Surface engineering of nanomaterials: Processing and applications

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Abstract

At present, nanomaterials (NMs) show extreme potential for a wide range of applications ranging from aerospace to energy storage applications owing to a number of properties which, in a number of contexts have been reported to be superior as compared to those of bulk counterparts. However, the high surface area to volume ratio which yields extraordinary properties to NMs also turns out to be the major limitation in a number of different contexts. For instance, the high surface area to volume ratio in these materials leads to a high reactivity, especially in electrochemical environments which are prevalent during energy storage applications. In this context, it is worthwhile mentioning that processing of NMs play a crucial role in influencing their mechanical properties. On the other hand, surface engineering has emerged as a powerful tool to deconvolute bulk properties from surface characteristics and has been reported to exhibit tremendous potential for overcoming the aforementioned limitation of NMs. The present review therefore, is aimed at highlighting the present status of research in the field of processing and applications of surface engineered NMs. Moreover, challenges and future perspectives in the aforementioned avenue have been discussed.

Keywords: Nanomaterials, Chemical Vapour Deposition, Atomic Layer Deposition, pseudocapacitors, batteries.

1. Introduction

As correctly pointed out by Richard Feynman in his book “There's Plenty of Room at the Bottom”, nanoengineered systems have the potential to revolutionise the field of materials research [1]–[3]. From a historical viewpoint, this may be considered as the origin of a new avenue of materials research for heterogeneous material systems which helps to separate the surface from the bulk properties [3]–[7]. Besides, this approach has been utilised to discover materials with excellent bulk and surface/interface properties [8]–[17]. Synthesis techniques for NMs may be primarily split into two groups: (i) top-down, and (ii) bottom-up approaches. Methods based on top-down approach involve comminution or dissociation of bulk materials into finer components whereas those for bottom-up approach are used for assembling atoms together [18]–[22]. The former was originally developed for the microelectronics industries [23]–[25]. However, with the development of techniques such as nanopatterning and thin-film deposition, this approach made its way into fabrication of NMs [18]. Methods based on this approach commonly include solid-state milling (such as ball milling), photolithography, laser machining, soft lithography, nanosphere lithography, colloidal lithography, ion implantation, and deposition [19]. Common examples of synthesis technique involving bottom-up approach include plasma arcing, chemical vapour deposition (CVD), atomic layer deposition (ALD), metal organic decomposition, laser pyrolysis, molecular beam epitaxy, solgel method, wet synthesis etc [19].

One of the areas where surface engineering of NMs is being explored (at present) is the design of electrode materials for energy storage applications [26]. This avenue utilises the excellent charge storage capacity and high rechargeability of NMs [27]. At present, commercial grade batteries (for energy storage applications) mainly use micro-scale materials for electrodes [28]. This may be attributed to: (i) fabrication challenges for NMs, and (ii) the high reactivity (due to high surface area to volume ratio) NMs which leads to the formation of solid electrolyte interphase (SEI) [29]–[31]. The two aforementioned factors may be held responsible for an increased consumption of electrolyte during the formation of electrode-electrolyte interface, consequently, degrading the charge storage capacity [32]. This is one of the challenges which may be overcome through surface engineering [33], [34].

In the context of electrochemical supercapacitors, SEI must be stable enough to prevent Faradaic charge transfer reactions and assist in forming electric double layer [35]. In the case of batteries and pseudocapacitors, SEI must facilitate charge transfer reactions for the purpose of storing and releasing energy without any degradation in charge storage and release capacity [34]. From a surface engineering viewpoint, it is extremely important to engineer electrode materials for energy storge applications [32], [36]. This necessitates isolation of electrode materials with enhanced bulk and surface properties for high electrochemical performance (including high storage capacity, internal resistance and so on [23], [24], [37], [38]. The present chapter is aimed at addressing the present state of research in the context of surface engineering based processing techniques and applications of NMs. This has been followed by a discussion on the challenges and future perspectives in the avenue of surface engineered NMs.

2. Surface engineering approach for NM fabrication

2.1 CVD and ALD

To the best of authors' knowledge, gas phase processing of materials (till date) is the most widely used technique towards surface engineering of NMs [39]. These kind of processing approaches primarily involve a mixture of precursor gases which flow through a chamber (maintained at high temperature) to react with the substrate surface [40]. In the context of CVD, reactions between the substrate surface and gas phase precursor are influenced by a number of factors which include: (i) precursor partial pressure, (ii) temperature, and (iii) reactivity of the electrode [41]. In the case of ALD (**Fig. 1)**, gas phase precursors react in a self-limiting process. As a result, ALD involves pulsing of a number of precursors (generally two or more) in an alternating manner [42], [43]. In this context, it is worthwhile mentioning that although CVD is a promising technique to engineer the properties (physical, chemical, and mechanical) of substrate surfaces, however, it is highly challenging to control the thickness [43]. For instance, deposition of carbon-based NMs on a variety of substrates (using CVD) has been reported to enhance the mechanical properties, corrosion resistance, and electrical conductivity [44]. Another interesting feature of CVD is the easy removal of gaseous impurities which leads to the deposition of high-purity films [44]. However, the high temperatures prevalent during CVD may lead to the decomposition of a number of substrates limiting the choice of gas phase precursors for a given substrate during the process [45], [46]. Moreover, conventional CVD techniques have a number of limitations which include (i) high temperature (of reaction), (ii) low deposition rates, and (iii) operation at low pressures. This has been the reason for the development of enhanced CVD techniques such as laser, hot filaments and plasma [46]. This has given way for the development of metal-organic chemical vapor deposition (MOCVD) [39], [46].

