Perspective

In Situ Engineering of Conducting Polymer Nanocomposites at Liquid/Liquid Interfaces: A Perspective on Fundamentals to Technological Significance

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Mini Mol Menamparambath*

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ABSTRACT: The conducting polymers have continuously been hybridized with their counterparts to overcome the intrinsic functional limitations compared to the metallic or inorganic analogs. Remarkably, the liquid/liquid interface-assisted methods represent an efficient and facile route for developing fully tunable metamaterials for various applications. The spontaneous adsorption of nanostructures at a quasi-two-dimensional interface is energetically favorable due to the reduction in interfacial tension, interfacial area, and interfacial energy (Helmholtz free energy). This Perspective highlights the fundamentals of nanostructure adsorption leading to hierarchical architecture generation at the interface from an experimentalist's point of view. Thereafter, the essential applications of the conducting polymer/nanocomposites synthesized at the interface emphasize the capability of the interface to tune functional materials. This Perspective also summarizes the future challenges and the use of the known fundamental aspects in overcoming the functional limitations of polymer/nanomaterial composites and also provides some future research directions.

Advantages of Interfacial polymerization
- Liquid/liquid (L/L) interface as soft template
- Spontaneous polymerization
- Crystallinity modulation
- Nanostructure tuning
- Controlled synthesis

Organic/inorganic nanocomposites

KEYWORDS: *Conducting Polymers, Interfacial Polymerization, Liquid/Liquid Interface, Interfacial Tension, Self-Assembly*
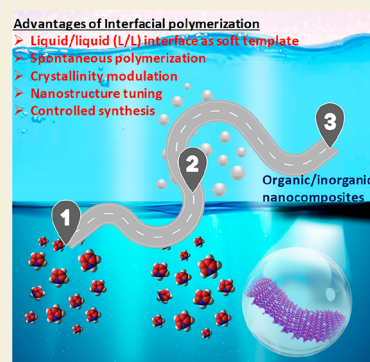
■ INTRODUCTION

In recent years, the development of polymer chemistry and its applications in novel technologies have expedited the amelioration of interfacial polymerization for the engineering of unique functional materials.[1] The increased interfacial free energy at the spatial boundary between two immiscible liquids has become a powerful fabrication technique for multifunctional polymeric nanostructures.[2] Further, the vivid efficacious attributes of nanoparticle-laden fluid interfaces have actively been employed for diversified applications such as oil-spill recoveries,[3,4] catalysis,[5,6] sensors,[7,8] electro-optics,[9,1] and more. The interface is a distinct entity with a thickness of less than a few nanometers, possessing characteristics substantially different from those of its organic or aqueous bulk phases. The immiscibility of the two liquid systems attributes to high interfacial tension (IFT) or "potential energy well" at the interface, where the nanostructures get impounded.[10] On the other hand, the stabilization of the energized interface is regulated by the durability of the adsorbed or assembled nanoparticles.[11,12] The immobilization of nanostructures at fluid interfaces is extensively achieved by cross-linking agents dispersed at different solvent phases or by encapsulating nanostructures using in situ polymerization techniques.[13,14] Moreover, the nanostructure encapsulation is the driving force for the self-organization of ultrathin polymeric films at the liquid/liquid (L/L) interface, whereas it is difficult in conventional methods due to their insolubility, dispersibility, or stringent deposition conditions.

Taking advantage of the competence of the high-energy interfacial layer to constrain the active monomers or oligomers in designing multifunctional polymer nanostructures at liquid/liquid interfaces is becoming ubiquitous among polymer technologists. Besides, the in situ engineering of inherently defect-free, highly crystalline, and uniform nanostructures is achieved by controlling the monomer concentrations or solvent systems during polymerization.[15] Further, the solution-based self-assembly technique offers the possibility to construct nanoscale or even molecular scale nanostructures from a bottom-up approach. Moreover, large-scale industrial processes are fascinated by exceptionally advantageous solution-based soft patterning techniques to construct nanostructures due to their cost effectiveness, high throughput, mild reaction conditions, etc.[2] Unlike previously reported methods on nanomaterial synthesis, the precise control of the dimensionalities without
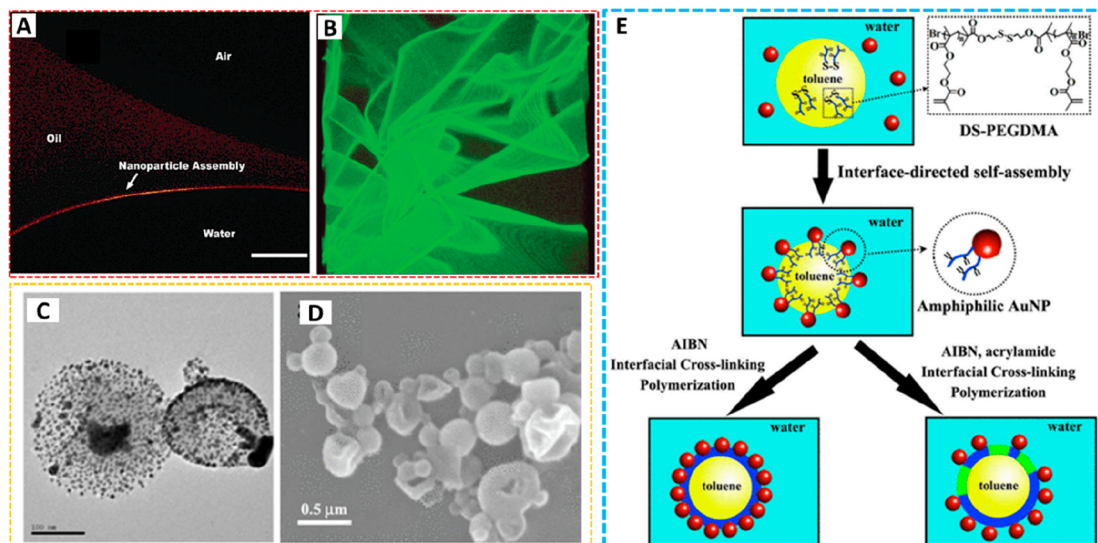
Figure 1. Fluorescence confocal microscopy illustrating the (A) preferential immobilization of tri-*n*-octylphosphine oxide (TOPO)-stabilized CdSe nanoparticles at the oil/water interface (scale bar: 70 μm) and (B) confocal microscope image of a nanoparticle sheet resulting from the cross-linking of associated organic ligands. The scale bar is 50 μm. Adapted from ref 20. Copyright 2003, American Chemical Society. (C,D) Transmission electron microscope (TEM) and scanning electron microscope (SEM) image of hollow capsules after being redispersed in tetrahydrofuran.[22] (E) Scheme for preparing amphiphilic AuNPs (one component and multicomponent) at the interface. Figures C−E were adapted from ref 22. Copyright 2012, American Chemical Society.

template imprints and simultaneous regulation of mesoporous structures provoked polymer technologists to invest a paramount interest in the interfacial polymerization strategy. It is important to note that tremendous efforts have been performed to utilize high-energy interfaces for chemical reactions ranging from polycondensation to the interfacial polymerization of the covalent organic frameworks.[2] However, the unbounded dissemination of the active sites during addition polymerization (including radical polymerization, anionic/cationic polymerization, and coordination polymerization) at the interface limits their utilization in the design of functional materials.

Motivated by the competency of exquisite properties like tunable band gap, high electrical conductivity, provisions for reversible doping or dedoping, and good biocompatibility, conducting polymers (CPs) and their hybrid systems are subjected to feasible nanostructure tuning. In addition, conducting polymers, whether utilized alone or in combination with other functional polymers, can be incorporated into nanostructured platforms that are utilized in different fields where electronic conductivity is essential. To date, numerous conducting polymers and their derivatives have gained significant acceptance, including polyacetylene, polypyrrole (PPy), polyaniline (PANI), poly(*p*-phenylenevinylene), poly-(3,4-ethylenedioxythiophene) (PEDOT), and polythiophene (PTh).[16] For example, the poly(vinyl alcohol) nanofibers that have undergone the most effective cross-linking through the incorporation of a conducting polymer, PTh derivatives, exhibited enhanced mechanical resistance to external forces, biocompatibility, water resistance, electrical conductivity, and hydrophobicity.[17] In short, the physicochemical tuning of CPs and multifunctional nanostructure embedded CPs are exceptionally efficient and can be tailored to a particular technique, such as in the context of biomedical or electronic applications.

