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Effect of annealing on the growth dynamics of ZnPc LB thin film and its surface morphology

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The ZnPc molecules in the thin film prepared by Langmuir-Blodgett (LB) process in asdeposited state has been found to have an edge on orientation with average tilt angle of 64.3° as confirmed from the Pressure-Area (π -A) isotherm and X-ray diffraction (XRD) study. The ZnPc LB thin film has been observed to have abnormal growth mode at higher annealing temperature and it is mainly driven by minimization of surface free energy which lead to large increase in crystallinity of the film. Kinetically favored orientational and structural transitions of ZnPc thin film during annealing and their effect on the surface morphology of the thin film has been studied using scaling concepts. The scaling exponents 1) root mean square (RMS) roughness σ , 2) roughness exponent α and, 3) in plane correlation length ξ are calculated from the HDCF $g(r)$ and ACF $C(r)$. The RMS surface roughness σ is found to be dependent on the as defined short wavelength undulations (ρ) and long wavelength undulations (χ). Both ρ and χ are the function of all the three scaling exponents. σ has been observed to be maximum for the ZnPc thin film annealed at 290°C , since the χ shoot to maximum value at this temperature due to the formation of small domains of ZnPc nanorods. The self affinity of the ZnPc thin film is found to decrease on annealing as obtained from both power spectral density (PSD) and HDCF $g(R)$ & ACF $C(R)$ study, which confirms that the dimension of surface morphology of the ZnPc LB thin film transform towards 2D with increase in annealing temperature. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4891177>]

I. INTRODUCTION

Langmuir-Blodgett (LB) technique provides an excellent means for constructing supramolecular assemblies or highly ordered molecular thin films of functional materials.^{1,2} Among the metal organic molecules, the metal-phthalocyanine (MPc) molecules have gained large attention because of their high thermal and chemical stability, high intrinsic charge carrier mobility, the ambipolarity of the charge carrier transport, and high absorption coefficient of order of 10^5 cm^{-1} .³ Hence they have been applied to wide varieties of fields such as optoelectronics and electronics devices,⁴⁻⁷ namely organic light emitting diodes (OLEDs),⁸ photovoltaic devices,⁹ memory devices,¹⁰ organic solar cells^{11,12} and sensors.¹³ Therefore it is necessary to have proper understanding of surface morphology and growth mechanism of MPc's compounds in thin films for their technical application. The surface and structural morphology of the thin film is very much dependent on the nucleation and grain growth process. It is important to tune the morphology of the organic semiconductor at the inorganic/organic, organic/organic or metal/organic interface to improve its charge injection. The anisotropy property of the MPc's molecules stress on the important role played by orientational degrees of freedom on the ordered orientational stacking of MPc's molecules in thin film which can lead to efficient

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Structural morphology study of Cd²⁺ induced Langmuir Blodgett multilayer films of arachidic acid

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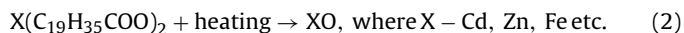
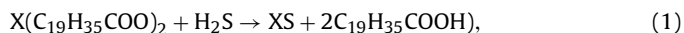
ABSTRACT

The organization and headgroup co-ordination of Cadmium Arachidate (CdAA) molecule in Langmuir–Blodgett (LB) multilayer films deposited on hydrophilic Glass (SiO₂) and Silicon (100) substrate at normal subphase pH (6.8) are studied. X-ray diffraction (XRD) and X-ray reflectivity (XRR) study reveals ordered layer by layer organization with uniform packing of CdAA molecules, and with a small tilt angle of alkyl chain of CdAA molecule equal to $6.8^\circ \pm 1.75^\circ$. Electron density profiles (EDPs) shows that the coverage of films remains almost constant with increase in bilayer thickness which indicate very little presence of pinhole defects. AFM study for 25 ML shows that coverage of the film remain intact upto 22nd ML and then decreases sharply due to presence of pinhole defects. Fourier transform infrared spectroscopy (FTIR) study is also consistent with XRD and XRR study of ordered deposition of CdAA molecule. FTIR and X-ray photoelectron spectroscopy (XPS) study indicates the formation of unidentate bridging metal-carboxylate coordination type headgroups consistent with one cadmium metal ion between two carboxylate (COO) groups in each headgroup structure.

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1. Introduction

Long-chain fatty acids have been extensively used as LB monolayers at the air–water interface [1–3]. They are amphiphilic molecules, where the hydrophilic groups attract the aqueous subphase and the hydrophobic groups point towards the air, thereby getting attached to the aqueous subphase. Due to this property of LB monolayers to array the amphiphilic molecules in a particular manner, it can successfully serve as a template for two-dimensional chemical reactions [4–6],



LB films are generated from LB monolayers deposited on a solid substrate layer upon layer, which have ordered molecular assemblies with planned structure. Through LB process, films of nanoparticles, nanowires and microparticles can also be synthesized [7–9]. It is a bottom-up assembly technique in nanotechnology and functional material application like chemical sensor, semiconductor light (CdS, CdTe), high temperature piezoelectric etc.

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In recent years, the LB Technique for preparation of ultra- thin films of various organic, metallorganic and polymer compounds have generated interest among researchers of various fields due to their potential applicability in molecular electronics, non linear optics, conducting thin films, sensors and as a templates for growing functional nanomaterials like quantum dots [10–15]. LB process though economical and with better molecular-level-control compared with other sophisticated techniques like molecular beam epitaxy (MBE), sputtering or metal-organic chemical vapour deposition (MOCVD) could not find much appealing application because of low reproducibility owing to presence of pinhole type growth defects. Therefore to apply LB films in various devices and technology, it is very important to control the ordered molecular assembly in each monolayer such that coverage area of film remains almost same with successive monolayer deposition. This aspect has been included in the present study.

The LB system of long chain saturated fatty acids (stearic, arachidic, behenic) are studied mostly because of their strong amphiphilic property and to incorporate different divalent cations of transition metals having considerable electronegativity (e.g., Cd²⁺, Ca²⁺, Mn²⁺, Zn²⁺, Ba²⁺, etc.) into their headgroup structure in comparison to amines, esters and alcohols. The floating LB monolayer of the required fatty acid on the water surface, can react directly with the ions of given divalent metal, dissolved in the water subphase in submillimolar concentration, to yield a nearly purified form of the fatty acid salt that can be deposited as multilayers on a suitable substrate by the successive vertical dipping technique

Observation of defect-assisted enhanced visible whispering gallery modes in ytterbium-doped ZnO microsphere

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Smooth surfaced and crystalline undoped and ytterbium doped zinc oxide (ZnO) microspheres having an approximate size of 3–5 μm were synthesized by hydrothermal process. Out of these microspheres, a single microparticle was chosen and engaged as a whispering gallery wave microresonator. The defect induced luminescence from an individual ZnO microsphere was investigated with micro-photoluminescence measurement in the spectral range of 565 to 740 nm under the excitation of a green laser having a centered wavelength at 532 nm. The defects-related emissions from a single ZnO microsphere show optical resonance peaks so-called “whispering gallery modes” (WGMs) which are confirmed with the theoretical calculation. Further, ZnO microspheres were chemically doped with the different molar percentages of Ytterbium (Yb), and enhancement in their emission properties was investigated. Our experimental results show that ZnO microspheres with 0.5 mol. % doping of Yb gives the strongest optical emission and has highest Q-factor which can be employed in the development of WGM based optical biosensor or laser. *Published by AIP Publishing.*

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I. INTRODUCTION

Whispering-gallery waves, which are originally observed for sound waves, have become a hot topic in photonic research due to the existence of a similar phenomenon in the light. In recent years, it has shown various applications in the areas of optoelectronics, sensors, lasers, etc.^{1–3} Particularly in sensing application, various forms of waveguide couple dielectric resonators that include ring, disc, spherical, toroidal, and cylindrical shape have been reported by many research groups.^{4–9} Among these reported optical resonators, the spherical shape could achieve the highest Q-factor and it has been exploited as an optical sensor.^{10,11} For example, silica microspheres of diameter 10 to 100 μm can support whispering gallery modes (WGMs) with highest Q-factor up to the order of 10^9 .¹² The excitation of the optical modes was achieved via coupling the laser light into a tapered fiber placed very close to the silica microsphere. Such spherical microsphere has shown its application as WGM based label-free optical biosensor for the detection of a single virus.² However, the limitation of such WGM sensing device is the requirement of very delicate and costly nano-positioning instruments, which makes it difficult for *in-situ* bio-sensing measurements. Several efforts have been attempted to overcome this technical difficulty by adopting dye or quantum dot doped polystyrene or silica microsphere.^{13–16} Although it could overcome the traditional light coupling scheme, such microspheres suffered photobleaching or blinking and required a prolonged doping process. In recent years, there are several reports on optical microcavities made of the semiconducting materials like In_2O_3 , ZnO, and TiO_2 .^{17–21} In these microcavities, the luminescence properties of the

semiconducting material itself acted as a light source and their structural geometry helps in trapping the light within. In this scenario, various types of ZnO micro/nanostructure based optical microcavities have attracted lots of attention in the development of WGM based UV lasers or sensors.^{19–22} Our earlier work has also demonstrated the existence of WGM in individual crystalline ZnO microsphere using micro-photoluminescence ($\mu\text{-PL}$) measurement under the excitation of 325 nm laser light.²³ We have further exploited WGM in ZnO microsphere for its application in refractive index sensing in the visible spectral region. However, our previous studies suggested that the quality factor (Q-factor) of the chemically synthesized ZnO microsphere compromises the sensitivity of our earlier proposed sensor and it requires improvement to use them as a reliable optical sensor or laser. Specifically, engineering the luminescence properties of ZnO microsphere is highly demanding to achieve high-quality factor WGM in the visible-NIR spectral region, which will enhance the sensitivity of the sensing device. Several studies have shown that doping of different materials such as rare earth material in ZnO thin films enhances the broad green luminescence,^{24–29} thereby providing a possible route to engineer defects assisted luminescence in ZnO.

