

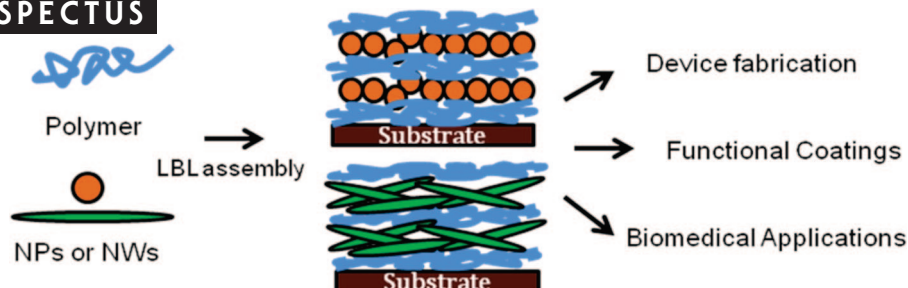
Composite Layer-by-Layer (LBL) Assembly with Inorganic Nanoparticles and Nanowires

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CON SPECTUS



New assembly techniques are required for creating advanced materials with enough structural flexibility to be tuned for specific applications, and to be practical, the techniques must be implemented at relatively low cost. Layer-by-layer (LBL) assembly is a simple, versatile, and significantly inexpensive approach by which nanocomponents of different groups can be combined to coat both macroscopically flat and non-planar (e.g., colloidal core-shell particles) surfaces. Compared with other available assembly methods, LBL assembly is simpler and more universal and allows more precise thickness control at the nanoscale. LBL can be used to combine a wide variety of species—including nanoparticles (NPs), nanosheets, and nanowires (NWs)—with polymers, thus merging the properties of each type of material. This versatility has led to recent exceptional growth in the use of LBL-generated nanocomposites. This Account will focus on the materials and biological applications of introducing inorganic nanocrystals into polymer thin films.

Combining inorganic NPs and NWs with organic polymers allows researchers to manipulate the unique properties in the nanomaterial. We describe the LBL assembly technique for introducing metallic NPs into polymers in order to generate a material with combined optomechanical properties. Similarly, LBL assembly of highly luminescent semiconductor NPs like HgTe or CdTe with poly(diallyldimethylammonium chloride) (PDDA) was used to create uniform optical-quality coatings made on optical fibers and tube interiors. In addition, LBL assembly with inorganic nanosheets or clay molecules is reported for fabricating films with strong mechanical and ion transport properties, and the technique can also be employed to prepare Au/TiO₂ core/sheath NWs.

The LBL approach not only will be useful for assembly of inorganic nanocrystals with various polymers but can be further applied to introduce specific functions. We discuss how the expanded use of NWs and carbon nanotubes (CNTs) in nanocomposite materials holds promise in the design of conductive films and new nanoscale devices (e.g., thin-film transistors). New photonic materials, sensors, and amplifiers can be constructed using multilayer films of NPs and can enable fabrication of hybrid devices.

On the biological side, inorganic nanoshells were used as assembly tools with the goal of detecting neurotransmitters (specifically, dopamine) directly inside brain cells. In addition, the stability of different cell lines was tested for fabricating biocompatible films using LBL. NP LBL assembly was also used for homogeneous and competitive fluorescence quenching immunoassay studies for biotin and anti-biotin immunoglobulin molecules. Finally, introduction of biomolecules with inorganic NPs for creating biocompatible surfaces could also lead to new directions in the field of biomedical applications.

Introduction

The ability to fine-tune the composition of nanostructured films or nanocomposites provides a

powerful tool for nano- and microscale assembly. Layer-by-layer (LBL)¹ assembly is a rich, versatile, and significantly inexpensive approach by which

thin films, particularly of oppositely charged layers, can be prepared. Researchers have been attracted to the fabrication of thin solid films using LBL for generating advanced coatings² and smart surfaces³ at the molecular level for various biological⁴ and material applications.⁵ The advantages of the LBL assembly technique also include simplicity, universality, and thickness control at the nanoscale level, compared with the other available assembly approaches. Formation of thin films from nanosized clay platelets or semiconductor, magnetic, or metallic particles with polyelectrolytes using LBL is a viable route for the construction of smart films. The variety of inorganic shapes and composition of the components (nanoparticles (NPs), nanosheets (NSs), and nanowires (NWs)) available for the LBL assembly process has led to an exceptional growth in the fabrication of LBL composites. LBL assembly of biomolecules with inorganic nanocomponents also leads to new direction in the field of biomedical research. Similarly, optical photonic materials using multilayer films of NPs or NWs can enable the fabrication of new devices.

Various assembly approaches have been employed to assemble polymers or NPs in an ordered manner and to investigate the scope of potential applications. Polymers⁶ and inorganic nanocrystals⁷ have been studied in detail to create unique architectures inspired from nature by manipulating the specific interactions. The LBL approach for assembling polymers with inorganic NPs provides the opportunity to combine the electronic, optical, and magnetic properties of inorganic nanostructures⁸ with unique physical responses of macromolecules.⁹ Once the components are available, combining the unique responses of inorganic clusters with polymers can lead to fabrication of hybrid devices. Similarly, the possible integration of biomolecules can lead to the development of new technologies for diagnostic applications. The LBL¹⁰ technique holds the promise of generating novel nanocomposites with optimal interfaces because (a) LBL assembly allows the introduction of various nanocomponents at the same time with high loading in the assembled layers, (b) the composition of each LBL prepared layer can be easily modulated from layer-to-layer to achieve the optimal structure for a specific application, and (c) LBL prepared layers can be assembled with controlled variable thickness for generating smart and biocompatible coatings.¹¹ LBL-based thin films have recently been applied to various applications that include drug delivery systems,¹² battery electrolytes, sensors, and thin membranes.¹³ In general, the LBL process is achieved by alternately exposing a substrate to positively and negatively charged polymers or particles (Figure 1). In LBL, steps 1–4 are repeated continuously until the desired numbers of “bilay-

