Controlled Self-Assembly of Nanomaterials through Highly Ordered Self-Assembled Monolayers and Genetically Engineered Polypeptides

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INTRODUCTION

Nanostructured materials represent a fascinating class of materials whose structural components, such as crystallites, atomic clusters or molecules, have at least one dimension between 1 nm and 100 nm. This size range is often equal to or smaller than the length scale that defines the physical characteristics of materials and at which intriguing phenomena are observed (for example, Coulomb blockade). Recent progress in synthetic methodologies has enabled the production of nanostructures of various metals and semiconductors, fullerenes (C_{60}), carbon nanotubes, organic and polymeric nanoparticles, and dendrimers. Similar advances have been made in molecular biology where polypeptides with specific recognition for an inorganic surface have been selected using phage or cell-surface display technologies and modified through genetic engineering to tailor their binding, functionality, and self-assembly properties. The next step towards applications of inorganic, organic, and biomolecular constructs is the development of parallel schemes to position them into desired configurations on substrates so that they could be interconnected and addressed to harness their properties in an operational device. We report the controlled self-assembly of nanomaterials through highly ordered self-assembled monolayers (SAMs) and genetically engineered polypeptides for potential applications in molecular electronics and optoelectronics, biotechnology, and nanophotonics.

RESULTS AND DISCUSSION

Highly ordered self-assembled monolayers for molecular electronics and optoelectronics. As part of our efforts on functional molecular assemblies, we have developed a series of anthracene- and pyrene-based self-assembling molecules with tunable energetic (π-π stacking, H-bonding, dipole-dipole interaction) and variable geometries. We discovered the conformation-dependent electrical properties of (4-mercapto-phenyl)(9-anthryl)acetylene (MPAA) molecules.[1] The presence of fused-rings in the structure of MPAA increases intermolecular π-π interactions and yields highly organized, densely packed, rigid SAMs of MPAA on Au. Amazingly, the arrangement of MPAA molecules within the SAM changes from 2-D stacked arrays to pseudo 1-D wires based on self-assembly time. Subsequently, we demonstrated that the current-voltage (I/V) characteristics depended on the local ordering of MPAA molecules.

With the goal of achieving novel electrical and optical properties, we incorporated C_{60} within the rigid conjugated molecular framework of MMPA to combine the physical and chemical properties of C_{60} with nanoscale ordering of MPAA.[2] Electrical properties of C_{60}-MPAA in both homo-assembly and co-assembly with MPAA showed semiconducting behavior. Importantly, we observed multiple peaks in I/V curves that suggest potential negative differential resistance (NDR) phenomena, which may be attributed to the weak charge transfer between MPAA and electron-affinitive C_{60} at the molecular junction of C_{60}-MPAA. In control experiments, neither C_{60} SAMs nor MPAA SAMs alone exhibited NDR-type peaks. Furthermore, we noted only weak (or no) apparent NDR effect on negative bias voltage, indicating that charge transfer takes place more strongly in one direction, that is, from electron-rich MPAA to electron-deficient C_{60}.

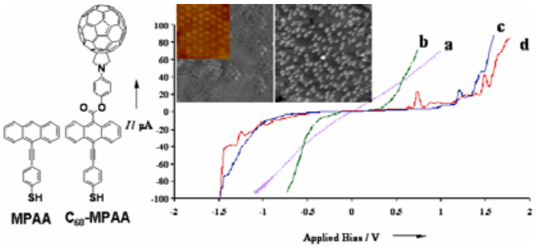

Figure 1. (A) Molecular structures of MPAA and C_{60}-MPAA. (B) Electrical measurements – a: Au(111); b: C60 only; c: C60-MPAA SAMs; d: C60-MPAA/MPAA composite SAMs (1:9 molar ratio). Insets: STM images of C_{60}-MPAA hybrid molecules in homo-assembly (left) and co-assembly with MPAA (right) after 24 hr.