In this work, we have systematically investigated the optical emission properties of individual Yb-doped ZnO (abbreviated as Yb-ZnO) microspheres and determined the optimum doping concentration that requires for achieving the highest quality factor of WGM. Such Yb-ZnO microspheres may possess potential applications in micro/nanophotonics for developing high performing micro-laser or optical micro-sensor for detection of the single biological molecule. We believed that this is the first report on engineering defect levels for achieving enhanced WGM and high-quality factor in ZnO microsphere in the visible-NIR spectral region.

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Defect engineered ZnO whispering gallery modes via doping with alkali metal ions for label-free optical sensors

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ABSTRACT

A systematic investigation on the proper utilization of defect levels present in ZnO is very much in demand to avail many applications of photonics in visible and near infrared (NIR) regions. In this paper, we have engineered intrinsic defects of zinc oxide (ZnO) to achieve high-quality intense whispering gallery modes (WGMs) in a single ZnO microsphere optical resonator by doping with alkali metal ions. Here, a single microsphere of undoped and doped ZnO was considered to investigate WGMs by recording luminescence spectra using a microphotoluminescence system under green laser excitation having a central wavelength of 532 nm and a fixed power of 55 mW/cm². We have found that there is a significant enhancement in the intensity of WGMs in the case of doped ZnO in comparison to undoped ones. Among all the doped ZnO microspheres, 2 mol. % Li-doped ZnO yields the strongest and intense WGMs, which are accompanied by high-quality (Q)-factors. Furthermore, the pump power dependence measurement performed in 2 mol. % Li-doped ZnO reveals the lasing action in the visible optical window by explicitly exploiting the defect levels present in the material. Thus, our proposed defect engineered ZnO microsphere may represent a promising optical microresonator for developing highly sensitive WGMs based optical sensors.

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I. INTRODUCTION

The designing of various optical microcavities possessing whispering gallery modes (WGMs) with enhanced optical performance represents one of the fascinating technologies in the field of photonics in recent years. Several research groups across the globe were involved in the development of different types of WGM resonators that possess a very high-quality factor (Q-factor).^{1–7} The traditional silica microsphere coupled through a tapered optical fiber has shown high coupling efficiency where light transmission in the optical fiber becomes almost zero due to the energy transfer to the silica microsphere.⁸ Such silica-based optical microresonators could achieve a high Q-factor value up to 10¹⁰ with a very promising sensing ability.⁹ However, it requires good coupling, expensive nanopositioning systems, and careful handling. Also, the instability and inability to be used in an uncontrolled environment demand the development of alternative active optical resonators where there is no requirement of coupling via tapered optical fiber.^{10–13}

The first among such active microresonators to be developed included a dye or quantum dot doped polymer microspheres. However, the major problems encountered in such optical resonators includes photobleaching of dye molecules during prolonged excitation, extensive doping procedure, nonuniform doping of dye molecules or quantum dots, desorption of dye molecules or quantum dots from the polymer microspheres, etc. In this regard, optical microresonators made of luminescent materials including semiconductors and phosphors represent very promising candidates for developing active WGM microresonators.^{14–18} In recent years, several semiconductor materials have emerged as optical resonators because they can emit, modulate, confine, and transmit light.¹⁹ Among semiconducting materials, the intrinsic properties possessed by ZnO makes it a very promising material for developing WGM resonators in the UV region. Several research groups have reported the observation of WGMs in ZnO micro/nanostructures and demonstrated their lasing capabilities in the UV region.^{20–24} In our earlier work, we



Enhanced photoconductivity of CdS-polyaniline multilayer nanocomposites



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ABSTRACT

In this letter, we show an efficient charge separation and charge transfer mechanism in case of Langmuir–Blodgett prepared CdS-polyaniline nanocomposite thin films. Bearing large interfacial area and low scattering loss, such nanocomposites show photoluminescence (PL) quenching with variation in number of layers which is due to the proportional increase of quinoid structure and efficient charge separation between CdS and polyaniline (PANI). Shifting of PL peak is also confirmed due to competitive fluorescence between CdS and PANI. The photoilluminated efficient charge separation and charge transfer between CdS and PANI make them highly suitable for optoelectronic applications.

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1. Introduction

The need to develop inexpensive, highly efficient, long-durable photovoltaic devices using conducting polymer nanocomposites continues to stimulate the present era of technology with new approaches of fabrication. Here, we aim to study the photoconducting behavior of the nanocomposite of polyaniline (PANI) by layer-by-layer deposition technique. The study of electronic transport properties of the polymer composites is very important because of their potential applications in different fields such as the photovoltaic cells, chemosensors, Schottky barrier tuning, light-emitting diodes, and photocatalytic activity [1–5]. Composites of polymers formed especially from the group II–IV semiconducting inorganic nanoparticles like CdS, and CdSe and the organic conducting polymers like PANI and Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) are such efficient systems where charge separation across the interface is looked at in order to explain their better photo response [6–9]. A hybrid system made up of inorganic nanoparticles and the conducting polymers has advantages in respect to charge separation as it is easy to process large-area devices out of these composites. It is also possible to tune the energy gap and ionization potential of the inorganic nanoparticles by the modification of the polymer chain [10,11]. Further thickness-dependent or layer variation conductivity study may be an effective way to evaluate the efficiency of such nanocomposite systems. In this communication,

we have studied the CdS incorporated PANI nanocomposite thin film by variation in number of layers in order to explore the charge separation and charge transport [8]. The deposition of the nanocomposite has been carried out by the Langmuir–Blodgett (LB) technique where formation of organized layer structures with designed architecture and functionality can be achieved [12].

2. Experimental detail

PANI in the emeraldine salt (ES) form is procured from Sigma Aldrich and is dissolved in ammonia solution (Merck, 25% GR) overnight to get in the emeraldine base (EB) form. A solution of PANI in EB form is made in a mixed solvent of m-cresol and chloroform (1:9 ratio v/v). The solution is sonicated in an ultrasonicating bath continuously until the whole solution becomes blue in color. Camphorsulphonic acid (CSA) in a proportion of 5:1 by w/w to PANI is added to the above solution and then the solution is stirred for 12 hours at room temperature. The role of the incorporation of CSA into PANI has been discussed elsewhere [13]. The prepared green color solution is filtered to separate undissolved macromolecules. Two separate solutions of 2 mM concentration of each of CdCl₂ and Na₂S are prepared using methanol as solvent separately. The prepared solutions are ultrasonicated for 1 hour to get transparent solutions. Now carefully 10 drops (~2 mL) from each of CdCl₂ and Na₂S solution are mixed with PANI-containing solution. An LB deposition unit (Apex Instruments Co., India) is used to deposit the films of the CdS-PANI-CSA nanocomposites over the glass substrates (with roughness of ~1.5 nm) and indium tin oxide (ITO)-coated glass

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Diffusion mediated agglomeration of CdS nanoparticles via Langmuir–Blodgett technique

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ABSTRACT

We have reported a diffusion mediated agglomeration of cadmium sulphide (CdS) nanoparticles within cadmium arachidate (CdA_2) film matrix. The structural morphology and formation of CdS nanoparticles are characterized by X-ray diffraction (XRD), X-ray reflectivity (XRR), atomic force microscopy (AFM) and ultraviolet-visible spectroscopy techniques. X-ray diffraction (XRD) results show a change in bilayer difference from 53.04 Å to 43 Å after the sulphidation. An epitaxial growth of the films by ~ 5 Å after sulphidation is confirmed from atomic force microscopy studies. The particle size calculated from UV–vis absorption edges are found to be varying from 2.6 nm to 3.3 nm for the different layers. A lateral dimension of 72–80 nm from AFM measurements and a size of 2.6–3.3 nm have confirmed one side flat pseudo two-dimensional disk-like nanoparticles. UV–vis reflectivity peak at E_1 (A) confirms the formation of hexagonal CdS nanoparticles along the *c*-axis.

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1. Introduction

Cadmium sulphide (CdS) nanoparticles have been studied extensively due to their large applications in the field of optoelectronics such as the window element for solar cells [1], photovoltaic cells [2] and optoelectronic sensors [3]. Fluorescent CdS nanoparticles are used efficiently in biology and medicine [4]. Other useful applications can also be found in humidity sensors [5], photo-catalytic activity [6], infrared photo-detectors [7], etc. In order to explore such useful semiconducting material one needs to investigate its properties to the fullest. Achieving ordered formation of such nano-entity has become a challenge where the modification in their physical properties as well as their configurations is needed [8,9]. In this respect, Langmuir–Blodgett (LB) technique for fabrication of nanoparticles might be a very effective tool [10,11]. An added advantage of the LB technique is that the nanoparticles can directly be synthesized onto a substrate for making devices [12].

