Functional nanomaterials for energy and sustainability

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ABSTRACT

In view of the continuous decline in fossil fuel reserves, at a time when energy demands are steadily increasing, a diverse range of emerging nanotechnologies promise to secure modern solutions to the prehistoric energy problem. Each one of those distinct approaches capitalizes on different principles, concepts and methodologies to address different application requirements, but their common objective is to open a window to a sustainable energy future. Consequently, they all deserve substantial (though not necessarily equal) consideration from the scientific and engineering community. In this review we present bottom-up strategies that show great promise for the development of a new generation of advanced materials for energy applications without compromising the public safety or the environment. Copyright © 2014 VBRI press.

Keywords: Nanomaterials; energy; sustainability; batteries; fuel cells.

Antonios Kelarakis is a Senior Researcher in the Centre for Materials Science, University of Central Lancashire, U.K. where he holds the Guild fellowship in research. Before undertaking his current position he gained extensive experience in both academic research and commercial development working in world-leading institutions in Europe and U.S.A. His research interests include colloids, biomaterials, polymer based nanocomposites and smart coatings. His investigations have been systematically directed to the design, synthesis and characterization of nanostructured polymeric materials for energy, safety and sustainability. Central to his work is the advancement of green approaches for the preparation of nanomaterials for environmentally conscious applications. He has authored more than 60 scientific articles in high impact journals and he has delivered numerous invited talks in national and international conferences.

Introduction

The enduring race for energy resources has always been progressed alongside the race for economic growth and cultural development. Even though fossil fuels will continue to have a prominent role in the next few years, a gradual transition to alternative energy technologies is unavoidable in the long run. Because it seems unlikely that a single approach will shortly take a clear lead to the energy race, parallel research efforts are in place to explore a wide range of strategies for improved energy production, transmission and distribution. Each one of those distinct approaches capitalizes on different principles, concepts and methodologies to meet different market needs [1-9].

The essence of the energy problem is to find a sustainable balance between the surging needs for reliable sources to power a vast array of portable and stationary applications, the public safety and the preservation of the natural environment. From a science perspective the challenge is to design a new generation of materials that can wisely produce and wisely consume energy.

Here, we review bottom-up strategies to synthesize nanoscale materials that can make the difference in the energy landscape. The macroscopic properties of those nanohybrids are governed by the thermodynamics of host/guest interactions, the dispersion level of the nanoparticles, the interfacial structure and dynamics and the morphological and topological characteristics of the systems. Following recent trends in the field and exemplifying representative cases from the literature, we

will highlight certain advantages in using nanomaterials for energy applications.

In particular, this paper focuses on nanostructured materials for energy saving (polymer nanocomposites and nanopatterned surfaces), energy harvest (nanoparticle induced piezoelectricity), energy production (membranes for fuel cells) and energy storage (electrolytes and separators for Li-ion batteries). It is noted that this article is strongly linked with a conference presentation of the author's research activities and it is not a complete review of the field. For additional information, the interested reader is referred to reports that cover a wider spectrum of energy nanomaterials [1, 2], and detailed articles about their application in Li-ion batteries [3,4], supercapacitors [5], photovoltaics [6], hydrogen storage [7], catalysts for fuel cells [8] and magnetic devices [9].

The objective of this review article is to provide an economical presentation of recent advances in the field and to demonstrate certain research directions that can contribute towards a safer planet and a sustainable energy future. Emphasis is given in presenting key design principles in nanomaterial engineering; composite formation, compatibilization, hierarchical organization, self-assembly, phase separation, soft and hard templation, directed crystallization, and surface patterning.