We have also studied the efficiency of photocurrent generation in C_{60}-MPAA SAMs. As shown in Figure 2A, when [Au/C_{60}-MPAA/MV^{2+}/Pt] cell was irradiated with a monochromatic wavelength of 400 nm, a stable cathodic photocurrent (ca. 1600 nA/cm^2) was generated. Photocurrent generation upon the application of different bias potentials is shown in Figure 2B. Semi-linear increase of cathodic photocurrent with an increase of negative bias (from +200 mV to -200 mV) to the Au electrode demonstrates that the photocurrent flows from Au electrode to Pt counter electrode through the SAM and electrolyte. Cathodic photocurrent dramatically increased as the potential bias is lowered below +100 mV. However, a further increase of negative bias beyond -300 mV to the Au electrode could not be realized due to a significant increase of the cathodic photocurrent as the dark current. Quantum yield of 14% was obtained for the photocurrent generation from C_{60}-MPAA SAM on Au, indicating the potential of C_{60}-MPAA hybrid molecules for mimicking photosynthesis in nature.

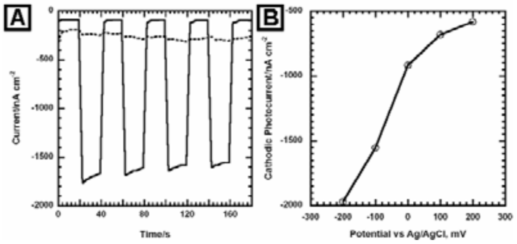

Figure 2. (A) Light-induced “ON” - “OFF” switchable photoelectrochemical response of bare [Au/MV^{2+}/Pt] cell (dotted line) and [Au/C_{60}-MPAA/MV^{2+}/Pt] cell (solid line). (B) Photocurrent vs applied potential curve for [Au/C_{60}-MPAA/MV^{2+}/Pt] cell. (Electrolyte: 0.1 M Na_2SO_4 solution containing 50 mM MV^{2+} as an electron carrier; input power: 260 mW/cm^2; applied potential – 100 mV vs Ag/AgCl.)

As an extension of the investigation on molecular optoelectronics, C_{60}-tethered 2,5-dithienylpyrrole triad was designed and synthesized.[3] The three-electron reduced C_{60} radical anions of C_{60}-triad both in solution and on gold substrate (as a SAM) were detected at room temperature. Photocurrent generated in [Au/C_{60}-triad/MV^{2+}/Pt] cell upon irradiation by a monochromatic wavelength of 400 nm is exceptionally large (3200 nA/cm^2) with high quantum yield (51%). The electron-rich characteristics of molecular architecture and the rigid conjugated molecular framework stabilize the C_{60} radical anions generated during electrochemical reduction and lead to a remarkable enhancement of photocurrent generation. A novel self-assembling molecule with coplanar anthraquinonyl and anthryl moieties linked by an acetylenic unit has also been designed and synthesized as an electron acceptor for efficient photocurrent generation.[4] Composite SAMs formed by co-assembling with an oligo(pyrrolethiophene) donor showed very promising photochemical properties. The amount of photocurrent generated (1425 nA/cm^2 with quantum yield of 23 %) under the illumination with a monochromatic wavelength of 360 nm is comparable to that obtained using a C_{60}-based molecule as the electron acceptor. This result demonstrates the feasibility of using anthraquinoneanthrylacetylene molecule as an efficient electron acceptor for constructing a molecular light-to-current converter.

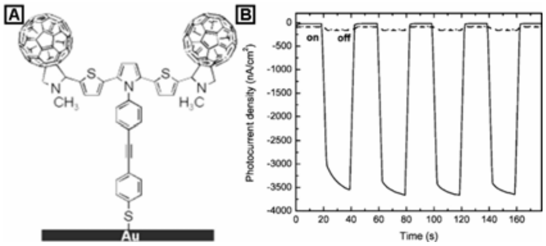

Figure 3. (A) Molecular structure of C_{60}-triad. (B) Photoelecrochemical responses of [Au/C_{60}-triad/MV^{2+}/Pt] cell (soild line) and [Au/MV^{2+}/Pt] cell (dotted line). (Electrolyte: 0.1 M Na_2SO_4 solution containing 50 mM MV^{2+} as an electron carrier; input power: 260 mW/cm^2; applied potential – 100 mV vs Ag/AgCl.)