In LB preparation of CdS nanoparticles, the organic fatty acid offers diffusion mediated agglomeration of CdS molecules along the film matrix. A chalcogenide gas, like hydrogen sulphide (H_2S) is allowed to react with the metallic salts of fatty acids such as CdA_2 to form the CdS nanoparticles [13]. In CdA_2 , cadmium ions are attached in between the polar head groups of fatty acids [14] and

this is sufficient to make two dimensional pseudo disk-like structures of CdS by exposing CdA_2 films to H_2S gas [13,15]. The layer by layer formation of the films manipulates the growth nature of the nanoparticles [16,17]. With such manipulation, LB prepared thin films in the ultrathin range have great use in the preparation of sheet semiconductor in nano-dimension [18]. One can also modulate the optical and electrical properties with respect to its definite bulk shaped CdS by varying the size to nano level [15,19]. Thus particles in nano-dimension size show equal importance in field of basic and applied interest.

We have studied the formation of CdS nanoparticles from CdA_2 by several techniques such as the X-ray diffraction (XRD), X-ray reflectivity (XRR), atomic force microscopy (AFM) and UV–vis absorption and reflectivity spectra. Diffusion mediated agglomeration of the CdS nanoparticles are dominated by the solution/substrate interfacial energy, critical Casimir induced aggregation [20] and the particle–particle interactions [21]. The definite phase transition during the agglomeration is not completely understood because of the non-equilibrium situation developed due to surface roughness, dewetting of the substrate by the subphase and other physical properties such as temperature, pH of the system. Both the XRD and AFM show the particular change in their characteristic measurements which confirms the formation of the CdS nanoparticles. Agglomeration of the nanoparticles can be studied by the calculation of fractal growths over the film surfaces. Such calculation is done from the logarithmic plot between radius of gyration and number of particles. The results show a definite power law which gives the variations in the fractal dimension (*D*) according to the layer numbers [20,22]. The blue spectral shift of

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Graphene oxide nanohybrids for electron transfer-mediated antimicrobial activity†

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and Dipankar Bandyopadhyay^{ID}*^{ab}

The rapid increase in the prevalence of antibiotic-resistant bacterial strains poses a global health risk. In this scenario, alternative strategies are needed to combat the alarming rise in multidrug-resistant bacterial populations. For example, metal-incorporated graphene derivatives have emerged as model nanomaterials owing to their intrinsic antibacterial activity together with their biocompatibility. Interestingly, photon-activated phthalocyanine sensitizers have also shown promising physicochemical biocidal effects against pathogenic bacteria populations when conjugated with diverse nanomaterials. Herein, we report the facile synthesis of graphene oxide incorporated zinc phthalocyanine (ZnPc–GO) nanohybrids showing bactericidal activity against Gram-negative *Escherichia coli* (*E. coli*) cells, in the absence of any photo-excitation. The ZnPc–GO hybrid nanomaterials were synthesized by the *in situ* deposition of GO flakes on ZnPc-coated indium tin oxide (ITO) substrates. Two types of morphologically different ZnPc molecules, potato-chip-like α -phase ZnPc, namely ZnPc(A), and nanorod-like β -phase ZnPc(B), were used for the synthesis of the ZnPc(A/B)–GO nanocomposites. The interactions of GO with the underlying ZnPc(A/B) entities in the ZnPc–GO systems were investigated using multiple characterization techniques. It was observed that the GO flakes in the ZnPc(B)–GO nanocomposite possess stronger π – π interactions and thus show a more efficient electron transfer mechanism when compared with the ZnPc(A) counterpart. Furthermore, the *E. coli* bacterial cells with an electronegative surface demonstrated a profound adherence to the electron-withdrawing ZnPc(B)–GO surface. The death kinetics of bacteria with ZnPc(B)–GO were further investigated using surface potential mapping and Kelvin probe force microscopy (KPFM) analysis. Upon direct contact with ZnPc(B)–GO, the adhered bacterial cells showed outer cell deformation and membrane protein leakage, induced by a proposed charge-transfer mechanism between negatively charged cells and the electron-withdrawing ZnPc(B)–GO surface. These new findings may provide insights into the design of potential ZnPc–GO-based novel antimicrobial nanomaterials or surface coatings.

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1. Introduction

The abrupt rise in bacterial mutagenesis has led to widespread antibiotic-resistant infections worldwide, thereby posing a serious threat to public health.^{1,2} Antibiotics are frequently administered to destroy or inhibit the growth of pathogenic bacteria. However, the exhaustive medical use and misuse of antibiotics has minimized their efficacy, which is attributed to the rapid emergence of antibiotic-resistant strains.³ In order to avert the antibiotic-resistance crisis, researchers are exploring innovative combat strategies to restrain the spread of bacterial

pathogens.^{4–7} In the recent past, the bactericidal and bacteriostatic efficacy of nanomaterials has been widely studied as a promising alternative to conventional antibiotic-based treatment.^{8–11} In this context, innovative methods like sensors,^{12,13} bacteriophage-based systems,¹⁴ thin film patterns¹⁵ and microfluidics^{16,17} have been employed for deactivation of pathogenic threats in the recent past. Amongst these methods, graphene-based nanomaterials^{18,19} have been extensively used as antimicrobial agents for numerous biomedical applications in recent years.^{20–22}

Graphene derivatives exhibit antimicrobial properties against a wide range of Gram-positive and Gram-negative pathogenic bacterial biofilms.^{23,24} The ease of surface modification by direct incorporation of functional groups or extrinsic mesoscale materials on the graphene surfaces promotes their usage for antimicrobial therapy.^{25,26} The antimicrobial efficacies of graphene derivatives can be further enhanced *via* surface functionalization with metals.²³ For example, metallic

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Structural and surface morphological studies of long chain fatty acid thin films deposited by Langmuir–Blodgett technique

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Surface roughness

ABSTRACT

In the present work we aim to study the structural and surface morphological characteristics of divalent cation (cadmium ion, Cd^{2+}) induced thin mono- to multilayer films of fatty acids such as arachidic acid and stearic acid prepared by the Langmuir–Blodgett (LB) technique. These ultra thin films of various numbers of layers were studied by X-ray diffraction (XRD), X-ray reflectivity (XRR) and Atomic Force Microscopy (AFM). In this specific Y-type deposition, it was found that as the individual layer thickness increases, the corresponding layer by layer interfacial electron density of the thin films decreases. Since the fatty acid chain tries to maintain its minimum value of cross-sectional area, tilting occurs with respect to its nearest neighbor. The tilt angle calculated for 9 layers of cadmium arachidate (CdA_2) and cadmium stearate (CdSt_2) are 18° and 19.5° , respectively. An asymmetric air gap of thickness $\sim 3 \text{ \AA}$ was also seen between the tail parts of 2 molecular chains. The RMS roughness and average height factors calculated through AFM studies show non-uniform surface morphology of both CdA_2 and CdSt_2 , although the calculated topographic variations were found to have more irregularity in case of CdSt_2 than in case of CdA_2 .

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1. Introduction:

LB films have shown wide application in devising sensors [1,2], molecular field-effect transistors [3], catalytic activity [4], synthesis of DNA–protein complexes [5], etc. Film deposition by this method is easy and cost-effective as compared to other processes like molecular beam epitaxy, sputtering technique, etc. In this method ordered orientation and molecular control over the layer by layer deposition of thin films of fatty acids of amphiphilic character can be achieved [6–10]. Fabrication of well ordered and efficient structures depends on proper handling of the molecular flexibility and complexity at the nanoscale region of the system. Defects [11] and instability [12,13] in metal–organic LB films, are treated as obstacles to the synthesis of films. The Pinhole defects [14] in such metal–organic LB films are infrequently observed. Reproducibility of the LB films is compromised due to presence of such defects. However by maintaining control over the subphase pH and further controlling the deposition parameters, reproducibility of the films can be achieved [15]. Parameters like compression pressure should be optimized and the rate of deposition is also controlled to get maximum interaction between the substrate and the hydrocarbon chain of film material. These features restrict overturning of the newly deposited layer [16].

Incorporation of a different divalent metal cation having different electro-negativity in the negatively charged head group of the organic acid also favors better deposition [17–19]. In many cases change of substrate can be found to be very effective [20].

In this report, detailed studies of the structural and surface morphological behavior of such cation induced fatty acids have been conducted. Since basic properties like the chain length, tilt angle, surface roughness, and height–height correlations are the most important parameters for the metal–organic LB films, one can take measures to handle these parameters to improve the film quality. The chain length and tilt angle are calculated from the out-of-plane X-ray diffraction (XRD) technique. In-plane XRD studies show a hexagonal structure for monolayers which steadily changes to an orthogonal structure for multilayer depositions [21]. A typical X-ray reflectivity study shows that an asymmetry (air gap) is associated with the individual bilayer structure. The RMS roughness measured through Atomic Force Microscopy (AFM) varies slower in case of CdA_2 than in CdSt_2 . The roughness, calculated from the XRR studies for bilayer deposition is also complemented with the AFM study.