On the other hand, ALD enables processing (near room temperature) for a number of depositions, providing favourable conditions even for thermally sensitive substrates [41], [42]. ALD involves a two-step process with an organometallic precursor and an oxidizing or reducing agent [43]. Inert gas such as Ar or N_2 is used to prevent a CVD reaction between precursors [45], [47]. The major advantage of ALD over CVD is (i) thickness control with high precision, (ii) lower operating temperatures, and (iii) coatings with high level of design complexity may be deposited on substrate surfaces [45]. However, ALD suffers from the high requirements of the precursor, viz. the precursor must be (i) volatile, and (ii) able to undergo a self-limiting reaction [43].

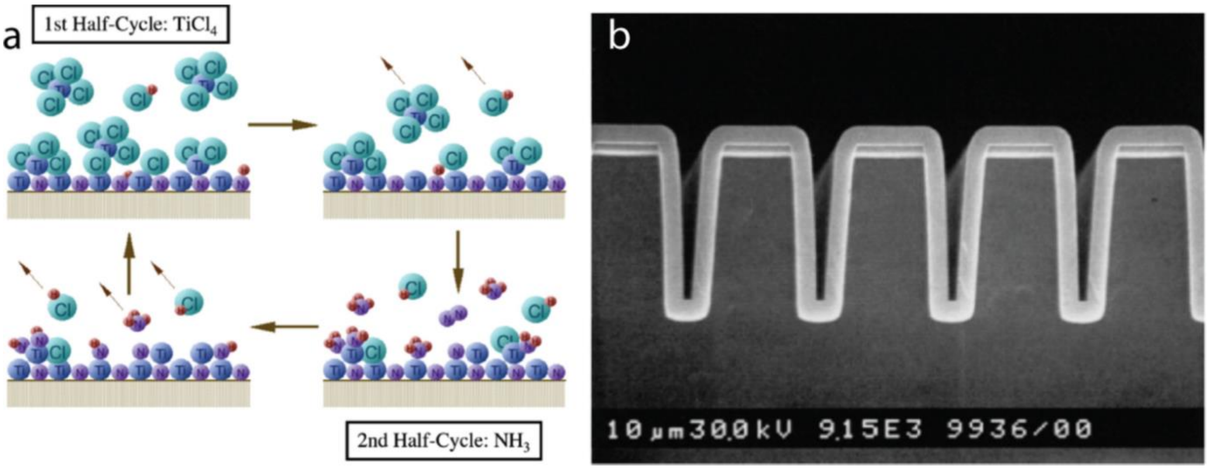

Fig. 1 ALD: **(a)** Schematic, and **(b)** Scanning Electron Microscope (SEM) image of a cross-section of 300 nm thick Al_2O_3 ALD film on a trench-structured Si wafer [42], [43].

2.2 Wet chemistry based surface modification

This approach uses reagents or solvents for the chemical modification or functionalization of the material surfaces [48]. In addition, this approach provides an additional control on the engineered interface. Either non-covalent interactions [40], [48] or covalent functionalization [41], [46] may be utilised to produce a coating using the aforementioned approach. An example of the former (i.e. a non-covalent surface engineered system) is an ionic surfactant (such as sodium dodecylbenzene sulfonate (SDBS)) coated carbon nanotube (CNT) [49]. In addition to maintaining the integrity of the CNT, the presence of an ionic surfactant prevents bundling and enables dispersion in liquid media [39]. On the other hand, chemical grafting of reactive functional groups (such as hydroxyl and carboxyl groups) to the surface (using strong oxidizers such as nitric acid and hydrogen peroxide) may be used to achieve covalent interactions. This leads to the formation of highly reactive defect sites through an increase in wettability. Although wet chemistry based methods are user-friendly, however, chemical selection for a particular reaction, is the most challenging in these methods [50]. In addition, wet chemistry-based chemical modification may result in the formation of functionalized surfaces which may undergo partial corrosion or dissolution in the solution [51]. Besides, strong oxidizers used for achieving covalent interactions are highly dangerous, especially for high temperature reactions [50]. As a result, several rinsing steps (time-consuming in nature) are essential to prevent the accumulation of harmful chemical residue after functionalization [46]. One of the dry chemical processes is reactive ion etching (RIE) which enables control of surface properties similar to that obtained using wet chemical modification techniques [52]. Besides, RIE may be used to fabricate finely controlled nanoscale features which are difficult to achieve with wet chemical processing techniques [27], [47], [52]. Surface properties such as the hydrophobicity and reflectivity can be controlled [52] [48].

2.3 Electrochemical or electrophoretic surface modification

Electrodeposition (ED), also known as electrochemical deposition, is a chemical precipitation technique. Ionic species in solution are attracted to the electrode using electric current where reduction/oxidation occurs followed by subsequent deposition. A variety of materials including metals, ceramics and polymers may be deposited using ED [49], [50]. A number of properties such as adhesion, hardness, and crystallinity may be controlled during ED [49]. Besides, a number of advantages are offered by ED which include fast deposition rates with deposition over a large area [53], no post-deposition treatment [51], and most importantly, low cost,. However, only a limited number of materials may be electrodeposited from aqueous solutions [53]. This may be attributed to the side reactions such as water electrolysis and the balance of diffusion into the pores and reactivity with the pore edge leading to non-uniform penetration into porous structures [54].

ED (or, electrophoretic deposition (EPD)) similar to ED, is a colloidal process for fabricating coatings from a stable suspension. However, unlike ED, EPD does not involve chemical reactions [55]. During EPD, application of a DC electric field to a colloidal suspension leads to the migration and subsequent deposition of charged particles on the oppositely charged electrode [52]. Stabilization of dispersed particles in the solvent is ensured by the addition of surfactants [56]. This, in addition, also provides charged sites to facilitate migration [48]. Recent EPD-based investigations by Carter et al. [57] and Oakes et al. [58] have demonstrated surfactant-free EPD of nanostructures (NSs) by the use of polar solvents. Teranishi et al. [59] have reported that a wide variety of materials (such as metals, nitrides, and oxides) may be deposited using EPD. Carter et al. [57] have demonstrated the fabrication of 3D foam materials with enhanced mechanical properties. In contrast to ED, EPD is highly scalable and economic [54]. Besides, EPD enables homogeneous microstructure [58], and densely packed coatings [53].

