**Focus In**

Colloidal Luminescent Nanoparticles: Semiconductor Nanocrystals and Lanthanide-doped Upconverting Nanophosphors

Quantitative Molecular Profiling of Biomarkers for Pancreatic Cancer with Functionalized Quantum Dots

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**Special Issue**


Flexible solar cells have attracted considerable attention as a means of generating green energy towards satisfying the growing energy requirements worldwide with a minimal environmental footprint. Compared to other types of solar cells, flexible dye-sensitized solar cells (DSSCs) fabricated on a conducting plastic substrate are particularly promising due to their economical high-throughput fabrication, in addition to their potential in a variety of applications such as portable and mobile ubiquitous power sources. As such, considerable effort has been directed towards fabricating flexible DSSCs on a plastic substrate. The susceptibility of the plastic substrate to thermal degradation at high temperatures (>450°C) used in conventional sintering processes has necessitated a low-temperature (<150°C) fabrication process. While methods such as chemical sintering and mechanical pressing have been proposed to fabricate TiO₂ photoelectrodes at low temperatures with improved interconnectivity of TiO₂ nanoparticles, the sub-optimal connectivity of the photoelectrode still remains a critical challenge. Furthermore, the degree of necking of TiO₂ nanoparticles and the unsatisfactory adhesion between the photoelectrode film and/or substrate found with low-temperature processes results in poor mechanical stability under deformation; inorganic photoelectrodes are so brittle that they easily fracture and delaminate from the substrate under an external bending force. In essence, the mechanical durability of the photoelectrode must be taken into heavy consideration in assessing the performance of the device.

In this study, we develop a novel composite photoelectrode – composed of nanostructured polymer nanoparticles and TiO₂ nanoparticles – via a spray-assisted electrosprining method as illustrated in Fig. 1. The resulting highly bendable composite film is used as the photoelectrode in DSCs. The structure of the polymer/ TiO₂ composite photoelectrode is similar to that of a fiber-reinforced composite in that PVDF nanofibers are embedded in the composite photoelectrode matrix containing TiO₂ nanoparticles (Fig. 2). To evaluate the mechanical properties of the composite-based film, a bending test is repeatedly performed with conventional (BF: binder-free) and composite-based (CF) films fabricated on a flexible ITO/PET substrate (Fig. 3). To apply constant strain on the film, the bending tests are performed in the following manner: a gradual external force is simultaneously loaded from the two edges of the specimen until the film completely wraps around a cylindrical rod with a radius of 7 mm. Before bending, both films have a uniform and crack-free surface as shown in Fig. 4 (a) and (d). The resulting crack formation in the BF-based electrode is completely different from that of CF-based flexible solar cells upon bending. In particular, only a few cracks are visible for the CF-based cells after 500 or even 1000 cycles (Fig. 4 (c)). On the other hand, numerous cracks are visible on the surface of BF-based cells after as few as 200 cycles, with the crack density increasing dramatically after 1000 cycles (Fig. 4 (e) and (f)). Furthermore, while the cracks of the CF-based film are short and deflected due to random PVDF fibers in the composite material, those of the BF-based film are long and vertical to the bending axis. These results clearly indicate a significant constraint in crack generation and propagation during repeated bending for the PVDF/TiO₂ photoelectrodes, which can be attributed to the relief of external stress through the polymer nanoparticles and the consequent prevention of delamination of the electrode. Moreover, the efficiency of the cell containing composite electrodes is comparable to that of a cell containing only TiO₂, suggesting that our proposed PVDF-nanofiber-reinforced photoelectrode is a promising candidate in high-efficiency flexible plastic DSCs.
Colloidal Luminescent Nanoparticles: Semiconductor Nanocrystals and Lanthanide-doped Upconverting Nanophosphors

