ACS APPLIED MATERIALS & INTERFACES

Review

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Nanostructured Energetic Composites: Synthesis, Ignition/Combustion Modeling, and Applications

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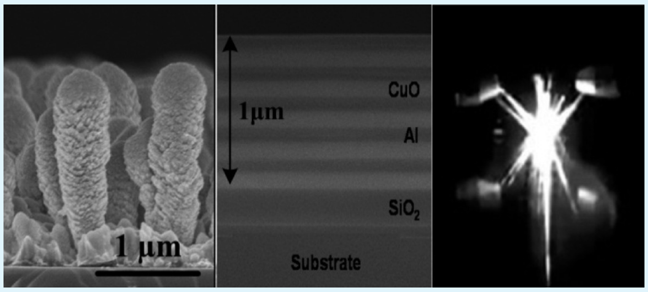

ABSTRACT: Nanotechnology has stimulated revolutionary advances in many scientific and industrial fields, particularly in energetic materials. Powder mixing is the simplest and most traditional method to prepare nanoenergetic composites, and preliminary findings have shown that these composites perform more effectively than their micro- or macro-sized counterparts in terms of energy release, ignition, and combustion. Powder mixing technology represents only the minimum capability of nanotechnology to boost the development of energetic material research, and it has intrinsic limitations, namely, random distribution of fuel and oxidizer particles, inevitable fuel pre-oxidation, and non-intimate contact between reactants. As an alternative, nanostructured energetic composites can be prepared through a delicately designed process. These composites outperform powder-mixed nanocomposites in numerous ways; therefore, we comprehensively discuss the preparation strategies adopted for nanostructured energetic composites and the research achievements thus far in this review. The latest ignition and reaction models are briefly introduced. Finally, the broad promising applications of nanostructured energetic composites are highlighted.

KEYWORDS: *Nanostructured energetic composites, synthesis strategies, ignition and combustion models, applications*

1. INTRODUCTION

Energetic materials can typically be categorized into propellants, explosives, and pyrotechnics according to their specific compositions, performances, and application areas.[1−3] Propellants and pyrotechnics are often composed of micrometer-scale individual fuel and oxidizers, and their compositions can be adjusted readily to maximize energy density. However, reaction rates are low because the chemical reaction is controlled by kinetic diffusion. As a result, propellants and pyrotechnics are often used in less brisant work as projectiles, propulsions, and decoys. They are also utilized in illumination. Meanwhile, explosives are usually generated by combining fuel and oxidizer moieties into one molecule. The reaction rate can be extremely high and detonation occurs. The energy density of molecular explosives can reach only half that of composite energetic materials, but the high reaction rate and gas yield enhances brisance. Thus, these explosives are often used in shattering work.[4] The difference between composite energetic materials and molecular explosives has long been clear; however, the advent of nanotechnology has fueled new interest in the field of conventional energetic materials because both a high reaction rate and energy density can be obtained concurrently.[2,5,6]

Ultrasonic powder mixing is the simplest and most commonly used method to prepare nanoenergetic composites. The stoichiometry can be adjusted readily to maximize energy density.[7−11] Various kinds of metals/metalloids have been considered as fuels for nanoenergetic composites, such as Al, Mg, Zr, B, and Si.[5] Among these fuels, nanoaluminum (n-Al) is the most frequently used component because of its low cost, commercial availability, high combustion enthalpy, and non-toxicity.[2,5] Therefore, most of the previous studies use ultrasonically mixed nanocomposites based on n-Al as reactive mixtures.[7−10] However, the intrinsic disadvantage of this method is the 4 to 8 nm thick aluminum oxide shell that typically forms around Al nanoparticles. This shell reduces energy density and degrades combustion performance. Furthermore, the distribution of fuel and oxidizer is nonuniform, and the interfacial contact is not intimate. Accordingly, combustion performance is significantly scattered and reliability decreases.[5] Thus, we believe that apart from accurate composition adjustment, improved control of nanoenergetic composite structures enhances the implementation of nanotechnology in energetics. The subsequent development of nanoenergetic composites should therefore focus on nanostructured energetic composites. In this study, we preliminarily define nanostructured energetic composites as nanoenergetic composites prepared through various techniques other than powder mixing, such as layered vapor deposition, sol−gel method, and arrested reactive milling (ARM). The initial results obtained are promising.

Excellent review papers that comprehensively discuss nanoenergetic materials with numerous citations can be referenced

Received: December 5, 2013
Accepted: February 19, 2014
Published: February 19, 2014

dx.doi.org/10.1021/am4058138 | *ACS Appl. Mater. Interfaces* 2014, 6, 3058−3074

for the benefit of this review.[2,5,6,12,13] In this article, we focus on nanostructured energetic composites, particularly developments over the past five years. The review paper is divided into five parts. Part I is the introduction. Part II comprehensively discusses the preparation strategies adopted for nanostructured energetic composites and some of the research achievements. Part III introduces the latest developments in ignition and combustion models. Part IV presents the broad applications of nanostructured energetic materials and cross-references nanoenergetic composites prepared by powder mixing. Finally, Part V states the conclusions and outlook.

2. STRATEGIES TO SYNTHESIZE NANOSTRUCTURED ENERGETIC COMPOSITES

2.1. Layered Vapor Deposition. Reactive multilayer nanofoil (RMF) is generated by alternately depositing two or more different materials. These materials can sustain a self-propagating exothermic reaction once it is initiated. Figure 1 shows typical cross-sectional images of multilayer foils prepared by layered vapor deposition.[14] Research on multilayer nanofoils dates back to the early 1990s. E. Ma et al. first reported on the self-propagating explosive reactions in Al/Ni multilayer nanofoils and established a simple model.[15] RMFs prepared by layered vapor deposition are mainly based on intermetallic (e.g., Al/Ni) and thermite reactions (e.g., Al/CuO).

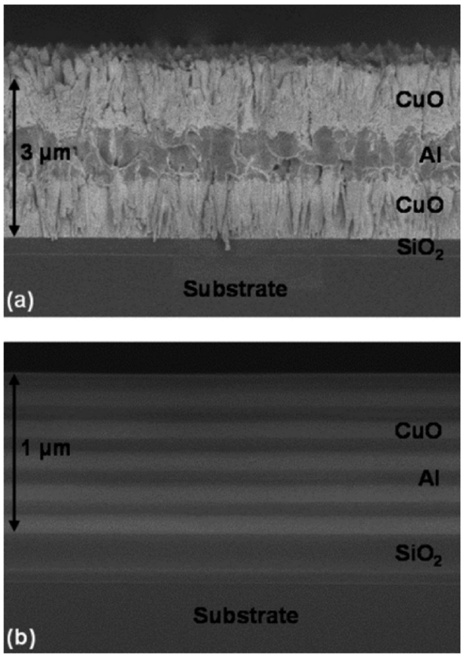

Figure 1. Cross-sectional images of CuO/Al multilayers by scanning electron microscopy (SEM). (a) Three layers of CuO (1 μm)/Al (1 μm)/CuO (1 μm). (b) 10 layers of CuO (100 nm)/Al (100 nm).[14]

Studies on intermetallic reaction mainly focus on the following three areas: reaction wave propagation, phase transformation and reaction process, and potential applications. To investigate the effects of premixing, bilayer thickness, and heat loss on the propagation of the reaction fronts of Al/Ni RMFs, Weihs et al. established analytical, empirical, and numerical models.[16−18] The influence of variations in the distribution of bilayer spacing on reaction heat and velocity has also been examined.[19] The effects of thermal properties on the reaction fronts of Al/Ni RMFs have been computationally studied by incorporating concentration, direction, and temperature dependence into the thermal conductivity model.[20] Early investigations into the phase transformation and reaction process of cases with low heating rate were conducted *ex situ*, but *in situ* techniques such as time-resolved X-ray microdiffraction through synchrotron and dynamic transmission electron microscopy (TEM) have been developed recently. Time-resolved X-ray microdiffraction through synchrotron has been used to examine phase transformations during the rapid heating of Al/Ni and Zr/Ni multilayer foils and has determined that the intermediate phases formed during self-propagating reactions differ from those formed at slow heating rates. Furthermore, *ex situ* characterization can generate misleading results.[21−23] Dynamic TEM has been used to characterize Al/Ni intermetallic reactions with an ultrahigh temporal resolution of 15 ns.[24−26]