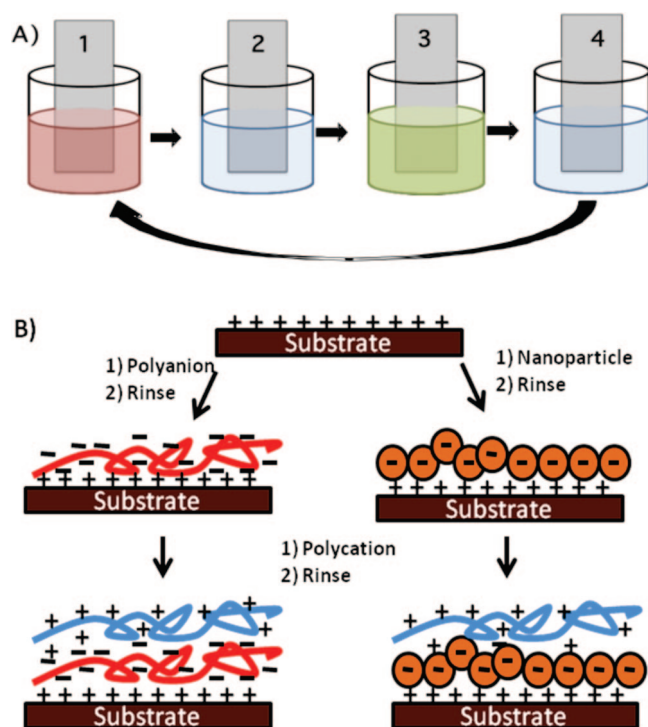


FIGURE 1. (A) Scheme of the LBL film-deposition. Steps 1 and 3 represent the adsorption of polyanion and polycation, steps 2 and 4 are washing steps. (B) Two adsorption routes, depicting LBL deposition for polymers and polymers with NPs.

ers” are achieved. Each individual layer thickness and LBL growth rate depends upon various factors including the chemistry used, charge density, molecular weight, temperature, deposition time, and concentration and pH of the species being deposited.¹⁴ The ability of LBL to control the coating thickness, properties of the nanocomponents and economic use of raw materials make the assembly tool greatly superior to other techniques.

In this Account, we discuss current efforts for constructing high-quality LBL films using inorganic nanocrystals and their advantages. Functional films for devices and biomedical applications by introducing the NPs in the LBL assembly will be discussed based on the alternating interaction of oppositely charged species, like positively and negatively charged polymers with inorganic NPs. Similarly, extending the concept of using different inorganic geometries like NSs for stronger mechanical properties and long NWs and CNTs for device fabrication is reported. Besides discussing material applications and general procedures for LBL, the use of LBL assembly for biological applications and other interesting uses is also illustrated.

LBL: Polymers as Building Blocks

LBL was originally developed for polyelectrolyte/polyelectrolyte systems; now the LBL technique is applicable for almost

any type of charged components, including inorganic clusters, NPs,¹⁵ NWs,¹⁶ NSs,¹⁷ organic dyes,¹⁸ dendrimers,¹⁹ polypeptides,²⁰ DNA,²¹ and proteins. This translates into an exceptionally broad range of morphological characteristics and functional responses. The forces that promote formation of LBL films are also not restricted to electrostatic interactions. Assemblies based on ionic charge transfer,²² hydrogen bonding,²³ covalent attachment,²⁴ biological recognition,²⁵ and hydrophobic interactions²⁶ have also been vigorously investigated. Availability of a wide-ranging spectrum of organic or inorganic components, variety of interactions and versatility in assembly approaches spectacularly enhances the uses of LBL technique.

In general, for the LBL assembly process, the common positively charged polyelectrolytes used are poly(allylamine hydrochloride) (PAH), poly(diallyldimethylammonium chloride) (PDDA), and polyethyleneimine (PEI). Once they are attached on the substrate, the net charge on the substrate surface becomes positive because of the adsorption of polyelectrolyte with positive charge. The films are consequently rinsed with pure water; the aim of rinsing is the removal of loosely adsorbed polyelectrolytes. To subsequently grow the LBL further, the films are introduced with negatively charged polyelectrolyte solutions. The common negatively charged polyelectrolytes are poly(acrylic acid) (PAA), poly(styrene sulfonate) (PSS), and poly(vinyl sulfate), which leads to the reversal of net charge on the substrate. As a result, a double layer of polyelectrolyte is built up on the substrate. With such cyclic depositions, one can achieve multilayer films on the substrates with desired thicknesses and structures. Different combinations using the same process of inorganic components with polyelectrolytes will be discussed in detail. LBL technique with inorganic nanocrystals for various useful applications will be also illustrated.

LBL Assembly with Inorganic Nanoparticles

LBL assembly with metallic NPs was used for introducing the unique responses of inorganic clusters in thin films. In the process, first the polymers are coated on the substrates, and then the adsorption of oppositely charged particles is used to build the multilayers. Au-NPs stabilized by the 4-(dimethylamino)pyridine (DMAP-Au) were investigated to interact with various polyelectrolytes using LBL assembly.²⁷ The results obtained indicated that the combined interactions originating from PAH and PSS with DMAP-Au NPs facilitated the preparation of stable thin films with tailored optical properties. In a similar study, Au-NPs and polyelectrolyte multilayer structures were also fabricated using spin-assisted LBL method.²⁸

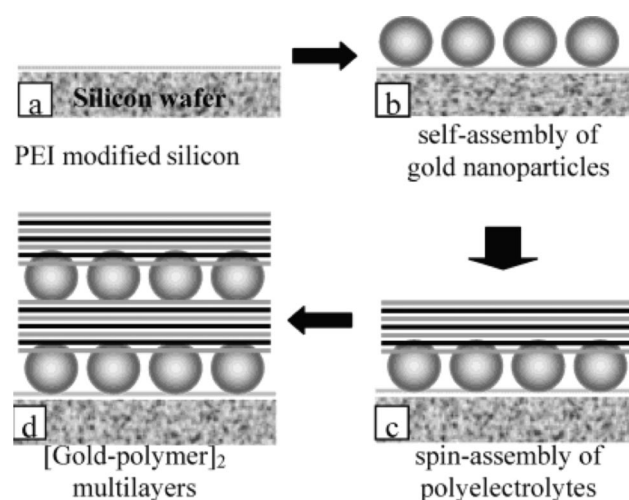


FIGURE 2. NP-polyelectrolyte multilayers: (a) PEI monolayer; (b) Au-NP monolayer deposited by adsorption on PEI; (c) Au/(PAH-PSS)_nPAH fabricated using LBL; (d) [Au/(PAH-PSS)_nPAH]₂ multilayers. Reproduced from ref 28. Copyright 2004 American Chemical Society.