2. Experimental details

Thin films of CdA_2 and CdSt_2 were prepared using the Langmuir–Blodgett apparatus (Apex Instrument Co., India). Stearic acid and

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Dynamics of roughening and growth kinetics of CdS–polyaniline thin films synthesized by the Langmuir–Blodgett technique

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Thin films of cadmium sulphide (CdS) nanoparticle induced polyaniline (PANI) nanocomposites have worked as a better system for application in photovoltaics due to the efficient charge separation and charge transfer. In this communication, we have chosen such a system of varying thickness deposited by the Langmuir–Blodgett (LB) technique in order to study the growth and roughness phenomena by dynamic scaling theory. Different techniques such as X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and X-ray reflectivity (XRR) are used for characterization of these films. In the study, the growth exponent, β , is found to have a correlation with the invariant logarithmic scaling law. A very large value of $\beta = 1.18 \pm 0.23$ as calculated is a result of the rapid roughening in the multilayer film growth process. We have investigated the dynamic scaling behavior of the multilayer system which shows a difference in the value of the coarsening factor and this confirms the breakdown of self-affinity as a consequence of some nonlocal growth effects. The normal grain formation with deposition at the initial stage and the increase in grain abnormality with increase in thickness is also verified in support of the dynamic scaling ansatz. In the present study the layer-by-layer deposition is confirmed by XRR fitting for a 3 layer film whereas the multilayer shows diffusing behavior due to H-bonding or electrostatic interactions.

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1. Introduction

Multilayer composites of semiconducting nanoparticles and conducting polymers provide large contributions in the field of photovoltaics, heterogeneous catalysis, sensors, actuators *etc.*^{1–6} In order to prepare a thin film of composite material for practical applications, we need a better understanding of the mechanism of their self-assembly at the molecular level. Optimized results for polymer composite devices can be achieved when molecular control over multilayer deposition is gained. However, this requires precise knowledge of the physics and chemistry of such materials.^{7,8} The improvement in properties by controlling the aggregation of semiconducting nanoparticles in polymer is a challenge as the nanoparticles are highly unstable in the polymer matrices. Research has been carried out by using the surfactant and other shielding agents to incorporate such nano-entities within the polymer chains. Although the approach for nanoparticle dispersion in polymer is successful

in some cases,^{2–5,9} in the present work we have found that the particles can exhibit self-assembly into some agglomerated structures. Reports confirming such aggregated dispersions show beneficial effects on the mechanical properties of the resulting nanocomposites.¹⁰

Polyaniline (PANI) is regarded as one of the most promising organic compounds due to its conductivity in the emeraldine salt (ES) form and also for the ease in the process of its synthesis.¹¹ In the emeraldine base (EB) form this polymer is chemically doped with different acids like hydrochloric acid (HCl), camphorsulphonic acid (CSA), dodecylbenzenesulphonic acid (DBSA) *etc.* to convert to ES form.^{12–14} The characteristic tunability of electrical and optical properties as well as the higher stability of PANI make them highly suitable for organic electronic devices. The properties of PANI are further enhanced by the change in the oxidation states or by blending with other nanosized semiconducting materials.¹⁵ In this respect, cadmium sulphide (CdS) incorporated PANI nanocomposites have been used in photovoltaic applications due to the formation of large internal area which can facilitate efficient charge transfer.^{15,16} Devices made out of such nanocomposites exhibit reduced light scattering effects and charges generated are easily transported by the respective carrier to the specific electrodes.¹⁷ It has been reported that the enhanced charge transfer is only possible if the charge carrying species find the easy paths for the electrode to carry the charges. Thickness variation of the

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PAPER

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Comparative study of optical, structural and electrical properties of zinc phthalocyanine Langmuir–Blodgett thin film on annealing

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Zinc phthalocyanine (ZnPc) in the mixture of *N*-methyl pyrrolidone (NMP) and chloroform (CHCl₃) [1 : 10 (v/v)] spreading solvent was observed to have only a monomeric absorption peak. However, on processing the solution into a thin film using the Langmuir–Blodgett (LB) technique, it shows absorption peaks corresponding to H, J and monomer aggregates, as confirmed by UV-Vis absorption spectroscopy. The Q-band absorption spectra of ZnPc LB thin film was observed to have a sharp change on annealing at 65 °C, indicating a change in the aggregation configuration of molecules over the surface. The annealed ZnPc LB thin film is found to have H and monomer aggregates only, which indicates that ZnPc molecules are arranged in an edge on face-to-face conformation. The ZnPc LB thin film remains in this aggregation until the higher annealing temperature. The ZnPc LB thin film shows an α -phase characteristic when annealed at 65 °C, and it remains intact in this phase up to 200 °C. The α – β phase transformation starts occurring from 200 °C and is completed at 290 °C. The large increase in crystallite size, as obtained from the XRD study, and the change in the shape of the ZnPc nanoparticles from spherical to nanorod structure, as observed from FESEM and AFM images, confirms the transformation of the ZnPc film from metastable α phase to stable β phase. Electrical conductivity is found to be enhanced considerably for β -phase with respect to α -phase in dark and under photoexcitation because of better charge carrier transport.

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Introduction

In organic electronic devices, the structural integrity and uniformity of the organic active layer on different interfaces is highly desirable for optimum device performance.¹ The control of the preferential orientation of the π -stacking direction in a thin film, *i.e.* the direction of favorable charge transport in conjugated materials, is essential to improve transport performances in devices such as organic field effect transistors (OFETs) and organic solar cells.² Among the organic semiconductors, the metallophthalocyanines (MPcs) have attracted significant interest because of their high thermal and chemical stability, high molecular symmetry, and favorable optical properties³ combined with unique electronic properties. MPcs consisting of a central metallic atom bound to π conjugated ligand and the chemical structure of these materials has a similarity with biological molecules such as chlorophyll and hemoglobin. Among the MPcs molecules, the zinc phthalocyanine (ZnPc) has been used largely because of its semiconductor property and high absorption coefficient (peak value of

$1.5 \times 10^5 \text{ cm}^{-1}$) in the wavelength range of 600–750 nm, and is a popular candidate for small molecules organic solar cells.^{4–6}

To tailor these materials for applications in efficient devices, it is important to have proper knowledge regarding the crystallinity and morphology of their thin films, their optical property and transport properties. This makes it necessary to understand the emergence of aggregation behavior of the molecules and polymorphism in thin films of these macrocyclic π -conjugated materials because it directly impacts device performances. The growth of organic molecules depends on the interaction of the molecules with different types of surfaces.⁷ The weakly interacting substrates have small surface free energy (mainly oxides such as SiO₂, glass, Al₂O₃ and polymeric substrate), which preferentially favor the upright standing growth of planar and nearly linear extended molecules for thin film deposition because the van der Waals and π – π interaction with neighbours is energetically preferred over the molecule–substrate interaction.⁸ Similarly, on strongly interacting metallic surfaces, the organic molecules adopt a flat lying molecular orientation.⁹

Supramolecular self-assembly is a very useful technique to fabricate molecular materials¹⁰ to investigate properties such as electrical conductivity and sensing. Phthalocyanine molecules have a tendency of self-aggregation to form dimers and higher order aggregates in solution and at the solid–liquid interface¹¹

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Growth and Structural Study of Cadmium Arachidate Multilayers Deposited by LB Technique

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Langmuir–Blodgett (LB) multilayer films of cadmium arachidate acid (CdAA) have been studied by X-ray diffraction and X-ray reflectivity techniques, which reveal uniform ordered packing of CdAA molecules with a small tilt angle of long alkyl chain equal to 6.8°. Electron density profiles reveal that the coverage of films remains almost constant with increase in bilayer thickness, which indicates very little presence of pinhole defects. FTIR studies confirm orthorhombic packing in CdAA LB films and the formation of unidentate bridging metal-carboxylate coordination type headgroups consistent with one cadmium metal ion between two carboxylic (COO) groups in each headgroup.

Keywords: CdAA LB film, monolayer, uniform stacking, tilt angle

Introduction

Highly ordered thin films of various organic materials having amphiphilic property are prepared extensively by Langmuir–Blodgett (LB) technique because of its great efficiency in controlling the film thickness and uniformity of the ordered multilayers.^[1,2] In LB films the organic amphiphilic molecules are arranged in a regular two-dimensional manner in each monolayer (ML) and the number of MLs to be deposited can be controlled to any desired value. Because of this layered and molecular order, LB multilayers are suitable precursor for the growth of nanoparticles, nanowires, and microparticles on solid substrate having better control over the size, shape, and distribution of them.^[3]

In recent years, metal-organic multilayers such as LB films have gained much importance among the researchers because of their potential applicability in molecular electronics, non-linear optics, and biosensors, and as templates for growing functional nanomaterials such as quantum dot.^[4,5] Because when different divalent cations of transition metals having considerable electronegativity such as Cd²⁺, Ca²⁺, Mn²⁺, Zn²⁺, and Ba²⁺ are incorporated into their headgroup structure of long-chain fatty acid, they play an important role in forming stable ML of fatty acid over water subphase. This greatly increases the ease of deposition of the ML over

substrate, which led to better ordered organization of LB multilayers on solid substrates.^[6] This ordered organization is mainly attributed due to the formation of headgroup-headgroup interfaces, which are stabilized by the strong electrostatic interaction with divalent metal cations at the expense of the headgroup-substrate and headgroup-water interfaces.^[7,8]

LB process is economical and has better molecular-level control compared to techniques such a molecular beam epitaxy (MBE), RF and DC sputtering, metal-organic chemical vapor deposition (MOCVD). However, low reproducibility owing to presence of pinhole type growth defects^[9,10] limits its applications. Therefore it is important to reduce the “pin-hole” type growth defects, which are formed due to the lack of deposition of the film-forming molecules and depend strongly on the subphase pH and dissolved metal ions.^[11] This defect can be reduced partially by increasing pH.^[12] This particular aspect has been considered in the present study to see the change in the surface property of the CdAA multilayer films with increase in pH value compared to the earlier work done at pH ~6.0.^[13]

The cadmium arachidate acid (CdAA) helps to improve the surface wetting properties (i.e., hydrophobic and hydrophilic property) of different substrate, which changes the surface energy of the substrate.^[14] Also CdAA ML forms a suitable matrix for the epitaxial growth of cadmium sulfide and that it can be used to control the morphology, size, and orientation of the growing crystals.^[15,16]

The growth and interfacial structure of these LB multilayer films have been characterized by X-ray diffraction (XRD) and X-ray reflectivity (XRR) technique. FTIR spectroscopy is useful to study the hydrocarbon tail packing and

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Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lrsrt.