Thermite reaction-based RMFs have received comparatively less interest, but they are significant because the thermite reaction is often much hotter than the intermetallic reaction.[27] The Al/CuO RMF was selected as the first research object in this area.[28,29] The thermite reactions of nano- and micro-multilayered Al/CuO RMFs were compared, and all of the energy in the nanostructured Al/CuO RMF was released before the melting point of Al was reached.[14] The effects of substrate material and thickness on the flame speeds of Al/CuO RMFs have also been examined both experimentally and theoretically through a combination of traditional 2D black box theory and a sandwich model.[30,31]

In RMF research, density functional theory (DFT) and molecular dynamics simulation have also been applied. In a recently published article, various techniques of experimental characterization and DFT calculation were integrated to determine the role of interfacial chemistry in Al/CuO thermite reactions.[32]

Layered vapor deposition is generally versatile because almost all of the frequently used metals, metalloids, and metal oxides can be prepared by choosing suitable deposition parameters, and it is convenient to control the thicknesses of the layers. Meanwhile, the dense and well-defined RMF geometry simplifies theoretical modeling and enhances accuracy. However, this technology is limited. First, the method is costly and difficult to scale up. Second, the premixing problem intensifies drastically when bilayer spacing is extremely small. Third, the prepared RMF is unstable in certain cases. Chemical, elastic strain, and interfacial free energies can destroy layering structure. Therefore, potential instability is a concern when reactants with highly varied properties in between or with substrates are deposited and/or when total RMF is extremely thick.[33]

2.2. High-Energy Ball Milling (HEBM). HEBM has been widely applied in the rapid combustion synthesis of materials and effectively generates nanostructured energetic composites. ARM is a typical example of this methodology, and other research groups have developed methods that are essentially similar to ARM. A recent review paper provides a comprehensive overview of mechanochemistry developments.[34]

2.2.1. ARM. To prepare nanostructured energetic composites, a mixture of powdered components (typically micrometer-sized) that can react chemically is milled under preset milling conditions. Milling time is accurately controlled to generate a compositionally homogenized nanocomposite just before the self-sustaining chemical reaction is initiated among the powdered components. The nanostructured energetic composites obtained are fully dense, micrometer-sized particles. Each component is incorporated into the matrix of another component, and the reactants are mixed on a scale of 100 nm.[35] Figure 2 displays typical backscattered electron images of Al/CuO nanocomposites prepared through ARM under different experimental conditions.[36]

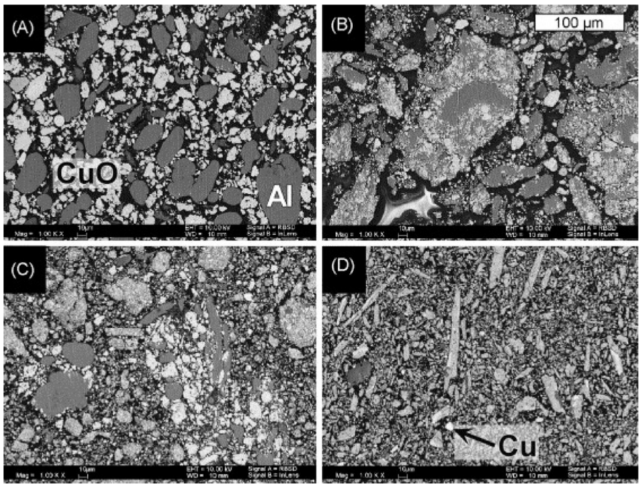

Figure 2. Backscattered electron images of Al/CuO nanocomposites prepared through ARM. (a) Original material. (b) After 2 min milling without hexane. (c) After 16 min milling with 1 mL of hexane. (d) After 60 min milling with 8 mL of hexane.[36]

ARM is an inexpensive and scalable technique that can be used with various reactive material compositions (e.g., Al/CuO, Al/MoO_3, B/Ti, Al/I_2, and Al/hydrocarbon). The contact among the reagents can be highly intimate. The cryomilling technique is based on ARM; in this method, powdered components are milled under cryogenic temperature generated through a liquid nitrogen bath. Through this technique, mixing uniformity and nanocomposite reactivity can increase.[37,38]

An ignition model of Al/CuO nanocomposites prepared through ARM has been established by combining the Cabrera−Mott (CM) oxidation mechanism[39,40] with an Al oxidation model.[41] Recent research on 2Al·3CuO suggests that the low-temperature redox reaction described by the CM kinetics generated a metastable CuO_{1-x} ($0 < x \ll 1$) phase with oxygen release. Therefore, despite a relatively small heat release, the gas evolution changed the thermal properties of the powder coating and consequently enabled its thermal runaway and ignition.[42] Another series of experiments conducted on 2.35 Al·Bi_2O_3, 4 Al·Fe_2O_3, and 8 Al·MoO_3 nanocomposites indicates that the low-temperature redox reactions occurring before ignition destabilizes the oxidizers and increases their susceptibility to rapid decomposition.[43]

2.2.2. Other Studies. The thermal explosion and high-temperature reaction kinetics of the Al/Ni system prepared through HEBM have been investigated by a research group at Purdue University,[44−47] and the findings show that mechanical treatment reduced ignition temperature and delay and apparent activation energy.[44−46] Several possible causes of the increased reactivity of Al/Ni nanocomposites generated by HEBM were evaluated, and the fact that nanometric Ni was embedded in the Al matrix without forming oxide barriers or intermediate layers is considered as a key mechanism.[48] In a study that mainly investigated the combustion and detonation of Al/Teflon nanocomposites, Russian researchers developed the term mechanically activated energy composites.[49,50] Components such as graphite, boron nitride, and MoO_3 were also milled with Al to prepare nanocomposites.[51]

In summary, HEBM effectively produces various nanocomposites and is also inexpensive and scalable. However, this method displays certain limitations: First, strict safety issues must be considered. In handling nanoenergetic materials, safety concerns require sufficient attention, particularly for the HEBM method. In this technique, high-energy impact and friction occur continuously throughout the preparation process. Operators must abide by all operational regulations and must be familiar with the materials to be handled. The amount of samples in each batch should be limited, particularly with respect to newly synthesized nanoenergetic composites. Personnel safety and health issues are discussed briefly in Part V. Second, the presence of impurities during milling, including contamination by the milling balls and process control agents, is inevitable, as are the undesirable partial reactions among original components. Third and most importantly, highly ordered nanocomposites are difficult to prepare through ball milling. Thus, nanoscale structural control is difficult as well.

2.3. Sol−Gel Strategies.

The sol−gel method was initially developed by researchers at Lawrence Livermore National Laboratory to synthesize nanostructured energetic composites made of Fe_2O_3/Al.[52] Either xerogel or aerogel can be obtained using different post-processing methods. Figure 3 depicts typical TEM images of the aerogel derived from Fe_2O_3/Al nanoenergetic composites.[53] N−Al particles are immobilized within the Fe_2O_3 skeleton to ensure intimate contact. However, impurities were detected in the obtained nanocomposites, potentially as a result of residual solvent, epoxide, and epoxide byproducts, which drastically retarded combustion speed. These impurities are unavoidable.[52,54] Sol−gel Ta/WO_3 nanocomposites were prepared and compared with conventional powder mixture, and both samples were consolidated using the technique of spark plasma sintering. The sol−gel composite released heat that was approximately 30% to 35% higher than that of the powder mixture. This result is attributed to the presence of carbon in the sol−gel composite.[55] Additional ignition tests show that the sol−gel Ta/WO_3 nanocomposite obtained is insensitive to friction, spark, and impact ignition.[56]

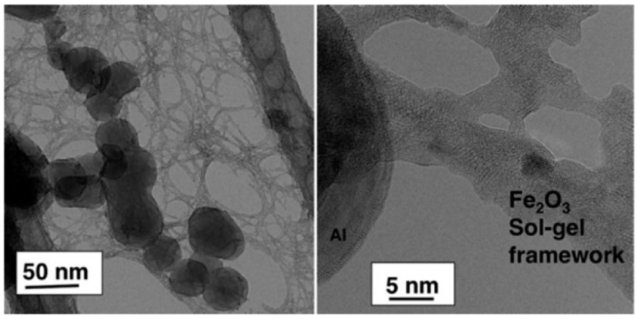

Figure 3. TEM images of the aerogel derived from Fe_2O_3/n-Al energetic composites; n-Al is embedded into the Fe_2O_3 framework.[53]

Apart from nanocomposites consisting of inorganic oxidizers as skeletons and fuel as filler, nanocomposites have also been generated from organic gel and inorganic oxidizers. Organic skeletons composed of resorcinol−formaldehyde (RF) and resorcinol–furfural were successfully filled with various oxidizers, including NH_4NO_3, NH_4ClO_4, and $Mg(ClO_4)_2$.[57] The one-pot synthesis method of interpenetrating CuO/RF aerogels was developed by simultaneously running two sol–gel processes.[58] The sol–gel method has also been used to generate nanocomposites consisting of high explosives and oxidizers.[59,60]

The sol–gel method is simple (preparation can be conducted within a beaker), and intimate contact among components can be ensured. However, impurity remains the most challenging issue because it significantly undermines performance. Therefore, it must be addressed creatively. As with the ARM method, the microstructures of sol–gel nanocomposites are difficult to manipulate.