2.4 Glancing angle deposition (GLAD)

This technique involves condensation of sputtered atoms on the substrate surface (**Fig. 2)** [63]. A number of physical and chemical phenomenon influence the thin film deposition process especially during the early stages of film growth [63]. The growth mode of the coating is influenced by a number of factors, viz. (i) temperature, (ii) crystallography, (iii) surface conditions of the substrate, (iv) energy of the condensed particles, and (v) nature of interactions between sputtered atoms and the substrate [27]. After the initial stages of film deposition, film growth becomes dominant. During thin film growth, two phenomenon: (i) atomic-level shadowing, and (ii) surface atom distribution [63]. A number of microstructural factors such as crystallinity, size, and density of nucleation sites influence film growth [63]. For the case of low temperatures on the surface of substrate ($\sim 0.1T_m$, where T_m is the substrate melting temperature), surface diffusion of incident (sputtered) atoms is reduced [27]. This is followed by the formation of a columnar structure by the condensation of the incident atoms at the nearest nucleation sites [27].

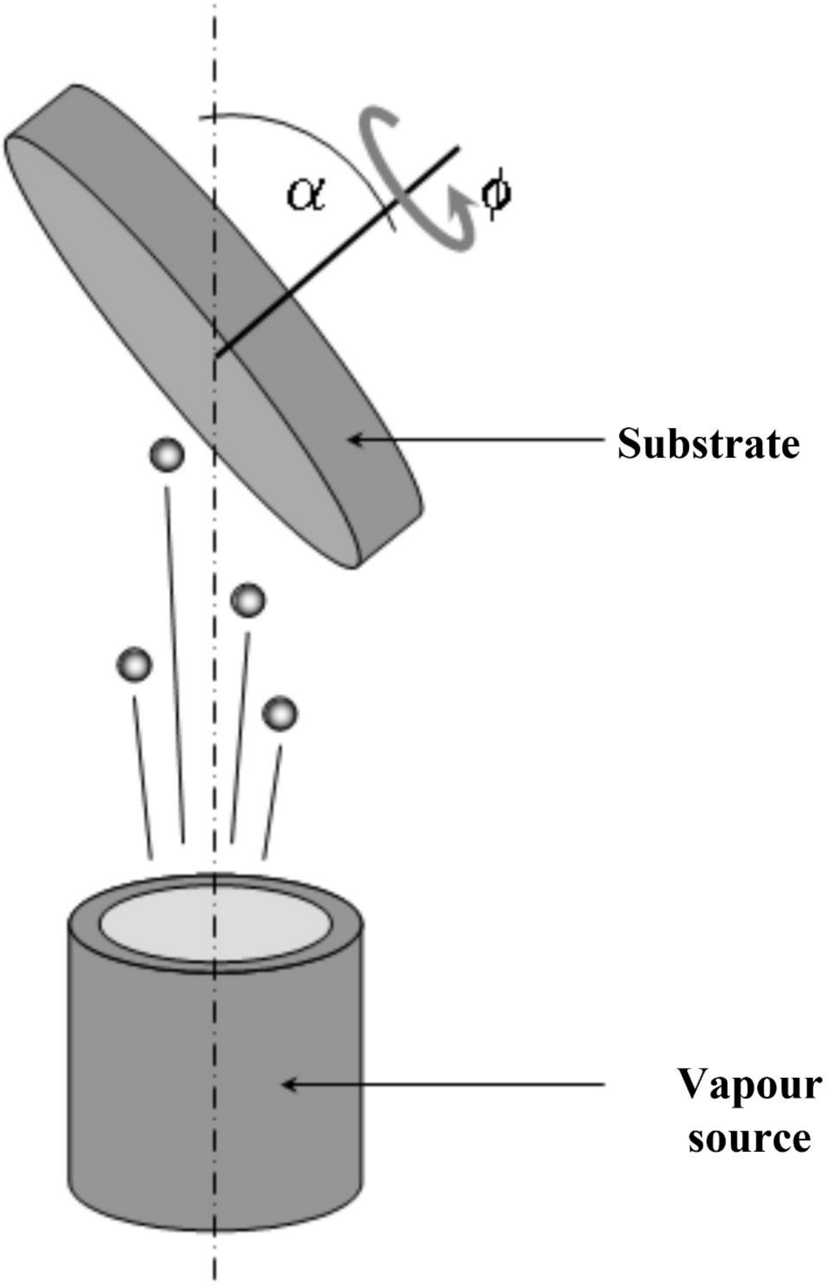

Fig. 2 Schematic of the experimental setup used for the GLAD technique. α is angle between the direction of incident vapour and the substrate normal. ϕ is the angle of rotation along the axis centered on the substrate [63].

When the flux of the sputtered atoms is incident at a non-perpendicular angle to the surface of a substrate, the nucleation sites intersect the incident atoms [27], [63]. This leads to a shadowing effect subsequently causing a tilted columnar grain growth (**Fig. 3**) [63]. It may be noted that during room temperature GLAD deposition, there occurs a competition for the growth of columnar grains [27]. This leads to the evolution of fractal microstructure columns, resulting in shadowing effect [27]. Considering that the sputtered atoms are incident on the substrate surface at an angle α with respect to the normal (to the substrate surface), columnar grains may be considered to grow at an angle β<α [60]. α and β may be related to each other using the "tangent rule" which is given by, [60]

$$\tan \alpha = 2 \tan \beta \tag{1}$$

For α < 60°, this rule shows a clear view of the columnar structure [63]. A modified version of equation 1 has also been proposed in this context. This is given as, [64]