UV-Ozone mediated miniaturization of dewetted polymeric nanostructures on graphene-oxide-flakes for enhanced Raman scattering



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ABSTRACT

Pre-decorating graphene-oxide (GO) flakes on silicon (Si) substrate led to the pattern directed dewetting of ultrathin polystyrene (PS) films. The size and periodicity of the PS droplets on the GO flakes were found to be much smaller than the same on the homogeneous Si substrate. Interestingly, when the dewetted PS droplets were exposed to UV-Ozone (UVO), polystyrene/polystyrene-oxide (PS/PSO) nanostructures of size less than 100 nm with sub-micron periodicity were formed. The UVO exposure facilitated, (i) catalytic conversion of PS into the lower molecular weight PS/PSO; (ii) heating beyond the glass transition temperature of PS/PSO because the UV rays concentrated at the GO-PS interface owing to the translucency (opacity) of the PS droplets (GO flakes); (iii) rapid spreading, thermal expansion, and breaking of PS/PSO droplets to form GOPSO nanocomposites. The nanocomposites enhanced the Raman signals of rhodamine6G (Rh6G) dye, which could be the highest among the recently reported chemical pathway of Surface-Enhanced-Raman-Scattering (SERS) of graphene and its derivatives. Density-of-states (DOS) computations uncovered that the defects induced strain effects on GO, confinement of light at the GO-PS/PSO interface, and the band gap reduction of GO cumulatively engendered the SERS effect.

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1. Introduction

Characterization of materials employing Raman spectroscopy (RS) has enriched diverse areas of science and technology such as solid-state physics [1], analytical chemistry [2], molecular biology [3], and forensic science [4], among many other domains. In the latter half of the previous century, perhaps, the discovery of LASER [5], and surface Plasmon resonance (SPR) have intensified the utility of the RS especially in the areas of materials science [6], nano- [7] and bio-technology [8]. Presently, the major focus of research has been in boosting the weak signals of the Raman active materials by embedding the specialties of quantum dots, 1D and 2D materials for diverse smart applications [1–8]. For example, the surface (surface enhanced Raman scattering – SERS) [7] of a material or the tip of an atomic force microscopy cantilever (tip

enhanced Raman scattering – TERS) [9,10] consisting of Au or Ag nanostructures, have shown their capacity to enhance the RS signals through localized surface Plasmon resonance (LSPR) [11].

However, most of these nanostructured surfaces are prepared employing costly fabrication techniques such as sputtering, lithography, reactive ion etching, or physical or chemical vapor depositions. Thus, of late, extensive research activities have been observed in developing cost-effective methodologies employing the smart materials, which can magnify the RS signals by many folds. For example, graphene and its derivatives have recently been experimented extensively to obtain SERS signals [12]. The studies suggest that although the SERS on the noble metals manifest through the electromagnetic mechanism (EM), the same can manifest in the graphene and its derivatives following the chemical mechanism (CM) [13–21]. Large enhancement of SERS due to GO with UV-Ozone (UVO) exposure [19] and use of graphene as the SERS probe have already been reported in the literature. In this study, we show a simple and cost-effective way to synthesize and self-organize nanostructures composed of graphene oxide (GO) and polystyrene (PS) nanocomposites, which is capable of

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Graphene oxide nanohybrids for electron transfer-mediated antimicrobial activity†

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and Dipankar Bandyopadhyay^{ID}*^{ab}

The rapid increase in the prevalence of antibiotic-resistant bacterial strains poses a global health risk. In this scenario, alternative strategies are needed to combat the alarming rise in multidrug-resistant bacterial populations. For example, metal-incorporated graphene derivatives have emerged as model nanomaterials owing to their intrinsic antibacterial activity together with their biocompatibility. Interestingly, photon-activated phthalocyanine sensitizers have also shown promising physicochemical biocidal effects against pathogenic bacteria populations when conjugated with diverse nanomaterials. Herein, we report the facile synthesis of graphene oxide incorporated zinc phthalocyanine (ZnPc–GO) nanohybrids showing bactericidal activity against Gram-negative *Escherichia coli* (*E. coli*) cells, in the absence of any photo-excitation. The ZnPc–GO hybrid nanomaterials were synthesized by the *in situ* deposition of GO flakes on ZnPc-coated indium tin oxide (ITO) substrates. Two types of morphologically different ZnPc molecules, potato-chip-like α -phase ZnPc, namely ZnPc(A), and nanorod-like β -phase ZnPc(B), were used for the synthesis of the ZnPc(A/B)–GO nanocomposites. The interactions of GO with the underlying ZnPc(A/B) entities in the ZnPc–GO systems were investigated using multiple characterization techniques. It was observed that the GO flakes in the ZnPc(B)–GO nanocomposite possess stronger π – π interactions and thus show a more efficient electron transfer mechanism when compared with the ZnPc(A) counterpart. Furthermore, the *E. coli* bacterial cells with an electronegative surface demonstrated a profound adherence to the electron-withdrawing ZnPc(B)–GO surface. The death kinetics of bacteria with ZnPc(B)–GO were further investigated using surface potential mapping and Kelvin probe force microscopy (KPFM) analysis. Upon direct contact with ZnPc(B)–GO, the adhered bacterial cells showed outer cell deformation and membrane protein leakage, induced by a proposed charge-transfer mechanism between negatively charged cells and the electron-withdrawing ZnPc(B)–GO surface. These new findings may provide insights into the design of potential ZnPc–GO-based novel antimicrobial nanomaterials or surface coatings.

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1. Introduction

The abrupt rise in bacterial mutagenesis has led to widespread antibiotic-resistant infections worldwide, thereby posing a serious threat to public health.^{1,2} Antibiotics are frequently administered to destroy or inhibit the growth of pathogenic bacteria. However, the exhaustive medical use and misuse of antibiotics has minimized their efficacy, which is attributed to the rapid emergence of antibiotic-resistant strains.³ In order to avert the antibiotic-resistance crisis, researchers are exploring innovative combat strategies to restrain the spread of bacterial

pathogens.^{4–7} In the recent past, the bactericidal and bacteriostatic efficacy of nanomaterials has been widely studied as a promising alternative to conventional antibiotic-based treatment.^{8–11} In this context, innovative methods like sensors,^{12,13} bacteriophage-based systems,¹⁴ thin film patterns¹⁵ and microfluidics^{16,17} have been employed for deactivation of pathogenic threats in the recent past. Amongst these methods, graphene-based nanomaterials^{18,19} have been extensively used as antimicrobial agents for numerous biomedical applications in recent years.^{20–22}

Graphene derivatives exhibit antimicrobial properties against a wide range of Gram-positive and Gram-negative pathogenic bacterial biofilms.^{23,24} The ease of surface modification by direct incorporation of functional groups or extrinsic mesoscale materials on the graphene surfaces promotes their usage for antimicrobial therapy.^{25,26} The antimicrobial efficacies of graphene derivatives can be further enhanced *via* surface functionalization with metals.²³ For example, metallic

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† Electronic supplementary information (ESI) available: Characterization of GO, XPS measurement data of samples, work function calculations, and FESEM images of bacteria. See DOI: 10.1039/c9na00272c



Enhancement of defect induced micro-photoluminescence intensity in Er doped ZnO

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Abstract—The enhanced micro-photoluminescence (μ -PL) emission property of Er doped ZnO was systematically investigated. The observed μ -PL spectra showed that ZnO microsphere doped with 3 mol% of Er gives the maximum intensity of optical emission.

Keywords— micro-photoluminescence, ZnO, microsphere

I. INTRODUCTION

Now-a-days the focus of photonics is extremely demanding as it deals with the enhancement in the light-matter interactions. Out of the various types of photonic structures whispering gallery mode (WGM) resonators are quite popular due to its multifaceted applications. Such kinds of resonators have been employed in the development of optoelectronic devices, sensors and lasers etc [1-2]. Specifically for the development of optical micro sensor, various shapes of resonators such as ring, disc, cylindrical, toroidal and spherical have been introduced by different research groups[3-7]. In recent years some optical microcavities based on semiconducting materials have been explored to solve the purpose. But the micro resonators made up of ZnO material have been widely used so far due to its tremendous optoelectronic properties. ZnO has attracted many researchers to investigate its potential applications in UV region due to its wide band gap around 3.37 eV [8]. But the presence of point defects in ZnO causes emission from visible to near infra-red region with proper excitation wavelength. So in the recent past the WGM from an individual ZnO microsphere was also explored by using visible excitation [9]. Here we targeted to get enhancement in micro photoluminescence intensity of a single ZnO microsphere through Er doping in the visible region. According to best of our knowledge the study of defect induced WGM of ZnO by doping with Er in the visible region is not reported so far.