Since the initial successful synthesis of nearly monodisperse semiconductor nanocrystals—a quantum dot (QD)—many reports have emerged on their syntheses and applications. In particular, most research on QDs has focused on Cd-based nanocrystals, such as CdS, CdSe, and CdTe, due to their tunable visible emission spectrum and their high quantum efficiency. Specifically, CdSe-based QDs exhibit full-color emission from blue to red and a quantum efficiency greater than 80% via the construction of a core/shell structure with a wider band gap material (e.g., ZnS) on the CdSe core. Consequently, there have been many trials in the application of such QDs, ranging from both in vivo and in vitro bio-imaging to their use in optoelectronic devices such as light emitting diodes and photovoltaic cells. However, Cd is a well-known toxic element and consequently, Cd-free luminescent materials have been placed under the spotlight. At KIST, we focus on using III-V compound semiconductor nanocrystals—InP QDs and lanthanide-doped inorganic nanocrystals called nanophosphors—and their size/doping element-dependent multi-color emission capacity as alternatives to Cd-based QDs.

Fig. 1 shows a digital camera image of blue, green, and red-emitting InP/ZnS core/shell QD solutions under a handheld ultraviolet (UV) lamp. Similar to CdSe QDs, the smaller InP QDs are able to emit light at a short wavelength. However, it is much more difficult to generate blue light from the InP QDs due to their smaller band gap energy compared to that of CdSe. To synthesize ultrasmall InP QDs capable of emitting blue light, we lowered the growth temperature used after the fast injection of P precursor solution into a reaction flask and hypothesized that InP QDs hold ultraviolet (UV) lamp. Similar to CdSe QDs, the smaller InP QDs are able to emit light at a short wavelength.

Reference
The detection of cancer biomarkers is important for diagnosis, disease stage forecasting, and clinical management. As tumor populations are inherently heterogeneous, a key challenge is the quantitative profiling of membrane biomarkers, rather than secreted biomarkers, at the single-cell level. The detection of cancer biomarkers is also important for imaging and therapeutic agents, as membrane proteins are commonly selected as targets. Many methods for detection of membrane proteins yield ensemble averages and hence have limited application for analysis of heterogeneous populations or single cells. Fluorescence-based methods allow detection at the single-cell level; however, photobleaching presents a major limitation in obtaining quantitative information. Quantum dots (QDs) overcome the limitations associated with photobleaching; however, realizing quantitative profiling requires stable quantum yield, monodisperse quantum dot–antibody (QD-Ab) conjugates, and well-defined surface chemistry. Here, we demonstrate quantitative profiling, spatial mapping, and quantitative multiplexing of molecular biomarkers associated with precursor lesions of pancreatic adenocarcinoma at the single-cell level using QD-Ab conjugates.

We selected three biomarkers for pancreatic cancer for quantitative imaging: prostate stem cell antigen (PSCA), claudin-4 (CLDN4), and mesothelin (MSLN). Furthermore, quantitative profiling of these biomarkers was studied in three pancreatic cancer cell lines: Panc-1 (derived from pancreatic ductal adenocarcinoma), MIA PaCa-2 (derived from epithelial pancreatic carcinoma cells), and Capan-1 (derived from a liver metastasis of a grade II pancreatic adenocarcinoma). The immunostained pancreatic ductal cell line HPV16 was used for comparison.

Targeting antibodies were covalently conjugated to the liposomized QDs by incorporating a COOH-terminated pegylated lipid (DPPE-PEG2k-COOH). Using zwitterionic lipids, the QDs are almost electrically neutral, with a zeta potential of <2 mV (Fig. 1 (c)). Introduction of 5 mol% of the COOH-PeG-lipid does not influence the hydrodynamic diameter but results in a small negative surface charge, corresponding to a zeta potential of about −7 mV (Fig. 1 (b)). The sharp size distribution and absence of aggregates is characteristic of successful conjugation and is crucial to minimizing nonspecific binding for quantitative profiling. The low concentration of carboxylated PEG-lipids minimizes aggregation during antibody conjugation and charge-induced nonspecific binding. The absorbance/emission spectra (Fig. 1 (d)) and the quantum yield (Fig. 1 (e)) of the QDs were not influenced by conjugation, and the quantum yield remained >40%.