1. Energy management

Effective energy management in transport vehicles means improved fuel economy and reduced gas emissions. Reduced fuel consumption can be achieved (among other factors) by decreasing the mass of the vehicle or the friction forces exerted on the vehicle. As described below, incorporation of nanostructured materials to the vehicle can contribute towards that goal.
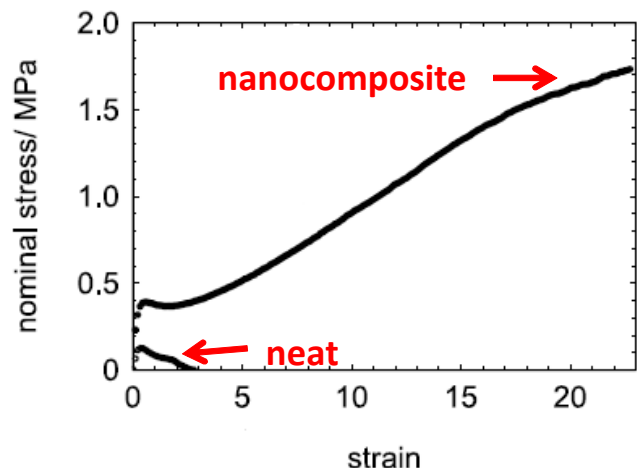

Fig. 1. Tensile curves of the neat ethylene/propylene elastomer compared to the 10wt% MCNF nanocomposite (T=55 °C). Reprinted with permission from Reference 15, Copyright 2005, Elsevier Ltd., Oxford, U.K.

Light weight, yet robust nanocomposites

Design principles: composite formation, compatibilization

Replacing conventional metallic, plastic or elastic parts of vehicles with super-strong, yet much lighter weight nanocomposites has a direct impact on fuel economy [10].

Introduction of functional nanoparticles to widespread polymers leads to materials with advanced macroscopic properties and superior mechanical response [11-14]. The overall behavior bears similarities to conventional microscale composites, but the critical filler loading to impart significant improvements is much lower in the case of nanocomposites. In contrast to microcomposites, that typically exhibit improved mechanical strength at the expense of toughness, nanocomposites oftentimes exhibit simultaneous enhancements in both toughness and strength. The reinforcement effect has been attributed to the large organic/inorganic interface that possesses fundamentally different dynamics compared to the bulk phase. The nanoparticles surrounded by their interfacial shells build up a percolated network that provides efficient load transfer and prevents catastrophic cracking [15, 16]. The profound role of this network can be clearly seen in **Fig. 1** that compares the tensile curves of an elastomeric ethylene/propylene random copolymer (in automobiles it can be used in tires or for weather stripping) to the corresponding nanocomposite material containing carbon nanofibers [16].
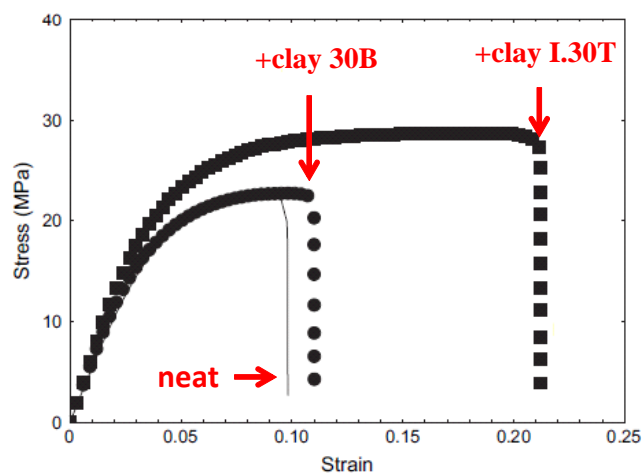

Fig. 2. Tensile curves of the unfilled blend (lines) comprised of poly(vinylidene fluoride)/ ethylene-vinyl acetate copolymer and corresponding nanocomposites containing 5wt% montmorilonite clay with the commercial names I.30T (squares) and 30B (circles), respectively. Reprinted with permission from Reference 19, Copyright 2007, Elsevier Ltd., Oxford, U.K.