This Perspective summarizes the recent progress in the physiochemical tuning of conjugated polymers and their composites at the interface of immiscible liquids accentuated by morphologically controlled unique properties. The develop-

ment of interfacial polymerization at a L/L interface is closely linked to stabilizing a solvent/nonsolvent interface with the adsorption of amphiphilic molecules. In this direction, the primary focus is devoted to the fundamental importance of the energetics of the interface and reaction dynamics at the interface. Further, the unique characteristics of reactive molecules, their interactions, and their affinity toward interface or bulk will be discussed. Besides, the electron and mass transfer at the interface and their influence on tuning the physicochemical properties of nanostructures will be reviewed. Subsequently, this Perspective focuses on the recent and illustrative approaches behind this technique that are readily scalable and have broad utility in practical applications.

FUNDAMENTALS OF INTERFACIAL POLYMERIZATION AT A LIQUID/LIQUID INTERFACE

The spreading of one immiscible liquid over another generates a liquid/liquid interface, and the collective interaction and forces give rise to the surface tension at the interface. Molecular aspects of nanoparticle adsorption and desorption to the interface are associated with the amphiphilicity of the surface-modified nanoparticles/reactive molecules involved in the polymerization process.[18] It is noteworthy that an optimal amalgamation of inter or intramolecular interactions such as $\pi-\pi$ stacking, van der Waals forces, hydrogen bonding, and metal coordination between the solvents and or reactive molecules regulates the self-assembly at the interface.[19] These intra/intermolecular interactions significantly affect the dynamics of self-organization of reactive molecules; as a result, the kinetics of polymerization. Intrigued by the advantages of the interactions at the interface, polymer technologists have taken advantage of the adsorption of reactive monomers or species in strategically developing distinct polymer/nanomaterial composites. The exploration of the high energy of the interface in adsorbing chemically modified nanoparticles and or monomer combinations and their advancement to interfacial polymerization is exemplified in this section.
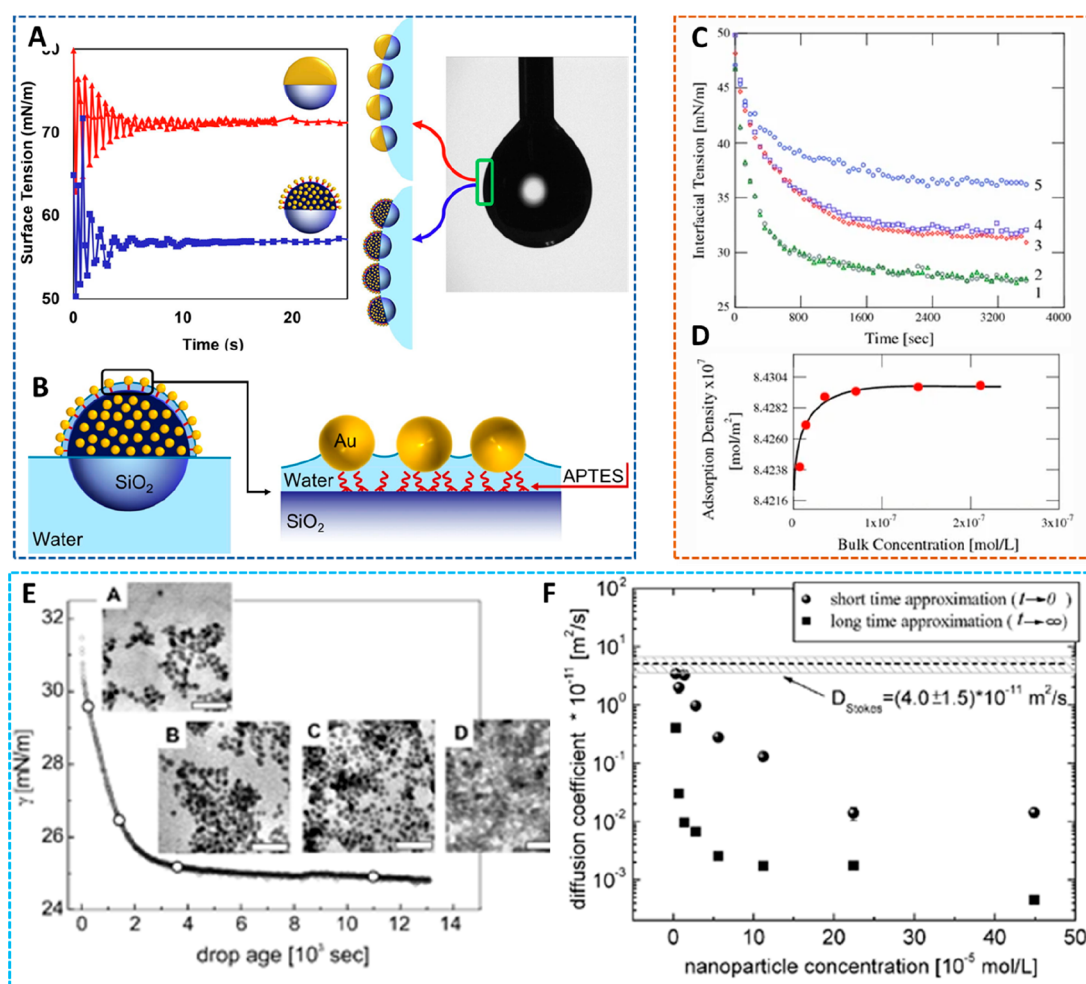
Figure 2. (A) An unexpected decrease in the effective surface tension in the presence of chemically modified Janus particles. (B) The schematics illustrate the immersion forces arising; the APTES linker molecule results in the proximity of gold nanoparticles to the core silica particle surface. Reproduced with permission from ref 26. Copyright 2020, Elsevier. (C) Interfacial tension of a water droplet in hexane with various concentrations of 2.8 ± 0.27 nm *n*-dodecane-1-thiol-capped gold nanoparticles and (D) their equilibrium adsorption density as a function of bulk nanoparticle concentration. Reproduced with permission from ref 28. Copyright 2011, Springer Nature. (E) Temporal evolution of interfacial tension at the toluene/water interface in the presence of 6.0 nm CdSe nanoparticles and (F) diffusion coefficients of CdSe nanoparticles at room temperature at different particle concentrations for short and long time approximations. Reproduced with permission from ref 32. Copyright 2007, Royal Society of Chemistry.

To mention a few, the immobilization of tri*n*-octylphosphine oxide (TOPO)-stabilized CdSe nanoparticles at the toluene/water interface achieved with the chemical cross-linking of the attached ligands arose as an excellent synthetic strategy for organic/inorganic composite membranes (Figure 1A,B).[20] It is remarkable that the adsorption of CdSe nanoparticles stabilizes the high-energy interface of the toluene/water system; furthermore, TOPO functionalization led to the subsequent free radical cross-linking between the nanoparticles. The aforementioned work is one of the early reports on the flexible route for fabricating ultrathin, flexible organic/inorganic composite membranes at a L/L interface.[20] However, elevated temperatures employed for free radical cross-linking enhanced the cracking of curved interfaces of droplets and made it undesirable. Therefore, a unique ring-opening metathesis polymerization/cross-linking employed at the oil/water interface established the stabilization of ultrathin capsules of CdSe/ZnS core–shell quantum dots.[21] Unlike the previous report, the strength of the self-assembled capsules was enhanced by interfacial cross-linking.[21] Moreover, the exquisite tailoring of

ligands regulated the controlled transport across the reactive interface and to the target of the ultrathin capsules. Further, the cross-linking polymerization of 2,2-azoisobutyronitrile was utilized to stabilize multicomponent hollow capsules with hybrid gold nanoparticles (NPs) and poly(acrylamide) at the water/toluene interface (Figure 1C–E).[22] In addition to the chemical cross-linking approaches at the interface, the tenacity of the nanoparticle assemblies is also enhanced by Pickering emulsion polymerization.[23]