$$\beta = \alpha - \sin^{-1} \frac{(1 - \cos \alpha)}{2} \tag{2}$$

This latter (equation 2) is much more accurate than the tangent rule (equation 1). This is because the latter calculates β with a much higher accuracy than that of the former, especially for high values of α (α~90°). Besides, the latter is based on a 2D geometric analysis. It considers that the structure of the films resembles columns with inclined hemispheric summits. Besides, surface diffusion and the minimum distance between the growth site of the particle flux and the top of columnar grains is also taken into account in equation 2. Nevertheless, unavoidable factors such as substrate polarisation, surface contamination etc. may give rise to discrepancies between the proposed theory [64] and experimental results. Hara et al. [65] have reported that the atoms incident on the film during its growth, undergo preferential diffusion. Beydaghya et al. [66] have calculated the inclination of the columns (β) by measuring the refractive index of evaporated Si films. Lintymer et al. [67] have reported that equations 1 and 2 are valid even for the case of sputter deposited thin films of Cr. It has been reported that sputtering pressure leads to significant deviations in theoretical inclination (β) predicted by the tangent rule (equation 1) [67]. Moreover, these deviations have been attributed to the reduction of shadowing effect is reduced with decreasing mean free path of sputtered atoms [67].

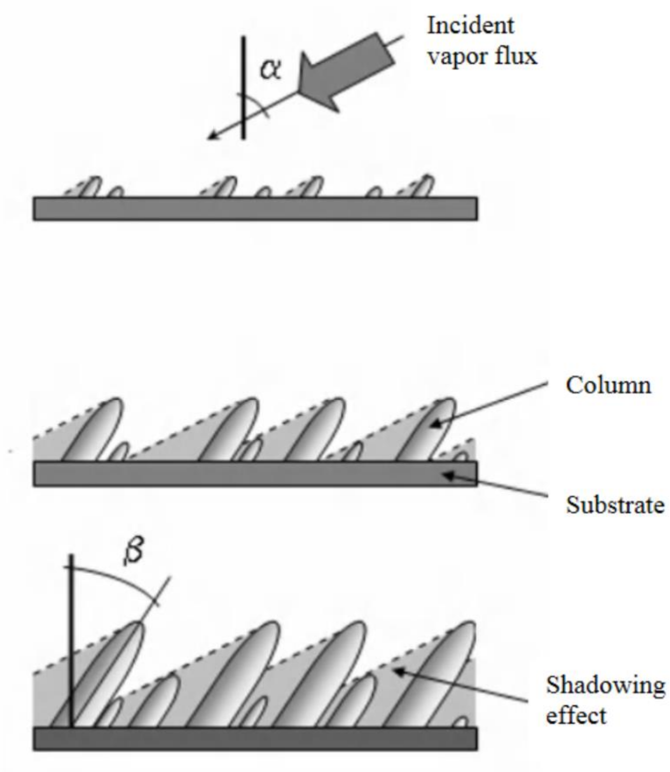

Fig. 3 Columnar grains with a particular orientation on a substrate. α is angle of incidence of the sputtered atoms on the substrate relative to the normal from the substrate. β is the angle of growth of the columnar grain with reference to the normal from the substrate [63].

Using GLAD, Nieuwenhuizen and Haanstra [68] have reported a chevron-like architecture of Al films deposited on a mobile substrate. The aforementioned architecture was reported to be obtained through an alternate tilting of the substrate by +α and –α with an equal deposition period [67]. The microstructure obtained was reported to comprise of columnar grains grown in a zigzag manner. Moreover, the morphology and size of the grains has been reported to be highly influenced by two different factors, viz. (i) angle of deposition, and (ii) rate of deposition [66]. This has been observed in the case of sputtered Cr films. In addition, the directional nature of columnar grain growth may also be utilised to obtain a wide variety of architectures [63]. This may be achieved by changing the position of the source (of sputtered atoms) with respect to the columnar grains during film growth [64]. During such an operation, it is only the substrate which rotates through he centre of the substrate [66]. The source of sputtered atoms remains stationary while the substrate is rotated [60] [63]. Such an instrument offers: (i) a rotation axis for the purpose of varying the angle of incidence of the particle flux (α), and (ii) a rotary axis at an azimuthal angle (φ) for an indirect modification of the sputtered source position [66]. Overall, GLAD technique significantly reduces the chances of shadowing which otherwise may be created by tilting the substrate and a change in the position of the substrate during the deposition process [65].

3. NMs surround our daily lives

In addition to the naturally existing NMs, it is possible to artificially fabricate NMs which are designed to match the different commercial requirements [45]. Synthetic (or artificial) NMs presently find extensive applications in a number of areas such as clothing, cosmetics, electronic goods, and many other items of daily use [47]. In the context of medical applications, these materials find extensive applications in areas such as drug delivery, diagnosis, and imaging. The unique properties of NMs (especially high room temperature mechanical strength and chemical reactivity) may be attributed to a high surface area to volume ratio and the onset of quantum effects in these materials [45]. There are a number of physical and chemical techniques for synthesis of nanoparticles (NPs) [47]. Moreover, there exist a number of natural sources of NMs such as ash (volcanic), fine sand, dust, biological matter etc. [19], [45], [47]. Practically, it is hard to control the shape and size of synthetic NPs [47]. This is because these NPs are obtained as by-products of human activities (such as combustion of automobile engines, mining etc.) and are comprised of a number of elements [45]. The size, shape, and chemical composition of synthetic NPs may be engineered by selecting an appropriate fabrication technique [47]. At present, a number of synthetic NPs are being investigated which include semiconductors (nanostructured), nanoceramics, nanosized magnetic particles and metallic powders etc [45].