In this experiment the temperature was set close to the melting point of the polymer, so that the effect of crystallinity is ruled out. Under those conditions the unfilled elastomer exhibits minimal mechanical strength, but the nanocomposite withstands substantial stresses and exhibits a 150 fold enhancement in mechanical toughness.
An additional reinforcement mechanism, which acts in parallel with that described above, has been proposed for immiscible polymer blends. In this case, the emulsifying efficacy of nanoparticles aids the dispersion of the minor phase and, thereby, improves the macroscopic properties [17, 18].

The driving force for this behavior can be kinetic (the preferentially nanoparticle enriched phase obstructs the diffusion and the coalescence of the suspended droplets) or thermodynamic (the presence of nanoparticle reduces the free energy of mixing of the two phases) in origin [19, 20].

As shown in **Fig. 2**, the tensile properties of a poly(vinylidene fluoride) (PVDF)/(ethylene-vinyl acetate copolymer) (EVAc) blend (PVDF:EVAc=70:30) are only marginally improved by the addition of the polar clay 30B. In contrast, substantial reinforcement is achieved by the non-polar nanoclay I.30T that shows stronger chemical affinity to the minor phase (it only contains 15 wt% polar units of vinyl acetate). Those trends highlight the profound role of the nanoparticle functional groups to induce favorable or unfavorable matrix-filler interactions at a localized level, an effect that drastically impacts the structure.

Nanoscale sculpturing at the interface

Design principles: self-assembly, phase separation, surface engineering

The biofilm deposition in marine vessels results in increased water-vessel frictional forces and excess propulsive fuel consumption. Early attempts to control the problem using biocides are now strongly discouraged due to their detrimental impact on the ecosystem. Systematic studies on conventional coatings support the conclusion that microorganisms adhere weakly to mechanically weak surfaces (and vice versa), but those coatings tend to be peeled off quickly and need to be reapplied frequently [21]. Nanoscale sculpturing at the vessel surface is a promising strategy to create non-toxic fouling release coatings [22, 23]. The approach aims to create surfaces with complex topological patterns so that attached microorganisms cannot get a firm grasp and are easily removed, for example by getting the vessel to speeding.

A snapshot of a recent demonstration of this strategy is given in **Fig. 3**. The polydimethylsiloxane (PDMS) is the standard fouling-release coating material for marine vessels, but has low elastic modulus and a smooth surface. Introducing polyurea segments or fluorinated chain extenders to the macromolecular structure leads to microphase separation that not only strengthens the material (by generating hard segments), but also induces surface roughness in a manner that mirrors the compositional heterogeneity of the bulk phase [24].
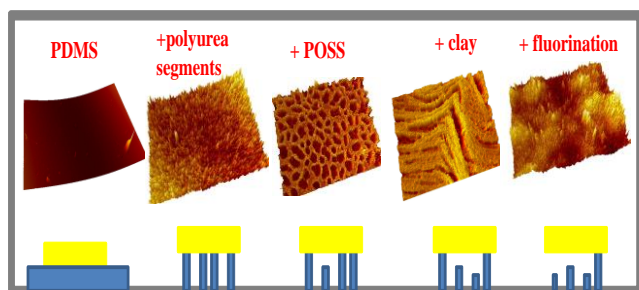

Fig. 3. 3-D profilometer images of a series of PDMS based materials and schematics showing the limited contact area of the adsorbed microorganisms (depicted in yellow) to the rough surfaces. The profilometer images are reprinted with permission from Reference 24, Copyright 2010, Elsevier Ltd., Oxford, U.K.

Moreover, addition of nanoparticles to the microphase separated matrix offers an additional level of architectural control and allows for the multi-level surface roughness

observed in those hybrid systems. Such irregular topographical features facilitate the removal of the sporelings by reducing the energy for detachment [24].

2. Energy harvest

Nanoparticle induced piezoelectricity

Design principles: composite formation, controlled crystallization

Piezoelectric materials generate voltage in response to mechanical deformation and, in doing so, they harvest, otherwise dissipated, energy from the ambient. For example piezoelectric transducers can be mounted to shoes or floors to capture energy from walking, or can harvest energy from ocean waves, wind, etc.