II. EXPERIMENTAL

Synthesis of bare ZnO and Er doped ZnO(Er-ZnO) microspheres were done by one-pot hydrothermal process as described in our earlier report [10]. For the preparation of undoped and doped ZnO microspheres zinc nitrate hexahydrate, hexamethylenetetramine and erbium (III) nitrate pentahydrate of Sigma-Aldrich and trisodium citrate of Merck were used. 0.5, 1.5 and 2.5 mM of erbium (III) nitrate were added to prepare 1,3 and 5 mol% of Er-ZnO .

III. RESULTS AND DISCUSSIONS

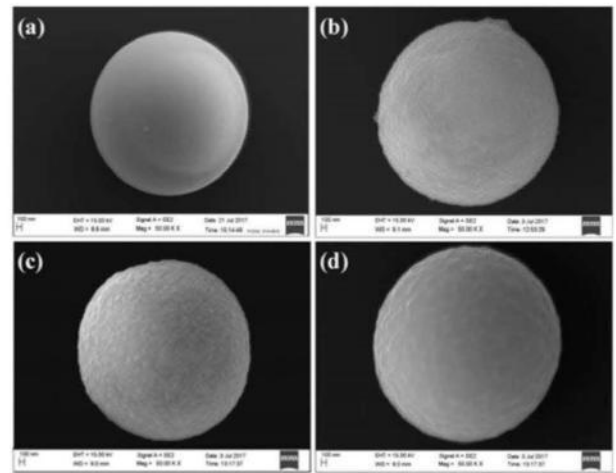


FIG. 1. (a)–(d) The FESEM images of single undoped ZnO, 1, 3 and 5mol. % of Er-ZnO microspheres, respectively.

From the FESEM images of FIG.1. it is cleared tht the surface roughness increases through doping.

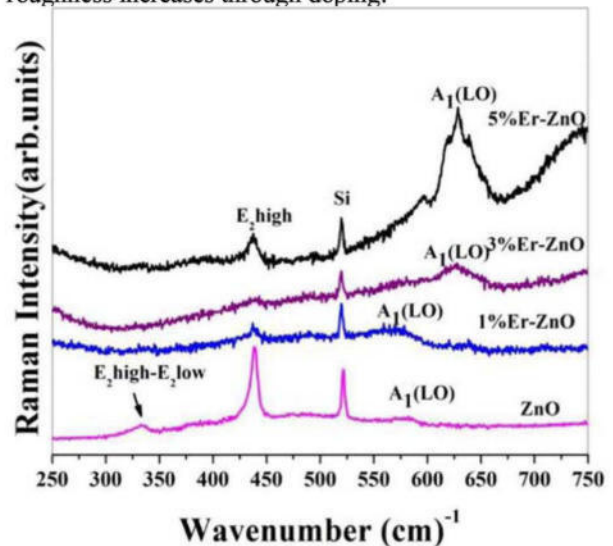






FIG. 2. The room temperature micro-Raman spectra of individual undoped ZnO, 1, 3 and 5 mol. % Er-ZnO microsphere.

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Microdroplet photofuel cells to harvest high-density energy and dye degradation†

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In this study, a membraneless photofuel cell, namely, μ -DropFC, was designed and developed to harvest chemical and solar energies simultaneously. The prototypes can also perform environmental remediation to demonstrate their multitasking potential as a sustainable hybrid device in a single embodiment. A hydrogen peroxide (H_2O_2) microdroplet at optimal pH and salt loading was utilized as a fuel integrated with Al as an anode and zinc phthalocyanine (ZnPC)-coated Cu as a cathode. The presence of n-type semiconductor ZnPC in between the electrolyte and metal enabled the formation of a photo-active Schottky junction suitable for power generation under light. Concurrently, the oxidation and reduction of H_2O_2 on the electrodes helped in the conversion of chemical energy into the electrical one in the same membraneless setup. The suspension of Au nanoparticles (Au NPs) in the droplet helped in enhancing the overall power density under photonic illumination through the effects of localized surface plasmon resonance (LSPR). Furthermore, the presence of photo-active n-type CdS NPs enabled the catalytic photo-degradation of dyes under light in the same embodiment. A 40 μL μ -DropFC could show a significantly high open circuit potential of ~ 0.58 V along with a power density of 0.72 mW cm^{-2} . Under the same condition, the integration of ten such μ -DropFCs could produce a power density of ~ 7 mW cm^{-2} at an efficiency of 3.4%, showing the potential of the prototype for a very large scale integration (VLSI). The μ -DropFC could also degrade $\sim 85\%$ of an industrial pollutant, rhodamine 6G, in 1 h while generating a power density of ~ 0.6 mW cm^{-2} . The performance parameters of μ -DropFCs were found to be either comparable or superior to the existing prototypes. In a way, the affordable, portable, membraneless, and high-performance μ -DropFC could harvest energy from multiple resources while engaging in environmental remediation.

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1. Introduction

Infusing the efficacies of nanoscale science^{1,2} in microfluidic devices for the development of affordable and portable energy harvesters with a significantly high power density has attracted major research attention in the recent years. The inventions of state-of-the-art thermoelectric, triboelectric, piezo-acoustic, electrokinetic, or Marangoni energy harvesters are directed towards this end.^{3–9} Interestingly, the traditional renewable¹⁰ or non-renewable¹¹ energy-harvesting technologies have also been

undergoing a paradigm shift from the regime of macroscopic to the very large scale integration (*e.g.* VLSI) of micro or nanoscopic prototypes for enhanced efficiency, higher throughput, and escalated power density.¹² Thus, it is not very surprising that a flurry of research activities has also been observed in the miniaturization along with process intensification¹³ of more widely employed commercial energy harvesters such as batteries,^{14,15} photovoltaic cells,¹⁶ or fuel cells^{17,18} for better efficiency.

In particular, since the path-breaking invention by Sir William Grove in the 18th century¹⁹ to convert chemical energy into the electrical one, fuel cells (FCs) have shown remarkable progress²⁰ despite numerous setbacks.²¹ For example, the utility of the FCs as isolated or distributed power resources has now been translated into a few megawatt plants for power supply.¹⁷ A large varieties of FCs composed of polymer electrolyte membranes, phosphoric acid, methanol or alkali have made appearance at different lengths and performance scales not only to power energy-intensive rockets but also to run miniaturized micro-transmitters or biomedical devices.^{22–25} Presently, the fuels utilized in the FCs are either hydrogen (H_2), methanol

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[†] Electronic supplementary information (ESI) available: Nanocomposites characterization, effect of pH on power generation in presence of additives, electrode characterization before and after analysis, cell characterization employing dye degradation moieties, optimal additive loading in VLSI, efficiency calculations and description of supplementary videos. See DOI: 10.1039/c9na00785g

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Visible whispering gallery mode lasing via Li⁺ ion doped ZnO microspheres

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ABSTRACT

Here we have fabricated ZnO based microcavity as optical resonator to achieve whispering gallery mode (WGM) luminescence through visible excitations. We have observed defect related WGM emissions by individual ZnO microsphere through visible laser excitations of 532 nm wavelength. Further, in order to get visible stimulated emissions, we have considered the doping of 2 mol.% of monovalent (Li⁺) ion to increase the number of defects in ZnO. Nevertheless, here the ZnO and 2 mol.% Li doped ZnO (Li-ZnO) microcavities (microspheres) are synthesized by using hydrothermal synthesis technique. Here we have considered four distinguished 2 mol.% Li-ZnO microspheres to check the consistency of the stimulated emission behavior. We have observed that the stimulated emissions are achieved through all the four Li-ZnO microspheres at threshold pumping power density of 48 mW/cm² of the laser source. Therefore, we have proposed these doped microresonators for their promising applications to design the WGM based visible laser cavities.

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1. Introduction

Due to the exceptional optical properties with tuneable band-gap and the presence of various defect energy levels in between the conduction and valence band makes ZnO more versatile semiconducting material. To employ ZnO material in various photonic applications, vigorous research is done on it by exploring its photoluminescence properties. However, its self-luminescence property in a broad region through proper excitation energy, including sub-bandgap energy levels, makes ZnO a more suitable material for UV-visible optoelectronic devices [1]. Due to the possibility of various shapes of nano/microstructures with different quality of morphology in ZnO facilitates to build a different type of electrical and optical sensors [2–4]. Due to the low-toxicity of ZnO based nanoparticles, it is not only applied to gas, chemical, thermal, and pressure sensors but also very much useful in label-free biosensors [5–8]. Being a non-toxic material ZnO also used for various photocatalysis processes in dye degradation and water purification in addition to environment cleaning purposes [9]. ZnO is also one

of the favourite choices for UV lasing devices due to its distinctive optical properties and polariton effect during excitonic emission [10–12]. Though the photonic confinement is difficult through bulk ZnO excitation, yet strong coupling of exciton and photon provides enough strength for typical random lasing of the material [12]. Hence, the bulk photoluminescence properties of ZnO show its different applications in the field of photonics such as sensing, lasing and photocatalysis, etc.[8,13,14]. Furthermore, lots of work has been done towards this regime by using the bulk nanomaterial of ZnO. But in the recent past, the WGMs of ZnO are quite popular by exploring the micro-photoluminescence property of the single microparticle. There are different types of structures of ZnO that have been used to confine the light such as micro disk, micro rod and microspheres etc.[15–17] Moreover, microspheres are among the simplest resonators due to its symmetry in the structure due to its high Q-factor and easy to couple the light into it. However, most of the WGMs studies based on ZnO are only limited to UV excitation, though defect-related visible emissions are always observed [18]. Here, we aim to get visible emissions by exciting ZnO microspheres through visible excitations only so that it could be less harmful to cells and more useful for various biological applications [19]. Further, various earlier reports have suggested