The partial wettability of the solid particles by the two immiscible phases results in the self-assembly of solid particles onto liquid/liquid or liquid/gas interfaces, referred to as Pickering stabilization.[23] In 1980, Pieranski investigated Pickering stabilization in terms of the reduction in interfacial free energy due to the segregation of nanoparticles at the interface. As asserted by the Pieranski equation, the minimization of interfacial energy (Helmholtz free energy) is significantly governed by the size of the adsorbed nanostructures.[14] The Pieranski equation is $\Delta E = -\pi R^2 \gamma \left(1 + \cos \theta\right)^2$, where R, θ, γ, and ΔE are the size of adsorbed particle,
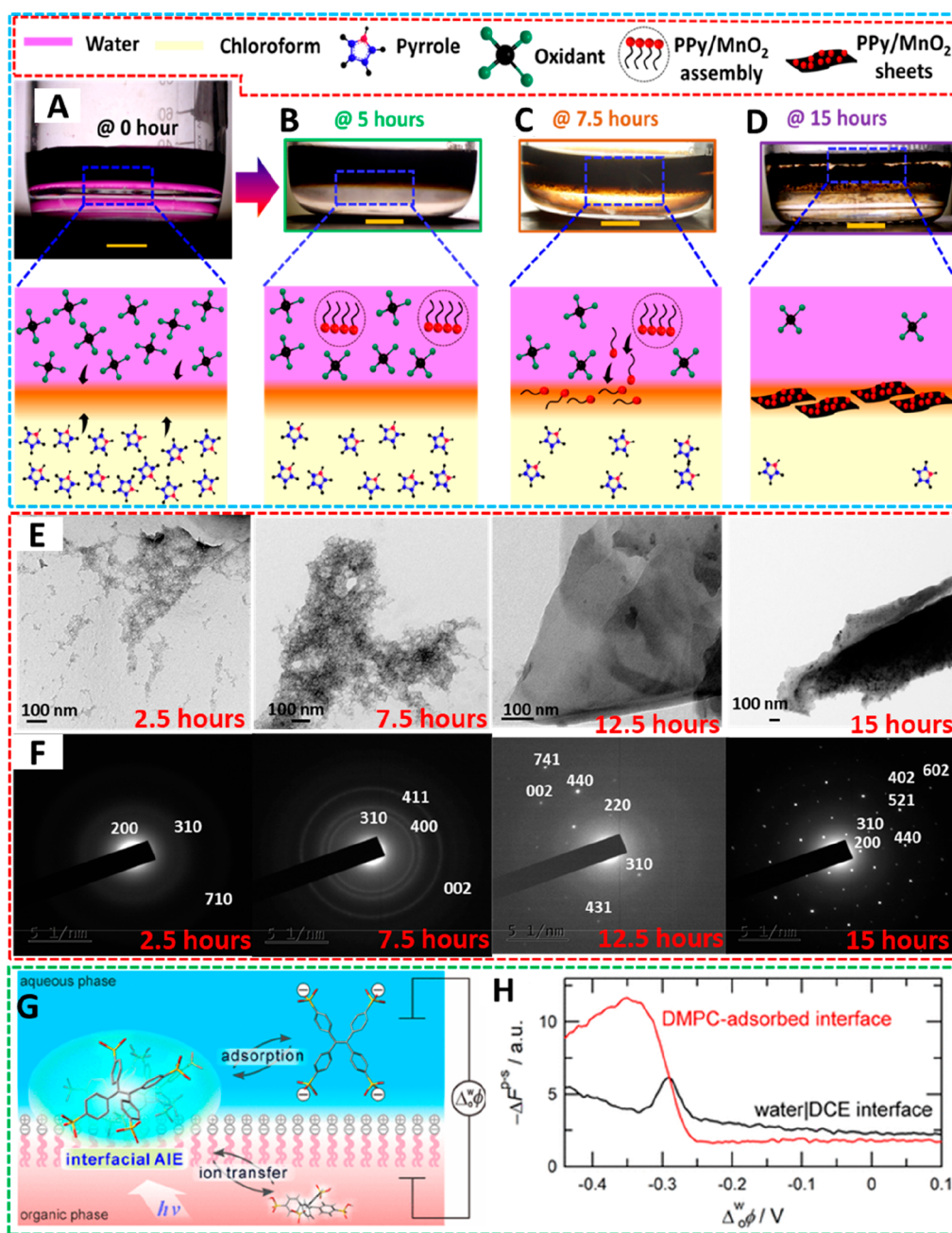
Figure 3. (A−D) Photographic images and schematic illustration of the interface-assisted polymerization of PPy/MnO$_2$ at different time intervals. Scale bar: 1 cm. (E,F) High-resolution transmission electron microscopic images and corresponding selected area electron diffraction images of PPy/MnO$_2$ synthesized at the water/chloroform bisolvent interface at varying time intervals. Reproduced with permission from ref 33. Copyright 2022, Royal Society of Chemistry. (G,H) The schematics and polarization-modulation total internal reflection (PM-TIRF) characteristics of water-soluble tetraphenylethene (TPE) aggregates at the water/dichloroethane interface. Adapted from ref 34. Copyright 2020, Americal Chemical Society.

wettability of the particle, surface tension, and change in Helmholtz free energy, respectively.[24,25] Thus, a detailed interpretation of the dynamics of nanoparticles at the interface has received significant attention in inventing distinct approaches for synthesizing novel functional materials or devices via size-selective particle self-assembly. One notable approach in this direction is the molecular dynamic simulations that validated the amphiphilic nature of Janus nanoparticles on the adsorption/desorption dynamics and hence stabilization at the interface.[18] Moreover, the adsorption of (3-aminopropyl)-triethoxysilane (APTES) modified Janus particles induced an unexpected reduction in the effective surface tension of the air/

water interface (Figure 2A,B).[26] The impact of the linker molecule on gold nanoparticles is crucial for reducing the IFT compared to physically modified Janus particles. It is noteworthy that the particle−particle interaction near the interface (between the particles approaching the interface from the bulk and the particles already adsorbed at the interface or particles leaving the interface) could result in an adsorption barrier.[27]

Dynamic interfacial tension measurements by pendant drop tensiometry is an appropriate experimental technique to comprehend the kinetics of nanoparticle adsorption at L/L interfaces (Figure 2C,D).[28] Dynamic surface tension measurements at the water/toluene interface for gold nanoparticles

protected by monolayers and protein conjugates emphasize that the adsorption of nanoparticles at the interface is the rate-controlling step of the self-assembly instead of diffusion.[29] Further, the temporal evolution of IFT ascertains a switch from diffusion-controlled kinetics to interaction-controlled kinetics for the adsorption of alkanethiol-stabilized gold nanoparticles at the interface from early to later stages.[30] Strikingly, a decay in IFT is in accordance with the diffusion toward the interface, ordering, and rearrangement of nanoparticles at the oil/water interface for trioctylphosphine oxide (TOPO)-covered CdSe nanoparticles.[31] A dipole–dipole interaction induced the clustering of CdSe nanoparticles to form large islands, subsequently directing the complete coverage of the oil–water interface during polymerization. The temporal evolution in the IFT measurements confirmed the IFT decrease consistent with the clustering and complete interface coverage by nanoparticles as observed in transmission electron microscope images (Figure 2E).[32] Further, a decrease in diffusion coefficient with increased nanoparticle concentration endorses variation in the adsorption mechanism from a diffusion-controlled to an interaction-controlled process at the interface (Figure 2F).[32] Insofar, it can be envisaged that a significant amount of research has been focused on stabilizing the interface using the adsorption of NPs, and their kinetics.[12,26,29,30] However, much less is known about the temporal evolution of IFT during polymerization at the interface and its impact on tuning the morphology and physicochemical properties of polymer/nanomaterial composites or hybrids.

It is impressive that the gradual decrease of IFT during in situ synthesis of polypyrrole/manganese dioxide hybrids (PPy/MnO$_2$ hybrids) was experimentally validated using pendant drop tensiometry.[33] Remarkably, a gradual in situ polymeric chain growth and crystallization of MnO$_2$ nanoparticles at the interface was concurrent with decreased surface tension with time.[33] The photographic images and schematics shown in Figure 3, represent the progressive change in the bisolvent system during in situ formation of PPy/MnO$_2$ hybrids. Figure 3A–D depicts the adsorption of NP-attached oligomers/short-chain polymers at the interface to form microscale PPy/MnO$_2$ sheets. In step 1 (Figure 3A), the monomers (pyrrole) and oxidant (KMnO$_4$) are mixed to initiate polymerization at the chloroform/water interface. Figure 3B (step 2) exhibits a dark coloration in the aqueous phase (KMnO$_4$ dissolved in water) due to the immediate transfer of MnO$_2$-attached oligomers toward the polar aqueous phase. However, steps 3 and 4 (Figure 3C,D) indicate the adsorption of MnO$_2$-attached oligomers/short-chain polymers toward the interface and the eventual formation of 2D PPy/MnO$_2$ sheets. Figure 3E shows the successive agglomeration of polymeric networks and growth of MnO$_2$-attached polymeric sheets as the reaction was advanced from 2.5 to 15 h. Further, the selected area electron diffraction images illustrated a gradual change in diffusive Bragg rings to bright Bragg spots, corresponding to the in situ crystallization of MnO$_2$ (Figure 3F). Conspicuously, this report validated the predominance of the interface in promoting the layer-by-layer growth of sheets by π–π stacking interactions of polymeric backbones. Intriguingly, The potential-modulated fluorescence and polarization-modulation total internal reflection (PM-TIRF) spectroscopy validated the potential-driven interfacial process of charged species and the orientation of the adsorbed species at the interface, respectively.[34] The adsorption of tetraphenylethene (TPE) derivatives bearing carboxylate and sulfonate groups at the dichloroethane/water interface

elucidated their mass transfer across the interface accompanied by the adsorption.[34] The schematics of the aggregation-induced emission (AIE) behavior of water-soluble TPE derivatives and PM-TIRF characteristics are shown in Figure 3G,H.

