Feature article

Application-driven multi-layered particles − The role of polymers in the architectural design of particles

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A B S T R A C T

Particulate systems, regardless micron or nano-sized, play an important role in various applications. In recent years, multi-layered, including core−shell, particles have been developed and exploited for a number of applications ranging from biomedical, catalysis, diagnostic, energy to wastewater treatment. While some multi-layered particles are designed to be wholly inorganic-based, a substantial proportion of these functionalized particles are designed using polymers. Polymers may play a role as a template, a material component of the particle or may be employed in the full design of the particle. In this review article, the key applications of multi-layered particles will be highlighted, while addressing to the role of polymers in the architectural design of these functionalized, application-driven particles.

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1. Introduction

Multi-layered polymer particles with specific functionalities, have become increasingly important in the recent years, arising from their potential role in various applications, such as catalysis, optical devices, electronics, energy-driven, biotechnological and biomedical applications [1,2]. For example, composite multi-layered particles can be employed as photo electrodes, using polymer particles as sacrificial templates, for hydrogen generation in photo electrochemical (PEC) cells towards energy-driven applications [3]. Alternatively, multi-layered fully polymeric particles can be utilized as a diagnostic or therapeutic tool for biomedical purposes [4]. Multi-layered particles are obtained when the surfaces of core particles are modified with a specific functional group or layer-coated with a different constituent. The aim is to endow functionalized particles with enhanced properties that are not present in their original, naked and non-functionalized state. In addition, the shell and layer thicknesses of these multi-layered particles can also be tuned, and their surface functionalities tailored to cater to very specific applications. This provides an array of possibilities in exploiting these versatile particles for a myriad of applications.

Given the current state-of-the-art, different types and configurations of multi-layered particles can be fabricated. These include core−shell particles, whereby particles may possess a metal-core and a metallic or non-metallic shell, a metal-core and polymeric shell, a polymer-core and metallic or non-metallic shell, and a polymer-core and polymeric shell comprising of different polymers; of which the latter examples are of interest in this review. Recently, a number of published papers were devoted to multi-layered metal-based nanoparticles such as iron, gold, platinum, and palladium. These have drawn interest because the properties of these nanosized particles are markedly different from their bulk materials [5]. For example, due to electron confinement and surface plasmon resonance effects [5,6], these metal−metal core−shell particles are utilized for a number of advanced functional applications, such as sensors, electronics, optoelectronics and catalysis [7−9].

Nonetheless, polymer-composing and hybrid particles have also attracted considerable interest within the industrial and scientific communities. For example, polymer-semiconductor-based particles, as a new class of materials, have found applications in electronics, as organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), sensors, and organic field effect transistors (OFETs). This is due to their advantages, such as low cost, flexibility and can be easily fabricated [10,11]. Likewise, fully polymeric multi-layered micro/nanomaterials and/or nanostructures are also widely explored [1,12]. Till date, a wide range of techniques can now be

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exploited to produce multi-layered polymeric particles. Examples of such techniques include immersive polymer assembly, electrophoretic polymer assembly, fluidized bed coating, spray coating, surface acoustic wave atomization, membrane filtration, microfluidic methods, and surface polymerization methods, with this list being non-exhaustive.

In this review, the objective is to give an overview of the various applications of polymer-composing multi-layered particles and to describe the role of the polymer in the design of these particles. The scope of this review will focus on polymer—polymer, polymer-inorganic and inorganic-polymer core—shell particles. Depending on the materials that compose the core and shell of these multi-layered particles, this paper will review how their properties can be modified, using polymers, to achieve functionalized, application-driven multi-layered and/or core—shell particles.

2. Polymer—polymer core-shell and multi-layered particles

Fully polymer-based particles, or polymer—polymer core—shell particles, with well-defined morphologies [13] have attracted immense interest in the recent years, and are widely reported in the literature. Polymeric core—shell particles can be obtained by layering polymers onto a polymeric core particle. The core material, if redundant, can serve as a sacrificial template to attain hollow-shell particles, or hollow capsules [14,15]. If required, the polymer core can be retained to serve as a part of the complete particle, where it provides additional functionalities.

2.1. Polymer—polymer core—shell particles

One key application of such polymer—polymer core—shell particles is in the biomedical field. Polymer-based multi-layered particles that exhibit pre-defined diameter and layer thicknesses may have better drug loading, offer improved drug stability, tunable release kinetics and profiles, while eliminating burst release, if any [16,17]. They can also be loaded with diverse bioactive agents that are separated from each other in individual particle, while preserving the bioactivity of these agents [18]. For example, multi-layered core—shell particles composed of fully biodegradable polymers can be used to store therapeutic agents in different polymer layers or compartments (Fig. 1). Such core—shell particles can be fabricated through a range of techniques, such as fluidized bed coating, dip coating, or spray drying, just to name a few. However, in this case

(Fig. 1), these core—shell particles are obtained through a one-step solvent evaporation technique [12,16]. Scanning electron microscopy (SEM) images show a distinctive core—shell structure, while Raman mapping validates the polymer composition at each layer. By varying the process parameters, a range of particles with different core—shell dimensions and sizes can also be achieved. The choice of polymers allow for different drugs to be loaded into different layers, thus achieving localized encapsulation within a single particle. Drugs are localized based on affinity to the polymer layers and allow for a selective loading of drugs in each particle compartment, i.e. core or shell. Understanding how various process parameters would give rise to different particle structures and morphologies thus enabling tailored fabrication of such polymer—polymer core—shell particles, through a single step fabrication process. Currently, these polymeric core—shell systems are explored chiefly for drug delivery applications. The application of polymer—polymer multi-layered particles as therapeutics is therefore emerging, with significant push to translate these technologies to the clinic.