Films showed red-shift in the plasmon resonance (optical response ~ 520 nm) because of the local dielectric environment. For films with sufficient density of gold NPs within the layers, the second strong peak was also observed around 640 nm, which is the collective plasmon resonance. The observations in tuning the independent and concurrent individual, intralayer, and interlayer plasmon resonances can be vital for sensing applications, which involve monitoring of optomechanical properties of ultrathin optically active membranes (Figure 2).

Inclusion of semiconductor NPs in the LBL films based on a similar alternating approach of oppositely charged species was also studied.²⁹ HgTe NPs and PDDA³⁰ were assembled into thin films with controllable thicknesses. LBL films were prepared according to the standard procedure: (i) first, the substrate was dipped into a solution of PDDA for 10 min, then rinsed with water; (ii) the glass substrate was dipped into the HgTe dispersion for 20 min, then rinsed with water. Each step resulted in a "bilayer" made of polymer/NP composites. The cycles were continued until the preferred thickness of the film was achieved, and each step was analyzed by UV-vis spectra.³⁰ The LBL films with HgTe NPs showed strong emission in the near-infrared region (peak around 1600 nm), covering the entire telecommunications spectral region. These LBL assembly of films containing NPs can be viewed as an inexpensive versatile method, enabling implementation of cost-effective high-capacity optical networks, optoelectronic emitters, and amplifiers.

The exceptional flexibility of LBL films is not limited to planar substrates but can also be applied for highly curved surfaces.

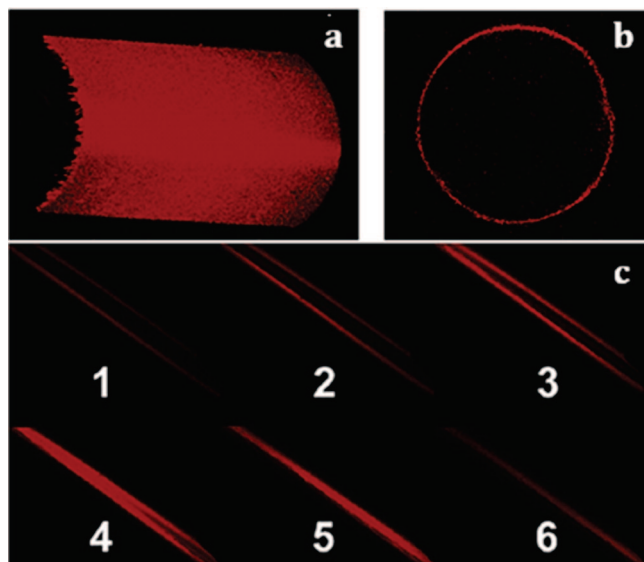


FIGURE 3. Confocal images of the optical fibers coated with (PDDA/CdTe)₈: (a) composite image of the fiber surface; (b) axial image of the fiber; (c) depth profile. Numbers 1–6 indicate gradual change of imaging depth. Reproduced from ref 31. Copyright 2003 American Chemical Society.

LBL sequential adsorption was utilized as a deposition method for nanostructured coatings on optical fibers, which was demonstrated with CdTe NPs. The fabrication of uniform optical quality coatings made of strongly luminescent NPs on optical fibers and tube interiors were analyzed. For this study LBL was performed using CdTe NPs and PDDA on optical fibers and glass tubings.³¹ Confocal microscopy demonstrated that CdTe/PDDA coatings were continuous and uniform (Figure 3). Strong coupling of the NP luminescence into the 600 μm glass optical fiber attributed to a high refractive index of CdTe/PDDA nanocomposites. Two unexpected results were detected: gradual red-shift of the luminescence spectrum with an increase in layer thickness and a significant improvement of the luminescence during the first 100 min of UV illumination. Similar trends were obtained for the coatings made for the glass tube interior, which can be considered as plain models of microfluidic devices with complex channels and sensing abilities.

Other than optical properties, the photocatalytic response of the LBL films consisting of polymers with TiO₂ NPs was also observed.³² Uniform distribution of TiO₂ NPs in the film was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Photocatalytic properties of the LBL films consisting of NPs were established by oxidation of iodide and decomposition of methyl orange. Other than electrostatic buildup, Wang et al. investigated a convenient LBL assembly approach to form similar multilayers of conjugated polymers and CdSe NPs using covalent attachments.³³ The stability of the resulting LBL film was tested by sonica-

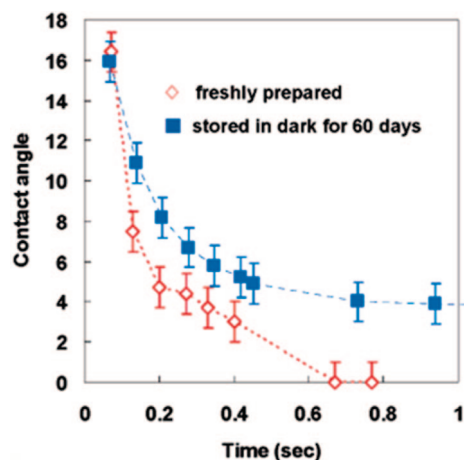


FIGURE 4. SiO₂/TiO₂ NP films showing changes in the contact angle of a water droplet on the freshly prepared and 60-day-stored multilayer-coated glass as a function of time. Reproduced from ref 35. Copyright 2006 American Chemical Society.

tion; no change in the thickness of the films was observed. Interesting photocurrent responses and photovoltaic properties were found in the LBL films. The results of this investigation demonstrate that the covalent-based LBL technique yields a distinctive method for the production of a variety of organic/inorganic hybrid films.