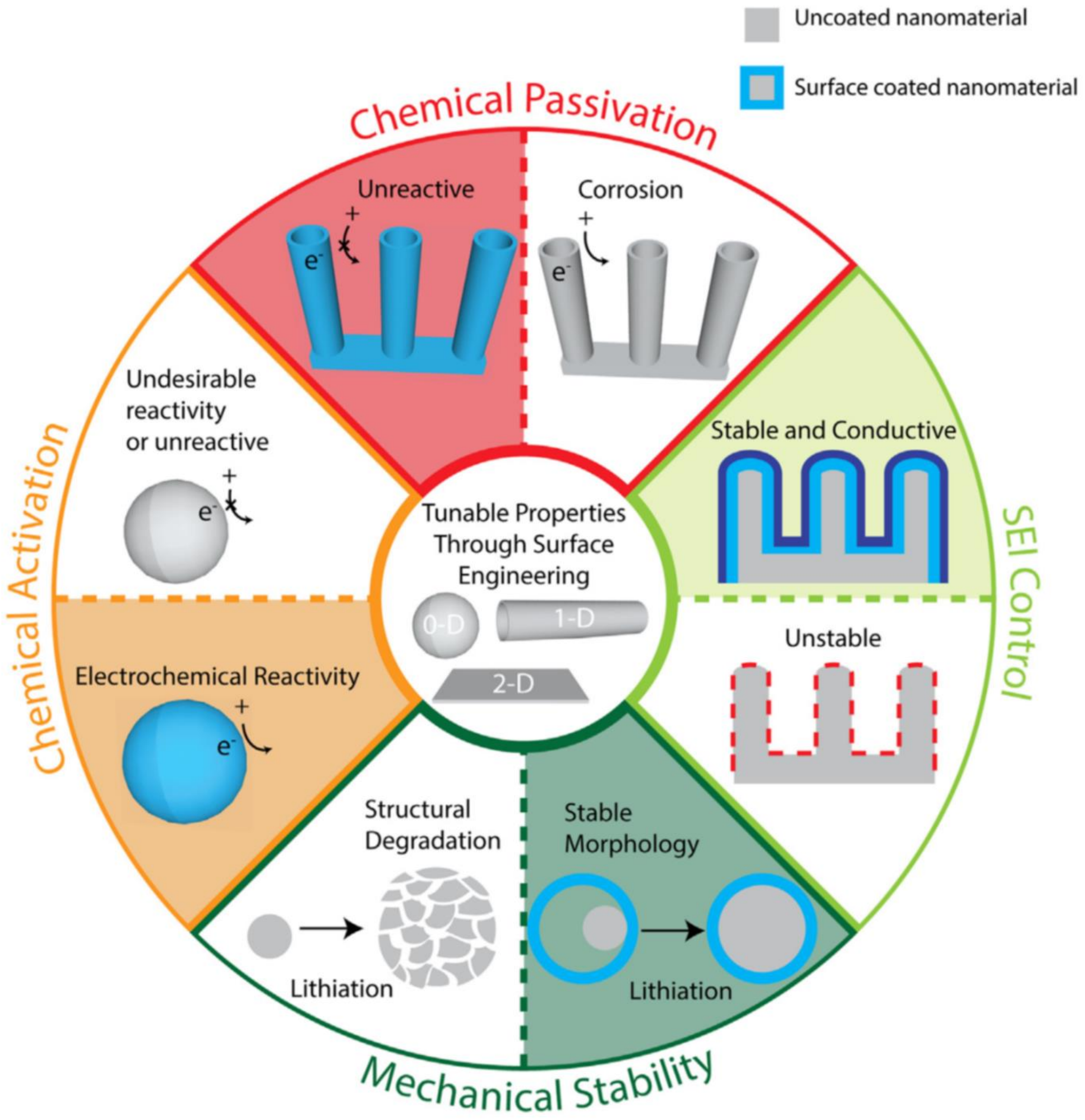

Fig. 4 Control of different properties of NMs (for energy storage applications) using surface engineering [31].

3.1 Energy storage: an emerging trend in surface engineering of nanomaterials

In the context of energy storage devices, pseudocapacitors (based on Faradaic storage mechanism) and hybrid super capacitors involve faster charging and discharging rates when compared with those of typical batteries [31], [67]. A schematic representing the role of surface engineered NMs in the context of energy storage applications is shown in **Fig. 4**. Moreover, the energy densities of these devices are higher than those of non-Faradaic supercapacitors [69]. This enables a pseudocapacitor to store charge over a wide voltage range. Common examples of pseudocapacitor electrodes include RuO_2 and MnO_2 [70-73]. Addiional cycles leads to the lowering of charge storage performance [78], [79]. This is because increased thickness may lead to an impediment of the mobility of charge carriers towards the surface and ionic diffusion through the formation of vanadium oxide [80].

Surface engineering may be used to overcome the limitations of pseudocapacitors and hybrid supercapacitors through an optimization of the bulk and surface [81], [82]. This enhances the rate of ionic diffusion in addition to providing high surface area [83]. These devices make use of metal oxides with high electrical resistance. Conductive pathways with short diffusion lengths must be provided by the engineered scaffolds [84]. These pathways are required for enhancing charge transfer with no irreversible reaction [85]. These shortcomings may be overcome during active metal deposition through (i) increasing surface area, and (ii) prevention of undesirable reactions by completely covering the substrate [85]–[87]. One of the most common ways to achieve these goals include nanostructured conductive carbon templates or nanowire core/shell [88], [89]. Surface engineering based processing of scaffolds and active materials involves a two-step process for optimising both surface area and chemical reactivity [90]. The high electrical conductivity of the substrate leads to an improvement in the capacitance [91], [92]. In addition, the high electrical conductivity leads to a decrease in the infrared (IR) drop in galvanostatic testing.