Recently, a generally more benign and physiologically-friendly approach, through a biomimetic strategy, was utilized to prepare polymer—polymer multi-layered particles [18]. This nature-inspired approach was developed by observing how water droplets behave on super-hydrophobic Lotus leaf surfaces. This knowledge allows for the preparation of compartmentalized multi-layered polymeric spherical particles. In brief, droplets of aqueous polymer solutions containing bioactive agents were dispensed onto super-hydrophobic copper surfaces. This type of super-hydrophobic surfaces were obtained by a chemical-based deposition method using copper as a substrate [19]. This maintains an almost perfect spherical shape and its droplet size can be tuned by the volume of solution [20]. Subsequently, through crosslinking and/or solvent evaporation of these droplets, spherical particles will be formed. Subsequent deposition of liquid droplets onto the preformed spherical particles followed by crosslinking with a suitable agent renders the first coating layer. Repeating this step will lead to multi-layered particles. From the work of Mano et al., dextran-based multi-layered hydrophilic particles were prepared containing three different fluorophores in different concentric layers [18]. Through the proposed bottom-up procedure, multi-layered hydrophilic particles were obtained (Fig. 2) [18]. One advantage of this technique is that high encapsulation efficiencies approaching ~100% can be achieved.
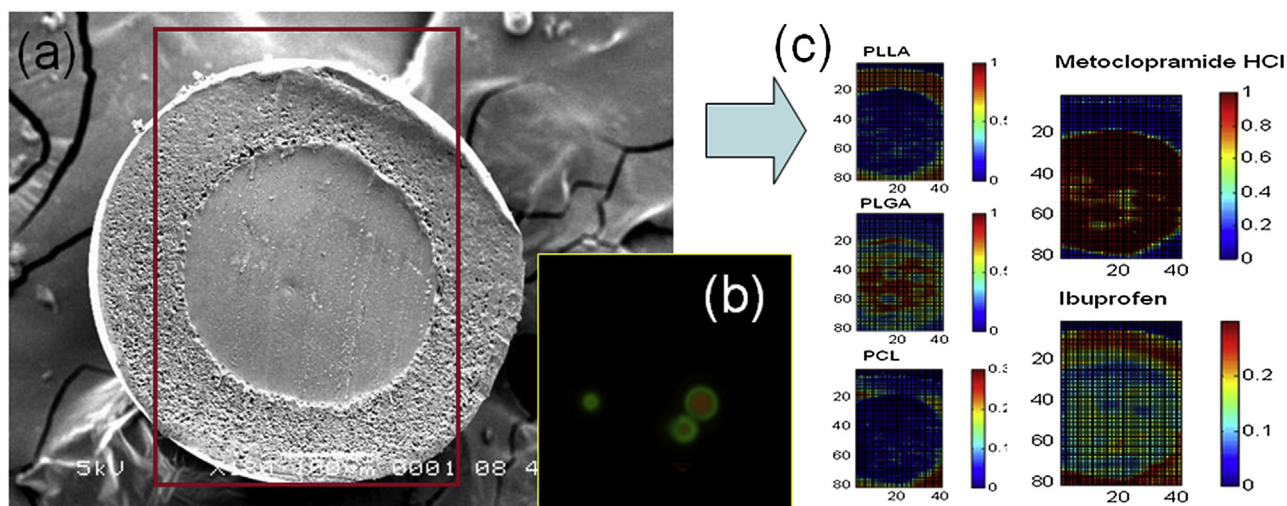

Fig. 1. (a) FESEM micrograph of core—shell microparticle; (b) Confocal image of sub-micron sized core—shell particles loaded with two different fluorescent dyes; (c) Raman mapping of polymers and drugs from core—shell microparticle (a) [12,16].
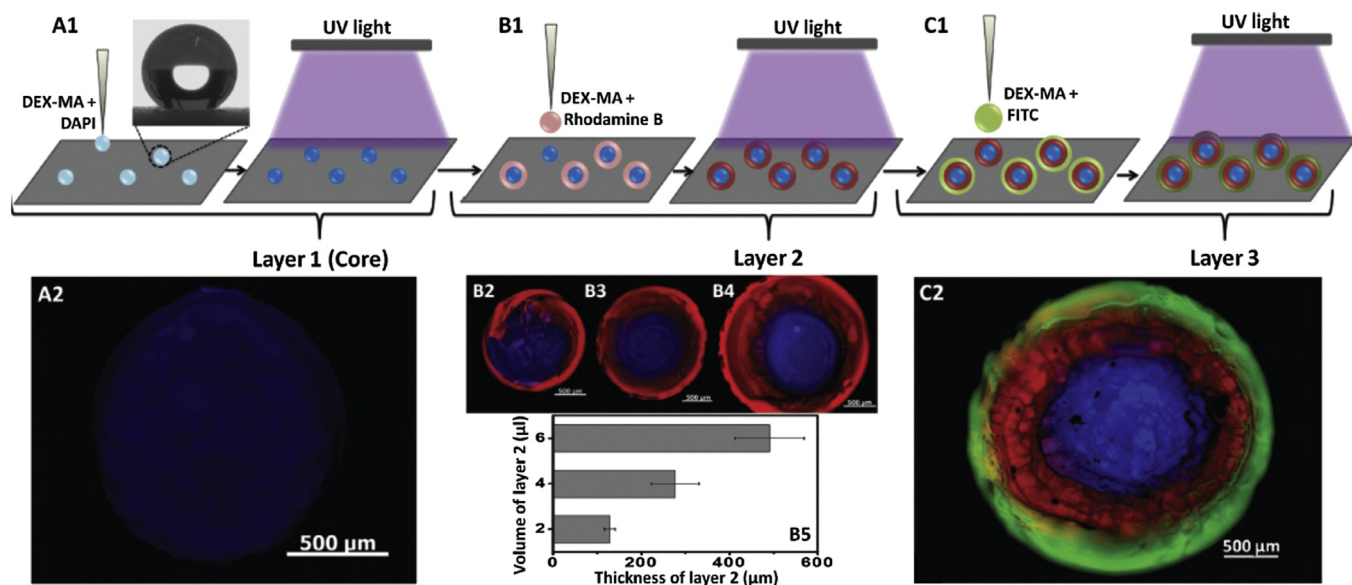
Fig. 2. Biomimetic approach using copper superhydrophobic surfaces to produce multilayered particles: (A1) the core (Layer 1) is produced dispensing DEX-MA (methacrylate modified dextran) + DAPI solution onto the superhydrophobic surface and then crosslinking by UV light exposure; (B1) the follow layer (Layer 2) is obtained dispensing DEX-MA + Rhodamine B solution around the previous obtained particle and again crosslinking by UV light exposure; and (C1) the third layer (Layer 3) is obtained following the same procedure but using DEX-MA + FITC solution. Fluorescent microscopic images (A2, B2, B3, B4 and C2) of the particles obtained in each step of the procedure; and (B5) thickness of the particle layers that were obtained by dispensing different volumes of polymeric precursor solutions in the second layer [18].

Besides the biomedical arena, polymer—polymer multi-layered particles have also been exploited in many other applications. For example, preparation of multi-layered core—shell latex-based particles has been reported [21]. These particles were synthesized via a surface cross-linking emulsion polymerization technique. Here, both the core and shell materials were made of latex. Polymerization was performed in a semi-continuous fashion monitored by dynamic laser scattering. Briefly, divinylbenzene (DVB) was added as the crosslinking agent to create the "hard" layers, so as to prevent molecular diffusion from the adjacent "soft" layers. The interesting concept was to utilize DVB to crosslink the odd-numbered layers, i.e. first, third, and fifth layer of the shells, counting outwards from the inside of the particles, while the core, second, and fourth layers of the shell were free of DVB. The core latex (latex I) was composed of low T_g copolymers, i.e. T_g lower than room temperature, whereas the first layer (layer 1) of the shell was composed of higher T_g co-polymers. The beauty of this technique is the ability to design each polymeric layer with alternating latex layers of high and low glass transition temperatures (T_g). A summary of the reaction scheme for these particles is shown in Fig. 3.