LBL also provides a versatile means to create all-NP coatings from different combinations of functional NPs (metallic, magnetic, and semiconductor NPs). The assembly of oppositely charged NPs without polymers was first reported in 1966.³⁴ In a recent study, Rubner, Cohen and co-workers³⁵ used LBL assembly for oppositely charged NPs without polymers, which exhibited antireflection, antifogging, and self-cleaning properties. LBL of positively charged TiO₂ (7 nm) and negatively charged SiO₂ NPs (7 and 22 nm) was performed on solid substrates. The porosity and chemical composition of the coatings were determined using a simple method that is based on ellipsometry and does not require any assumptions about the refractive indices. The presence of nanopores in the TiO₂/SiO₂ NP coatings results in superhydrophilicity as well as antireflection properties. The superhydrophilicity of contaminated coatings was readily recovered and retained after ultraviolet irradiation. Unlike TiO₂-based coatings, which lose their superhydrophilicity in the dark, SiO₂/TiO₂ NP-based coatings retained their superhydrophilicity even after being stored in dark for 60 days (Figure 4).

Nanosheets and Nanoplates for LBL Assembly

LBL of NPs can also be extended to inorganic sheets, which are of great interest for their unique material properties. Fer-

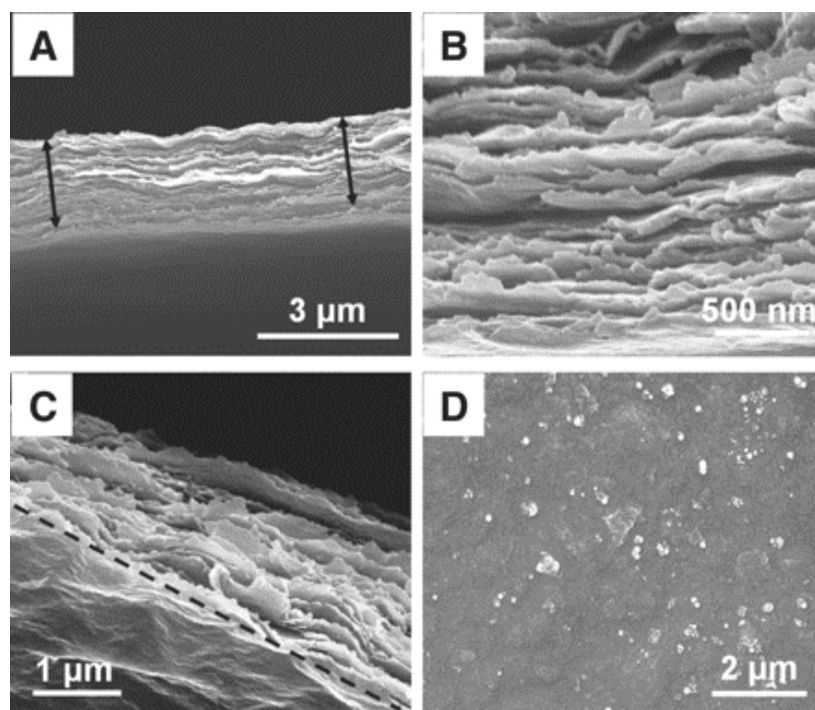


FIGURE 5. SEM of PVA/MTM nanocomposite: (a) cross-section of the film; (b) close-up of the cross-section; (c) top-down view of a fracture edge of the composite after tensile testing; (d) top-down view of the composites surface. From *Science* (www.sciencemag.org), ref 37. Copyright 2007. Reprinted with permission from AAAS.

guson et al. reported LBL of the positively charged polyelectrolytes with silicate mineral hectorite individual sheets. The assembly allowed controlled, stepwise formation of multilayer thin films.³⁶ Each nanocomponent presented rapid adsorption by an ion-exchange mechanism and X-ray diffractometry. Film thicknesses greater than $0.2 \mu\text{m}$ were found for the silicate/polymer assembly. The large lateral area of the silicate sheets permitted each layer to completely coat any packing cracks in the underlying film. The careful picking of the NSs or plates in the LBL film can be exploited as an assembly tool for the preparation of films with a variety of technological significance. Because NSs cover the defects in the films, Podsiadlo et al.³⁷ prepared ultrastrong layered polymer nanocomposites using poly(vinyl alcohol) (PVA) and montmorillonite (MTM) clay. Characterization of the assembly verified dense coverage of the nanoplatelets and their strictly planar orientation (Figure 5).³⁷ Evaluation of mechanical properties for PVA/clay composites displayed four times higher strength and 1 order of magnitude higher Young's modulus when compared with pure PVA polymer. Glutaraldehyde cross-linking increased the strength and stiffness of both pure PVA and the PVA/MTM composite. The ultimate tensile strength increased by a factor of 3 over the un-cross-linked PVA/MTM strength and 10-times in comparison with pure PVA (high values up to 480 MPa). The modulus of the PVA/MTM with glu-

taraldehyde exceeded that of un-cross-linked PVA/MTM by 1 order of magnitude and that of pure PVA by 2 factors, with the highest values reaching 125 GPa. These results indicate the possible variability in the physical properties of the LBL assemblies by modulating the components used in the buildup.

Other than mechanical properties, Hammond and co-workers described ion transport properties of polymer-clay structures from a combination of PEI, laponite clay, and poly(ethylene oxide).³⁸ This trilayer LBL structure was assembled using hydrogen bonding and electrostatic interactions. The films were characterized using ellipsometry, atomic force microscopy (AFM), and electrochemical impedance spectroscopy (EIS). Results demonstrated a layered, anisotropic structure that showed in-plane ion transport 100 times faster than cross-plane at 0% relative humidity. Similarly, Shi and co-workers³⁹ prepared LBL films from Bi_2WO_6 nanoplates, which had higher visible-light photoactivity ($\lambda > 420 \text{ nm}$) than Bi_2WO_6 nanoplate powders and P25TiO_2 films (Figure 6). Thickness and photoactivity of the films was also modified by changing the deposition cycles. Bi_2WO_6 films showed spectral selectivity of the photocatalytic degradation of rhodamine-B. Under a wavelength greater than 300 nm, the rhodamine-B molecules tend to be transformed to rhodamine over Bi_2WO_6 films. On the contrary, under shorter wavelength ($\lambda = 254 \text{ nm}$) light irradiation, the rhodamine-B molecules can be photodegraded completely. Generally,