Notably, current research focuses on developing polymer/nanomaterial composites at the interface through interfacial polymerization to take advantage of the capability of the interface to confine the nanostructures of pristine polymers or their surface-modified hybrids. The interface is analogous to a biological membrane where an energy conversion reaction occurs due to a potential gradient from ion transfer across the membrane.[35] The spontaneous electron transfer between the monomers dissolved in an organic phase and metal ions in the aqueous phase in the absence of an external electric field is a promising strategy for an energy-efficient method to produce polymer/nanomaterial composites. Our research group is actively exploring the spontaneous electron transfer between the monomers of conducting polymers and metal ions. Strikingly, the composites of PPy, such as PPy/Ag, PPy/Au, PPy/Cu, PPy/Pt, and PPy/metal oxides have been morphologically tuned to two-dimensional (2D) sheets at the interface of chloroform/water.[13,36,33] Thus far, during polymerization, electron transfer at the interface can be considered as a spontaneous electrochemical process without an external electric field. Contrary to spontaneous electrochemical reactions reported at the interface, interfacial polymerization is also conducted in an applied electric field or at an electrified interface.[37] More recently, simultaneous Au nanocluster electro generation and polymerization of a dithiafulvenyl substituted pyrene molecule at a miniature interface between two immiscible electrolyte solutions (ITIES).[38]

From all these observations, the dynamics of the confinement of polymer/nanomaterial hybrids at the L/L interface leading to well-defined morphologies, pore structures, compositions, and dimensionalities can be summarized as follows.

1. A well-defined interface is generated between two immiscible phases upon mixing.
2. By virtue of the asymmetric forces at interfaces, the reactive molecules on both phases reorganize and adsorb at the interface to counterbalance the asymmetric forces.
3. As mentioned earlier, the adsorption would facilitate the electron transfer between the reactive species to initiate polymerization.
4. Due to the poor affinity of the oligomeric chains or short-chain polymer units in either of the immiscible liquid phases, the structural units prefer to adsorb at the interface, reducing the IFT, as attested by the pendant drop tensiometry.

However, depending on the surface nature of the oligomers and subsequent interactions with the interface/solvents, the dynamics of adsorption–desorption and ensuing confinement are categorized into three pathways.[36,39]

1. If the oligomers are doped with nanostructures, the interface attracts and stabilizes the nanostructure-attached oligomers or short-chain polymers as a result of the inherent nature of the interface to reduce high IFT. Thus, the interface promotes the confinement of oligomers, hence oriented growth of polymers leading to an end morphology of 2D sheets or films.[13]
2. On the other hand, if the oligomers are undoped with nanostructures, the oligomer/short-chain polymer interaction with the solvent exceeds the attractive forces from
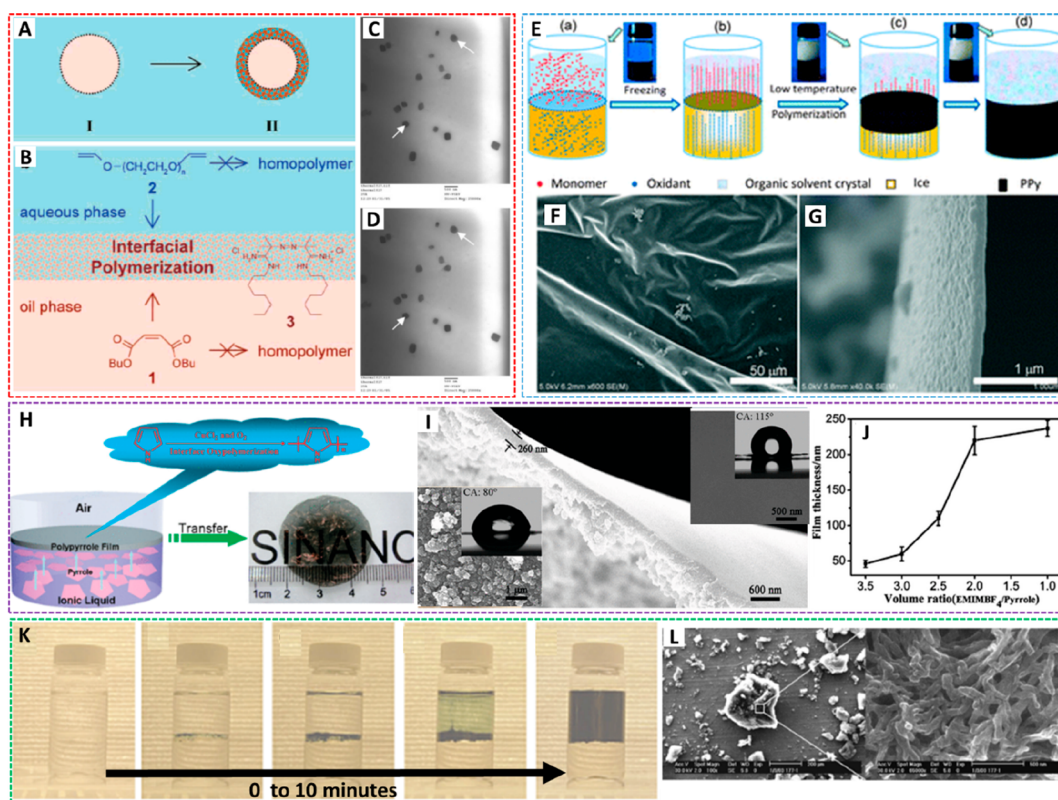
Figure 4. (A) Interfacial free-radical polymerization of mini emulsion oil drops (I) to form liquid-core polymer capsules (II).[51] (B) alternating copolymerization of dibutyl maleate (1) and hydrophilic PEG divinyl ether (2), initiated with surface active initiator (3) at the oil/water interface. (C,D) TEM images of originally intact (~280 nm diameter) capsules are damaged using 5 min electron beam irradiation, revealing hollow cores. Figures A−D were adapted from ref 51. Copyright 2005, American Chemical Society. (E) The schematic representation of the freezing interfacial polymerization method and the photographic images show the samples during the synthesis.[55] (F,G) SEM images from the top and cross-section views of the PPy films were prepared by the FIP method. Figures E−G were reproduced with permission from ref 55. Copyright 2012, Royal Society of Chemistry. (H) Schematic illustration of the formation of the Ppy film at the air/ionic liquid interface and the photograph of the film.[56] (I) Cross-sectional SEM image of an asymmetrical free-standing film. The inset shows the top-view SEM image of (b) the rough side and (c) the smooth side of the film with the corresponding water contact angle.[56] (J) Variation in film thickness with the reaction time. Figures H−J were adapted from ref 56. Copyright 2010, American Chemical Society. (K) Snapshots of the interfacial polymerization of aniline in a chloroform/water system from a reaction time of 0−10 min.[57] (L) SEM images of polyaniline after filtration at different magnifications show the agglomeration of nanofibers. Figures K,L were adapted from ref 57. Copyright 2004, American Chemical Society.

the high-energy interface. Therefore, oligomers could diffuse to the appropriate solvent phase (organic or aqueous phase), leading to aggregation into an agglomerated end morphology of 0D or 1D in the bulk solvent.[13,36]

3. Interestingly, despite having nanostructure doping in oligomeric chains, predominant interaction between the solvent and the nanostructure-attached oligomers could diffuse them to appropriate solvents.[40] Thus, the aggregation of nanostructure-attached oligomers in bulk solvents could generate an end morphology of 0D in the bulk solvent.