Such latex composite particles have many applications in a broad range of technologies, such as impact modifiers, adhesives, and coatings [22—27]. Such multi-layered structures are desired in cases where a combination of multiple polymer phases in one latex particle would provide superior physical properties as compared to a single phase latex particle. In addition, while there is an abundant literature regarding the simple core—shell emulsion, i.e. the latex which consists of a core and a one-layer shell, there have also been some works that report on the preparation of multi-layered core—shell latexes. Such particles with periodical multilayer structures have potential applications in optical limiting, three-dimensional optical data storage, security data encryption, chemical or biochemical sensing, and dielectric resonators [28].

Because the T_g of such multi-layered latex-based particles (Fig. 3) in every layer are alternating, and the alternating changes on the degree on the deformation of latex particles with the number of layers can be used to prove the layer-by-layer structure of these latex particles. This can be proven by the alternating changes of film-formation properties of the latex emulsion at room temperature with increasing number of layers. Results showed that latex particles with only a single coating (latex II) cannot form a continuous film at ambient temperature. Likewise, the even-numbered layers (i.e. latexes IV, and VI) are broken and cracked on the glass substrates, whereas the films formed by odd-numbered layers (i.e. latexes I, III, and V) are continuous, without any cracks on the glass substrates. This is because the T_g of the core and layers 2 and 4 polymers are below the ambient temperature. This illustrates how different layer properties can influence film formation of these polymer—polymer multi-layered particles. Indeed, the deformation of the latex particles is largely dependent on the nature of the polymer in the outermost layer of the latex particles.

Electrophoretic image displays (EPID) have been of intensive research and development in the recent years [29—32]. For dual-particle EPID, its working principle lies in two kinds of coloured and oppositely charged particles that are suspended in a dielectric medium, i.e. the electrophoretic ink, and placed between two flexible electrodes. Under the influence of an electric field, the particles move towards the electrode of opposite charge. The front electrode is transparent, whereas the back electrode is used for pixel addressing. Each pixel therefore takes on the colour of the particles that have migrated to the front. In EPIDs, multi-layered latex particles with surface functional groups make them suitable for use as electrophoretic particles in electronic inks [29]. A recent paper presents the synthesis of such latex particles for use in dual particle electrophoretic ink without any surfactant [28]. For this purpose, acidic and basic particles of contrasting colours are synthesized, and the mixing of these will lead to spontaneous transfer of a proton from the acid to the base, without the need of any micelles to stabilize the counter-ions (Fig. 4). Countercharging of particle will therefore result in improved lifetimes of the display and reduced power consumption.

From the work by McCleskey et al., sterically stabilized electrophoretic particles with dyes are used. Particle colouration is
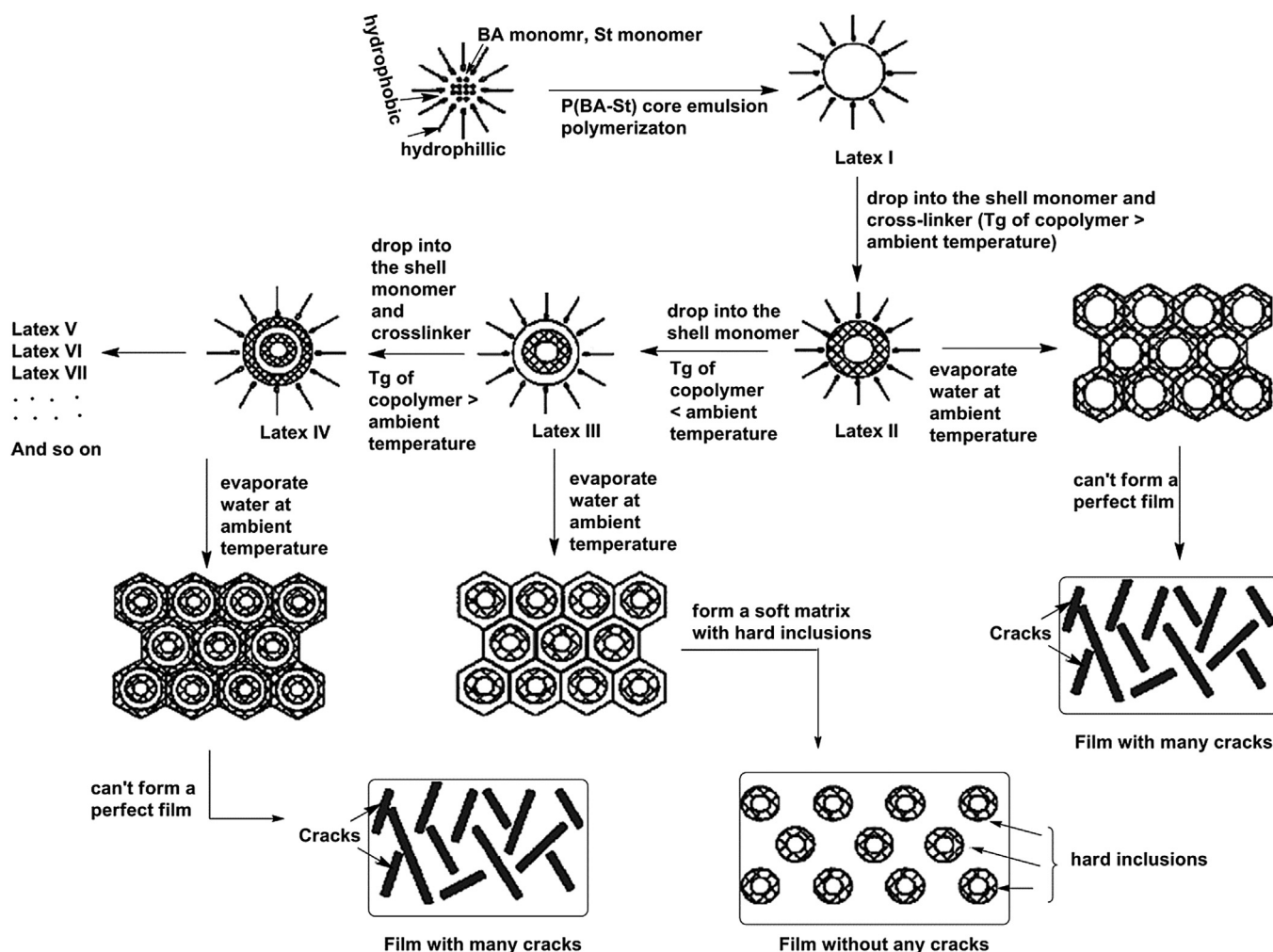
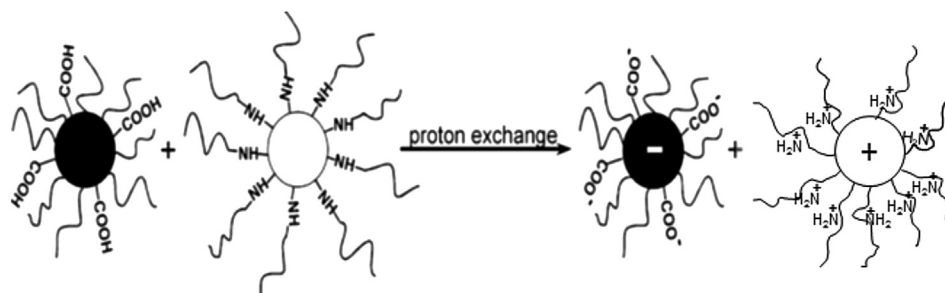**Fig. 3.** Schematic of the preparation of multilayered latex particles [21].