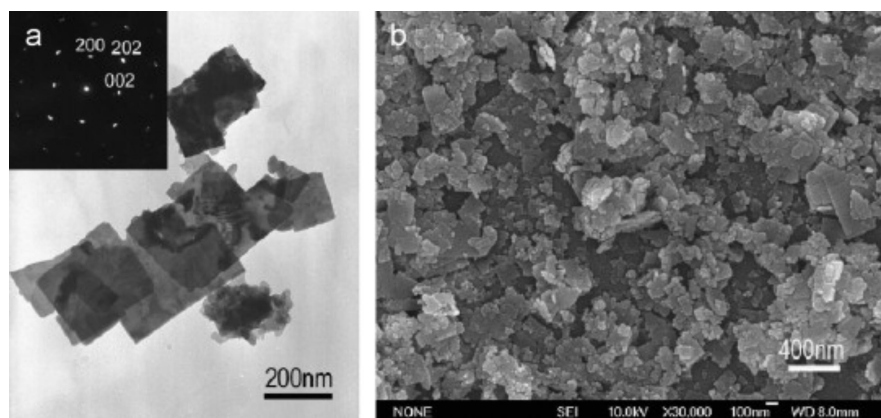


FIGURE 6. (a) TEM image of Bi_2WO_6 nanoplates and (b) SEM of a Bi_2WO_6 multilayer film with eight deposition layers. Reproduced from ref 39. Copyright 2007 Elsevier.

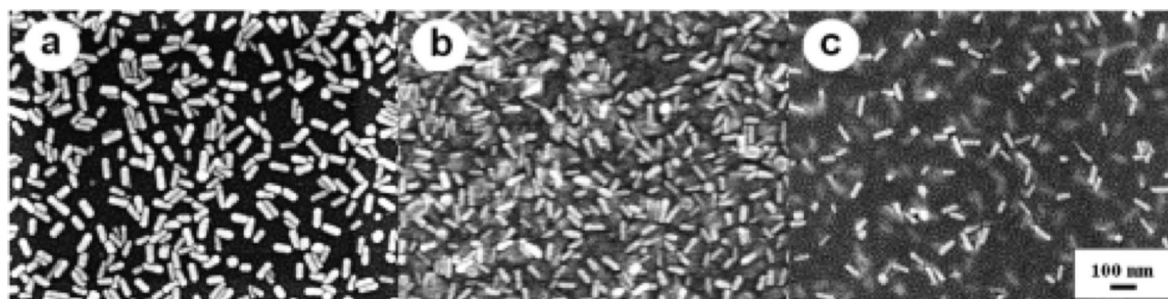


FIGURE 7. TEM of Au-NW LBL films with four layers separated by a single PDDA layer (a); PDDA/PSS bilayers (b), and PDDA/PSS/PDDA/PSS multilayers (c). Reproduced from ref 41. Copyright 2007 American Chemical Society.

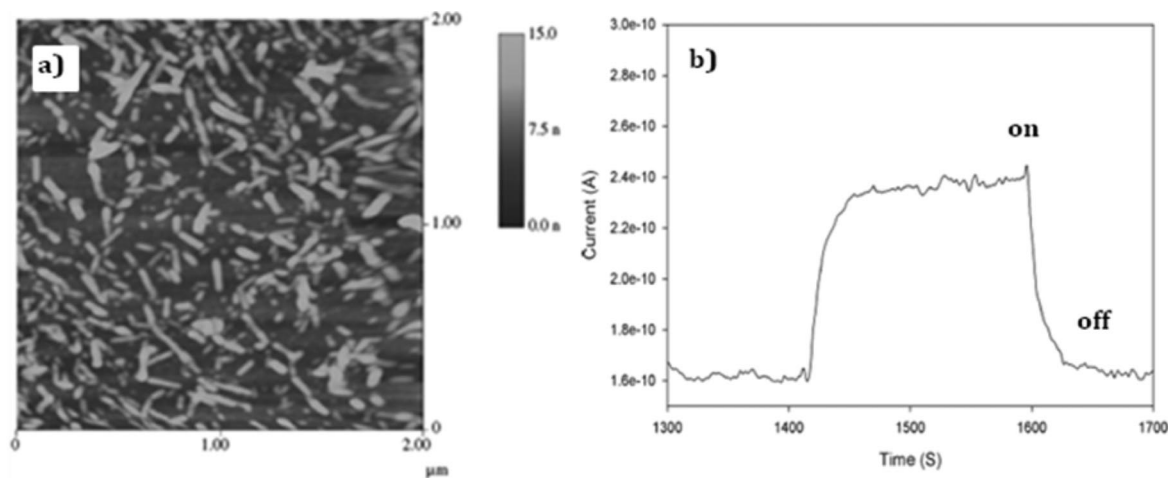


FIGURE 8. (a) AFM image of $(\text{PDDA}/\text{NW})_1$ and (b) photoresponse of Te films for repetitive switching between “on” and “off” states. Reproduced from ref 42. Copyright 2006 Wiley-VCH.

Bi_2WO_6 films have potential application in selective oxidation, photosynthesis, and photodegradation of dyes by different wavelength light irradiation. Use of NSs for LBL demonstrates the ability of the technique to enhance the physical responses of the materials. Recently, titania sheets in the LBL assembly were used as reactors for the in situ formation of Ag metals in thin films from silver ions.⁴⁰

LBL Assembly and One-Dimensional Nanowires

LBL assembly using NWs and CNTs is a new area of research. One-dimensional nanomaterials are likely to play a key role in fabricating devices of the next generation. The LBL assembly approach was also extended to NWs by alternative adsorption of polymers and inorganic wires. Recently, Liz-Marzán and