2.4. Porous Silicon Embedded with Oxidizers.

Porous silicon-based nanocomposites are typically capable of highly heated reactions because strong oxidizers, such as perchlorates, are often embedded in these composites to react with silicon rather than metal oxides. The distribution of nanopores is uniform in the porous silicon layer, and the contact between the embedded oxidizers and the silicon is intimate. This material is particularly advantageous because it can be integrated readily with silicon-based microfabrication technology. The methods of electrochemical etching[61−66] and galvanic corrosion etching[67,68] have both been used to prepare the porous silicon. Aside from porous silicon, porous copper can also generate nanostructured energetic composites.[69]

Porous silicon was first recognized as a potential component of energetic materials in 1992 when the application of concentrated HNO_3 to the surface of porous silicon produced using the anodization method resulted in a violent reaction.[70] Porous silicon has since been comprehensively investigated as a component for nanostructured energetic composites along with various candidate oxidizers for embedding.[61,62] The combustion behaviors of porous-Si/$NaClO_4$ have been systematically studied, and the effects of porosity and pore depth on burning rate have been investigated in both confined and unconfined conditions. The velocities measured in confined conditions are constantly higher than those measured in unconfined conditions. Combustion velocity increases with the porosity of porous silicon until approximately 69% porosity is reached. It also increases with pore depth until it plateaus at approximately 400 m/s.[65]

Efforts to control reaction dynamics have also been made. Gas generation/propagation velocity has been tuned without affecting total energy output by annealing porous silicon in oxygen prior to oxidizer embedding.[64] In another study, microfabrication techniques were used to create ordered pillar structures on heavily doped silicon substrates. Electrochemical etching was utilized to realize the multiscale structure. After embedding with $Mg(ClO_4)_2$, flame propagation speed in these multiscale composites was significantly higher than that in nanocomposites produced by the simple electrochemical etching of porous silicon, thereby indicating that reaction propagation can be controlled by structural modifications.[71]

Apart from the widely used process of electrochemical etching, the technique of galvanic corrosion etching has also been developed.[67] In one study, an on-chip device to diagnose velocity and a high-speed technique of video recording both measured the combustion propagation velocity of porous silicon/$NaClO_4$. Average combustion velocity reached 3050 m/s in porous silicon with a specific surface area of approximately 840 m^2/g and porosity ranging from 65% to 67%. This velocity is potentially the highest reported in the field of nanoenergetic composites.[68] The velocity diagnostic device and a typical combustion frame are presented in Figure 4.

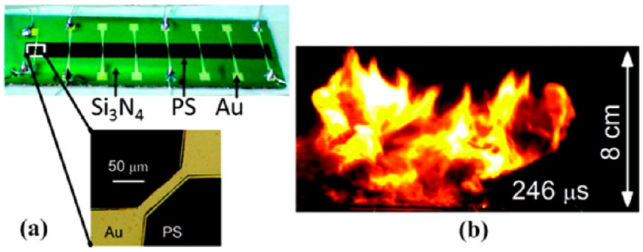

Figure 4. (a) Optical image of the microfabricated device that diagnoses velocity with integrated Au wires positioned at a distance of 5 mm. (b) Typical combustion phenomenon of porous silicon/$NaClO_4$.[68]

Nanostructured energetic composites based on porous silicon have also been integrated with microelectrochemical systems (MEMS) to realize multifunctional devices. Microhotwires have been incorporated into nanoenergetic composites to prepare microigniters. Patterned arrays of energetic devices with independent addressability have also been fabricated.[61,63,72] Furthermore, an integrated system that includes nanoporous silicon, a hotwire initiator, and a MEMS acceleration switch has been established.[63,64]

Nanoenergetic composites based on nanoporous silicon are generally capable of high-energy output and are beneficial to MEMS integration. The structure of the porous silicon layer can be effectively controlled by adjusting the operational parameters. Nevertheless, efficiently embedding the nanopores with oxidizers to increase filling ratio remains a challenge, and the hygroscopicity of the various oxidizers commonly used in previous studies can cause instability with respect to long-term storage. Finally, the high sensitivity of nanocomposites composed of porous silicon should be considered in practical application.

2.5. Self-Assembly Method.

Self-assembly is an efficient bottom-up method of preparing nanostructured energetic composites. The driving forces in the self-assembly of fuel and oxidizers include electrostatic force,[73−75] surface modifiers [e.g., poly-4-vinylpyridine (P4VP)],[76−80] and biomolecules.[81,82]

2.5.1. Electrostatic Self-Assembly.

In a pioneer study on the electrostatic self-assembly of nanoenergetic materials, particles of Al and Fe_2O_3 aerosol were first oppositely charged and then mixed. The electrostatically assembled nanocomposite was compared with randomly assembled (Brownian) mixtures by a spark ignition test and analyzed by differential scanning calorimetry (DSC). The results indicate that the energy release rate and reaction heat of the electrostatically assembled nanocomposite were significantly increased.[75] On the basis of electrostatic self-assembly and hydrogen bonds, nanowire membrane-based nanothermite was prepared. MnO_2 nanowires were first synthesized using a hydrothermal method. The nanowire surfaces were then modified using polydiallyldimethylammonium chloride to obtain positive charges. The positively charged MnO_2 nanowires were self-assembled with negatively charged Al nanoparticles in a water-based solution. The flexible membrane structure was then constructed by simple suction filtration.[74] Subsequently, a ternary thermite membrane composed of MnO_2/SnO_2/n-Al was developed. α-MnO_2 nanowires were synthesized using the same hydrothermal method. Then, SnO_2 nanostructures were prepared on the surface of MnO_2 to generate a hierarchical structure. The n−Al particles were self-assembled with MnO_2/SnO_2. The free-standing thermite membrane was formed after vacuum suction filtration. The introduction of SnO_2 changed the apparent activation energy and the onset reaction temperature of the Al/MnO_2 nanocomposite.[83]

2.5.2. Self-Assembly Based on Surface Modifiers. Surface modifiers have been widely used to assemble nanoenergetic composites. Polyvinylpyrrolidone is a candidate polymer to immobilize nanoparticles because of the strong affinity of the pyridyl group to metals and because it can bond with polar species through hydrogen bond.[84] The self-assembled Al/Fe_2O_3 nanothermite performed more effectively than the conventional physical mixture in the reference with respect to ignition and pressurization behavior. The findings also suggest that interfacial contact is more important than the size effect.[78,85] Various CuO nanorods/nanowires have been self-assembled with n-Al particles by P4VP. Their flame speeds and pressurization rates are higher than those of randomly mixed nanocomposites.[76,77] Hybrid nanoenergetic formulations composed of self-assembled CuO nanorods/Al mixed with either NH_4NO_3 or secondary explosives, namely, 1,3,5-trinitroperhydro-1,3,5-triazine and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, were investigated in different weight proportions. The results show that extremely high pressure can be generated and that nanothermites trigger the explosives under fully confined geometry.[80]

2.5.3. Bio-Based Self-Assembly. DNA-directed assembly has been explored recently. Al and CuO nanopowders were first suspended and stabilized in aqueous solution. Thiol-modified oligonucleotides can be bound directly to CuO nanoparticles. Neutravidin was attached to the alumina shell around Al nanoparticles, followed by grafting with biotin-modified oligonucleotides. Hybridizing the complementary DNA strands eventually produced a nanostructured energetic composite composed of Al/CuO through self-assembly. The self-assembled Al/CuO nanocomposites exhibited a lower onset reaction temperature and higher reaction heat than those of their physically mixed counterparts.[82] Protein cages also assisted in the assembly of nanoenergetic materials; cationized ferritin protein cages loaded with FeO(OH) cores were assembled with n-Al particles. The reaction kinetics improved mainly because of the reduced diffusion distance between reactants. Furthermore, FeO(OH) was successfully replaced by ammonium perchlorate in the protein cages; thus, the n-Al/ammonium perchlorate system reacted more quickly and energetically. Building multiple layers of protein cages around the n-Al facilitates the adjustment of the stoichiometric ratio.[81] Figure 5 schematically shows the assembly of n-Al particles with cationized ferritin loaded with either iron oxide or ammonium perchlorate.