Fig. 4. Countercharging of functionalized multilayered latex particles in the electrophoretic dispersion medium [29].

achieved *via* two different methods: dyeing by polymer particle swelling using the versatile method of supercritical CO_2 [33], and polymerization in the presence of black dye Nigrosin, in a single-step process. The coloured particles obtained have been tested in a dual particle electrophoretic ink, containing white TiO_2/polymer particles as the second type of particles. When the white particles have migrated to the front of the electrophoretic test-cell, the light is scattered by the pigments and the cell appears white. On the contrary, when the black particles migrate to the front of the display, the light is absorbed by the Nigrosin contained in the black particles and the display appears black [32].

2.2. Polymer-polyelectrolyte multilayer (PEM) core—shell particles

Several approaches have been devised to prepare poly-electrolyte multi-layered particles (PEM [34—36]. Among the various approaches, layer-by-layer (LbL) assembly is an influential domain in the use of non-covalent interactions which is mostly based on electrostatic interactions i.e. the absorption of alternating cationic and anionic species. In addition to electrostatic interactions, other complementary interactions include hydrogen bonding [35], hydrophobic interactions [37], covalent bonding [38], DNA hybridization [39], van der Waals [40], and guest—host

interactions [41]. The popularity of LbL technique is mainly due to its simplicity in engineering multi-layered particles with a range of tunable properties, i.e. stiffness, permeability, biofunctionalization, biodegradability etc., and has found applications from drug delivery to catalysis [1].

PEM particles are typically assembled through a sequential deposition of charged polymers *via* complementary interactions onto a template or substrate [15,42]. In short, electrostatic interactions between polyions in solution and an oppositely charged interface are key to the final structure of the polyion-layered thin film. During layering process, polymer adsorption proceeds until the surface charge is reversed. This is followed by the adsorption of a counter-polyion. The final PEM particle consists of layers of nanometer thickness.

Hess et al. [43] pointed out one very interesting property of PEM particles, whereby the yield stress of PEM-modified suspensions exhibits a surprising dependence on the polyelectrolyte conformation of multilayer films. They have demonstrated that control over the polyelectrolyte conformation of PEM films (in the case of strong polyelectrolytes) serves as a versatile platform to tailor the dynamic yield stress of colloidal suspensions (Fig. 5). Specifically, low dynamic yield stress values can be achieved by adsorbing polyelectrolytes in a flat conformation provided the ionic strength of the background fluid has significantly less impact on the yield stress. Alternatively, low yield stress values can also be produced by adsorbing the polyelectrolytes in a brushy conformation and dispersing them in a low ionic strength background fluid. On the contrary, polyelectrolytes have to be adsorbed in a brushy conformation and dispersed in a high ionic strength background fluid in order to achieve high yield stress values. Therefore, a wide range of the dynamic yield stress is achievable for brushy polyelectrolyte multilayers just by fine-tuning of ionic strength of the background fluid. Hess et al. study shows that well-defined, homogeneous polyelectrolyte multilayers are a promising method for the design of colloidal suspensions.

3. Polymer-inorganic core-shell and multi-layered particles

3.1. The role of polymer as a sacrificial template

Polymer–inorganic hybrid core–shell particles are studied for various applications, in drug delivery, cosmetics, electronic devices, and chemical analysis [44]. Several routes have been explored in coating an inorganic core with a polymeric shell [45,46]. Among these, surface graft polymerization, in particular, is of wide interest due to its versatility. This involves polymerization after the attachment of a polymerization initiation group or polymerizable group on the surface of the core particle. Wakiya et al. [47] introduced a stepwise formation method for micron-sized, multi-layered core–shell particles comprising of an inorganic core, polymer inner shell, and an inorganic outer shell (Fig. 6a). Here, a silica core was coated with a polystyrene seed layer, followed by surface seed polymerization with styrene, to afford the inner shell. These particles were then coated with an additional layer of silica (outer shell) by surface sol–gel reaction with tetraethoxysilane. The usefulness of the combination of surface seed polymerization and sol–gel method is emphasized by the precise control achieved over particle diameter as well as shell thickness and count. Moreover, they have also described how the inner organic shell can be easily removed by calcination to afford a single-core micro-capsular structure (Fig. 6b).

An attractive thermal deposition method has been utilized by Kim et al. for the fabrication of multi-layered superparamagnetic particles [48], which can be utilized as a magnetically cell sorting device. Polystyrene spheres are used as a template, and their surfaces were coated with a magnetic element (i.e. Ni) by thermal deposition that was isolated with SiO_2 layers. By controlling the thicknesses of Ni to be less than 3 nm and SiO_2 layers to be more than 10 nm, superparamagnetic particles could be obtained (Fig. 7). Fig. 7 also shows the importance of the thickness of Ni layer in order to achieve superparamagnetic property of the particles. One advantage of using polystyrene as template is easy fabrication of particles with various diameters ranging from 100 nm to 100 μm, by changing the polystyrene particle size. Another advantage is the possibility of fabricating hollow superparamagnetic particles when the polystyrene template is removed. Such hollow superparamagnetic particles would be potentially useful as a cell sorting device for cell collection in the void space of the hollow structure [49–52].