To sum up, the above-mentioned underlying principles of reorganizing and adsorbing reactive intermediates while lowering the interfacial tension and consequent product formation at the interface form the basis of interfacial polymerization. Strikingly, the goal of polymer technologists is to evenly incorporate functional nanostructures into the polymer matrix. Thus, the fundamental aspects of the reorganization of reactive molecules are utilized to adsorb the polymer and nanostructure counterparts simultaneously at the interface for the in situ generation of polymer/nanomaterial composites. Furthermore, during interfacial polymerization, the gradual upsurge in the film

thickness could eventually develop a diffusion barrier and cease the further growth of the film.[41] A comparative evaluation of the thickness of the 2D films of PPy/metal composites using atomic force microscopy images proved the predominance of the L/L interface in confining the self-assembly of nanoparticle-attached oligomers or short-chain polymers at the interface and thinning the polymeric composite sheets up to 1.1 nm.[36] The thickness was further approximated to three repeating layers of PPy backbones owing to the self-assembly of oligomers or short-chain polymers at the interface.[36] Notably, though the film thickness is self-limiting, the film thickness is also controlled by the size of the nanoparticles encapsulated in the polymeric matrix for polymer/nanomaterial hybrids synthesized in situ.[33,36] Besides, the rapid growth of the film at the initial stages and hence the thickness of the film are proportional to the square root of monomer concentration. In an urge to minimize the IFT, the reactive molecules diffuse rapidly toward the interface; hence, the interface is covered expeditiously.[42] Therefore, a rapid decrease in the IFT during the initial stage of polymerization attested to the adsorption and coverage of the interface. However, a judicious interface regulation by appropriate choice of solvent systems could successfully tune

the thickness of multilayer films or even generate monolayers.[43,44]

Subject to the dissemination of reactive species either in the solvent or nonsolvent phase, an imperative membrane asymmetry (possessing smooth and rough surfaces on opposite sides) was identified in thin films and membranes. Moreover, as observed during interfacial polymerization, the membrane was increasingly disordered with expanding thickness.[42,45] To a greater extent, the thin film shows 2D growth parallel to the interface; however, secondary 3D growth perpendicular to the interface conceivably extends the thickness of the films. Recently, a remarkable extension of film thickness up to ∼850 nm during interfacial electrosynthesis, along with a propitious porous 3D structure, has been reported.[37] Moreover, the free energy of the particle as a function of distance to the interface and its nucleation at liquid/liquid interfaces controls the membrane asymmetry. It is also reported that the particle should be sufficiently large enough to be surface active and to adsorb at the interface rather than small particles being pushed out of the interfacial region. Apart from these observations, it is reported to annihilate the interfacial confinement of nanostructure-attached oligomers or short-chain polymers when the concentration of monomers is very high.[33] This phenomenon is attributed to the particle–particle interaction at the interface.[27] In addition, the liquid/liquid interface favorably alters the reaction kinetics; in other words, it acts as a catalyst, depending on the charges of the reactants and the dielectric permittivity of the organic phase.[46] Further, the rate-determining step in an electron transfer reaction is the "interfacial" diffusion of a redox species across the oil/water interface.[47,48] Overall, the kinetics of interfacial charge transfer are regulated by the charges of the reactants, their location with respect to the interface, and the dielectric properties of the two immiscible phases forming the interface.[49] Driven by the inferences mentioned above, diverse parameters influence the growth mechanism of nanostructures during interfacial polymerization and offer a new platform for regulating polymer properties.

■ PIVOTAL RECORDS ON INTERFACIAL POLYMERIZATION

The paramount importance of interfacial polymerization is attributed to its ability to develop controllable polymerization at standard temperature–pressure conditions. During the early stages of the development of interfacial polymerization, the monomers or reactive molecules were organized at the interface to minimize the high IFT. Upon which external stimuli such as radiation or oxidants are introduced to initiate the polymerization, leading to monolayers or thin-film confinement at the interface. To provide a few examples, even though there are more, monomolecular and Langmuir–Blodgett films of butoxycarbonyl methylurethane diacetylenes are constructed by illuminating ultraviolet light on the adsorbed monomers at the air/water interface.[50] A first report on interfacial free-radical alternating copolymerization of dibutyl maleate and hydrophilic poly(ethylene glycol)-divinylether in forming liquid-core polymeric capsules at organic/aqueous interface is shown in Figure 4A−D.[51] As a result of the introduction of conducting polymers, the oxidative polymerization of pyrrole to polypyrrole at the organic/aqueous interface was reported back in 1986.[52] Intriguingly, the morphology of PPy from thin, flexible, transparent films to dark brown thick sponge-like sheets were modulated by adjusting the concentration of pyrrole monomers during polymerization. Furthermore, the PPy composites

deposited on thin polyethylene films or rubber latex sheets exhibited an electrical conductivity of 10−30 Ω^{-1} cm^{-1}.[52] In addition, the incorporation of large negatively charged functional groups into PPy films through electrostatic interaction between PPy chains and the dopant was highly efficient at vapor/liquid interface.[53] Likewise, the electroactive polyaniline films at a liquid/liquid interface formed from the network of randomly oriented tubular forms exhibited redox behavior similar to conventional electrodeposited polyaniline.[54] On the whole, the interfacial polymerization strategy is superior to the conventional electrochemical synthesis of conducting polymers in terms of (i) low-cost reagents, (ii) fabrication of large-area thin films, (iii) short reaction times, (iv) excellent control of the reaction kinetics, etc.

The Nobel Prize in 2000 for Heeger, MacDiarmid, and Shirakawa for their pioneering work in conductive polymers motivated polymer technologists to develop conductive polymer composites of remarkable properties and progressively explore the interfacial polymerization technique. An in situ freezing interfacial polymerization (FIP) was superior to conventional interfacial methods in improving the conductivity (up to 2000 S cm^{-1}) of PPy sheets (Figure 4E−G).[55] By virtue of low reaction temperature and confined space, FIP could evade unfavorable branching or cross-linking during polymerization, consequently constructing highly ordered polymeric structures with longer conjugation lengths.[55] Interestingly, through oxidative polymerization, PPy films with controlled film thickness from ten to hundreds of nanometers were spontaneously formed at an air/ionic liquid interface (Figure 4H−J).[56] As explained in the previous section, the membrane asymmetry was evident from the scanning electron microscopy images, where the side facing air is very smooth whereas the side facing ionic liquid is rough. Owing to the high surface energy of PPy,[58] increasing surface roughness decreased the contact angle of polypyrrole films. Further, controlling the monomer and oxidant concentrations could regulate the thickness of the films from 50 to 250 nm.[56] Intriguingly, the polyaniline nanofibers made by interfacial polymerization in a methylene chloride/water system were reported to exhibit 30 to 120 nm diameter with the choice of appropriate dopant acid (Figure 4K,L).[57] Although the monomer and oxidants were taken in the organic and aqueous phases, the polyaniline nanofibers migrated into the water phase after a short induction period. Further, the migration of the camphor sulfonic acid-doped polyaniline differently to organic and aqueous layers in carbon tetrachloride/water and chloroform/water systems illustrated the counterion-induced solubility of polyaniline in organic solvents.[57] Remarkably, interface manipulation in a bicontinuous microemulsion system from pure interface to other interfaces such as cationic, nonionic, and anionic offers the generation of 2D PPy nanosheets to 3D PPy or their composites.[59] Besides, in the absence of the molecular layer, the pure interface offers relatively thicker 2D nanosheets compared to cationic, nonionic, and anionic interfaces.

Apart from the typical interfacial polymerization, where the counterions attached to active monomers govern the diffusion of the polymeric backbone to respective solvents or their confinement at the interface.[60] The in situ generation of Ag nanoparticles together with PPy polymerization resulted in the spontaneous growth and entrapment of Ag NPs in the growing polymer chains. Further, the indicated in situ method efficiently and uniformly incorporates nanosized particles with a narrow size distribution, contributing up to 60% of the total weight of the composites.[60] The role of various oxidants (metal ions) in
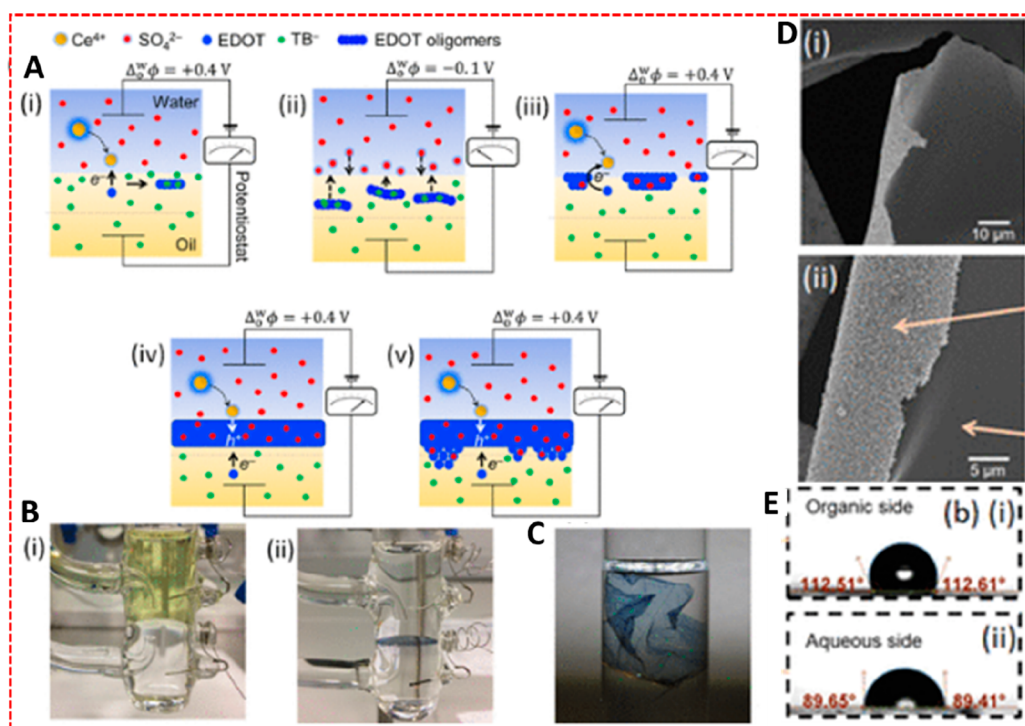
Figure 5. (A) Mechanism of PEDOT interfacial electrosynthesis at the interface between two immiscible electrolyte solutions.[37] The schematics represent the initiation of radical cation generation to the formation of PEDOT oligomer islands, and their successive growth to 2D films of PEDOT is represented in (i)−(v). (B) Four-electrode electrochemical cell (i) before and (ii) after interfacial electrosynthesis.[37] (C) As synthesized, PEDOT films are stored in an acetone/0.2 M H$_2$SO$_4$ mixture. (D) SEM images of an electro-synthesized free-standing 2D PEDOT film illustrating the membrane asymmetry on both sides. (E) Contact angle showing the difference in the hydrophobicity of the films on both sides. Figures A−E were adapted from ref 37. Copyright 2022, American Chemical Society.