The most popular macromolecular piezoelectric materials are based on PVDF, which tends to crystallize on its inert α-phase. When the α-crystals are subjected to uniaxial stretching, the polar C-F bonds are aligned perpendicular to the polymer axis to give the all-trans conformation of the β-phase [25]. Alternatively, crystallization in the presence of nucleating agents and nanoparticles such as nanoclays, carbon nanotubes, graphene, Ag nanoparticles promotes the formation of β phase [26-29] (**Fig. 4**).
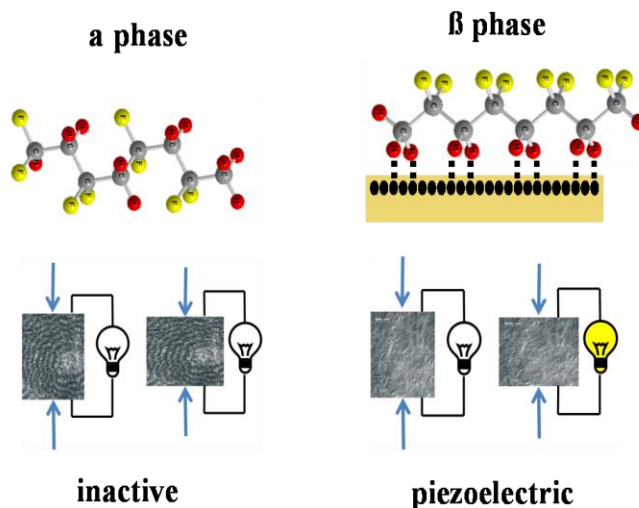

Fig. 4. Molecular configuration of the inert α-phase (left) and the piezoelectric β-phase of PVDF (right) that is induced and stabilized in the presence of nanofiller.

It has been demonstrated that various types of nanoparticles not only induce the β phase of PVDF and its copolymers in a cost effective manner, but they also confer simultaneous improvements in the mechanical toughness of the material [29].

3. Energy production

Nanohybrid membranes for fuel cells

Design principle: composite formation

In proton exchange membrane fuel cells energy is produced from the catalytic recombination of oxygen with protons (produced by the oxidation of a fuel such as hydrogen,

methanol, ethanol, etc) permeating across a suitable membrane. The efficiency of the cells largely relies on the catalytic activity of the (typically platinum) nanoparticles and the quality of the Nafion proton exchange membrane. Nafion is composed of a tetrafluoroethylene backbone functionalized with perfluorovinyl ethers bearing terminal sulfonic acid groups to impart remarkable ionic properties to the, otherwise highly hydrophobic, macromolecule. In the microphase separated polymer, the ionic clusters accommodate large amounts of water, creating a well interconnected network that is ideal for proton transportation [30-32]. At the same time, the Teflon-like backbone maintains the mechanical and chemical stability for the water-swollen system.

When methanol is used as fuel (in direct methanol fuel cells) it tends to permeate the Nafion membrane alongside with water. The phenomenon, known as "methanol cross-over", adversely affects the efficiency of the cell. Incorporation of high aspect ratio impermeable nanoparticles is a common strategy to improve the barrier properties, because it creates a more tortuous and, thus, longer pathway for diffusion (**Fig. 5**).
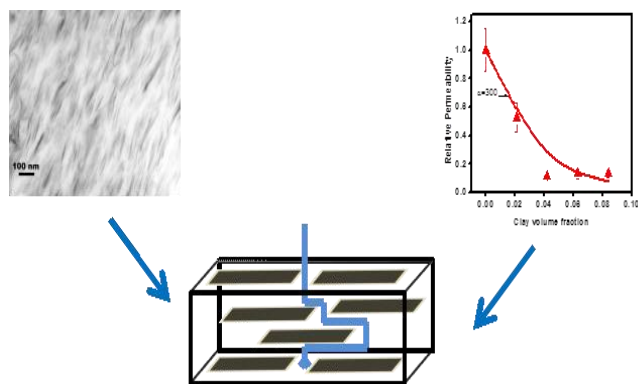

Fig. 5. A longer and more tortuous diffusion path in well dispersed Nafion/clay membranes (TEM image is shown on the left) is responsible for the dramatic decrease in methanol permeability (plot is shown on the right). Reprinted with permission from Reference 33, Copyright 2009, Elsevier Ltd., Oxford, U.K.