Dubal et al. [94] have used chemical bath deposition to deposit MnO_2 on Si nanowires (NWs) with a complete coating on the array of NW. This prevents the reaction between Si NWs with the electrolyte. This gave them the opportunity to optimize the ionic liquid electrolyte each having a 2.2V range [94]. As reported by Ghodbane et al. [95], the ionic conductivity and reactivity may be controlled through an appropriate optimisation of active material crystal structure. Besides, a separate processing of the bulk and substrate surface (enabled by surface engineering) results in an optimisation of the active material during deposition [95]. Aqueous ammonia has been reported to optimise the crystallinity, morphology, and surface area of $Ni(OH)_2$ during chemical bath deposition process [96]. Less amounts of ammonia was reported to result in thin nanowalls with a high surface area resulting in a low resistance to charge transfer [96]. On the other hand, while the $Ni(OH)_2$ was observed to act as an active material [96]. Carbon based materials such as graphene [94], and CNTs [70] have been reported to provide high surface area conductive substrates for faradaic metal oxides by acting as supercapacitors themselves. However, collective effects of carbon and metal oxides leads to an enhancement in the overall capacitance [86], [87], [97]. For instance, deposition of a thin layer of carbon on a pseudocapacitor provides a conductive wrapping leading to an increase in the overall capacitance by ~20% [89], [98].

3.2 SEI control through surface engineering

As briefly described in the Introduction section (**section 1**), SEI forms from electrolytic reaction on the electrode surface [98]. Moreover, a number of parameters such as type and morphology of electrode, and testing parameters influence the composition and function of the SEI [98]. Although this layer provides a stable interface, however, it has also been reported to impede ionic diffusion [99]. In addition, exposure of additional material may be caused due to a volumetric expansion of the electrode [92], [100]. This in turn may lead to the formation of high amounts of SEI with subsequent irreversible consumption of ions and electrolyte [102]. It has been observed that additives such as vinylene carbonate [65], [103] and CO_2 leads to the formation of SEI with a much lower interfacial resistance as compared to that in case of additive free electrolytes [103]. The final aim for SEI based surface engineering is to form a surface which is stable, ionically conductive surface and most importantly shows minimal degradation over a prolonged period of time [93], [105]. Hence, an appropriate control of SEI is essential for a separate engineering of the bulk and surface of NMs which tend to be highly reactive in electrochemical environment owing to their high surface area to volume ratio [106].

ALD has been reported to emerge as an important deposition technique towards manipulating SEI [106], [107]. In the context of ALD coatings, the most effective deposition occurs on the assembled electrode in order to ensure rapid transfer of electrons [104]. As briefly mentioned in **section 2.1**, ALD materials such as Al_2O_3 and ZnO have the ability to control SEI formation through protection of electrode on account of possessing low ionic conductivity. As highlighted by Cheng et al. [108], ALD deposited $LiAlO_2$ has a much higher ionic conductivity as compared to that of $Li_2O–Al_2O_3$ [108]. It was reported that application of ALD-based surface coating to the anode in a full cell leads to a significant enhancement in the number of cycles for charge storage [108]. Besides, the anode is protected from chemical attack by the cathode comprising of transition metals [108]. In this context, Al has been been reported to prevent mechanical failure through Li intercalation, compression of Si, and a change in SEI composition [109]. The surface coating with the highest coulombic efficiency (over 100 cycles) was achieved for the case of 3wt.% Al [109]. Even annealing may be used to modify the electrode surface promoted enhanced SEI formation [109]. Han et al. [110] have reported that removal of chemically adsorbed water and hydroxyl groups from annealed TiO_2 surface results in the formation of SEI with low ionic resistivity.

3.2.1 SEI: Characterisation

One of the approaches towards developing surface engineering approaches for controlling SEI formation is through understanding the reactions occurring in the SEI [111-113]. This further necessitates an understanding on the composition of SEI. A number of characterization techniques such as Atomic Force Microscopy (AFM), Electrochemical Impedance Spectroscopy (EIS), Fourier Transform Infrared Spectroscopy (FTIR) etc. [110]. Spectroscopic investigations on the SEI have revealed the presence of ionic insulators such as Li_2CO_3 and LiF [108]. The use of Secondary Ion Mass Spectroscopy (SIMS) and X-Ray Photoelectron Spectroscopy (XPS) has revealed that SEI on Al_2O_3 coated electrode is much thinner as compared to that of LiAlO2 which has been shown to possess excellent ionic conductivity of Li^+ [109]. Lipson et al. [114] have investigated SEI formation for ALD-deposited Al2O3 coating on MnO electrode using Scanning Ion Conductance Microscopy (SICM) topography. It was shown that 3Å of Al_2O_3 leads to a partial prevention of thick SEI layer formation [114]. On the other hand, 9Å of Al_2O_3 was reported to completely prevent the formation of thick SEI layer **(Fig. 5)** [114]. Formation of SEI on Si NWs with hydride and methyl terminated surfaces was investigated with FTIR and XPS [111]. The termination of methyl group on the surface of Si renders the surface relatively unreactive [107].