the initiation and growth of polymers into 2D sheets was extensively investigated for the polymerization of PPy.[36,61] The spontaneity of electron transfer between the electrode couple (monomer and metal ions) at the interface via a spontaneous electrochemical pathway in the absence of an external electric field was predicted from the standard reduction potentials of the electrode couple.[36] Further, the chloroform/water interface is reported to be a potential template for the self-assembly of Zr-doped cryptomelane nanostructures attached to PEDOT oligomers or short-chain polymers.[39] The wise choice of mixed oxidants (KMnO$_4$ and ZrOCl$_2$.8H$_2$O) resulted in the in situ generation of Zr-doped cryptomelane nanostructures embedded in the PEDOT matrix at temperatures ranging from 5 to 50 °C.[39] Consistent progress in the self-assembly of nanoparticles to the spontaneous in situ generation of polymer/ nanoparticle composites is very evident from the aforementioned reports.

In distinction to these reports, interfacial charge transfer reactions in an applied electric field-induced interfacial electropolymerization along with in situ generation of nanostructures have been disclosed.[37,62] The electrosynthesis at the oil/water interface directly produced PEDOT thin films with distinct molecular architectures inaccessible in bulk solution, Figure 5A−E.[37] The schematics given in Figure 5A show the interfacial electron transfer between oxidant and monomer at an electrified interface (i), ion-pairing and interchange between reactive intermediates (ii), coalescence of individual and rapidly growing PEDOT islands to highly compact 2D PEDOT thin film (iii−v). The electropolymerized biocompatible films <50 nm thick were also extracted and stored for long-term use. Besides, controlled secondary growth of 3D porous structures up to ∼850 nm thick

toward monomer consisting organic phase was also observed. The thin film formation at the immiscible liquid interface in a four-electrode electrochemical cell is evident from Figure 5B, and the large-scale PEDOT film is redispersed and stored in an acetone/0.2 M H$_2$SO$_4$ mixture (Figure 5C). Further, the membrane asymmetry of PEDOT thin films was confirmed from the scanning electron microscopy images and contact angle measurement (Figure 5D,E). Similarly, an electrified dichloro-ethane/water microinterface could electropolymerize terthio-phene along with Au nanoparticle generation; further, a heterogeneous electron transfer between an aqueous couple (Ce(IV)/Ce(III)) and the terthiophene monomer led to electropolymerization of terthiophene.[63,64] Similarly electrified immiscible electrolyte interface was employed to generate AuNP/poly 2,5-dimercapto-1,3,4-thiadiazole films.[65] Regardless of the resemblance in interfacial polymerization, various microstructures of conducting polymers such as membranes,[54] films,[55,66] fibers,[57,67] and nanoneedles[15,68] are reported.

FUNCTIONAL MATERIALS FROM INTERFACIAL POLYMERIZATION FOR VARIOUS APPLICATIONS

Despite the unique electrical characteristics, the development of conductive polymers for various applications cannot be commensurately compared to their metallic or inorganic semiconductor counterparts. Consequently, continuous efforts have been made to develop polymer/nanomaterial hybrids or composites to overcome the inherent limitations of demonstrating for electronic or optoelectronic applications. Nonetheless, the spontaneous self-assembly of conventional polymeric films at the L/L interface is also competent enough to design and devise functional materials from their organic/inorganic
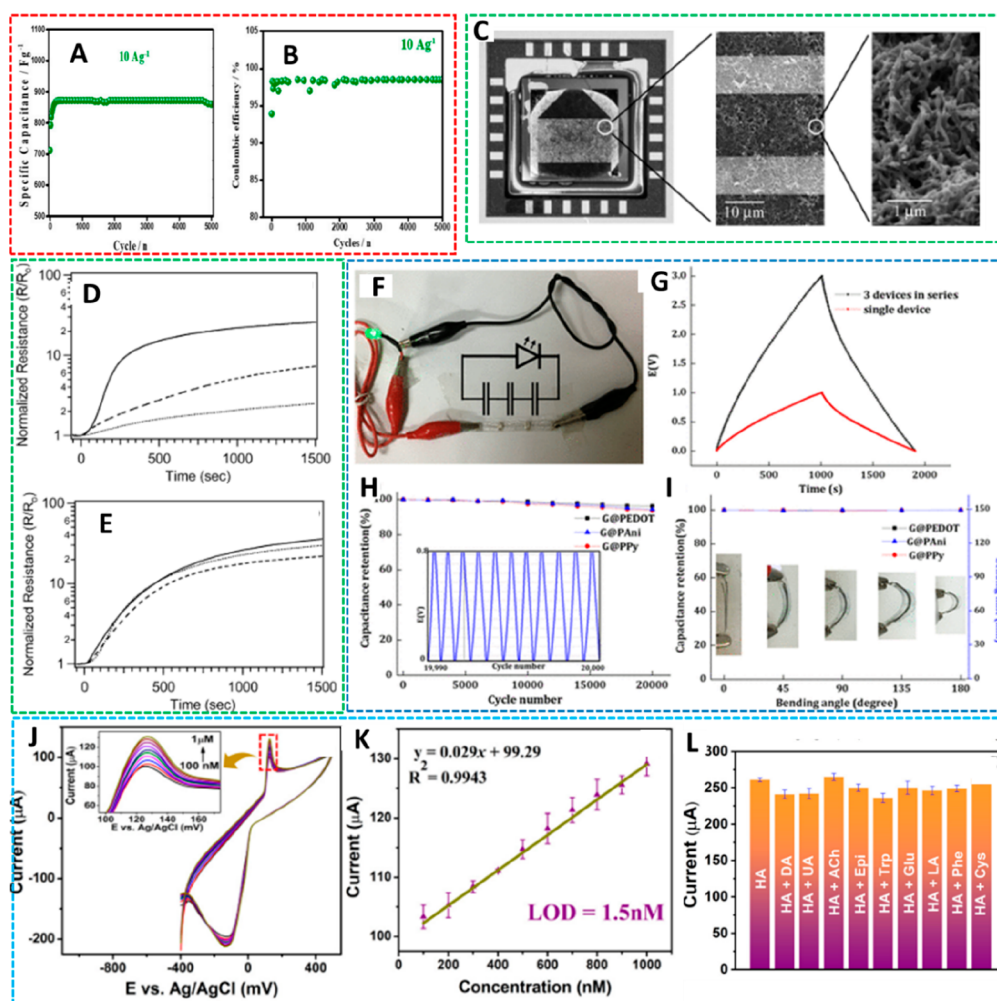
Figure 6. (A,B) Variation of specific capacitance and Coulombic efficiency of a P−DBSA‖P−DBSA device, with a continuous cycling life at 10 Ag^{-1}. Adapted with permission under a Creative Commons (CC-BY 4.0 license) from ref 70. Copyright 2019, MDPI. (C) Interdigitated electrode sensor substrates fabricated by using standard photolithographic methods. The scanning electron microscope images of films deposited on interdigitated electrodes.[71] (D,E) Response of conventional and nanofiber polyaniline films to 100 ppm gaseous NH$_3$ of various thickness ranging from 0.2 to 2 μm. Adapted from ref 71. Copyright 2004, American Chemical Society. (F) Photograph showing a serially connected three G@PEDOT fiber supercapacitor that lights up a green LED. (G) Galvanostatic charge−discharge profiles of the serially connected supercapacitor device shown in (F) compared to a single device. (H) Cycle life of G@PF supercapacitor devices.[72] Inset is galvanostatic charge−discharge profiles of G@PEDOT after 19899 cycles up to 20000 cycles at 1.05 A/cm³. (I) Capacitance retention under bending up to 180° for a maximum time of 150 min. Insets show photographs of bent fiber supercapacitors. Adapted from ref 72. Copyright 2017, American Chemical Society. (J) Cyclic voltammograms of the PEDOT/Au−Ag modified GCE in the presence of varying concentrations of HA in the range of 100 nM to 1 μM at pH 7.2 and scan rate 50 mVs^{-1}, (K) calibration plot of anodic peak current vs concentration, (L) comparison of the anodic current response of the PEDOT/Au−Ag modified GCE in the presence of 100 μM HA and 1 mM of various interfering groups. Adapted with permission from ref 40. Copyright 2023, Royal Society of Chemistry.