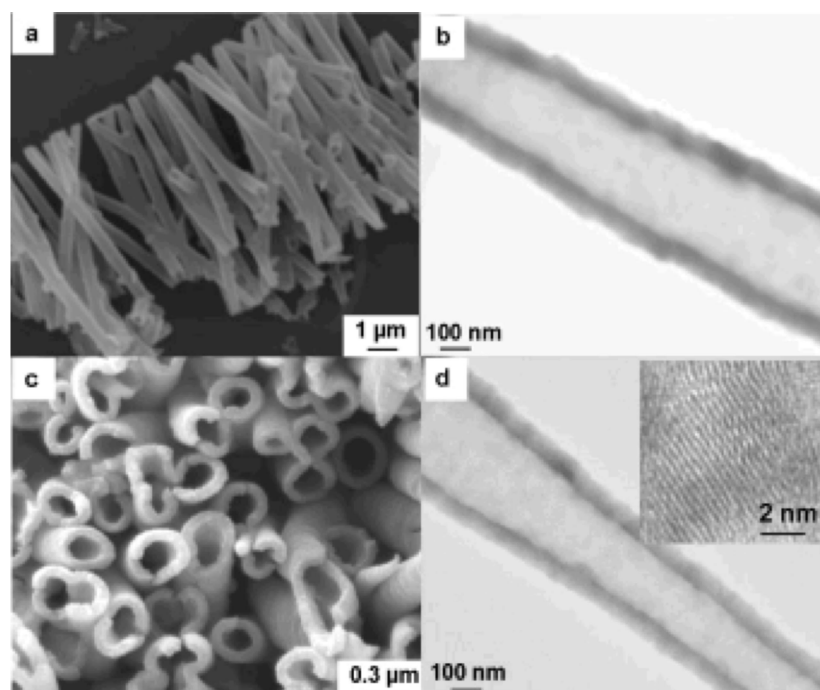


FIGURE 9. SEM (a, c) and TEM (b, d) of titania nanotubes obtained from $(\text{PEI}/\text{TALH})_{12}\text{PEI}$ coated membranes after heating at 95 °C for 24 h (a, b) and 450 °C for 10 h (c, d). Reproduced from ref 44. Copyright 2007 Wiley-VCH.

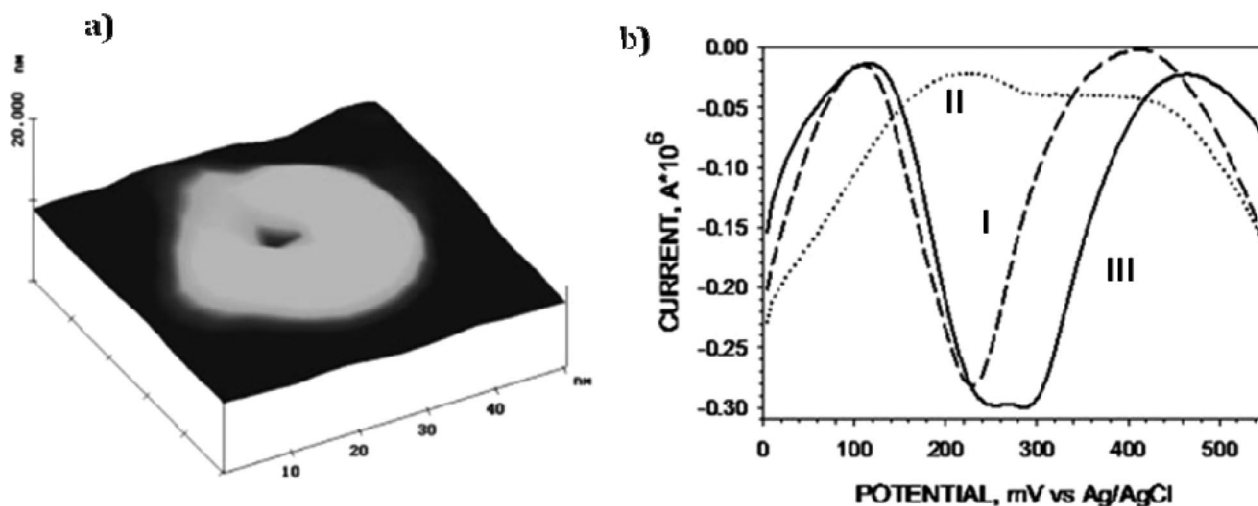


FIGURE 10. (a) AFM image of TiO_2 nanoshells and (b) differential pulse voltammograms of (I) dopamine, 1 mM; (II) ascorbic acid, 1 mM; and (III) a mixture of 1 mM dopamine and ascorbic acid in 0.1 M buffer coated with PDDA(PDDA-PAA). Reproduced from ref 47. Copyright 2002 Wiley-VCH.

co-workers⁴¹ reported LBL films using the standard polyelectrolytes and Au wires. The control of NW density in monolayers was achieved by varying deposition time and interlayer separation in multilayer films (Figure 7), which was varied through the assembly of an increasing number of polyelectrolyte monolayers. In all cases, plasmon coupling (leading to extensive red shift and broadening of the longitudinal surface plasmon band) could be efficiently tuned by keeping the particles separated at distances longer than the Au-NW short axis. This systematic study of the optical effects derived from

plasmon coupling in mono- and multilayers of metallic NWs was presented.

LBL assembly of NWs was also performed by transforming CdTe NWs to Te NWs by using the Cd complexing agent EDTA.⁴² Te NWs exhibited a uniform diameter with lengths ranging from 200 to 800 nm. LBL films of Te NWs on glass were fabricated by dipping the substrate alternatively into negatively charged NWs and PDDA (Figure 8).⁴² To characterize the conductive and photoconducting properties of the films made from Te NWs, PDDA/NW was fabricated and electrical

contacts were made by attaching silver wires to the Te surface. The electrical resistance measurements of the Te NW films were carried out in the dark and under light. The "light-on–light-off" cycle was shown to be very stable at room temperature, but the photocurrent increase and decrease kinetics was found to be relatively slow. The observed results are promising and offer the potential to construct photoactive switches with higher loadings of NWs. The photocurrent study of the thin films also demonstrated that Te thin films can be reversibly switched between lower and higher conductivity states after exposure to external light. The photoconducting NWs could also serve as light detectors for various optoelectronic applications, in which the binary states can be optically addressed.