Based on this observation, proton exchanged nanoclays were introduced to Nafion membranes to generate hybrids that exhibit up to 10 times lower methanol permeation, while maintaining high levels of ionic conductivity. In addition, the nanocomposites exhibit superior thermal and mechanical properties, a behavior that allows the use of thinner membranes with lower internal resistance [33].

Extensive triple phase boundaries for fuel cells

Design principles: hierarchical organization, controlled crystallization, templation

In fuel cells the triple phase boundaries (TPB) are defined as the contact points between the gas reactants (flowing through the pores), the ionic conductor (Nafion) and the electronically conductive catalyst support. A facile strategy to enlarge the TPB and maximize the current flow and cell efficiency is described below. The method is based on ice templating of a suitable aqueous dispersion; as the solvent freezes, spontaneous phase segregation confines the

dispersed particles to the area between the crystals, so that after the solvent is removed by sublimation, it leaves behind a highly porous scaffold [34]. In the approach shown in **Fig. 6**, an aqueous suspension comprised of Nafion, graphite oxide and chloroplatinic acid (**Fig. 6**, left) was subjected to ice templating (**Fig. 6**, middle), followed by *in situ* mild reduction via hydrazine to generate graphene supported platinum nanoparticles on a microporous Nafion scaffold (**Fig. 6**, right) [35].
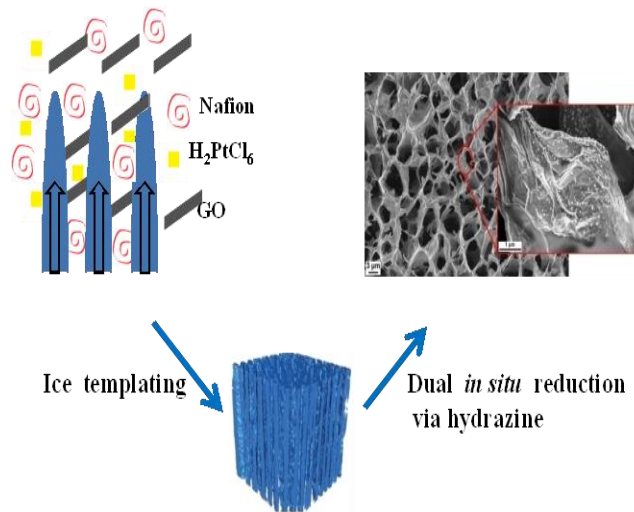

Fig. 6. Synthesis of macrocellular scaffolds of Nafion containing graphene supported platinum nanoparticles. The approach is based on ice-templating followed by mild chemical reduction via hydrazine. TEM images (on the right) are reprinted with permission from Reference 35, Copyright 2011, American Chemical Society

5. Energy storage

Nanocoated separators for Li-ion batteries

Design principles: surface coating

The design principle of a Li-ion rechargeable battery relies on the reversible intercalation/deintercalation of Li-ions within the cavities of the electrodes and their diffusion across the electrolyte during the successive charge/discharge cycles. The separator is an integral part of the battery that prevents physical and electrical contact between the electrodes, while permitting ionic current flow. The separator itself does not participate to any chemical reaction; it has nevertheless a major impact on the cell performance. A common problem encountered in polyolefin separators is their poor wetting from polar electrolytes (e.g. ethylene carbonate, propylene carbonate), an effect that increases cell resistance and reduces the efficiency. Various surface treatments focus on chemical grafting of hydrophilic groups or physical absorption of surfactants, but the latter are eventually washed away during repeating electrochemical cycling [36].