An interesting example shown by Gao *et. al* [3]. in which they have successfully fabricated hollow sphere-nanofilms with precisely tunable numbers of layers using Ta_3N_5 hollow sphere-nanofilms as an example. This was achieved through the oil-water interfacial self-assembly combined with the control of the sol–gel reaction of precursors [Fig. 8]. A bunch of well-defined poly(styrene-co-acrylic acid) (PSAA) colloidal particles were self-assembled on smooth substrates using oil-water interfacial self-assembly strategy to form polymer nanofilms [53–55]. Due to the monodispersibility and stability of polymeric colloidal particles, high-quality multilayer polymer particle nanofilms were more easily controlled than organic/inorganic core–shell composite particles as building blocks [56]. After introducing ethanolic solution of tantalum ethoxide to the particles, it infiltrated into the
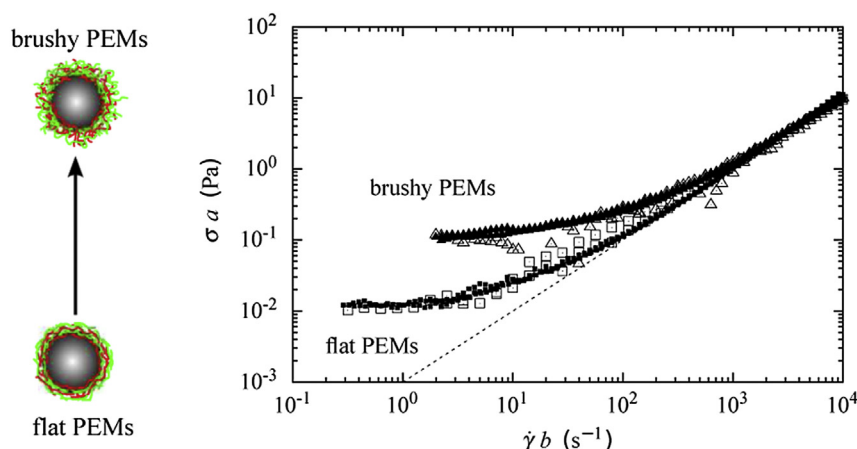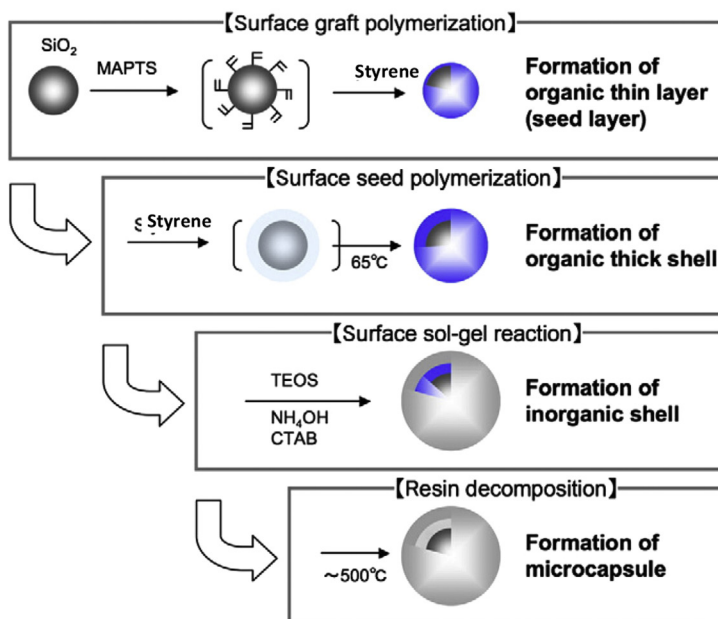

Fig. 5. Using the polyelectrolyte conformation of the PEM's to tune the dynamic yield stress. Typical curves of normalized shear stress as function of normalized strain rate [43].
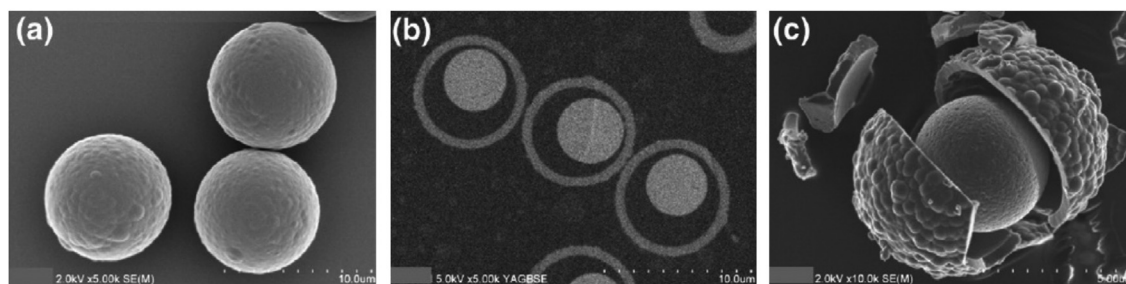
(a)

(b)

Fig. 6. a – Schematic illustration for the stepwise preparation method of various polymer–inorganic hybrid core–shell particles [47]. b – SEM images of the multilayered particle with silica outer shell prepared by surface sol–gel reaction [47].
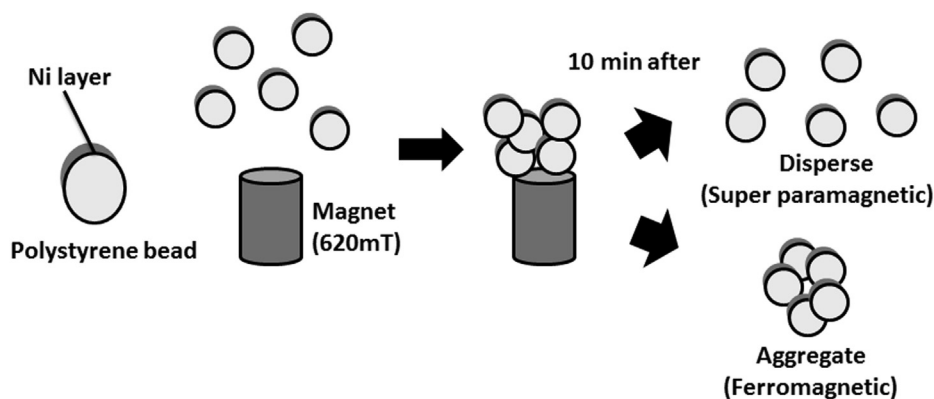

Fig. 7. Qualitative confirmation of superparamagnetic properties of particle achieved by tuning the layer thickness of Ni [48].

voids between PSAA colloidal particles *via* capillary forces and its hydrolysis/condensation reactions occur during drying. Because the monodisperse PSAA colloidal particles were composed of hydrophobic PS-enriched cores and carboxylic-acid-group-enriched shells, they quickly captured small Ta_2O_5 nanoparticles derived from the sol–gel reaction of tantalum ethoxide due to the strong interactions between polymer particles and the inorganic phase.