counterparts. Although much work has been disclosed on conducting polymers, this Perspective aims to focus extensively on the polymer/nanomaterial composites engineered at the liquid/liquid interface. Furthermore, the resultant product can be readily isolated from the reaction medium using either an uncomplicated filtration method or a meticulous film transfer strategy depending upon the targeted applications. The polymer nanocomposites that have been reported in this Perspective hold significant importance in various applications that require a consistent distribution of nanostructures of a few nanometers in size within the polymeric matrix. A binary composite film of PPy and PANI, with a large density of PANI particles covered with a porous PPy membrane, exhibited hexavalent chromium adsorption for water purification technologies. On the other hand, high-quality PANI nanotubes synthesized with the aid of decylphosphonic acid at a xylene/water system exhibited

corrosion protection of mild steel.[69] The highly efficient PANI doped with dodecylbenzenesulfonic acid (DBSA) is endowed to have high specific capacitance, excellent reversibility, rate capability, and superior cycling stability, with a meager solution resistance (R_s = 0.61 Ω) and a potential drop (IR = 0.0191 V).[70] As shown in Figure 6A,B, the pseudocapacitor electrode exhibited a constant current density of 10 Ag^{-1} for 5000 cycles, and Columbic efficiency was retained until 98.5% after 5000 potential cycles.[70] A better performance in sensitivity and time response toward sensing of various gases such as HCl, NH$_3$, N$_2$H$_4$, etc. was reported on PANI nanofibers of high surface area, small nanofiber diameter, and porous nature (Figure 6C−E).[71] Owing to the fine-tunability of the unique electrical, chemical, and physical properties of polyaniline nanofibers synthesized through interfacial polymerization, the response mechanisms of polyaniline chains are different during sensing. Impressively,

acid doping, base doping, reduction, swelling, and polymer chain conformational changes could alter the electronic resistance of PANI during the sensing of HCl, NH_3, N_2H_4, $CHCl_3$, and CH_3OH, respectively.[71] Due to the superior antibacterial activity of Ag, Ag NPs (∼100 nm) incorporated onto biocompatible PPy sheets at the chloroform/water interface exhibited antibacterial activity toward *E. coli* and *S. aureus*.[61]

Closer π–π stacking distances and lateral separations of PEDOT chains in nanoneedles achieved using interfacial polymerization could also revolutionize the polymer electronics at the nanoscale. In consequence, scanning tunneling microscopy revealed a field-induced conductance switching in the order of millisecond response times in PEDOT nanoneedles.[15] A dichloromethane/water interface ensured N and Cu codoped porous graphene fiber cores were uniformly coated with semiconducting PEDOT shell layers and exhibited superb electrochemical characteristics (Figure 6F–I).[72] Exceptional components and nanoarchitecture helped to optimize the electron–ion transfer between shell and core, enabling their tolerance to cyclic fatigue due to continuous redox reactions.[72] The in situ alloying of Au–Ag nanoparticles and concealing them in a PEDOT matrix at the hexane/water interface was reported for the first time. The electrochemical sensor was developed from Au–Ag/PEDOT hybrids to detect histamine, demonstrating its competency in food spoilage monitoring and practical viability in health monitoring devices (Figure 6J–L).[73] A concomitant electropolymerization of 2,2′:5′,2″-terthiophene (TT) and reduction of Cu^{2+} to Cu nanoparticles at the micro interface between two immiscible electrolyte solutions could develop a flexible electrocatalytic composite.[49] The Cu/polyTT composite modified glassy carbon electrode testified to be a promising carbon capture material. Furthermore, a series of surface active pyrrole derivatives were interfacially polymerized by an electron transfer between a monomer dissolved in the organic phase and $Ce(SO)_4$ in the aqueous phase.[74] In addition to the polymer/nanohybrids, owing to the intriguing properties of 2D materials, the interfacial electrochemical self-assembly of MXene nanosheets at metal template substrates signifies the importance of liquid/liquid interfaces to generate functional architectures. In addition to the 2D stacking, the gelation approach could generate three-dimensional open porous aerogels for supercapacitors and electromagnetic interference shielding applications.[75] In summary, numerous methodical approaches have ascertained the high-energy interface-driven adsorption and polymerization of distinct polymer/nanomaterial composites. To this point, the interfacial polymerization successfully composited inorganic or organic counterparts and enhanced their potential in applications ranging from point-of-care diagnostics to sustainable energy technologies.

◼ COMPARATIVE ASSESSMENT OF INTERFACIAL POLYMERIZATION WITH CONVENTIONAL POLYMERIZATION TECHNIQUES

In light of the general nature of the synthesis strategies for the polymerization of CPs as a whole, chemical polymerization techniques are the sole focal point. The chemical polymerization process mainly follows an oxidative polymerization pathway, wherein the initial nucleation stage entails the introduction of diverse dopants or oxidants, which leads to the formation of a monomer radical cation. Electrochemical polymerization is considered to be the optimal technique for the fabrication of conducting polymers due to its favorable yield and electronic characteristics. The monomer of the conducting polymer is

oxidized at the anode to a radical cation (initiation step of polymerization) due to the low anodic potential and high susceptibility to electrophilic substitution. A significant amount of research has been focused on numerous synthetic strategies to overcome the intrinsic limitations of conducting polymers; electrochemical polymerization is one of the most explored synthetic strategies. During electrochemical polymerization, polymer chain growth follows a radical–radical coupling; eventually, reactive radicals terminate in the vicinity of the electrode. Therefore, a comparative evaluation is conducted between the conventional electropolymerization of conductive polymers and interfacial polymerization as an effective method for producing polymer/nanomaterial composites. Importantly, the conventional electropolymerization approaches must require specialized workstations, including an electrochemical cell consisting of a three-electrode setup (working electrode, reference electrode, and counter electrode) dipped in a solution of monomer and dopant.[19] Conversely, interfacial synthesis offers two modes of polymerization: (1) spontaneous electron transfer between the monomers and dopants across the interface and (2) an external electric field-induced oxidation of monomers leading to polymerization. It is important to mention that the spontaneous electron transfer between the monomer and metal ions dissolved in the respective solvent phases facilitates the in situ generation of conducting polymer/nanomaterial composites through interfacial polymerization. The interfacial polymerization is exceptional in terms of less energy input than conventional oxidative polymerization. Further, a relatively new approach where the miniature ITIES controls the formation of nanocluster-embedded film rather than the homogeneous growth of polymers. As mentioned earlier, the miniaturization of the ITIES could avoid the large overpotential during polymerization, thus the overoxidation of the thin films.[38]

Electropolymerization techniques conspicuously focused on single-solvent systems, leading to inhomogeneous nanodomains in bulk conducting-polymer systems.[15,76,77] On the contrary, the interfacial polymerization process stimulates the simultaneous crystallization of single-crystalline polymers, for example, PEDOT nanoneedles.[15] Additionally, crystallization during chain growth aids closer π–π stacking distances and lateral separations in nanoneedles.[15] It is a fascinating reminder that a judiciously formulated interface is exceptional in the controlled mass transfer of reactive molecules at the interface between a good and poor solvent, resulting in the controlled addition of building blocks during polymerization. The controlled addition of monomers is challenging due to the three-dimensional diffusion of monomers in a single-solvent-mediated oxy-polymerization or electropolymerization. Apart from these, polymers often strongly bind to the electrode surface during electropolymerization, making it challenging to set loose from the anode or obtain free-standing films. At the same time, interfacial polymerization at a liquid/liquid interface is a template-free and intrinsically defect-free method for fabricating 2D flakes or sheets. Furthermore, sheets of dimensions ranging from nanometers to micrometers or free-standing, flexible, and large-scale films could be produced through interfacial polymerization. Moreover, the interfacial polymerization at the L/L interface is an appropriate method for in situ generation of polymer/nanomaterial hybrids in bulk quantities.[78] The liquid/liquid interfaces demonstrated an exceptionally restricted two-dimensional space to synthesize multidimensional nanostructures of uniform size and crystallinities. Additionally, these

methods are indeed feasible at low temperatures with slow and controlled addition of reactants and improved yields and molecular weights.