A novel coating approach has been recently developed that focuses on the electrostatic immobilization of positively charged nanoparticles to the plasma treated substrates in order to create a uniform and persistent surface coverage [37]. The advantage of the method is that it allows the deposition of nanoparticles not only to the exterior of the membrane, but also to the internal pores at a depth of several microns. Owing to this surface coverage,

the contact angle of the nanocoated membrane against propylene carbonate is virtually zero, compared to 66 $^\circ$ for the pristine separator (**Fig. 7**). At the same time, the electrolyte uptake is 4 times higher for the coated membrane and the ionic conductivity of the wet membranes exhibit a 5-fold increase. As a result, cells equipped with the nanocoated separators exhibit superior electrochemical performance [37].
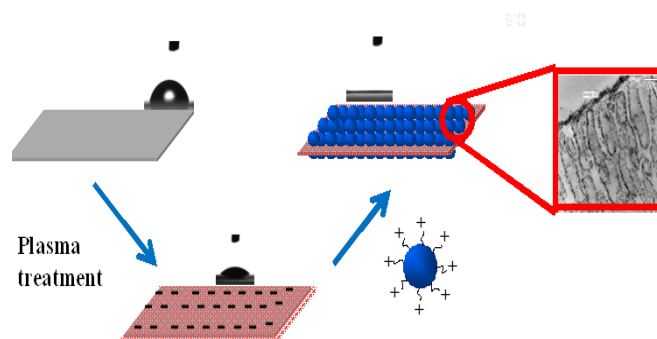

Fig. 7. Preparation scheme of nanocoated separators by electrostatic immobilization of nanoparticles to the plasma treated surface. The contact angles of propylene carbonate are shown against the uncoated separator (left), the plasma treated surface (middle) and the nanocoated substrate (right). Reprinted with permission from Reference 37, Copyright 2011, Royal Society of Chemistry.

Nanoscale electrolytes

Design principle: composite formation

A large variety of nanoscale ionic electrolytes can be easily prepared by introducing functional inorganic nanoparticles (silica, zirconia, carbon, etc.) to poly(ethylene oxide) or ionic liquids [38, 39]. The polymeric chains are covalently attached or electrostatically adsorbed to the nanoparticle surface, to generate well-dispersed, highly homogenous nanohybrids (**Fig. 8**).
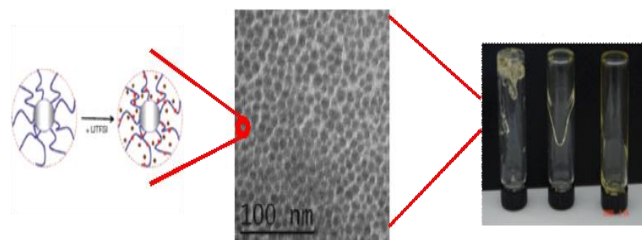

Fig. 8. Nanoscale electrolytes are comprised of well dispersed (middle) functional nanoparticles (left) within a conductive medium and exhibit tunable fluidity (right). Reprinted with permission from Reference 38, Copyright 2010, John Wiley and Sons, Inc.

This design motif allows multiple parallel handles by varying, for example, the nanocore shape and size, the nature of the functional groups and the architecture of the tethered chains. Thus, a broad range of physical properties can be accessed varying from amorphous to crystalline materials and from self-suspended fluids to soft glasses that only flow at high deformations. It has been demonstrated that these hybrids electrolytes retard the lithium dendride growth, exhibit superionic conductivity, high lithium transference numbers, wide redox stability window and enhanced thermo mechanical stability [38, 39].

Conclusion

Research efforts towards the development of advanced materials for energy generation, storage and distribution are expected to be more intense and more systematic in the years to come. Capitalizing on well-established engineering principles (composite formation, compatibilization, hierarchical organization, self-assembly, phase separation, soft and hard templating, directed crystallization, and surface patterning), a wide range of energy materials has been developed. The improved physico-chemical properties of those materials can support innovative energy technologies that are critical for a sustainable energy future.

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