In summary, the self-assembly method is highly promising in preparing nanostructured energetic composites. The borders of the three aforementioned self-assembly strategies are not strict; for instance, electrostatic force plays a key role in the self-assembly process based on protein cages. In the future, additional principles must be implemented for the design of new and interesting self-assembly techniques. Minimizing the introduction of other additives (e.g., hydrocarbon ligand) is beneficial as these additives either lower total energy density or even undermine performance drastically. However, introducing additives may also be advantageous; for instance, the DNA strands used for self-assembly can be exploited further to produce "smart" nanostructured energetic composites as envisioned by the researchers.[82]

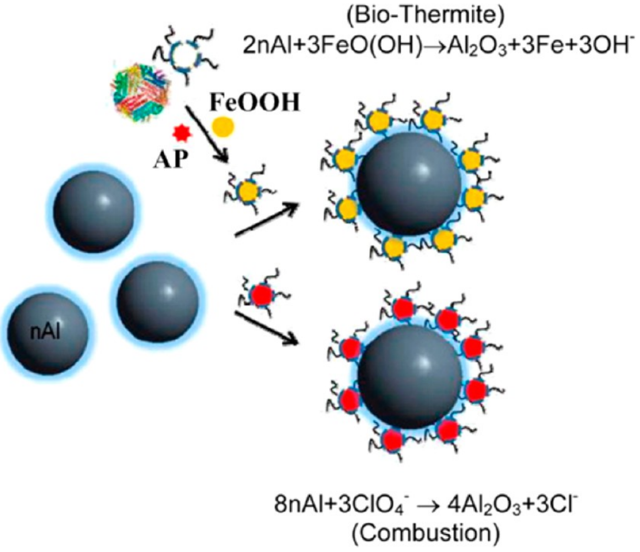

Figure 5. Assembly of n-Al particles with cationized ferritin loaded with either iron oxide or ammonium perchlorate.[81]

2.6. Core/Shell Energetic Materials Based on Nanowires/Nanorods. Fe_2O_3 nanowire arrays were partly embedded into thin Al films to obtain extremely high packing density, intimate contact, and precise control of oxidizer/fuel dimensions in a pioneer study on nanowire-based energetic materials conducted in 2004.[86] However, the preparation method, which consists of eight steps, is rather complicated.

A considerably simpler technique based on CuO nanowires was later developed. A thin Cu film was first deposited onto silicon substrate. CuO nanowires were then synthesized by thermally annealing Cu films in static air. Finally, n-Al was deposited around the CuO nanowires and on the surface of the underlying CuO/Cu_2O film.[87] The advantages of this method include enhanced contact, reduced impurity, tailored dimensions, and easy integration into the microsystem.

After this study, additional investigations into core/shell energetic materials based on CuO nanowires have been conducted.[88−92] The mixing uniformity and activation energy of Al/CuO nanocomposites based on CuO nanowires were significantly improved and reduced, respectively, compared with those of nanoparticle-based Al/CuO mixtures.[91] As the number of CuO nanowires obtained in the annealing process increased, the heat released in the first exotherm of Al/CuO increased. Meanwhile, ignition delay and ignition energy were reduced.[90]

However, the formation of CuO nanowires through the thermal annealing of Cu thin films inevitably results in the undesirable generation of a micrometer-scale Cu_2O/CuO layer beneath the CuO nanowires. To overcome this limitation, purely nanostructured Co_3O_4/Al was developed. Co_3O_4 nanorods were prepared by annealing $Co(OH)_2$, which was synthesized through chemical bath deposition. Then n−Al was deposited around the Co_3O_4 nanorods by thermal evaporation to produce energetic materials that are purely nanostructured. Total reaction heat, particularly the exothermic reaction prior to Al melting, was significantly enhanced.[92]

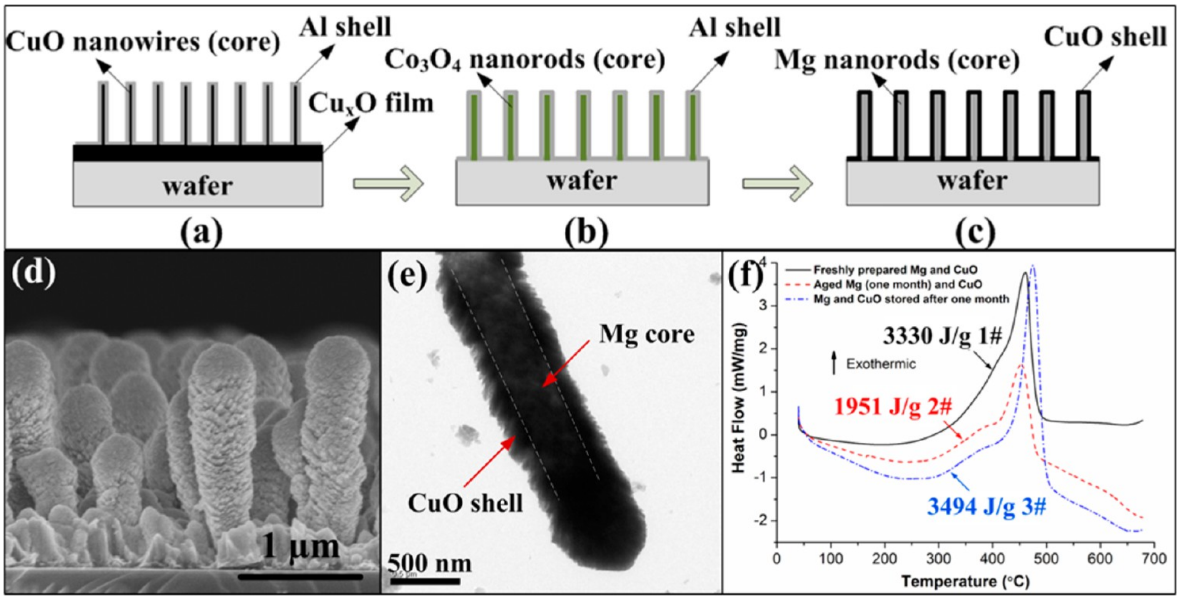

Figure 6. (a−c) Schematic diagrams of the evolution of the design concept. (a) Concept for.[87−91] (b) Concept for.[92] (c) Concept for.[93] (d) Cross-sectional SEM image of the Mg/CuO arrays. (e) TEM image of the core/shell structure. (f) DSC analyses of the Mg/CuO nanoenergetic arrays.[93]

The aforementioned core/shell nanostructures all possess a metal oxide core and a metal shell, which can reduce available chemical energy after long-term storage. This phenomenon is attributed to the fact that nanometals are active and readily oxidized. Novel core/shell nanoenergetic arrays composed of an Mg nanorod core and a CuO shell have been developed recently. The Mg nanorod arrays were first prepared onto silicon substrates through glancing angle thermal evaporation. Then, CuO was deposited by reactive magnetron sputtering. Figure 6 displays the schematic diagram of the evolution of the design concept, as well as the main experimental results. The newly designed nanostructured energetic composite exhibited a good anti-aging property, as proven by the well-maintained reaction heat (as indicated by the comparison between samples 3 and 1), whereas the aged sample lost considerable chemical energy (as indicated by the comparison between samples 2 and 1).[93]

Core/shell energetic material based on nanowires/nanorods is a new and promising field of research. This material is derived from layered vapor deposition but has greater potential for exploration than relatively mature RMF. The unique structure of this energetic material may be exploited to obtain added value. For instance, superhydrophobic property is often related to nanotextures; thus, waterproof nanostructured energetic composites can be envisioned.