As emerged from various electropolymerizations, synthesis of pristine or blends of conductive polymers is more prominently reported. Moreover, ex situ integration of nanomaterials into the electrochemically polymerized matrix has to be employed to synthesize multifunctional polymer/nanomaterial composites.[79,80] On the other hand, facile in situ interfacial polymerization successfully amalgamated inorganic nanostructures into a polymeric matrix simultaneously to develop multifunctional composites.[36,33,40] Furthermore, the progression of the interface between two immiscible solvents (hexane/water) to a reactive template mitigated the solubility issues of organic (monomers) and inorganic (metal salts) counterparts in comparison to polymerization in a single solvent.[40] At the same time, the miscibility constraints of the reactants in a single phase hamper the in situ generation of inorganic counterparts during polymerization. Further, the screening action of sheathing layers of polymers evolved concurrently on the nanoparticles during interfacial polymerization could stabilize them from further aggregation in solution.[40] Whereas in most cases, the nanocomposites formulated through alternative methods are devoid of high shelf life due to the severe aggregation of nanostructures in solution. It is awe-inspiring that, similar to conventional techniques, the dopant functionality and concentration regulation could tune the diameter of the polymer fibers in a template-free interfacial polymerization.[67]

FUTURE OUTLOOK AND SUMMARY

With a history of several centuries, tremendous efforts have been made to optimize the chemical compositions and structural assembly of functional materials to have more opportunities for potential applications. The interface of immiscible liquids has been reported to be an ideal template for a bottom-up strategy for devising 2D materials to realize their best performance in a broader range of applications. Further investigations need to be focused on generating functional polymer/nanomaterial composites possessing high mechanical flexibility and strong interlayer interactions. Further, much effort is needed to explore the built-in membrane symmetry/asymmetry while constructing the hierarchical 2D films. The membrane asymmetry could be advantageous in developing the membrane-potential sensitive sensor probes in biomedical applications, especially noncovalent labeling of liposomes and exosomes. Hence, the importance of the L/L interface in mimicking biological membranes should be an exciting aspect of research. Additionally, the advantageous biocompatibility of conducting polymers and their composites could be ideal for mimicking biological membranes and functions. Further, regulating the functional group on the monomers during polymerization could standardize the porous and physicochemical nature of the membranes across the thickness of the films. A direct, one-step interfacial polymerization of immiscible hydrophilic and hydrophobic vinyl monomer solutions resulted in a macro-scale hydro/organic binary cooperative Janus copolymer films through interfacial polymerization.[81] The difference in the chemical nature of the hydro/organo enables the smart shape or responses against various stimuli, which may be easily adapted to the conducting polymer/nanomaterial composites.

Apart from all these observations, simultaneous electrogeneration of nanoparticles and electropolymerization using an electrified liquid/liquid interface is an emerging strategy that makes use of electrochemistry and surface chemistry in tuning the polymer/nanomaterial composites. The reaction kinetics of electrochemical nucleation at the liquid/liquid interface is sparsely explored to understand the relevance of IFT to electrochemical phase formation. Apart from these, cyclic voltammetry and chronoamperometry studied the influence of surfactants on nucleation and electrodeposition of nanoparticles at liquid/liquid interfaces.[82] The exploration of in situ nucleation and controlled growth of polymer/nanomaterial hybrids could substantially unfold and improve the new advanced thin film nanofabrication regime. Conventional electropolymerization techniques provide overoxidized polymeric chains; instead, controlled oxidation of monomers using miniaturized electrified interfaces yielded polymeric films. Further research would be required to unravel the in-depth underlying mechanisms of stress generation due to the low grain boundary and nano geometries to fulfill the miniaturization scale devices. It can be seen that the growth mechanisms of those nanostructures directly affect stress generation, which is significantly correlated with the performance of miniaturized electronic devices.

The dielectric nature of interfaces, type (micro/macro/flat) of the interface, the concentration of monomers and oxidants, doping levels, monomer-cross-linker-oxidant ratio, and the nature of nanoparticle anchoring were found to predicate the morphology and electrical properties of conducting polymer/nanomaterial composites. Notably, the interfacial tension at the interface of the two liquids ultimately results from the asymmetrical interaction of their constituent phases. The contributions of coexisting phases to the overall value of interfacial tension were investigated through molecular dynamics simulation studies.[83] The minimum energy structure at the interface, according to Hore et al., is a compromise between hydrogen-bonding geometry optimization and dipole compensation.[84] Based on the current understanding of the author, while there have been several attempts to construct L/L interfaces utilizing an organic solvent and an aqueous solvent, comprehensive studies examining the impact of different L/L interfaces on the tailoring of multifunctional polymer/nanomaterial composites are seldom explored. Recently, Nesleena et al. investigated the effect of different liquid/liquid interfaces on the tailoring of the physicochemical properties of conducting polymer/nanomaterial composites.[85] The selection of solvent combinations (e.g., hexane/water, dichloromethane/water, and chloroform/water) and the resulting interfacial tension were crucial factors in confining the products to distinct phases and, consequently, modifying the nanostructure morphology of the composites from zero to two dimensions to a combination of zero and two dimensions.[85]

On top of that, the polarity and thickness of the interface are crucial in regulating the electron, ion, and mass transfer across the interface; hence, nano/microstructure tuning of polymer composites is an intense aspect of future research. Furthermore, the major constraints of interfacial polymerization for the in situ generation of two-dimensional polymer/nanomaterial composites are diffusion-limited cease of film growth, imperative membrane asymmetry, particle size dependence on adsorption at the interface, and solvent-polarity-controlled diffusion of products to their respective solvent phases. Considering the few nanometer thicknesses of the composite films confined at the interface, meticulous film transfer strategies are also necessary to retain the 2D nature of the composites. Owing to the unique properties of alloys, the simultaneous in situ alloying of metals

and polymerization at the L/L interface is another striking aspect of research that needs to be investigated for developing multifunctional materials. Beyond the fundamental aspects, depositing the composites onto appropriate substrates pertaining to spreadability or wettability on different materials is an essential research focus. Therefore, further exploration of functional electronics can be achieved with rapid development in the synthesis, morphology control, and novel properties of conducting polymer/nanomaterial composites.

■ AUTHOR INFORMATION

Corresponding Author

Mini Mol Menamparambath − *Department of Chemistry, National Institute of Technology Calicut, Calicut 673601 Kerala, India;* ⊙ orcid.org/0000-0001-6845-0815; Email: minimol@nitc.ac.in

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsmaterialsau.3c00068

Author Contributions

M.M.M.: manuscript conceptualization, visualization, project administration, resources, writing-original draft, writing-review and editing. CRediT: **Mini Mol Menamparambath** conceptualization, project administration, resources, visualization, writing-original draft, writing-review & editing.

Notes

The author declares no competing financial interest.

Biography

Mini Mol Menamparambath is an Assistant Professor in the Department of Chemistry at the National Institute of Technology Calicut (NITC), Kerala, India. Previously she was a DST-Inspire Faculty at the same institution. Between March 2014 and December 2015, she was a Postdoctoral Fellow under the Brain Korea 21+ program of the National Research Foundation, South Korea. She completed her primary education in India and her Ph.D. from Sungkyunkwan University, South Korea under the guidance of Prof. Seunghyun Baik. Investigating liquid/liquid interfaces for the strategic design of functional materials with potential applications ranging from sustainable energy technology to point-of-care diagnostics is the focus of her research group. In addition, a solid understanding of the interfacial properties could be essential for the efficient development of advanced nanostructures and for narrowing the gap between fluid interface chemistry and polymer technology across different domains of application. The research aspects have led to several professional recognitions, such as Women in Materials Science and Women in Nanoscience, as a part of International Women's Day 2023 by the Royal Society of Chemistry. She has been invited as a delegate at Faraday Discussions: Electrosynthesis, 2023, organized by the Royal Society of Chemistry. Further, her research work entitled 'In-situ engineering of Au−Ag alloy embedded PEDOT nanohybrids at a solvent/nonsolvent interface for the electrochemical enzyme-free detection of histamine' has been selected for the "Most popular" anniversary collection to celebrate 10 years of high quality, impactful and timely research in Journal of Materials Chemistry B of Royal Society of Chemistry.

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