Fig. 2 shows a panel of fluorescence images after incubating Panc-1, MIA PaCa-2, and Capan-1 cells with the QD-Ab conjugates. To quantitatively determine the expression levels we confirmed that all target biomarkers on the cell surface were saturated and generated a standard curve relating the fluorescence intensity to the QD concentration. Fig. 3 (a) shows the resulting average biomarker density for PSCA, CLDN4, and MSLN in the three pancreatic cancer cell lines. The expression levels of these markers (molecules per square micron) are in the range from 30 μm⁻² to 470 μm⁻². Furthermore, we demonstrated the capacity to spatially resolve biomarker density using our system (Fig. 3b).

Herein, we demonstrated quantitative profiling of biomarkers for pancreatic cancer at the single-cell level using QD-Ab conjugates. The key requirements for quantitative profiling of membrane biomarkers using a QD probe are that one QD-Ab conjugate is bound to one target molecule, with no aggregation or nonspecific binding. Using our lipid-coating strategy for water solubilization and antibody coupling using pegylated lipids, nonspecific binding and aggregation are negligible, allowing quantitative profiling of biomarkers for pancreatic cancer. The ability to measure quantitative expression levels of membrane proteins has potential impact in a number of fields. For example, profiling of biomarkers in tissue samples would complement conventional histological staining and morphometric analysis, and may improve staging of disease progression. Similarly, profiling of single cells from blood samples, for example circulating tumor cells, may allow improved diagnosis and clinical management.
Polymer solar cells have attracted a substantial amount of interest as a renewable energy source, particularly in light of the desire for a flexible, economical, and a large-area manufacturing process. The generation of a photocurrent in polymer solar cells is governed by a four-step cascade: (i) generation of excitons (electrically neutral bound electron-hole pairs) via photon absorption by a polymeric electron donor (D), (ii) subsequent diffusion of excitons to the heterojunction interface between the donor and the acceptor (A), (iii) dissociation of the excitons into free charge carriers, and (iv) the transport of these carriers to the electrode contacts (Fig. 1). In particular, to achieve efficient charge separation within polymeric materials, the limited diffusion length of excitons (ca. 10 nm) must be overcome. While bulk-heterojunctions (BLHs) consisting of a polymeric electron donor (D) and a fullerenic electron acceptor (A) have emerged to bring forth a significant breakthrough in polymer solar cells, they continue to possess uncontrollable and unstable architectures. Moreover, the search for optimum fabrication conditions of a high interfacial area of both D and A domains—to limit excessive phase segregation for the generation of carrier traps to increase the recombination of excitons—is demanding and must be conducted for each and every new material combination.

In this regard, nano-structured bilayer systems with vertically bi-continuous and interpenetrating heterojunction structures have been the recipient of reignited interest. In particular, their active layer morphology with a large high interfacial area allows for a reduction in the charge recombination loss and an increase in the vertical charge transport efficiency. Such bilayer heterojunction nanostructures have been demonstrated via soft lithography, nano-imprinting, and replica molding utilizing a nano-template, and have showed a substantial improvement with regards to the power conversion efficiency (PCE) of bilayer solar cells, almost approaching that of BHJ solar cells. In this study, we introduce a facile method for the fabrication of efficient bumpy-nanostructured bilayer polymer solar cells using a blend of conjugated and insulating polymer. The spontaneous phase separation of the poly(3-hexylthiophene) (P3HT)/polyethylene glycol (PEG) blends during the spin-coating process yields a characteristic bumpy electron donor layer with circular depressions (Fig. 2(b)). The diameter of the depressions are in the range of 350 – 750 nm with variations in height of approximately 40 nm for a P3HT:PeG blend containing 6% PeG. A cross-sectional SEM image of the P3HT:PEG blend clearly shows multiple-scale depressions of the film (Fig. 2(c)). We also confirmed that the circular depressions on [6:6]-phenyl-C61-butyric acid (PCBM), a fullerene electron acceptor sequentially deposited onto a P3HT:PEG blend film via spin-coating in a dichloromethane solution, were retained without any damage. Interestingly, upon immersion of the blend film in acetone for the selective removal of the PEG phase, we observed the detachment of the film from the PEDOT:PSS coated ITO glass. Consequently, to verify the vertical phase segregation of our P3HT:PEG blend, we took X-ray photoelectron spectroscopy (XPS) measurements with argon sputtering (Fig. 2(d) inset) [1]. When considering that (i) the surface energy of P3HT (47.8 mJ/m²) is higher than that of P3HT (28.7 mJ/m²), and closer to the surface energy of PEDOT:PSS (41.6 mJ/m²), and (ii) the tendency for a component with low surface energy to segregate at the air/film interface to reduce interfacial tension, we can reasonably infer the preferential localization of the PEG and P3HT phase at the substrate surface (PEDOT:PSS layer) and the air-film interface, respectively [1]. Such vertical phase segregation in polymer blends is typically governed by the conditions during film formation, such as the surface treatment, solvent evaporation, viscosity, and blend composition. In particular, the initial phase separation can take place in a surface-oriented manner and form a bilayer structure when a polymer phase has a preference for a substrate.