2.7. Other Methods. *2.7.1. Electrophoretic Deposition (EPD).* EPD has been used to deposit energetic composites composed of Al/CuO.[94,95] Micrometer-sized Al particles and nanosized CuO particles were first dispersed in ethanol (EtOH)/H_2O solution to obtain positive surface charges. With a custom-built EPD cell, a composite layer was formed on the negative electrode. The mixing and combustion velocities of the films prepared using EPD were considerably more uniform and faster, respectively, than those of composites produced by the "drop-cast" method. Both n−Al and nano-CuO particles were also used in EPD to prepare nanocomposite thin films.[95] The direct-ink writing technique was combined with EPD to prepare Al/CuO nanocomposites on patterned 2D and 3D electrodes, and various architectures exemplify the versatility of this new method.[96]

2.7.2. Electrospinning Method. To realize a nanostructured energetic composite, nanothermite was electrospun into the nitrocellulose (NC) polymer matrix.[97] Here n−Al and nano-CuO particles were first dispersed into collodion solution. Ether and EtOH were added and stirred vigorously. The suspension was then ultrasonically mixed and magnetically stirred. The nanostructured energetic composites were prepared by electrospinning the suspension through a home-made setup. The burning of the Al/CuO-based NC was significantly more luminous than those of pure NC and NC incorporated with n-Al, and combustion propagation velocity increased dramatically. Electrospinning was also used to generate Al/Fe_2O_3/NC energetic fiber, and the introduction of Al and Fe_2O_3 catalyzed NC decomposition.[98]

2.7.3. Macroporous Metal Oxide/Metal Composite Ordered in 3D. A macroporous Fe_2O_3/Al nanocomposite film ordered in 3D was prepared based on a polystyrene sphere template.[99] Polystyrene spheres were first synthesized using an emulsion polymerization method to generate a suspension, which was then transferred to the surface of a microslide substrate. The voids among polystyrene spheres were filled with an $Fe(NO_3)_3{\cdot}9H_2O$ precursor solution. After calcination, the macroporous Fe_2O_3 film ordered in 3D was formed. Finally, an Al film was integrated by vapor deposition to generate nanostructured energetic composites made of Fe_2O_3/Al.

2.7.4. Metallized Fluoropolymer Composites. A novel energetic composite called aluminized fluorinated acrylic (AlFA) composite was developed.[100] Al nanoparticles were first treated with phosphoric acid 2-hydroxyethyl methacrylate ester (PAM) to yield PAM-*co*-nano-Al, and then AlFA-X (where X denotes the particle content wt %) composites were prepared by *in situ* polymerization of 1H,1H,2H,2H-perfluorodecyl methacrylate with varied mass of PAM-*co*-nano-Al. Another new kind of nanocomposite was developed by incorporating perfluoropolyether coated n-Al blend with epoxy resin.[101] The new nanocompsite was moldable, machinable, and stable in open air. Fluorine is the most

Table 1. Comparison of Various Strategies in Preparing Nanostructured Energetic Composites

preparation methods	figures of merit						
	cost	scalability	impurity/prereaction	safety concern	green operation	controllability on nanostructures	integration with MEMS
powder mixing	low-cost	scalable	serious impurity[b]	medium	generally green	not controllable	difficult
layered vapor deposition	expensive[a]	difficult to scale up	high purity[c]	safe	green	excellent controllability	easy
mechanically assisted methodology	medium	scalable	impurity/prereaction existing	precaution needed	generally green	poor controllability	difficult
sol−gel/Aerogel strategies	low-cost	scalable	serious impurity	precaution needed	not green	partially controllable	difficult
porous silicon with embedded oxidizers	low-cost	medium	impurity being possible	precaution needed	medium	partially controllable	easy
self-assembly method	generally low-cost[d]	scalable	serious impurity	medium	dependent[d]	good controllability	difficult
core/shell nanostructures	expensive[a]	difficult to scale up	high purity	safe	generally green	good controllability	easy

[a] The cost is mainly due to vacuum deposition equipment. [b] The high impurity originates from the metal oxide shell surrounding the nanometal core. [c] Except those with ultrathin bilayer thicknesses. [d] Dependent on the specific self-assembly method used.

electronegative element and the fluorination of metals usually generates substantial heat of reaction. Fluorocarbons normally contain a high amount of fluorine and are ready to generate reactant gases when heated. Therefore, various kinds of fluorocarbon-based energetics are promising for applications. Further information is presented in a recently published book.[102]

2.7.5. Carbon Nanotubes (CNTs) with Embedded Oxidizer. KNO_3@CNTs was reported as a promising new energetic nanocomposite.[103] KNO_3 was first embedded into CNTs by wet chemical method to form KNO_3@CNTs nanoenergetic material, and then KNO_3@CNTs was electrophoretically deposited onto a Cu microbridge to achieve an energetic micro initiator. The energetic micro initiator showed higher electrical explosion temperature and more violent explosion phenomena than the pure Cu microbridge.

2.8. Summary. After a comprehensive review of the various strategies adopted in preparing nanostructured energetic composites, an overall comparison must be conducted. Attention is focused on those main strategies. Seven factors are chosen as figures of merit, i.e., production cost, scalability of the method, possibility of impurity/prereaction, safety concern, green operation (minimizing the use of hazardous chemical reagents), controllability on the nanostructures, and the ability to be readily integrated with MEMS. Integration with MEMS is proposed as a factor because the combination of nanocomposite and MEMS to form nanoenergetics-on-a-chip indicates profound effects on the microenergetic-related field. Table 1 displays the comparison results and powder mixing technique is also included as a reference. The interpretation of the table can rely on different practical conditions. For example, the layered vapor deposition may be not suitable for preparing large amounts of free-standing material. However, because the layered vapor deposition is easily integrated with MEMS, large batches of reaction units can be simultaneously fabricated on a silicon chip. This concurrent fabrication demonstrates the "scalability" of the method.

3. IGNITION AND COMBUSTION MODELS

As mentioned, the dense and well-defined geometry of RMFs makes theoretical modeling easier and more accurate. Researchers have been working on RMFs for a number of years. Therefore, the modeling of nanostructured energetic composites focuses mainly on RMFs. A review paper has discussed the early research results.[13] The present paper concentrates on the developments of modeling work on RMFs in recent years. The newly proposed ignition model for Al/CuO prepared by ARM is also presented in this paper.

Modeling of nanoenergetic composites is generally classified into two categories. The first category is the well-known lumped modeling that mainly deals with reaction modeling of nanoparticles.[41] In these models, the temperature and/or heat flux can be depicted versus time, in which these two features (temperature and/or heat flux) are not related to direction because the models are intrinsically lumped.[41,104] The second category of modeling deals with heat conduction with heat source.[19,20,31,105−109] In this type of modeling, two coupled partial differential equations that may be converted into a system of ordinary differential equations[13] or one partial differential equation that assumes special conditions[31,107] are challenged. Temperature and heat flux can be calculated in any position and time in nanoenergetic foils, and more importantly, the speed of flame propagation can be easily addressed because of the coupling effects of time and coordinates that are considered in these simulations. It is important to highlight that the propagation velocity in multilayer foils can be analytically calculated by assuming a simple relation between heat generation and composition of foils, as well as making certain mathematical simplifications and assuming steady-state part of the solution.[16,110,111] Moreover, the effects of heat transfer from different substrates on quenching of flames can be investigated by using heat conduction equation with moving heat source and with the experimentally determined flame velocity data.[31] This method is coupled with experiments, but it can provide a practical tool to model flame propagation in nanoenergetic foils even with commercial software such as COMSOL.

3.1. Lumped Modeling. The ignition model of Al/CuO nanocomposite prepared by ARM[41] is first introduced. To clarify the steps of calculations, we can consider the general model

$$\dot{T} = \dot{P} + \dot{E} - \dot{C} - \dot{R} \qquad (1)$$

where $\dot{T}$ is the heating rate of the system, $\dot{P}$ is the heating rate incorporated into the system from an external source such as Joule heating and/or laser heating, $\dot{E}$ is the rate of released heat that results from chemical reaction within the system, and $\dot{C}$

and $\dot{R}$ are rates of heat losses due to convection and radiation, respectively.