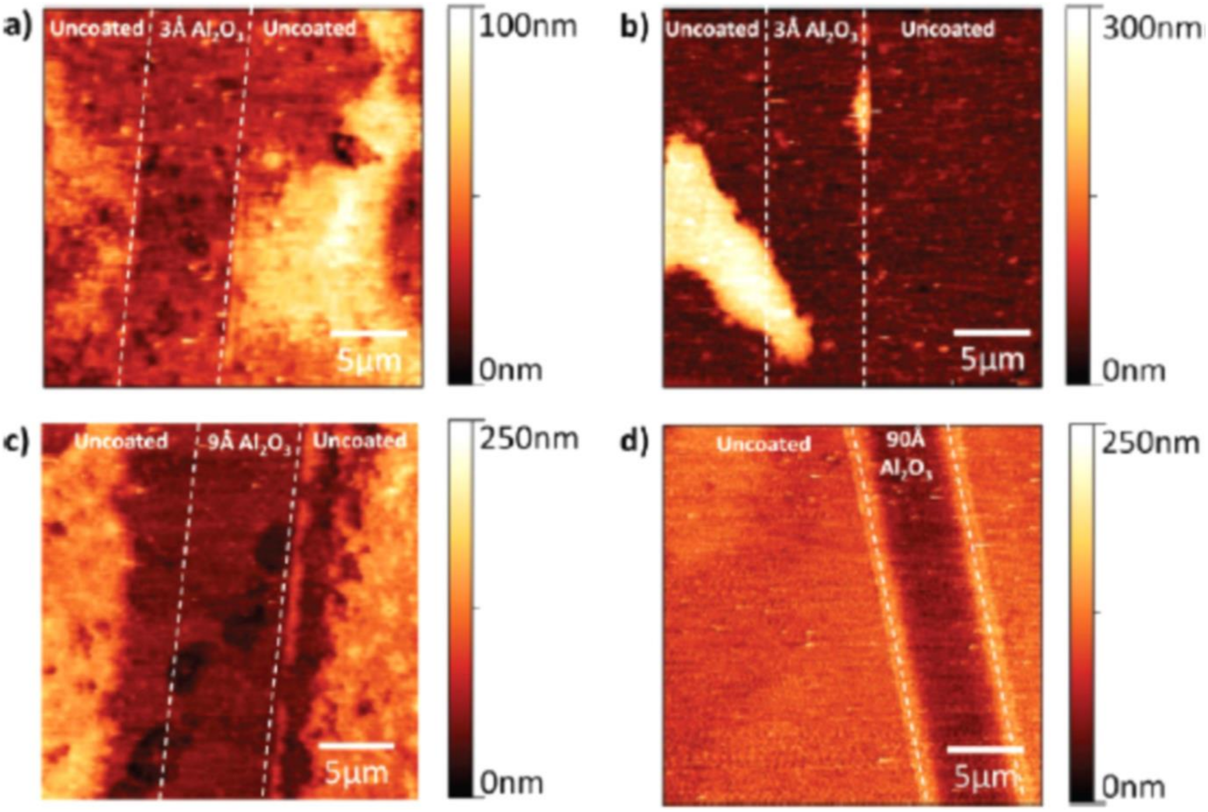

Fig. 5 SICM tomography images showing a striped ALD Al_2O_3 with thickness of **(a,b)** 3Å (**(a)** and **(b)** represent two different regions), **(c)** 9Å, and **(d)** 90Å on MnO substrate surface [114].

3.3 Chemical passivation

Owing to the reduced dimensions (typically less than 100 nm), NMs possess high surface area to volume ratio. This leads to a high surface energy, which leads to a high reactivity in many environments [111]. Supercapacitors are composed of an electrolyte between two electrodes and store energy through electrostatic attraction between opposite charges [112]. In other words, ions in the electrolyte are attracted to the oppositely charged electrodes leading to the formation of electric double layer on the electrode surface [113]. This is unlike most of the other energy storage devices which are based on charge storage using Faradaic electron transfer reactions [110]. The electrostatic nature of the supercapacitors leads to very fast charge and discharge [109]. In addition, chemical passivation of NMs may lead to the use of a whole new range of chemically compatible materials with high charge storage durability for applications in supercapacitors [107]. This, in principle, may also be used to increase the capacitance of highly porous nano-electrodes [104]. Surface engineering with high precision (at atomic-scale) may lead to partial dissolution of ions in solvents [114]. This leads to an enhancement in the overall capacitance [116]. Chmiola et al. [115] have demonstrated the aforementioned approach in carbide-derived carbon. Porous Si has been demonstrated to provide the high surface area required for a supercapacitor electrode [115]. Electrochemical etching as been reported to optimize electrodes for ionic conductivity, surface area, and penetration of electrolyte in porous Si [114]. It has been shown that porous Si reacts with ionic liquid electrolytes. This makes it a poor electrode material for supercapacitors [114]. In order to overcome the aforementioned problem, CVD-based thin coating of graphene on the surface of porous Si has been shown to extend the voltage window to ~2.7 V, with increase in discharge times by over 20 times [114]. Besides, nanostructured in aqueous and organic media has also been reported to be stabilised by carbon coating [111], [114]. Passivation of porous Si by TiN using ALD has been reported in Ref. [115]. Mesoporous Si may also act as a support for porous carbon with subnanometer-sized pores [108]. A number of coatings on Si NWs may lead to a prevention of undesirable reactions, leading to an increase in the voltage window [107].

4. Influence of surface engineering on the mechanical properties

In the context of energy storage systems with high charge storage capacities, mechanical properties play a very important role. This is because volumetric changes often promote cracking. This leads to the loss of active [108], [114]. Surface engineering may be used as a potential tool to provide mechanical support for the purpose of minimising active material loss [107]. In the context of Li-ion batteries (LIBs), it has been reported that alloying materials such as Ge, Si, and Sn and metal oxides have high Li ion storage capacities [104]. This leads to high volume expansion (~300–400%). For the case of conventional bulk counterparts, volumetric expansions lead to mechanical fracture and subsequent degradation of active material (electrode) [95]. This ultimately leads to battery failure [93]. At present, two strategies have been devised to overcome these difficulties. The first strategy involves designing NMs for the purpose of accommodating large volume expansions while the second one involves the use of thin surface coatings as an adhesive during the storage of Li [70]. Both these strategies are highly essential for the purpose of overcoming these mechanical challenges [72]. A number of surface engineering approaches have been devised to minimise the amount of mechanical expansion and degradation [73]. One of these approaches is to use an external bulk coating on the entire electrode. The other approach As reported by Lu et al. [116], involves using conductive carbon coating on an electrode made of Si NP. Besides, it was also highlighted that the use of individual NPs as coating materials leads to mechanical fracture of the coating. The other strategy, as shown by Nguyen et al. [117], involves the use of individual NM or NW as a protective coating. $NiSi_x$ NW was initially grown using a silane CVD technique, subsequently followed by the growth of amorphous Si layer using an additional silane CVD step [117]. Finally, ALD based coating of Al_2O_3 was deposited. A high cyclability with 150 cycles at a full discharge capacity as high as upto ~ 3000 mAh/g and with 700 cycles at a partial discharge capacity of ~1200 mAh/g, was reported [117]. As highlighted in Ref. [116], Al_2O_3 coating undergoes fracture even after repeated cycles of charging and discharging shows high cyclability. Similar observations have been observed for Si core-shell structured NPs with in-situ polymer coatings [112] and Fe_3O_4 with carbon coatings [114]. Moreover, it was also highlighted that although the aforementioned coatings improved cyclability, however, mechanical fracture during the cycles could not be prevented [107]. This led to the development of a yolk/ shell structure [106]. The main difference between a yolk/shell and core/shell structure is based on the difference in the structure of the inner core [94]. In other words, the inner core completely fills the outer shell in a core-shell structure whereas, there is a void space (between the inner core and outer shell) for a yolk/shell structure [69]. Accomodation of volume expansion occurs with the help of the void space (in the yolk-shell structure). This is subsequently supported by the outer shell [74]. Application of external loads on a multi-layer NP followed by the removal of the outer layer of the NP has been reported for the fabrication of yolk/shell structures [1], [75], [120], [121]. Liu et al. [119] have demonstrated that a pomegranate- like design leads to enhanced performance (total capacity: ~3000mAh/g with a small amount of degradation even after 1000 cycles). A similar approach has been used to enhance the overall performance in S/TiO_2, S/Carbon, and Sn/C yolk-shells [119]. In addition, there have been a number of recent experimental investigations highlighting the efficiency of yolk-shell and core–shell structures towards improving the overall cyclability of Na ion batteries (SIBs) [1].