Well-defined PSAA/Ta_2O_5 core–shell spherical nanofilms were produced at high humidity [57]. Finally, PSAA colloidal particles (core) were removed by calcination *via* different routes in order to produce hollow sphere nanofilms of Ta_3N_5. Accordingly, calcination in ammonia provides Ta_3N_5 hollow sphere-nanofilms with precisely tunable layers (Route A in Fig. 8). However, at low humidity, the Ta_2O_5 sols formed closely packed three-dimensional skeletons
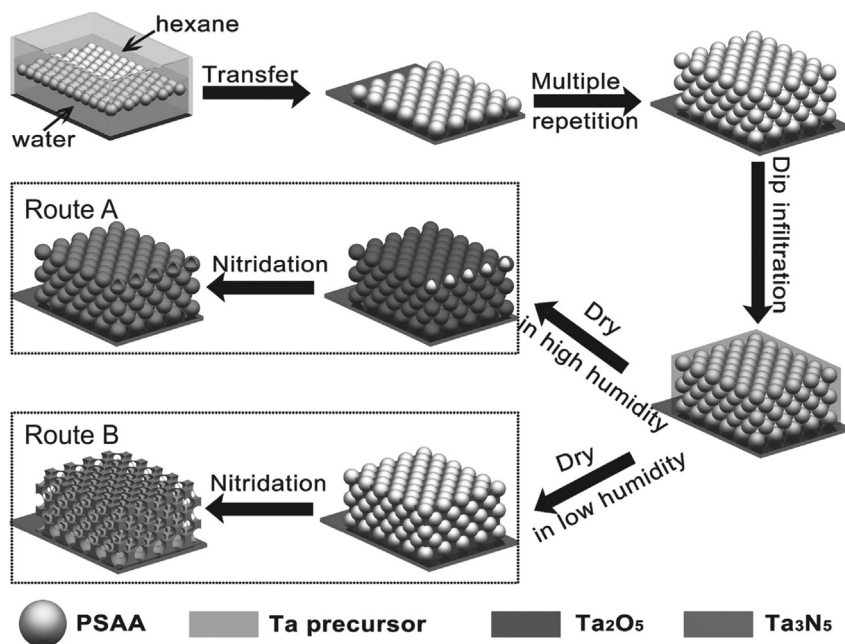
Fig. 8. Schematic illustration for the formation of multilayer Ta$_3$N$_5$ hollow sphere- and inverse opal-nanofilms [3].

due to the low rate of the sol–gel reaction. After calcination, Ta$_3$N$_5$ monolayer- and multilayer ordered pore structures (inverse opal-nanofilms) were produced (Route B in Fig. 8). Ta$_3$N$_5$ is an important photocatalyst suitable for solar hydrogen production because it has a narrow band gap of 2.1 eV, making it suitable for the collection of more than 45% of incident solar energy [58]. Photoelectrodes based on Ta$_3$N$_5$ thin films, nanoparticles, nanotube arrays and nanorod arrays have displayed excellent visible-light activity for photoelectrochemical (PEC) water splitting [59]. In their study, Gao et al. also found out that Ta$_3$N$_5$ hollow sphere-nanofilms based photoelectrodes exhibited significantly enhanced visible-light water splitting ability and superior stability. The PEC performance of the hollow sphere-nanofilms was also found to be highly dependent on the numbers of layers used [60].

3.2. The role of polymer as a retainable core particle

Self-assembled colloidal core–shell nanoparticles with polystyrene as core and gold nanoparticles as shell have been designed by Tian et al. [61]. They have also investigated the application of these core shell-structured colloidal particles for protein separation. Similarly, colloidal particles with polystyrene-(PS) coated magnetic nanoparticles in the core were also prepared by this strategy [61]. Briefly, hydrophilic citrate-stabilized AuNPs (gold nanoparticles) were dispersed in water and PS with thiol terminal groups (PS-SH) was dissolved in toluene. Finally by mixing the two solutions *via* sonication, a stable emulsion was obtained. In the emulsion, AuNPs were present at the liquid–liquid interface. Colloidal particles with PS cores and AuNP coronae were prepared by adding the emulsion to excess methanol, where the colloidal particles were stabilized by hydrophilic AuNPs in the coronae. In the same way, PS-SH/PS-coated Fe$_3$O$_4$NPs were dispersed in toluene, and then colloidal particles with PS/Fe$_3$O$_4$NPs in the cores and AuNPs in the coronae were prepared (Fig. 9). The morphology of colloidal particles can be easily controlled by varying the weight ratio of PS-SH to AuNP. The commonality across these examples is that the polymer serves as the permanent core material upon which other inorganic materials were decorated. As illustrated, AuNP in the coronae of colloidal particles provide active sites for

chemical reactions and protein adsorption, and Fe$_3$O$_4$NPs in the cores of colloidal particles can be used in the separation of the colloidal particles from the solution. On the basis of this approach, many different hydrophobic compounds/particles can be included in the cores of colloidal particles, and functional colloidal particles can be produced. These colloidal particles are especially valuable in the fields of catalysis, biomolecule separation, and gene therapy.

4. Inorganic-polymer core-shell and multi-layered particles

Like polymer-inorganic core–shell multilayer particles, inorganic–polymer microspheres are also attracting much interest considering their unusual and possibly unique optical, mechanical, rheological, electrical, catalytic, and flame-retardant properties. A huge variety of inorganic materials has been used to prepare such hybrid cores, with silica (SiO$_2$) being the most widely used. Colloidal silica spheres are popular not only because of the uniformity in size, shape and compositions of these particles, but also their usefulness in electronics and biomedical applications [62–64].
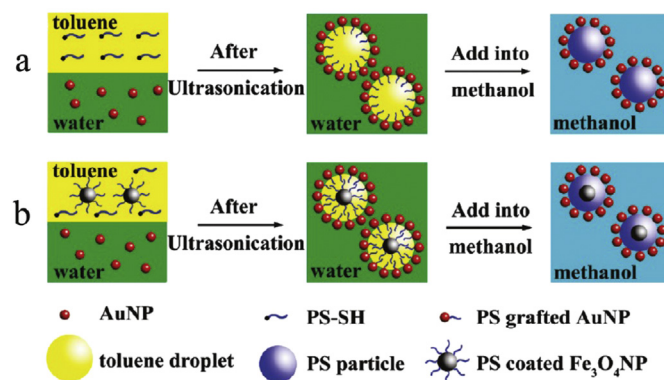

Fig. 9. Schemes for the preparation of (a) colloidal particles with PS cores and gold nanoparticle (AuNP) Coronae and (b) Colloidal particles with PS/Fe$_3$O$_4$NP cores and AuNP coronae [61].