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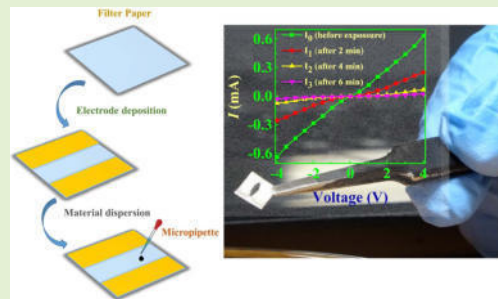
Paper Based Enzymatic Chemiresistor for POC Detection of Ethanol in Human Breath

Nirmal Roy, Shirsendu Mitra, Nayan Mani Das, Nilanjan Mandal, Dipankar Bandyopadhyay^{ID}, Harshal B. Nemade^{ID}, *Member, IEEE*, and Tapas K. Mandal^{ID}

Abstract—A paper based chemiresistor has been fabricated to selectively sense ethanol in human breath. The chemiresistor was composed of a sensing mixture of multiwall-carbon-nano-tubes (MWCNTs), poly (diallyldimethyl-ammonium chloride) (PDDA), alcohol dehydrogenase (ADH), and coenzyme (NADH). The aluminum electrode was deposited on the paper surface, followed by drop-casting of the aforementioned sensing mixture. The resistance of the sensors was measured by exposing the same in gas-vapor mixture as well as the sample solution. The surface-modified MWCNTs specifically broke down ethanol present in the gas-vapor mixture or in a solution to generate a quantitative electronic response proportional to the ethanol concentration.

Subsequently, the interference of other volatile organic materials was also tested to prove the selectivity and sensitivity of the sensor towards ethanol in the presence of different volatile organic compounds (VOCs). The variation of the resistance during the interaction between sensor and ethanol was also characterized by measuring the surface potential of the channel material under ethanol exposure using Kelvin probe force microscopy (KPFM). The sensor was integrated with a voltage divider circuit, a display, and a microcontroller unit to make a proof-of-concept prototype for the point-of-care (POC) detection of ethanol in human breath.

Index Terms—Chemiresistor, ethanol sensor, MWCNTs, paper.



I. INTRODUCTION

EXPOSURE to volatile organic compounds (VOCs) either as indoor or outdoor pollutants cause various ailments

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ranging from eye, nose, lung, liver, kidney to the central nervous systems [1]. The major sources of VOCs in the air are paints and their solvents, wood additives, aerosol sprays, cleansers and disinfectants, repellents, fuels, and automotive products [2]–[4]. Since most of the VOCs have a negative impact on the environment and subsequently on human health, point-of-care (POC) detection of them is perhaps the need of the hour [5]. For example, portable, inexpensive, and user-friendly VOC detection devices are already in use in the industries like food and beverage, paint, biomedical, pharmaceutical, and oil, among others [6], [7].

Apart from industrial gaseous or volatile effluents, VOCs are also present in human breath depending on abnormal metabolism or intoxications [8], [9]. Thus, of late, the POC detection of toxic VOCs in human breath has also become important to measure the quality of human health. Intake of alcoholic beverages can increase the concentration of ethanol in the exhaled air, which is an intoxicated state of health condition. In particular, driving under the influence (DUI) of alcohol has been deemed illegal beyond a permissible breath alcohol concentration (BrAC) of 0.05% - 0.08% owing to its fatal accidental consequences across the world [10]. Further, due to its flammable properties, sensing and detection of ethanol vapor are also essential during the large scale production of ethanol and fuel processing [11]. In this direction,

Optical and surface morphology study of zinc phthalocyanine Langmuir Blodgett thin film

Dhrubojyoti Roy, Nayan Mani Das, M. Gupta, V. Ganesan, and P. S. Gupta

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Optical And Surface Morphology Study of Zinc Phthalocyanine Langmuir Blodgett Thin Film.

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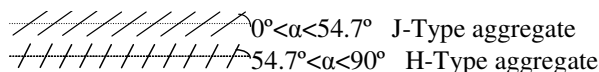
Abstract. The UV-Vis absorption spectroscopy analysis reveals that prominent J-aggregation of ZnPc molecules was observed in the LB films while no such aggregation was found in the solution. Change in fluorescence color of ZnPc LB film from its solution confirms the appearance of new aggregation.

Keywords: Langmuir-Blodgett Film; Aggregation; Fluorescence; Atomic Force Microscopy.

PACS: 68.47.Pe; 87.15.nr; 35.50.Dq; 68.37.Ps.

INTRODUCTION

Metallophthalocyanine (MPcs) nowadays are promising materials for advanced technical and medical applications. MPcs due to their semiconducting property properties are attractive for photodetectors, organic transistors, sensitive gas sensors, and photovoltaic cells. The inherent – stacking abilities of MPcs owing to large π system make these macrocycles easily organizable into supramolecular structures [1]. The optical and electrical properties of thin films of MPcs can be significantly different from those of single crystals or molecules in solution due to different stacking and aggregation behavior of MPcs in different medium. Therefore, in order to improve the performance of devices it is very much in need of having better knowledge of these thin layers MPcs samples. The aggregates can be classified as three types as face to face (H-type aggregate), monomer and edge to edge (J-type aggregate) [2].



EXPERIMENTAL

Spreading solution for LB Film deposition was prepared by dissolving the ZnPc at concentration of 1mg/ml into a mixture of N-methyl pyrrolidone (NMP) and chloroform [1:10 (v/v)]. Monolayer

formed by spreading the solution over the milli-Q water (pH~ 6.0 and resistivity~18M Ω cm) subphase in Langmuir trough was compressed to a pressure of 35 mN/m and was transferred onto quartz substrate using vertical deposition method of varying layers. A 40 L LB film of ZnPc is deposited here.

RESULTS AND DISCUSSION

UV-Vis Absorption Study

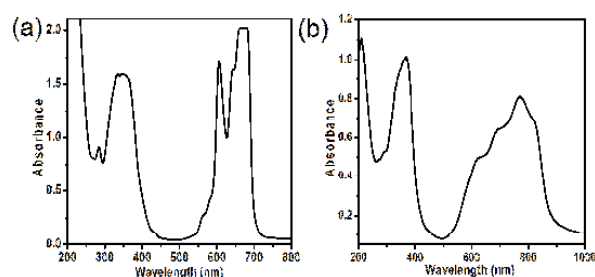


FIGURE 1. UV-Vis Absorption Spectrum of (a) ZnPc in (1:10) NMP+ Chloroform Solution, (b) 40 L ZnPc LB Thin Film.

The UV-Vis absorption spectra shown in Fig.1 are studied thoroughly, in order to investigate the possible aggregation behaviors of the ZnPc molecules in solution and in LB Thin Film. From the absorption spectra it is seen that the ZnPc solution has a strong

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Study of polymorphism of ZnPc LB thin film on annealing

Dhrubojyoti Roy, Nayan Mani Das, Mukul Gupta, and P. S. Gupta

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Study of Polymorphism of ZnPc LB Thin Film on Annealing

Dhrubojoyoti Roy^{a*}, Nayan Mani Das^a, Mukul Gupta^b, P. S. Gupta^a

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Abstract. The average molecular orientation in the as-deposited Zinc Phthalocyanine (ZnPc) Langmuir-Blodgett (LB) film has been obtained to be 47° w.r.t to substrate surface from polarized Raman spectroscopy analysis. Absorption spectroscopy confirms the phase transition of ZnPc thin film from α -phase to β -phase on annealing however, such confirmation could not get established from Raman spectroscopy.

Keywords: LB Thin Film, Phase Transformation, Annealing, Aggregates.

PACS: 68.47.Pe, 81.40.Vw, 81.40.Ef, 61.43Hv

INTRODUCTION

The core structure of the metallophthalocyanine (MPc) is formed by four isoindole units endowing the molecule with 2D conjugated π electron system. MPc occurs in many polymorphic phases α , β , χ and ε connected with different crystalline structure. The most popular are metastable α -phase and stable β -phase [1]. The both phase having herringbone structural arrangement. The main difference is the angle of inclination of the molecular plane w.r.t. the crystallographic ac-plane within the columns and the arrangement of the common columns in the crystalline structure. In α and β -phase, this is equal to 25°-35° and 40°-49° respectively [2]. These parameters play a significant role in the change of conductivity along the stacking molecules. The preferred orientation is usually determined by sample preparation conditions such as the type of substrate, temperature, and method of deposition.

EXPERIMENTAL

Initially, LB trough was filled with Milli-Q water having pH (~6.0). The ZnPc (Sigma-Aldrich) spreading solution was prepared by dissolving it at a concentration of 1mg/ml into a mixture of Trifluoroacetic Acid (TFA) and Chloroform (CHCl₃, Merck, Analytical Reagent) [1:10 (v/v)] solvent. Then using a microliter syringe 200 μ L of solution was spread and left undisturbed for 20 min for evaporation of the solvent. Then surface pressure – molecular area (π -A) isotherm was recorded by compressing the

spread monolayer over water surface at a rate of 5 mm/min. The spreading monolayer film was then transferred onto solid substrates using the vertical dipping method at a surface pressure π ~35 mN/m. We deposited a multilayer film of 33 layers ZnPc.