5. Surface engineering: Future perspectives

5.1 Prevention of micro-cracks

Typical magnitudes of Li intercalation potentials (with respect to Li/Li^+) used for most of the cathodes are ~4V [114]. Most of these are highly stable and presently find applications in commercial batteries [121]. However, Li metal oxides ($LiMO_x$) are brittle ceramics. Hence, Li intercalation, leading to lattice distortions, may often lead to microcrack formation thereby resulting in a degradation of the electrodes ability to intercalate Li [106].

5.2 Prevention of Polysulfide shuttlng

In terms of the charge storage capacity, Li-S batteries pose a major challenge to the conventional LIBs [1], [119]. However, these batteries suffer from a number of limitations, rendering them unsuitable for commercial applications [1]. A conventional Li-S battery makes use of a Li anode and S cathode and typically involves C networks for immobilization of S for the purpose of providing electrical connectivity across the electrode [118]. Similar to the other high-performance electrodes, S cathodes also show large volume expansions [2]. However, there are a number of challenges in these electrodes. During the reaction of S cathode with Li, two things may occur: (i) active material may undergo huge large volume expansions, (ii) intermediate phases may be formed (in Li/S reaction chain) [112]. The former leads to large volume expansions resulting in an agglomeration of active S and consequently leading to losses in ionic conductivity [113]. The latter is unique to S cathodes. Seh et al. [123] have used wet chemical processing to fabricate S/TiO_2 yolk/shell electrodes with a cyclability of ~800mAh/g for 1000 cycles. Moreover, pairing of these electrodes with pre-lithiated Si/C yolk-shell particles has been reported to enhance energy density in LIB [123]. In addition, the other challenge to be overcome in the context of Li-S batteries is the shuttling of polysulfide i.e. reduction in the active S content in the cathode through dissolution of polysulfide into the electrolyte [122], [124]. Recent experimental investigations have highlighted that thin metal oxide coatings, such as Al_2O_3, indium-tin oxide (ITO), and vanadium oxide results in strong interface (surface) binding of polysulfides, minimising the detrimental effect of polysulfide shuttling [125]. In the context of Li-S battery research, this is a recently emerging research avenue with a high potential towards designing cathodes with cyclability as high as ~100 cycles with more than 90% of the initial S capacity [121]–[124].

5.3 Prevention of dendritic growth for metal anodes

In the context of rechargeable LIBs, Li metal was initially used as the anode. However, dendritic growth in these anodes was reported to lead to a quick mechanical. The coating techniques devised to prevent dendritic growth led to a a low cyclability of LIBs. Drop cast based deposition of polystyrene NPs on a Cu foil followed subsequently by flash evaporation of carbon fibers has been reported in Ref. [125]. A conductive carbon yolk-shell structure for enhanced cycling performance in Li metal anodes was designed [125]. Most importantly, this electrode was shown to possess high cyclability with a coulombic efficiency of ~ 99.9% for 150 cycles [125]. The other strategy involves the use of ALD for the purpose of coating thin layers of Al_2O_3 on a metallic foil of Li [114], [125]. In both approaches, the performance of Li metal anode was improved. Similar to the Li ion systems, Na ion systems have also been shown to suffer from the same problem of dendritic growth the metal anodes (Na anode in this context). Kazyak et al. [126] have demonstrated that a 2–3 nm Al_2O_3 coating on the Li metal anode led to the high stability of the device (for ~1200 cycles). Nevertheless, the two aforementioned approaches have been successfully demonstrated to prevent dendritic growth in Li metal anode [126]. Besides, dendritic growth in Na ion systems and K ion systems in Potassium Ion Batteries (PIBs) is an avenue which is largely unexplored at present. This avenue is expected to offer tremendous potential towards exploration of Ca and Mg in the rechargeable battery systems.

6. Conclusions

The present review highlights that microstructural evolution in surface engineered NMs is highly influenced by the fabrication (deposition) techniques. In the context of energy research (especially high-performance energy storage devices), this has opened up a number of new avenues which include enhanced chargeability, high durability (for electrodes), and high energy density. A decoupling of the space characteristics from the bulk properties enables one to separately optimize the properties of the surface coatings with those of the underlying substrates. Besides, surface engineering may also be used to overcome a number of challenges, primarily associated with the utilisation of nanostructures in the aforementioned devices.

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