Similarly, magnetic particles have also attracted much attention in recent years due to their novel physicochemical properties such as their response to an external magnetic field, ability to generate heat under an alternating magnetic field, reduction in relaxation time of surrounding small molecules like water for magnetic resonance imaging and so forth [65]. Surface grafted polymerization is an efficient method to endow these magnetic nanoparticles with multi-functionality through the use of surface polymers [66]. For example, surface-grafted functional polymer brushes not only efficiently improves the solubility of magnetic particles in different solvents, but also endows the particles with a series of functionalities for antibacterial properties [67], immobilization of metal nanoparticles [68], controlled drug release [69], just to name a few.

In the work by Liu et al. [70], to obtain multifunctional inorganic (magnetic) core and polymer shell particles, the functional poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) brush was grafted onto the alkylbromide-modified magnetite/silica/poly(N,N′-methylenebisacrylamide-co-2-hydroxyethylmethacrylate) (Fe$_3$O$_4$@-SiO$_2$@PHEMA) tri-layer microspheres *via* the surface-induced atom transfer radical polymerization (Fig. 10). Typically, the bilayer microspheres with surface alkyl bromide groups were prepared by a sol–gel process for the synthesis of Fe$_3$O$_4$@SiO$_2$ core–shell inorganic component and then distillation-precipitation polymerization was followed for the formation of PHEMA shell (third layer) together with the subsequent esterification of the surface hydroxyl group and 2-bromoisobutyryl bromide. Furthermore, gold nanoparticles were loaded onto the functional PDMAEMA brushes through the *in situ* reduction due to their strong coordinate interaction. These PDMAEMA brush-stabilized gold nano-colloids can be used as a catalyst. For example, the reduction of 4-nitrophenol to 4-aminophenol as a model reaction, revealed a high catalytic efficiency and good reusable property of Fe$_3$O$_4$@SiO$_2$@PHEMA-g- PDMAEMA/Au microspheres [70]. Due to excellent stabilization ability of the grafted polymer (PDMAEMA) brush to gold nanocolloids, the catalytic activity was well retained even after at least six cycles of usage, significantly better than previous reports [71,72].

Another of such example would be the fabrication of SiO$_2$/organic/Fe$_3$O$_4$ tri-layered particles. These microspheres are of interest because of the wide application potential of these magnetic materials in magnetic bio separation, drug delivery, magnetic resonance imaging contrast enhancement, and targeted drug delivery [67,73–75]. A simple process has been developed to prepare magnetically modified aminated silica (SiO$_2$) particles [76]. Submicron-sized SiO$_2$ particles were modified with poly(methylmethacrylate–co-methacrylic acid) through seeded polymerization without any stabilizer. The role of polymer (poly(-methylmethacrylate–co-methacrylic acid) here is to protect silica particles as well as to provide surface functional groups to allow further modification. Hence, the carboxyl groups localized near the particles surface were then covalently linked with ethylene diamine to prepare aminated composite particles. Iron ions were then precipitated on the surface of aminated composite particles in order to achieve magnetically doped functional SiO$_2$ particles.

In addition to magnetic nanoparticles (iron (II) and iron (III)), zerovalent iron nanoparticles (nZVI) have also been studied in recent years for environmental remediation applications such as the degradation of chlorinated organic contaminants such as trichloroethylene (TCE) and polychlorinated biphenyls (PCB) from water [77]. The most common way to overcome limitations related to the transport of nZVI is to add a polymer stabilizer to limit aggregation and hence, enhance the particle reactivity [78]. The other method to enhance particle reactivity has been to limit particle size through novel synthetic techniques. Petersen et al. [79] studied the effect of particle size as well as polymer coating and polyelectrolyte multilayer (PEM) synthesis conditions on degradation of chlorinated contaminants (TCE and PCBs). They have used two different synthetic techniques: 1) An LbL approach at different pH values i.e., sorption of iron (II) on multi layered polyelectrolytes decorated glass beads followed by iron reduction to get PEM stabilized nZVI and 2) iron reduction in the presence of varying concentrations of poly(acrylic acid) to get PAA stabilized nZVI. Zero valent iron nanoparticles produced by both techniques yielded higher degradation rates than free nZVI without stabilizer. Their investigation revealed that hydrophobicity and sorption to the multilayer impacts the availability of the hydrophobic compound to the nZVI. Particle size also had a major role whereby smaller particles having stronger dechlorination rates. This study highlights the importance of polymeric surface coatings or PEM characteristics on the application of nZVI for environmental applications and suggests that by carefully designing nZVI nanoparticle/polyelectrolyte combinations, it is possible to achieve specific goals under various subsurface environmental conditions.

Recently, a new class of core/shell particles, namely rattle particles [80,81], have shown promise in applications such as catalysts [82–84], drug delivery vehicles, [85–89] nanoreactors [90–92] and optical materials [93]. For example, rattle particles, composed of a catalytic core and mesoporous shell, can be utilized in the area of heterogeneous/selective catalysis when specific substrates
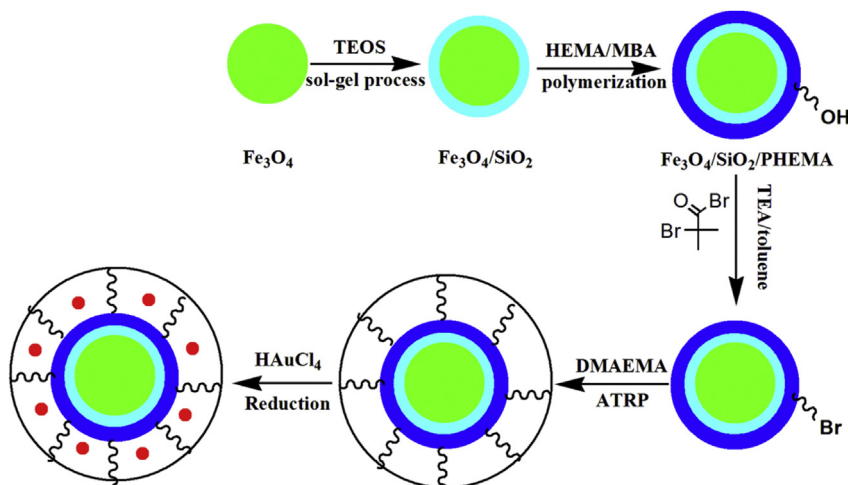