The photovoltaic properties of the nanobumpy heterojunction bilayer of solar cells (P3HT:PeG/PCBM) are compared to those of a typical planar bilayer device (P3HT:PCBM), as shown in Fig. 2(c). The increase in photocurrent due to the bumpy interface morphology results in a significant enhancement in the PCE (PCE = 3.7 %) over that of a bilayer polymer solar cell with a typical planar interface (PCE = 2.8%). Given that photocurrent generation in organic solar cells is determined by light absorption, charge transport, recombination and dissociation, and the charge-collection efficiency, UV-Vis absorption and X-ray diffraction (XRD) measurements were taken and indicate no significant difference in the light absorption property and crystallinity of the homo-P3HT and P3HT:PEG blend films. Furthermore, by estimating the field-dependent possibility of charge separation, we found that charge extraction is more efficient than charge recombination in the bilayer devices and that the increase in the interfacial area of solar cells with a bumpy interface leads to the generation of more electron-hole pairs at the interface [1]. Ultimately, we believe that our direct strategy in the control of the interfacial morphology of polymer bilayer solar cells has advantages of being mold-free, simple, cost-effective, and versatile. 

References
Flexible devices are light-weight, durable under mechanical impact, and implantable on various substrates such as clothing or human skin. Not surprisingly, recent years have witnessed the development of various prototype devices, including but not limited to the following: paper phones, flexible displays, e-skins, and flexible batteries. Despite such ongoing advances, the repeated deformations experienced by electrodes bring the design and fabrication of reliable electrodes to the forefront in the field of flexible devices. Conventionally, the most commonly identified failure in continuous metal films is the fatigue-induced gradual degradation of mechanical and electrical properties due to repeated deformation. The evolution of fatigue damage in a thin metal film is a two-fold process: crack initiation and crack propagation. Crack initiation related to collective dislocation motions is followed by crack propagation, which in turn degrades the electrical properties of the metal electrode such as conductivity. In essence, the ability to control crack initiation and suppress crack propagation is needed to realize highly stable flexible metal electrodes.

To achieve these purposes, we adopt nanohole arrays in Cu electrodes, which can enhance the reliability. Prima facie, the idea that nanoholes in metal electrodes can improve both mechanical and electrical stability seems counterintuitive due to the decrease in electrical conduction path and the localization of stress by the holes. However, upon further investigation, recent experimental results using wavy, arc or horseshoe structured electrodes underscore the importance of controlled structures for the achievement of such reliabilities. Our proposed novel nanostructured metal electrode dramatically improves fatigue damage resistance. A nanohole Cu electrode is fabricated on a plasma-etched nanostructured PI substrate. The nanoholes in the electrode act as a buffering structure to reduce stress evolution, thereby suppressing crack initiation by preventing damage formation, and retarding crack propagation by reducing the stress level through crack blunting. Furthermore, this nanohole Cu electrode can be deformed in any direction, and can withstand both tensile and compressive stress. In fact, the nanohole Cu electrode shows significantly improved electrical stability – its electrical resistance increased by less than 10% over 500,000 cycles while retaining high conductivity, compared to 300% in the case of a normal electrode having the same thickness. Our results provide a key guideline in the design of a fatigue-free flexible metal electrode, and envision its application towards preventing mechanical and electrical failure of metal layers during repeated bending deformation.