Specific attention was given to address the chemical heat release rate. A numerical model was proposed to calculate the growth rate of alumina, which was based on the CM oxidation mechanism. The CM mechanism deals with initial and low temperature process combined with an aluminum oxidation model that describes different alumina polymorphs at increased film thickness and higher temperature.[41] Oxidation growth of amorphous and γ-Al_2O_3 were considered. The proposed model adopted CM mechanism for the initial growth of amorphous alumina. Arrhenius-type kinetics was introduced for the thermally activated growth of the amorphous oxide and the oxidative growth of γ-Al_2O_3 after phase change. Accordingly, the total heat flow can be given as follows:

$$\dot{E} = n\left(\frac{\mathrm{d}m_{\mathrm{am}}}{\mathrm{d}t} + \frac{\mathrm{d}m_{\gamma}}{\mathrm{d}t}\right)\Delta H_{\mathrm{Al_2O_3}} \tag{2}$$

where n is the number of inclusions per unit of mass in the nanocomposite particle. Simulation results were compared with experiments in which two models of heating were considered for the particles. The considered models were the filament ignition model that was similarly applied in[112] and the laser ignition model that was also implemented in.[113] Heat losses by convection and radiation were incorporated in both models. The gas released from decomposing CuO could probably affect the filament ignition process. However, the released gas was not included in the modeling work.

In another study, Vohra et al. developed a numerical method to predict the temperature field and heat release in a nanocalorimeter that contained a Ni/Al bilayer.[104] Thermal loss caused by convection was ignored because the device was triggered under vacuum. The differential equation of modeling the system temperature was introduced as follows:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\Delta H}{\overline{\rho c}}\frac{\mathrm{Vol}_{\mathrm{bilayer}}}{\mathrm{Vol}_{\mathrm{stack}}}g(\tau)\frac{\partial \tau}{\partial t} + \frac{V'I}{\overline{\rho c}Vol_{\mathrm{stack}}} - \frac{\sigma}{\overline{\rho c}\mathrm{Vol}_{\mathrm{stack}}}(\varepsilon_{\mathrm{top}}A_{\mathrm{top}} + \varepsilon_{\mathrm{bottom}}A_{\mathrm{bottom}})(T^4 - T_{\mathrm{a}}^{4}) \tag{3}$$

$$\frac{\partial \tau}{\partial t} = \frac{D(T)}{\delta^2} \tag{4}$$

where τ is the normalized time variable and $g(\tau)$ is the canonical solution of heat equation, which is a known function. In the computations, eq 4 was discretized by using an explicit second-order Adams–Bashforth scheme, and eq 3 was discretized with a fourth-order Runge–Kutta scheme for Joule heating and radiative heat loss terms. An exact integration was used for the reaction source term. The Arrhenius pre-exponent and activation energy of the atomic diffusivity were determined by employing the Arrhenius model for combining Ni and Al, and by using experimental data to estimate the rate of heat release.

3.2. Heat Conduction Modeling with Heat Source.

Fourier's law and the equation of energy conservation were used in this kind of modeling to introduce partial differential equation of heat conduction as follows:

$$c\rho\frac{\partial T}{\partial t} = \nabla(k\nabla T) + \dot{Q} \tag{5}$$

where the last term is the heat generated from the reaction of nanofoils. This heat of reaction depends on the concentration of material. Thus, eq 5 is coupled with the equation of motion of the concentration field (equation of diffusion), as follows:

$$\frac{\partial C}{\partial t} = \nabla(D\nabla C) \tag{6}$$

where D is the atomic diffusivity and is commonly assumed to follow Arrhenius model of temperature dependent. The temperature, heat flow, and flame speed in nanolaminated material can be estimated by solving eqs 5 and 6 together. The conduction mode of heat transfer is dominant for thick free-standing foils. However, in connection with thin reactive foils deposited on a substrate, heat conduction to the substrate, convection, and radiation to the atmosphere can also be important and can affect the self-propagation reaction.

To simplify the coupled system of eqs 5 and 6, in most simulations, we can assume that the temperature field is constant in normal direction and that diffusion occurs merely in normal direction. Therefore, the aforementioned equations take the following forms:

$$c\rho\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right) + \dot{Q} \tag{7}$$

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial y}\left(D\frac{\partial}{\partial y}C\right) \tag{8}$$

Another promising technique for modeling flame propagation in nanofoils is by converting $\partial T/\partial t$ in eq 7 to $V(\partial T)/(\partial x)$.[114] If flame velocity can be measured through experiment and heat generation can be considered within the boundary conditions, then the partial differential equation below can be obtained.[31]

$$c\rho V\frac{\partial T}{\partial t} = \nabla(k\nabla T) \tag{9}$$

The effects of different boundary conditions or substrates on the quenching effects can be considered by analyzing eq 9. In connection with this equation, a traditional two-dimensional black box theory was used in conjunction with the sandwich model to estimate the appropriate heat flux on the substrate that accounts for the heat loss to the surroundings.[31] The observations from computations were firmly consistent with the experiment measurements.[30] A similar mathematical model can be applied to simulate temperature distribution in solders and components during reactive bonding process with reactive multilayer foils as local heat sources.[115,116]

4. PROMISING APPLICATIONS

Nanostructured energetic composites are adopted in numerous applications in both military and civilian areas. Some application-driven investigations based on ultrasonically mixed nanocomposites are discussed in this section. These power mixtures can be readily replaced with nanostructured energetic nanocomposites without affecting the design concept and architecture of any related device. Using nanostructured energetic composites is even beneficial because of its easy integration with MEMS. High heat of reaction is mostly exploited as the driving force of many application fields, including reactive bonding, micro ignition and rapid initiation, processing of materials, and micro power generation. Gas released in the reaction is also relevant to application fields, including microactuation/micropropulsion, gas generators, and pressure mediated molecular delivery. Reaction products can also be utilized for synthesis of materials and inactivation of microorganisms.

Table 2 displays the rough classification of various applications according to different attributes, including heat release, gas evolution, and specific reaction products. Cross reference can exist, e.g., microactuation is based on gas generation, but heat release also contributes in the course of actuation/propulsion.

Table 2. Various Applications of Nanoenergetic Composites

attributes	applications
heat release	reactive bonding[115−123]
	micro ignition and rapid initiation[64,69,72,124−137]
	materials processing[138−141]
	micro power generation[142]
gas evolution	micro-actuation/propulsion[63,143−147]
	pressure mediated molecular delivery[148,149]
reaction products	material synthesis[105,138,150−152]
	inactivation of biological agent[153−156]
others	propellant additives[157−159]
	hydrogen production[160,161]
	nanocharges[162]

4.1. Reactive Bonding. The RMFs (especially Al/Ni) are extensively investigated as heat sources for soldering, brazing, and welding. These processes are generally termed reactive bonding.[115−122] The self-propagating reaction velocity, reaction temperature, and total heat of reaction can be readily tailored by changing the bilayer spacing, total foil thickness, and composition ratio, which makes RMFs an ideal candidate for precisely controlled reactive bonding. Moreover, the characteristics of localized heating and rapid cooling associated with reactive bonding allow RMFs to join temperature-sensitive materials and components with extremely different coefficients of thermal expansion.

Self-propagating exothermic reaction of Al/Ni multilayers was applied in the joining processes of metallic glass,[117] titanium alloy,[119] stainless-steel specimens,[118] silicon wafers,[116] and bio-MEMS systems.[122] The duration of melting process and the maximum temperature at solder/component interface generally determine the quality of the joint. Parameters, including applied joining pressure, total foil thickness, and solder selection, can be adjusted to achieve good bonding results.[120] Figure 7 depicts the schematic diagram of the reactive bonding of two components by using reactive foil, solder, and applied pressure.[118] Au and Ni coating is used to enhance bonding, and the coating may vary according to different solders and specimens. Apart from conventional individual reactive bonding, in which relatively thick reactive foil is used, integrated reactive system via patterning technology is also developed to reduce the required thickness of reactive foil.[123] Nanocomposites were also studied for reaction-assisted bonding process[163−165] in which additional heating source (e.g., furnace) was needed. However, these investigations are not highly engaging because they do not differ significantly from the conventional bonding process.