Fig. 10. Preparation of the Fe$_3$O$_4$@SiO$_2$@PHEMA-g-PDMAEMA microspheres with the grafted PDMAEMA brush [70].

permeated through the shell can be selectively catalysed by the cores [82–84]. Another application area of rattle structure would be in photonics. If the core of the colloidal photonic crystals of rattle particles is movable and magnetic as well, then its position can be easily manipulated by an external magnetic field [93]. Okada et al. [94]. observed the rattling of silica rattle particles (which has a micron-sized silica inner sphere) with an optical microscope and proved the movability of the inner spheres when it is in suspension. The multi-layered rattle particles (silica sphere/polystyrene (PSt) inner shell/silica outer shell) were prepared with a combination of soap-free emulsion polymerization, silica-coating and removing the polymer component by pyrolysis. In order to achieve silica rattle particles without any residual polymer component, they have removed Polystyrene by heating the multi-layered particles at 500 °C for 4 h. Here, polystyrene mainly acts as a removable template to provide free space for rattling of the inside spheres. An AC field was applied to the suspension to form a pearl chain structure composed of dielectric rattle particles fixed with each other [95]. Because of low optical perturbation at the shell interfaces, it has been predicted that clear images of the inner spheres are obtained with the microscope especially when the shell surfaces can be preferentially attached to each other under the electric field. Fig. 11 shows a transition from the disperse state to pearl chains of the rattle particles under AC field and this transition took about 20 min. They have also showed that at the AC application time of 20 min, where the rattle particles were slightly moving due to Brownian motion, but still softly fixed with each other in the laterally moving chain and most of the inner spheres were also attached to the inner wall of silica shells. A viscosity enhancer (PVP) was added to the suspension of rattle particles in order to further reduce the Brownian motion of the silica shell in suspension. There were two reasons to choose PVP with a very high molecular weight of 360 kDa: 1. to increase the viscosity of suspension and 2. to reduce the permeability through the silica shell. However, it was found that at this condition only less than 10% of inner spheres in the pearl chain of particles were able to move independently in the compartment of the silica shell. Diluted NaOH solution was used to etch silica rattle particles so as to detach the inner spheres from the inside

wall of the silica shell and thus increase the percentage of inner spheres (75%) that could move freely under the applied electric field. This interesting work initiates the high potential of the responsive cores whose positions in the hollow structure can be easily controlled by external fields. This is the first direct observation of freely movable inner single spheres without adhering to the inside wall of the shell compartment, possible only through the use of a sacrificial polymeric template.

5. Perspectives

Over the last decade, significant developments were made in the field of multi-layered polymer-comprising particles. Depending on their architectural designs, there are different types of multi-layered particles, such as polymer–polymer, polymer-inorganic, inorganic-polymer type of configurations, whereby most of these are core–shell structures. They represent a new class of polymer composite materials that can be used for applications in catalysis, photonics, water treatment, as sensors, and in biomedical applications, depending upon the structure of the particles, and the choice of polymers and their counterparts (polymer/inorganic). These polymers play a critical role in the design of such functionalized particles. For example, inorganic nanoparticles can be made to be water soluble by modifying their surface with hydrophilic polymers, rendering them to be re-dispersible in water (i.e. inorganic-polymer). Alternatively, polymeric particles can be used as a template upon which nanoparticles can be deposited to render other functional properties (i.e. polymer-inorganic). Multi-layered particles can also be made wholly from polymers where different polymers can be used to coat an underlying polymer core particle (i.e. polymer–polymer and polymer-PEM). The possibilities of such particles are immense, giving rise to new particulate designs for very specific applications.

However, significant challenges still remain in the field of research, where polymers play an indispensable role in shaping the use of such multi-layered particles. Although the opportunities for such functionalized particles are vast, to date, it is still unclear whether all these potential uses can be readily translated into commercial products for economic benefits. The aforementioned fabrication methods are not sufficient for the bulk production of different multilayer polymeric particles considering that most of these methods cannot be used for large-scale production. Hence, further efforts must be made into the development of robust and reliable strategies that can be utilized for fabricating various high-quality multilayer particles on large scales. The use and exploration of such highly functionalized particles are probably still at its infancy where many more application-driven studies are required to fully appreciate their commercial potentials. For example, only in recent years, more *in vivo* studies have been conducted to fully appreciate the use of multi-layered particles as pharmaceutical drug carriers. Moreover, challenges associated with such drug delivery systems, *viz.* long-term stability, biocompatibility and immunogenicity are still yet to be fully understood. Although a lot of potential applications, such as catalysis, drug delivery, diagnostics and water remediation systems have been mentioned here, most of them still remain to be realized in terms of its potential as a future commercial product. Therefore, in order to gain in-depth understanding, more structure–property–application relationships must be investigated. Nonetheless, as highlighted in this review, polymeric-based multi-layered particles do possess unique properties and functionalities that would render them useful for specific applications. This is because of the versatility and robustness of polymers that allow for tunable properties to be imparted onto core particles, be it polymer-core or inorganic-core. The role that polymers play therefore adds a new dimension to the
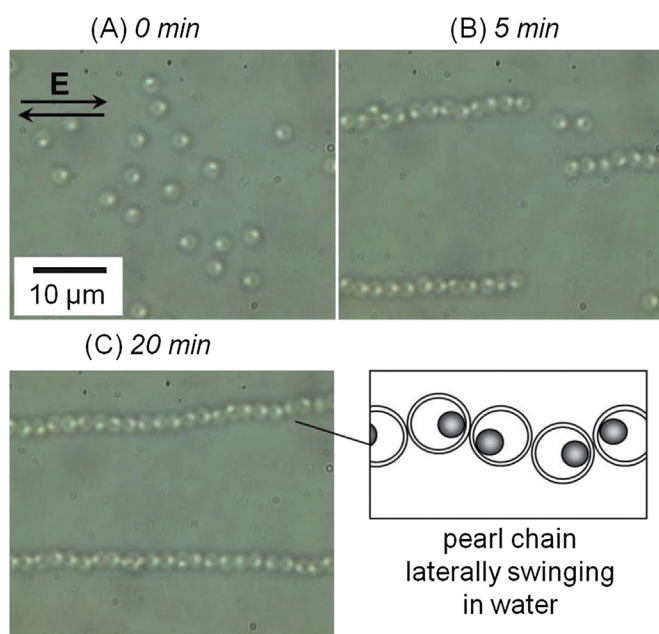

Fig. 11. Optical microscope images to show a transition from the disperse state to pearl chains of the rattle particles under an alternative electric field [94].

architectural design of multi-layered, highly functionalized particles.

Acknowledgements

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