weak.

K. Golberg, A. Elbaz, R. McNeil, A. Kushmaro, C. D. Geddes, and R. S. Marks\*. 2014. Increased bioassay sensitivity of bioactive molecule discovery using metal-enhanced bioluminescence. Journal of Nanoparticle Research 16:2770 (DOI 10.1007/s11051-014-2770-y).

# 5. Highly sensitive detection of E. coli by a SERS nanobiosensor chip utilizing metallic nanosculptured thin films

A nano-biosensor chip, utilizing surface enhanced Raman spectroscopy (SERS) on nanosculptured thin films (nSTFs) of silver, was shown to detect Escherichia coli (E. coli) bacteria down to a the concentration levels of a single bacterium. The sensor utilizes highly enhanced plasmonic nSTFs of silver 10 on a silicon platform for the enhancement of Raman bands as checked with adsorbed 4-Aminothiophenol molecules. T-4 bacteriophages were immobilized on the aforementioned surface of the chip for the specific capture of the target E. coli bacteria. To demonstrate that no significant non-specific immobilization of the bacteria occurs, a different bacterial strain, Chromobacterium violaceum (CV026) was used. The present sensor performs a fast, accurate and stable detection of E. coli with ultra-small 15 concentrations of bacteria down to levels of single bacterium as compared to conventional methods of detection.

#### 6. Designed Amphiphilic β-Sheet Peptides as Templates for Paraoxon Adsorption and Detection

Amphiphilic peptides were designed to fold into a  $\beta$  -sheet monolayer structure while presenting the catalytic triad residues of the enzyme, acetylcholinesterase (Glu, His, and Ser), to a solution containing the organophosphate, paraoxon. Three peptides, in which the catalytic triad residues were arranged in different orders along the strand, were generated to reveal potential differences in interactions with paraoxon as a function of the order of these amino acids. One additional peptide with amino acids introduced in random order was studied to highlight the contribution of the  $\beta$  -sheet secondary structure to any interactions with paraoxon. Langmuir isotherms, Brewster angle microscope at interfaces, and circular dichroism measurements in bulk showed that both the  $\beta$  -sheet conformation and the order of the amino acids along the strand influenced the interactions of paraoxon with the peptides. Compression isotherm curves as well as Brewster angle microscopy images provided evidence for enhanced adsorption of the paraoxon to the monolayers of peptides, which present neighboring Glu and Ser residues along the hydrophilic face of the  $\beta$  -strand. Circular dichroism revealed that the peptide most sensitive to interactions with paraoxon was that with the triad residues in the order Glu, Ser, and His, which appears to be appropriate for supporting a catalytic mechanism similar to that in the acetylcholinesterase enzyme. These rationally designed peptides may be further used for the development of technologies for organophosphate adsorption and detection.

<u>K. Yaakobi</u>, Y. Liebes-Peer, **A. Kushmaro** and H. Rapaport<sup>\*</sup>. 2013. **Designed amphiphilic β-sheet peptides as templates for paraoxon adsorption and detection**. *Langmuir* 29 (23): 6840-6848.