Prima facie, the idea that nanoholes in metal electrodes can improve both mechanical and electrical stability seems counterintuitive due to the decrease in electrical conduction path and the localization of stress by the holes. However, the nanoholes act to suppress crack initiation by preventing protrusion formation and the subsequent damage propagation via crack tip blunting, resulting in an extremely low change in electrical resistance during bending fatigue.

References

A large number of light-trapping technologies have been explored in an effort to boost the optical absorption in thin film solar cells, particularly near the optical band gap. Among these, a plasmonic approach via the incorporation of metal nanoparticles in buffer or active layers is of particular promise. In this case, the size of the metal nanoparticles determines whether they act as a local field enhancer or a light scattering center. Moreover, the shape of the nanoparticles and their proximity to active layers are key design parameters for effective light trapping. Here, we investigate the influence of these geometrical parameters on the optical absorption in organic solar cells, and subsequently propose an optimal nanostructure design based on numerical calculations.

Embedding metallic nanograting on the frontcontact or backcontact of solar cells is another promising approach; in this case, incident light scattered by nano-grating is coupled into waveguide modes or surface plasmon polariton (SPP), resulting in the enhancement of optical absorption. In this particular architecture, nanograting provides momentum in the in-plane direction for scattered light to be coupled into propagation modes. Therefore, geometrical parameters of nanograting such as period, height, and width must be carefully designed to achieve maximal absorption enhancement. We perform a systematic study on plasmonic nanograting design to exploit waveguide mode coupling for light trapping in inverted polymer solar cells, and show via numerical calculations that the incorporation of the optimal design of plasmonic one dimensional (1D) nanograting on the backcontact leads to significant absorption enhancement in a thin polymer active layer (Fig. 1). We introduce an optical spacer layer, TiO2, between the active layer and cathode, which also acts as an electron transport layer. This spacer layer increases the optical thickness and in turn, optical modes into a waveguide. In order to optimize the metallic nanograting design, we use an Eigen mode solver in the modal analysis of the multilayered solar cell structures and identify polarization-dependent waveguide and SPP modes. The FDTD (Finite-Difference-Time-Domain) calculations combined with the modal analysis allow for the optimization of nanograting for maximization of optical absorption under a standard solar radiation. We demonstrate an absorption enhancement of over 20% in a random polarization with optimal design of plasmonic nanogratings (Fig. 2). Finally, upon further investigation into the absorption enhancement mechanisms, we show that the excitation of the TE0 and TM0 modes mixed with the SPP lead to the absorption enhancements in TE and TM polarizations, respectively.

References
Interactions Between Mesenchymal Stem Cells and T Cells on a Single Cell Level

The immune system, put together by multiple layers of complexity, can be simplified as a constant source seeking to maintain balance through any means possible. A key player in this system is the T cell, impaled with various modes of protective functionality. Oftentimes, however, T cells are negatively associated with pathological diseases, namely those of the autoimmune type. To manage and reduce the sensitivity of the T-cell-mediated immune system, immunosuppressive medication, such as corticosteroids, cyclophosphamide, and tacrolimus, has unfortunately become a rather prescriptive mode of treatment. Specifically, the attenuation of the entire immune system, and the consequent overarching repercussions on the body has researchers and clinicians open to a different form of treatment.

Mesenchymal stem cells (MSCs) have recently been identified for their ability to target a site of inflammation and thereby modulate the immune system in a biocompatible manner. Emerging as a potential mode of immunotherapy for many autoimmune diseases, the use of MSCs have been verified in a limited set of pre-clinical models for their therapeutic capacity, and have opened up a new area of research. For instance, an immune system protected by MSCs is thought to be a potential mode of therapy for the treatment and prevention of graft versus host diseases (GvHD) and allogeneic graft rejection. Recent literature indicates that these results are likely due to the interaction between MSCs and various immune cells through a range of mechanisms. A number of different hypotheses have become a crucial point of contention as current studies continue to show highly controversial findings with no conclusive results in determining the key underlying mechanism of MSC-mediated T cell suppression.