RESULT AND DISCUSSIONS

UV-Vis Absorption Spectroscopy

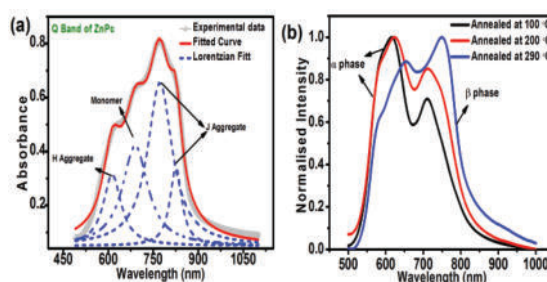


FIGURE 1. Q-band absorbance spectra of ZnPc thin film (a) in as-deposited state, (b) at different annealing temperatures.

The ZnPc molecules in the LB thin film over solid substrate shows three types of aggregates i.e. H, J and monomeric. Change in the aggregation or orientation of the ZnPc molecules takes place over the substrate surface on annealing has been confirmed from the change in Q-band absorption spectra (Fig.1) which occurs only after 55 °C. The annealed ZnPc LB thin film is comprised of H and monomer aggregates in

Structural, optical and electrical properties of CdS–polyaniline Langmuir–Blodgett films

Nayan Mani Das, Dhrubojyoti Roy, M. Gupta, V. Ganesan, and P. S. Gupta

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Structural, Optical and Electrical Properties of CdS– Polyaniline Langmuir–Blodgett Films

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Abstract. Structural, optical and electrical properties study of the cadmium sulphide (CdS) incorporated polyaniline (PANI) thin films with varying layers have been carried out. It is seen that layer variation enhances the particle mean sizes with quenching of photoluminescence and an increase in rectifying nature of current-voltage measurements.

Keywords: Langmuir-Blodgett Film, Atomic Force Microscopy, Photoluminescence, Electrical Properties.

PACS: 68.47.Pe; 68.37Ps; 78.55.-m; 73.61.Ey

INTRODUCTION

Organic materials including polymer assemblies are of immense importance due to their unique characteristics such as flexibility, self-organization and stimuli responsiveness. These physical parameters are highly responsible for practical applications in electronic systems such as organic semiconducting devices, organic solar cells, photovoltaics etc [1]. Such properties can also be enhanced by the change in the oxidation states or by blending with other nanosized semiconducting materials. In this respect, CdS incorporated PANI-camphorsulphonic acid (CSA) have been of great importance in photovoltaic applications due to the formation of large internal area which can enable the efficient charge transfer [2].

EXPERIMENTAL DETAILS

A solution of PANI in the emeraldine base (EB) form was prepared with 1 mg/ml concentration using m-cresol as solvent. CSA in a ratio 1:5 with PANI was added to the prepared solution. Adding chloroform in 9:1 with m-cresol the whole solution is diluted and is sonicated for 2 hours. Two separate solutions of cadmium chloride and sodium sulphide were prepared in methanol with 2 mM concentration and stirred to mix them completely. 10 drops from each of the solution were added to the PANI-CSA solution. The characteristic deep green color of the PANI-CSA solution turned into slightly yellowish-green color.

Langmuir-Blodgett thin film deposition technique was used for the film deposition purpose. 3 layers, 7 layers and 9 layers of the composite films were prepared.

RESULTS AND DISCUSSIONS

Structural Study

Fig. 1(a)–1(c) shows the AFM images of 3 layers, 7 layers and 9 layers of CdS incorporated PANI-CSA films. We used WSxM software for characterizing the AFM images. From the Fig. 1 it can be seen that as the number of deposition goes on increasing the thickness variation also shows the analogous trend. The particle sizes also exhibit an increasing property. The 3 layers in Fig. 1(a) show the uniform aggregation of the composite nanostructures over surface. This may be attributed to the Ostwald ripening of the nanoparticles. The particles with respect to its size variation can be interpreted by addressing the number of counts with the height variation as histograms, shown in the Fig. 1. The distribution can be fitted with the log-normal envelop from which the average diameter can be calculated.

$$y = \frac{1}{\sqrt{2\pi}\sigma D} \exp\left[-\left(\frac{\ln^2(D/D_c)}{2\sigma^2}\right)\right] \quad (1)$$

Where, σ and D_c are standard deviation and mean particle size. D represents the diameters particles.

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Chapter 2

Pathways to Translate the Biomedical Prototypes



Tamanna Bhuyan, Surjendu Maity, Devi Rupa Saha, Nayan Mani Das,
and Dipankar Bandyopadhyay

1 Introduction

Recent decades have witnessed remarkable technological advancements in healthcare devices that have been responsible for early and precise diagnosis, more successful treatments, and helping patients to lead healthier lives [1, 2]. However, because new technology primarily drives healthcare expenditures and product risks against benefits, a careful evaluation of primary critical paths, including product initiation, formulation, design, final validation, and product launch, is increasingly necessary for clinical practice [3–5]. The target audience for these activities is scientists, clinicians, and technologists to translate novel medical technologies from academia to the market [6, 7]. The global medical device industry is significantly technology-driven and progressing rapidly. However, in India, it is still in the nascent stage with restricted levels of availability of infrastructure, penetration, lack of trained human resources, adoption and out-of-pocket expenditures [8–10].

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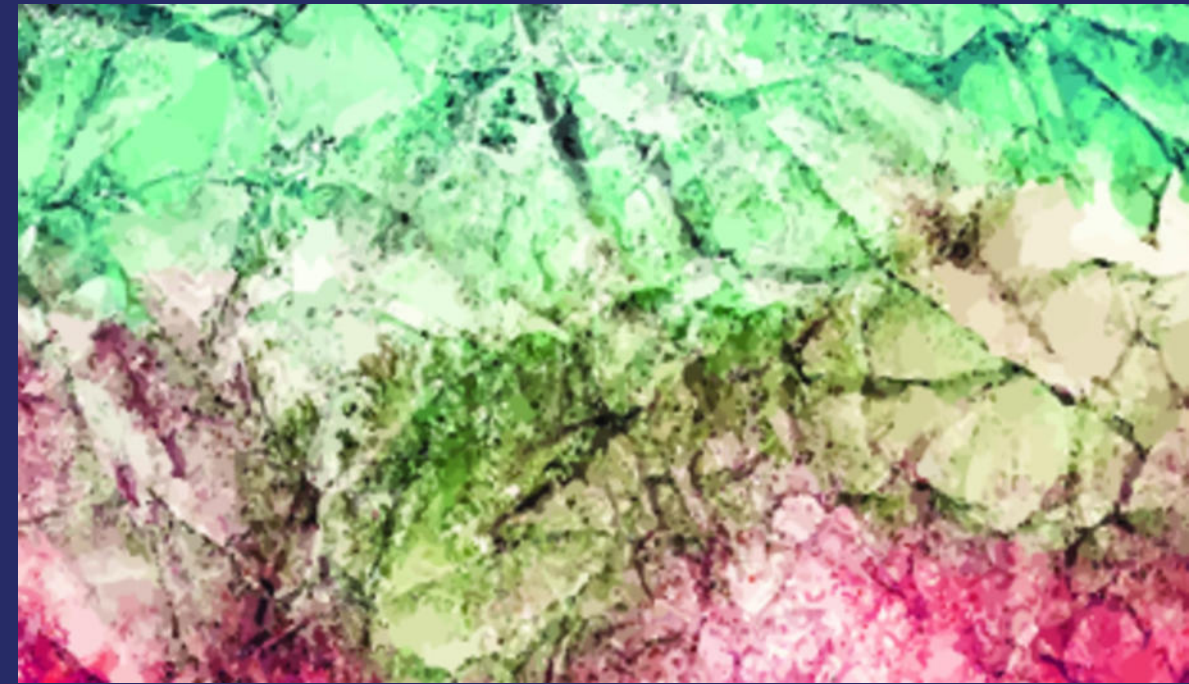
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Ultrathin Langmuir-Blodgett Films

Thin films based research finds application due to their compatibility with real life phenomena (such as bio-membranes, lipid-protein interactions) and fabrication of devices. Moreover, the ease in processing techniques and their flexibility towards the practical applications make them technically more reliable in today's modern era of technology. Apart from inorganic metal or semiconductor thin films, recently the most preferred and the important topic of research have been related to the subject of organized organic and polymer composites ultrathin films. For uniform and low cost synthesis, a number of chemical and physical synthesis processes have been applied throughout the last century and so. In the present work the fabrication of such important organic/polymer thin films have been tackled by the Langmuir-Blodgett (LB) deposition technique which is considered to be one of the best methods to handle uniformity in a system of monomolecular dimension.

Nayan Mani Das
Partha Sarathi Gupta

Structural dynamics study of ultrathin Langmuir- Blodgett films

Detail strategy to work on monomolecular organic
and composite films by Langmuir-Blodgett technique

• Dr. Nayan Mani Das has received his master and PhD in applied physics from IIT (ISM) Dhanbad in the years of 2010 and 2015 respectively. He is now pursuing his post doctoral research at IIT Guwahati. • Prof. Partha Sarathi Gupta has got his PhD from IIT Kharagpur and he is a professor now in the department of applied physics IIT (ISM) Dhanbad.



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