The strategy of LBL assembly was also employed for NW formation. To prepare Au/TiO₂ NWs, ordered arrays were fabricated using LBL assembly of cationic polyelectrolytes and inorganic precursors on template-grown Au NWs. The wires formed were investigated with SEM, TEM, and X-ray energy analysis.⁴³ This technique is useful in fabricating core/sheath NWs. Though LBL assembly, titania tubes were also successfully fabricated by deposition of water-soluble titania, titanium(IV) bis(ammonium lactato)dihydroxide (TALH), and oppositely charged PEI (Figure 9).⁴⁴ Tubular structure was prepared by deposition of the above-mentioned materials inside the cylindrical pores of a polycarbonate membrane template, followed by calcination. The titania tubes exhibited very interesting photocatalytic properties, demonstrated by the degradation of the azodye methyl orange. They were easily separated from the reaction system by simple centrifugation, allowing for straightforward recycling. The reported procedure provides a versatile technique to fabricate titania-based tubular nanostructures, which could easily be applied to construct other tubular structures and can find uses in catalysis and chemical sensing.

Another class of one-dimensional material is CNTs; LBL assembly using single-walled carbon nanotubes (SWNTs) can be applied to develop unique electronic devices due to their outstanding mechanical, thermal, and electrical responses. In a recent study, the fabrication of high-mobility thin-film transistors (TFTs) using LBL assembled SWNTs for the semiconducting material and SiO₂-NPs as the gate dielectric material were investigated.⁴⁵ The channel length and the effective thickness of the SWNT–semiconductor layer were 50 μm and 38 nm, respectively. The effective thickness of the SiO₂ dielectric layer was 180 nm. The gate voltage V_G sweeps were collected from –10 to 0 V with 2 V steps. The SWNT-TFT exhibited p-type semiconductor characteristics and operated

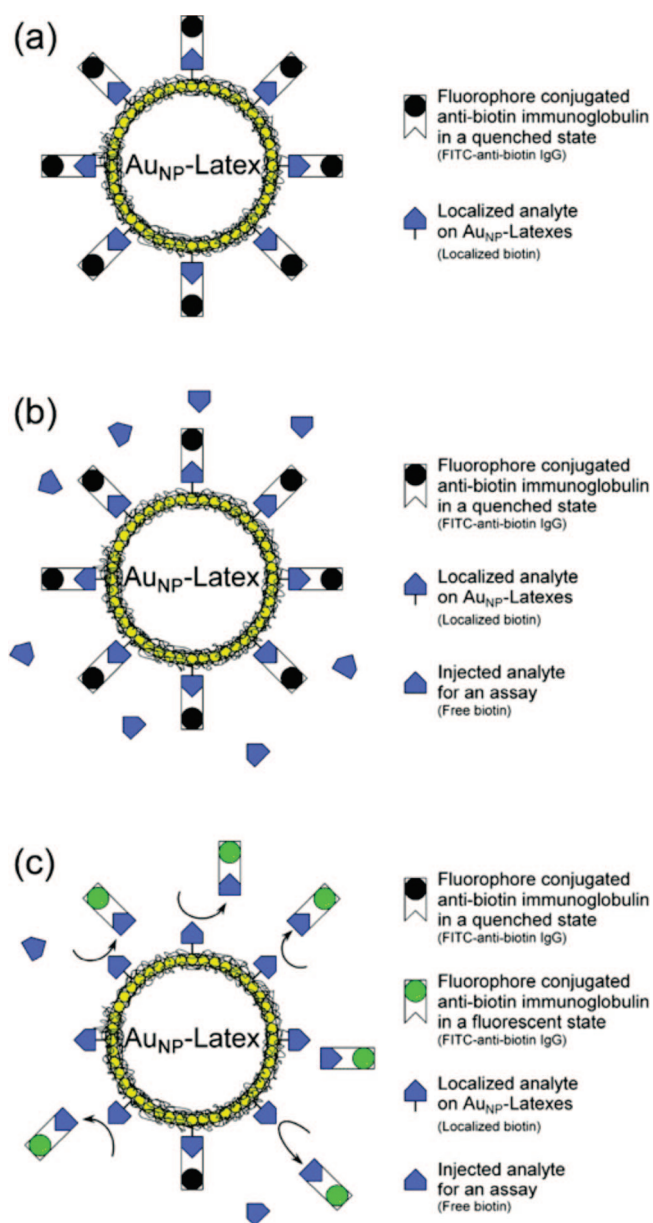


FIGURE 11. Schematic of immunoassay using NP/polyelectrolyte-coated latexes: (a) fluorophore-labeled antibodies are quenched before injection of analyte; (b) injection of analyte; (c) fluorophore-labeled antibodies fluoresce after being released by biotin. Reproduced from ref 49. Copyright 2005 American Chemical Society.

in the accumulation mode. The combination of LBL and microlithography provides a simple, low-temperature, and highly efficient approach to fabricate TFT devices.

LBL Using Inorganic Nanoparticles for Biological Applications

Here we discuss mainly the use of inorganic NPs as assembly tools for biological applications. LBL assembly of NPs with polyelectrolytes provides the opportunity to introduce biocompatibility and fabricate biomaterials. For biocompatible

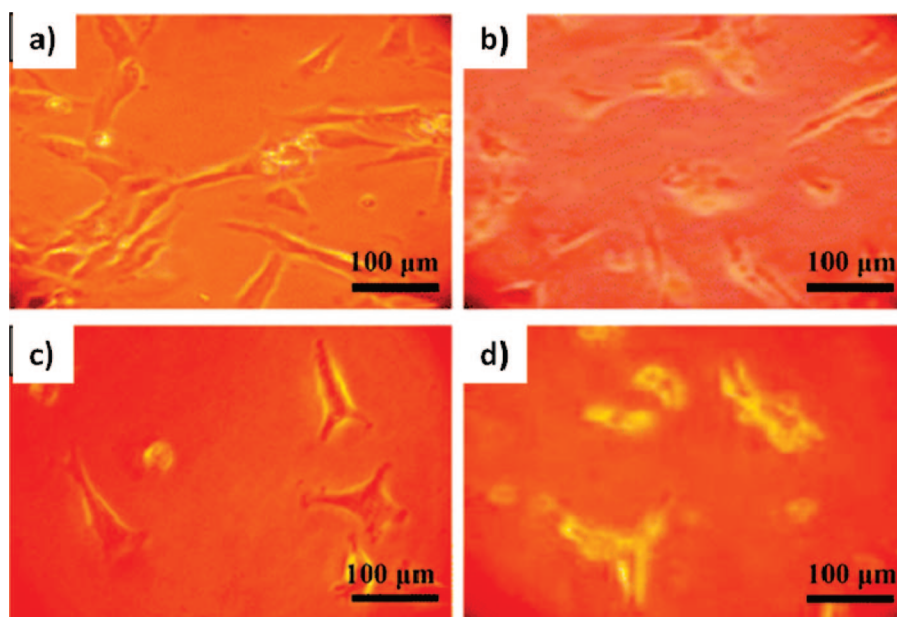


FIGURE 12. Optical images of human osteoblasts (ATCC, CRL-11372) cultured slides (A, B) and slides coated with (PDDA/MTM/PDDA/AgNPs)₁₀ (C, D) for 3 days. Reproduced from ref 50. Copyright 2005 American Chemical Society.