Arrays of covalently bonded single gold nanoparticles. To obtain reproducible measurements of electron transport, organic conjugated molecules need to be covalently bonded to the electrodes - usually Au - through terminal groups such as thiols. The imbedding of thiolated molecular assemblies in an insulating matrix of alkanethiols with gold nanoparticles (AuNPs) as top-contacts provides an attractive platform (or test-bed) for studying molecular electronics since individual AuNPs can be easily located and reliably connected with a STM tip or a conducting AFM tip.

We have developed a bottom-up approach to form 2-D arrays of asymmetric molecular assemblies with covalently bonded Au-NPs as potential top-contacts for electrical addressing by a scanning probe.[5] We were able to achieve sub-100 nm domains of organic conjugated molecules insulated by alkanethiols through a combination of layer-by-layer scheme and surface chemical reaction to produce metal-organic-metal junctions of well-controlled size and interspacing. Arrays of single AuNPs are achieved by taking advantage of the interplay of electrostatic interactions and covalent bonding, in conjunction with the positional constraint on the template.

Figure 4. Arrays of covalently bonded single AuNPs on thiolated molecular assemblies.

Integration of functional organic molecules with genetically engineered polypeptides for nanoparticle assembly and biotechnology. In the last decade, use of phage and cell-surface display technologies has emerged as a powerful strategy to screen peptides/polypeptides with recognition for inorganic materials. Combinatorially selected peptides can identify a specific inorganic elemental composition, crystallographic orientation and structure, or morphology of an inorganic entity. Moreover, as molecular linkers, recombinant peptides can be covalently bonded with organic functional molecules to construct hybrid superstructures which are potentially tunable in terms of physico-chemical and optoelectronic properties. As a proof-of-concept demonstration using gold-binding polypeptide (GBP-1), we explored the patterning – physical or chemical – of genetically engineered polypeptides using high-resolution microcontact printing.[6] In chemical pattering, surface chemical reaction localized by the patterns on a PDMS stamp, enabled the generation of patterns as well as the formation of organic-peptide conjugates simultaneously. We demonstrated the utility of laterally structured GBP-1 as templates for the site-specific assembly of AuNPs.

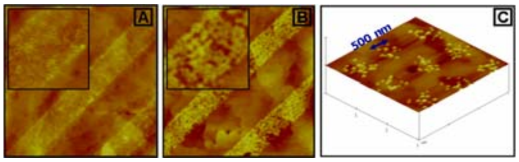

Figure 5. Chemically (A) and physically (B) patterned GBP-1. (C) Assembly of AuNP into arrays of 500-nm squares using chemically patterned GBP-1.

We have also employed GBP-1 in the immobilization of alkaline phosphatase (AP) to fabricate enzymatic protein microarrays. Attachment of proteins onto solid supports with high affinity and materials selectivity is a central issue in many applications of biotechnology including proteomics. Existing methods, based on thiol or silane anchors, result in the immobilization of proteins in a random orientation and consequently a loss of biological activity due to non-specific binding on the substrate. There has always been a compromise between maintaining biological activity of proteins and having the advantages of surface-bound proteins. We fused GBP-1 to AP through genetic engineering to create a bi-functional molecular construct (AP-GBP) that possesses an enzymatic activity and an inorganic-binding activity at the same time. Significantly, in comparison to AP-WT (wild type), we measured a dramatically higher level of enzymatic activity of AP-GBP as a result of specific binding on the substrate, proper orientation, and higher packing density.

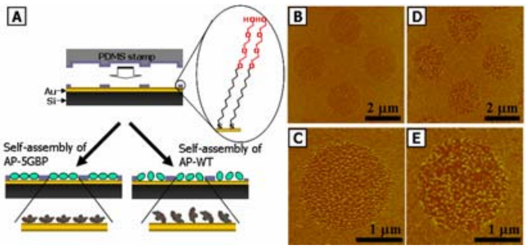

Figure 5. (A) Schematic illustration of experimental procedure to fabricate enzymatic protein arrays. Immobilization of AP-GBP (B-C) and AP-WT (D-E).

CONCLUSIONS

A significant challenge in the application of organic, inorganic, and biomolecular building blocks for various applications is the development of self-assembly approaches. We have presented a systematic strategy to achieve nanostructured systems by controlling the self-assembly of nanomaterials through highly ordered SAMs and genetically engineered polypeptides.

ACKNOWLDEGEMENT

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