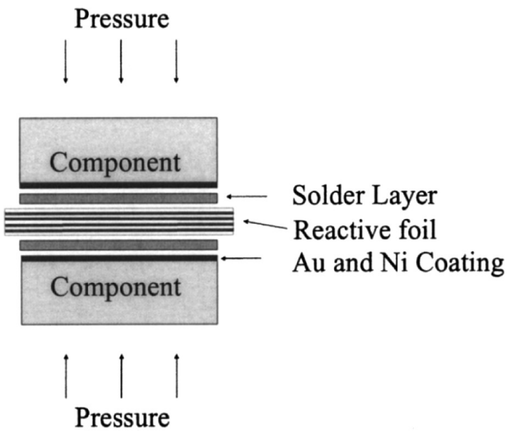

Figure 7. Schematic showing the reactive bonding of two components.[118]

4.2. Micro Ignition and Rapid Initiation. Nanoenergetic materials are integrated with micro-heaters because of the exothermic nature of the former. Accordingly, this integration occurs to realize functional energetic devices, which can enhance the energy output as both electrical energy resulting from Joule heating and chemical energy originating from chemical reaction can be collected.[61,64,124−129,131,132,137] Micro ignition and rapid initiation are based on this concept. The difference between the two mechanisms lies in the mode of stimulations and the potential application areas. Small-current stimulus mode (typically within several amperes) is usually applied for micro ignition process, which is related to the applications in the firing system.[64,69,124,125,131,132,136] Rapid initiation refers to the fast electro-explosion process induced by pulse high current density (exceeding 10^6 A/cm^2), which is often employed in detonation systems, e.g., exploding foil initiator (EFI).[126,127,130,135] Potential applications of reactive multilayers on semiconductor bridge were also investigated.[133,137]

Layered vapor deposition and porous silicon-based nanostructured energetic composites have been widely investigated in this field because they can be readily integrated with silicon-based microelectronics and microsystems. Nanoenergetic composite is typically deposited onto micro-heater arrays patterned by photolithographic technology. The rising temperature of micro-heater by Joule heating process initiates the chemical reaction after reaching the firing point of the nanocomposite. A typical microigniter based on CuO/Al nanocomposite and Pt micro-heater is displayed in Figure 8.[125] Efforts were made to directly transfer the electric current through nanocomposites that can conduct electricity (e.g., Al/Ni RMFs). This direct passage means that Joule heating and chemical reaction both occur within nanocomposites.[132]

The application of micro ignition has shown promising results, and the ejected high-temperature reaction products observed in numerous investigations are believed to further enhance the ignition ability.[125,129,137] However, the potential in rapid initiation process remains ambiguous because of two aspects. The first is that rapid initiation is usually completed in a very short time (sub-microsecond magnitude). Therefore, nanocomposites do not easily react completely in such a limited period, which means that the chemical energy cannot effectively contribute to the rapid initiation process.[127] The second aspect is that the input energy is relatively high because of the required high current density. In other words, it may not be efficient because the total available chemical energy may amount to only a small portion of the input electrical energy.[126,130,135]

4.3. Synthesis and Processing of Materials. Energetic composites have long been used in synthesis and processing of materials, e.g., thermite reaction between Al and Fe_2O_3 is well-known for its use in track welding that forms molten Fe. A

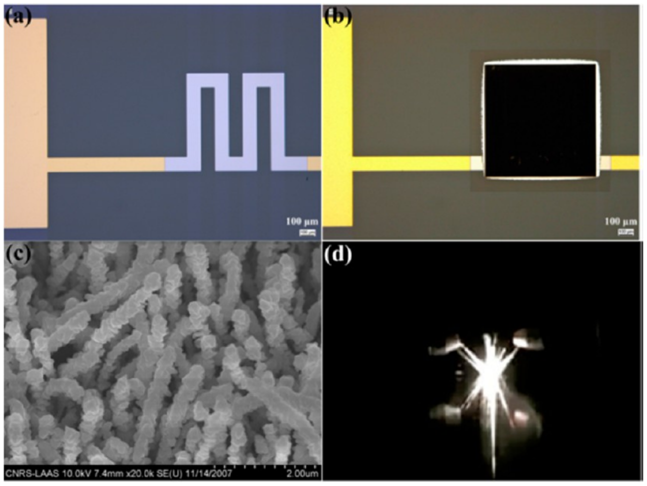

Figure 8. A typical micro igniter based on CuO nanowires/Al and Pt micro-heater. (a) Au/Pt/Cr micro-heater, (b) a micro-heater with integrated CuO nanowires/Al, (c) SEM image of CuO nanowires/Al, and (d) a typical combustion frame after ignition.

paper published in 1993 reviewed the applications of thermite reactions in this field.[166] The emergence of nanoenergetic composites further stimulates and revives this field with the development of nanotechnology. Synthesis of intermetallic compounds[105,138,151,152] and crystallization of amorphous silicon[138−141] are two typical examples.

The self-sustaining reaction of binary metallic nanomultilayers can also be exploited to produce intermetallic compound with minimal energy expenditure similar to the aforementioned reactive bonding.[105,152] Uniform heating of the whole sample is another way to produce the intermetallic compound. Thermal exploding mode or annealing mode can explain the reaction mechanism depending on the adopted heating rate.[105,151] Poly-Si is a promising material to fabricate solar cells and thin film transistors. Crystallization of amorphous silicon with nanoenergetic composites is advantageous for its local heating and swift processing, and is suitable for large area production.[139,141] Figure 9 shows a schematic of the crystallization of amorphous silicon induced by thermite reaction of Al/Fe_2O_3 nanocomposite. SiO_2 and Ag layers were deposited to prevent metal diffusion during processing and retain thermal energy transportation. The residual products and Ag/SiO_2 buffer layers were etched away after the reaction to leave the crystallized poly-Si thin film.[139]

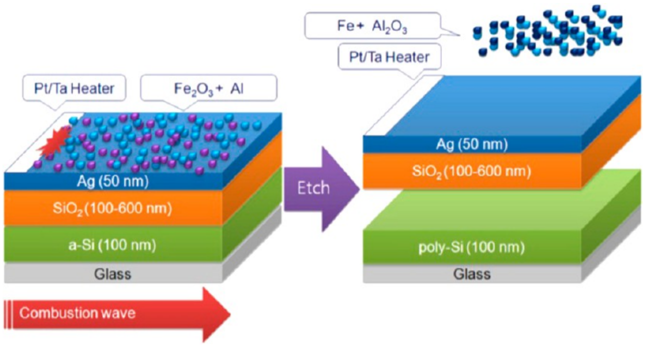

Figure 9. Schematic of amorphous silicon crystallization with Al/Fe_2O_3 nanocomposite.[139]

4.4. Micro-Actuation/Propulsion.

Certain reactions can produce gas products in normal environmental conditions (e.g., porous-Si/$NaClO_4$). The reaction products are typically in the solid state under standard conditions for many thermite reactions. However, the high reaction temperature enables vaporization of some reaction products and reaction intermediates; thus, gas generation is feasible.[167−170] The high reaction temperature also heats and pressurizes the air trapped among the nanocomposites. All these factors contribute to the promising application called micro-actuation/propulsion.[63,143−147] Numerous formulations of nanoenergetic composites have been investigated for potential gas generation. Maximum pressure and pressurization rate are typically chosen as the parameters for comparison.

In this study, a microactuator was fabricated for disposable lab-on-chip applications. The microactuator consists of an inflatable elastic membrane and is characterized by small size (<0.25 mm^2 × 100 μm), good bio-compatibility, and high efficiency (>10 kPa overpressure with <100 mW electrical power). Figure 10 shows the schematic diagrams of 3D cut view and the functioning principle of the device. When actuation is required, the energetic powder is heated and gases that inflate the PDMS membrane are liberated. Subsequently, the accumulated pressure moves the fluid into the micro-channel.[146]

Nanoenergetic composites were also investigated for applications in a microthruster. The first autonomous jumping microrobot was fabricated by the integrated assembly of control, sensing, power, and actuation functions onto a polymer platform. Nanoporous Si-based energetic composite was chosen to be the energy source for propulsion because of the reduced complexity. The fabricated robotic hexapod could detect an increase in light intensity and respond by jumping.[145] Al/Bi_2O_3 and Al/CuO nanothermites were recently evaluated for micropropulsion applications. Al/Bi_2O_3 exhibited a higher average thrust, longer burning duration, and larger specific impulse than Al/CuO. Bulk packing density and confinement geometry influence the average thrust and burning duration. Adding small amounts of nitrocellulose is also effective in increasing the specific and volumetric impulses of the nanothermites.[147]

4.5. Biomedicine-Related Applications.

Nanoenergetic composites were recently studied for biomedicine-related applications. A high reaction temperature can be used to inactivate certain biological agents and some halogen-containing reaction products can further enhance this capability. An extremely high reaction propagation velocity of certain nanoenergetic composites induces shock wave, which can be exploited to achieve pressure-mediated cell transfection.