Furthermore, the implications of such uncertainty—an argue, thwarted by the failure of two late-stage clinical trials by Osiris Therapeutics, the largest MSC therapeutic company—underscores the pressing need to better understand MSC-mediated immunomodulatory mechanisms, and the development of technology that can facilitate this understanding. Unfortunately, most current technology and assays have the potential to be misleading, primarily due to their inability to generate single-cell information from a group of cells. The problems due to the lack of single-cell analytical capability is further magnified when considering that MSCs expanded in vitro are of a heterogeneous population with different physical properties and differentiation abilities.

In essence, it is important to resolve cellular properties at an individual level, which may then provide key insights into the molecular regulation of stem cell maintenance and differentiation, and ultimately, the sub-type identification of MSCs. This type of sub-profiling would allow us to more effectively study MSC-T cell communication by providing an avenue to correlate various markers (soluble factors and cell surface markers) to different cellular functions (e.g. T cell suppression by MSCs on a level that cannot be found in a bulk assay (Fig. 1). We propose herein a microarray system with the capacity to take real-time single-cell measurements, such as the proliferation rate and secretory profile of cytokines, in a high throughput manner (Fig. 2 (a)). To investigate the key mechanism involved in the immunosuppressive process of MSCs on T cells, we employ a single cell co-culture system in conjunction with microengraving technology, and test three different soluble factors (IL-10, PGE2, and TGF-1) known for their association with immunosuppressive effects. The average rates of secretion of the three soluble factors in the selected microwells are higher than those from microwells with only T cells (Fig. 2 (b)). Overall, measuring the interactions of CD4 T cells and MSCs using the microwell assay technology with both single-cell and temporal resolution increases the dimensionality of data available. This data could be used to evaluate the delay of T cell proliferation.

In essence, such a microarray system would allow us to more effectively study MSC-T cell communication by providing an avenue to correlate various markers (soluble factors and cell surface markers) to different cellular functions (e.g. T cell suppression by MSCs on a level that cannot be found in a bulk assay. Unfortunately, the first two late-stage clinical trials by Osiris Therapeutics, the largest MSC therapeutic company, underscore the pressing need to better understand MSC-mediated immunomodulatory mechanisms, and the development of technology that can facilitate this understanding. Unfortunately, most current technology and assays have the potential to be misleading, primarily due to their inability to generate single-cell information from a group of cells. The problems due to the lack of single-cell analytical capability is further magnified when considering that MSCs expanded in vitro are of a heterogeneous population with different physical properties and differentiation abilities. In essence, it is important to resolve cellular properties at an individual level, which may then provide key insights into the molecular regulation of stem cell maintenance and differentiation, and ultimately, the sub-type identification of MSCs. This type of sub-profiling would allow us to more effectively study MSC-T cell communication by providing an avenue to correlate various markers (soluble factors and cell surface markers) to different cellular functions (e.g. T cell suppression by MSCs on a level that cannot be found in a bulk assay (Fig. 1). We propose herein a microarray system with the capacity to take real-time single-cell measurements, such as the proliferation rate and secretory profile of cytokines, in a high throughput manner (Fig. 2 (a)). To investigate the key mechanism involved in the immunosuppressive process of MSCs on T cells, we employ a single cell co-culture system in conjunction with microengraving technology, and test three different soluble factors (IL-10, PGE2, and TGF-1) known for their association with immunosuppressive effects. The average rates of secretion of the three soluble factors in the selected microwells are higher than those from microwells with only T cells (Fig. 2 (b)). Overall, measuring the interactions of CD4 T cells and MSCs using the microwell assay technology with both single-cell and temporal resolution increases the dimensionality of data available. This data could be used to evaluate the delay of T cell proliferation.
On November 8, 2012, KIST officially inaugurated its Cheonbuk branch. The Cheonbuk branch first opened in 2008 with a strategic goal of conducting pioneering research on composite materials in Korea. Currently, 20 Ph.D. and 70 researchers are working in the Soft Innovative Materials Research Center and the Carbon Convergence Materials Research Center. They plan to hire 100 additional Ph.D. researchers until 2014 with aspirations to conduct world-leading research on composite materials. KIST President Kil-Joo Moon predicts that the Cheonbuk branch will play an important role in increasing the global competitive power of Korea and in taking a lead in the expanding market of composite materials worldwide.