surfaces, an LBL sequence using (PDDA/CdTe)_x/PDDA/(PAA/collagen)_y was prepared.⁴⁶ When mammalian cells were cultured on (PDDA/CdTe)_x, only dead cells were observed. When NP films were coated with a single PAA/collagen, the cells attached in large quantities. Thus biocompatibility of the film can be engineered depending upon the cell type used. LBL was also used to create ion-selective/biocompatible films using TiO₂ nanoshells. Hollow titania spheres were fabricated from TiO₂ and Ag-NPs.⁴⁷ To make nanoshells with ion-sieving properties, the silver core was removed by treatment with ammonia solution. Once the titania shells were formed, LBL assembly of TiO₂ nanoshells and negatively charged PAA was carried out. UV-vis was used to analyze the buildup of TiO₂/PAA films. The morphology of the hollow-sphere shells in the LBL films provides large surface area and porosity. The ion-permeable properties of the nanoshells were analyzed by cyclic voltammetry using potassium ferricyanide as the probe molecule.

LBL films of TiO₂ nanoshells with high pore density showed similarities with the biomembranes. Recently there has been substantial attention in developing new detection techniques for the secretion of neurotransmitters from the cells present in the brain. To understand the system of secretion and metabolic rate is an important key factor to cure diseases (for example, Parkinson's disease). Dopamine is one important chemical present in the nervous system. The electrochemical response to dopamine and ascorbic acid was studied to test the LBL films (Figure 10).⁴⁷ Results indicated that LBL coatings with nanoshells showed a drastic difference in the elec-

trochemical signal response for ascorbic acid compared with dopamine. The ion-selective capabilities of the nanoshell films for the successful detection of dopamine in the presence of ascorbic acid represent a significant biological problem and demonstrated improvement in detection sensitivity. The LBL films were found to be compatible with other cell lines, which opens the pathway for their exploitation as smart coatings for in vivo monitoring of brain activity.

To study the LBL of NPs with biomolecules, Zhou et al. prepared multilayer thin films of Au-NPs and myoglobin on solid substrates.⁴⁸ In another report, Au-NP/polyelectrolyte coated latex particles were prepared using LBL technique to investigate the competitive fluorescence quenching immunoassays.⁴⁹ Quenching efficiency (QE) for the plane LBL films is related to the cube of the spacing between the layers. Achieving QE = 50% at a distance of ~15 nm indicated that the Au-NP/polyelectrolyte is suitable for detecting release/binding measures for antibodies. A reliable, competitive binding immunoassay for biotin was fabricated on Au-NP/polyelectrolyte-coated polystyrene colloids (488 nm), as quenchers for the fluorescein-isothiocyanate labeled anti-biotin immunoglobulin (FITC-anti-biotin-IgG). Molecules of biotin were attached on the NP/polyelectrolyte composites by adsorbing a layer of biotinylated poly(allylamine hydrochloride) (B-PAH). FITC-anti-biotin-IgGs was subsequently bound to the particles through biotin. Characterization using TEM and quartz crystal microgravimetry established the multilayer formation on latex particles. The NP/polyelectrolyte-coated latexes removed FITC-anti-biotin-IgG upon addition of free-biotin, with a sensing

ability of 1–50 nmol. These results indicate that NP/polyelectrolyte-coated composites can be used as smart sensors (Figure 11). This study supports the importance of LBL with NPs to be used for sensors and delivery applications.

LBL assembly from MTM-clay and PDDA was also used to study antibacterial activity, which was introduced by alternating clay with starch-stabilized silver-NPs.⁵⁰ The resulting composite showed excellent structural stability with no detectable levels of silver lost over a 1-month period. Estimation of the antibacterial response presented almost total growth inhibition of *E.coli* over a period of 18 h. The quantity of silver eluted from the LBL films over 30 days was determined to be just 0.5–3.0 $\mu\text{g/L}$. This loss in concentration of silver did not stop the growth of the mammalian culture tissues. The LBL nanocomposite offered high biocompatibility with the human osteoblast cell line used (Figure 12).⁵⁰

LBL assembly based on sequential absorption of polymers with inorganic nanocrystals is a unique approach to combine the physical responses from both the components into the nanocomposite material. Different mechanisms were reported to explore the ability of the LBL method to create advanced functional films. This approach allows playing with the chemistry of the nanocomponents used in the assembly to introduce biomimetic features and to design advanced devices. The high loading of NPs or NWs into the polyelectrolyte films with potential applications can be utilized further for future materials. In particular, the use of NPs holds a great promise for manufacturing infrared opto-electronic emitters, amplifiers, and sensors. For biomedical applications, LBL assemblies with nanoshells and NPs can be used for understanding neuron communication and to fabricate biocompatible surfaces. Introducing NSs, NWs, and SWNTs in the LBL assembly adds to the versatility of the approach for constructing transistors and conducting films.

BIOGRAPHICAL INFORMATION

Sudhanshu Srivastava received his masters degree in Chemistry from Indian Institute of Technology, Roorkee. He then completed his Ph.D. degree in 2007 from Department of Chemistry at the University of Massachusetts, Amherst, under the guidance Professor Vincent M. Rotello. Currently, he is working as a Research Fellow under Professor Nicholas A. Kotov. His current research is focused on the spontaneous assembly of nanoparticles for construction of nanowires and other advanced architectures. He is also investigating exponential layer-by-layer assemblies for loading and unloading of nanoparticles and nanotubes.

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FOOTNOTES

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