The threat of biological weapons is a major concern that stimulates efficient neutralization of spore-forming bacteria. Various reactive materials, including Al, Mg, B/Ti, Al/MoO_3, and Al/I_2, were seeded in hydrocarbon flame to quantify their differences in biocidal effects. Compared with pure hydrocarbon flame, powder-seeded flame (without iodine) enhanced the inactivation efficiency of bacterial spores one order of magnitude, whereas the iodine-containing material further increased the spore inactivation by two more orders of magnitude.[154] Al/I_2O_5 and Al/Ag_2O were also tested for this purpose. Al/I_2O_5 produced iodine gas that effectively interacted with the spores and neutralized bacteria growth, whereas Al/Ag_2O could not vaporize silver because of a relatively low

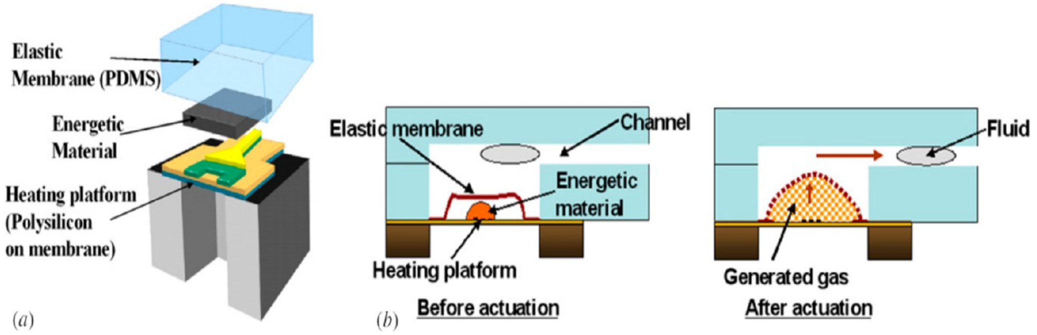

Figure 10. (a) 3D cut view of the microactuator and (b) functioning principle of the device.[146]

reaction temperature, which limits its ability to neutralize bacteria growth.[155]

Bi_2O_3/Al/nitrocellulose-based actuator was designed to induce intranuclear molecular transport. The cross-sectional schematic diagram, which is composed of a MEMS initiator, gel tube, and cell suspension vessel, is shown in Figure 11. A transient pressure pulse, which consisted of a shock wave superimposed on a broad pressure pulse, was generated upon initiation. Accordingly, cell membrane permeability was temporarily altered and molecular transport was facilitated. Shock wave was induced by the supersonic nanothermite combustion and the broad pressure pulse was generated as a result of gel protrusion into the suspension vessel following thermite reaction. Both the high intranuclear delivery efficiency and high cell survival rate were achieved in the tests. The technology can be further extended to deliver numerous other biologically related molecules into various cell types.[149]

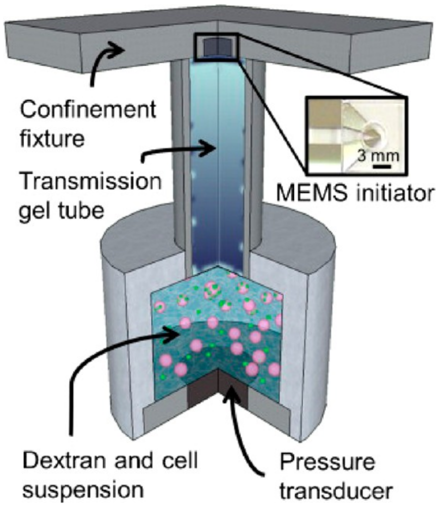

Figure 11. Cross-sectional illustration of MEMS-based actuator for pressure-mediated molecular delivery.[149]

4.6. Propellant Additives. Micrometer-sized metals (particularly Al) are widely used as additives to increase the performance of solid propellant. However, the tendency to form large agglomerates during the combustion process is disadvantageous. Adding nanometric fuel particles to the propellant results in increased burning rate and small agglomerate structures, but the drawbacks lie in the low active material content and processing difficulty caused by high specific surface area. Therefore, nanocomposites produced by the HEBM method were investigated as promising alternatives to mitigate the aforementioned difficulties.[157,158]

A mechanically activated Al/Ni nanocomposite with particle diameters ranging from 25 to 53 μm was used to substitute a portion of Al fuel in the AP/HTPB propellant. Both enhanced burning rate exponent and reduced condensed phase agglomerate size were achieved. As the weight percentage of Al/Ni increased, the reinforced effects became more evident.[158] Figure 12 shows the dependence of burning rate on the amount of Al/Ni used. The mass percentages of Al/Ni in propellant formulations were 0%, 7.5%, and 11.25% for samples A, B, and C, respectively. In another paper, reactive nanocomposites, including B/Ti, Al/CuO, and Al/MoO_3, were added to micrometer-Al powders. Then, the mixture was aerosolized and ignited in a constant volume chamber. Additives of Al/MoO_3 and B/Ti were found effective in increasing both pressurization rate and maximum pressure. This finding indicates the potentiality of Al/MoO_3 and B/Ti as propellant additives to replace the traditional micrometer-Al powders.[157]

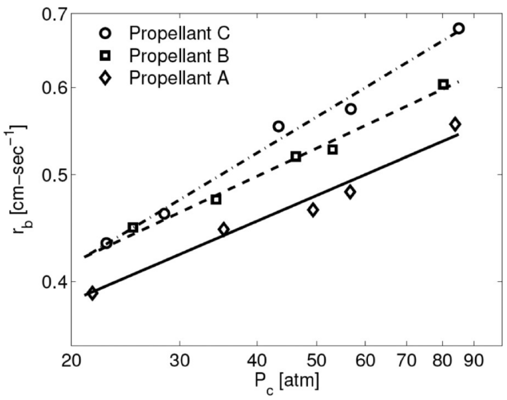

Figure 12. Dependence of burning rate on the amount of Al/Ni used. The mass percentages of Al/Ni in propellant formulations are 0%, 7.5%, and 11.25% for samples A, B, and C, respectively.[158]

Gelled aluminum microspheres that contain a small mass fraction of energetic binder nitrocellulose were recently prepared by a simple electrospray method. The microspheres possessed nanofeatures. The heater wire ignition experiments demonstrated the superior reactivity of the gelled aluminum microspheres compared with original nanoparticles. The newly developed gelled microparticles are expected to circumvent the processing challenges encountered when nanometallic fuels are used.[159]

4.7. Other Applications. *4.7.1. Hydrogen Production.* Mechanically milled Al-based intermetallics and Al/metal oxide composites were investigated to produce hydrogen by reacting with water. Adding Bi and Sn could significantly enhance the reactivity of Al with water. The addition of other metals or compounds to the Al/Bi alloy was also studied to obtain an optimized formulation for high hydrogen generation rate and large hydrogen yield.[160] In another study, an Al/Bi_2O_3 composite prepared by ball milling reacted fast with water, and the Al—water split reaction could be effectively stopped and restarted by controlling the temperature of the flask. Metallic Bi was obtained after the reaction, indicating that Al—water split reaction and thermite reaction occurred concurrently.[161]

4.7.2. Munitions. From the beginning of nanoenergetic material research, nanoenergetics has been considered as useful in improving components of munitions.[171] A lead-free percussion primer, which was composed of nanosized Al/MoO_3 powders or Al/PTFE powders, was patented.[172] Another patent described a reactive fragment, which consists of an energetic material and a polymeric binder material. The energetic material was in the form of a thin film, which was composed of metal or metal hydride as fuel and metal oxide as oxidizer. The fragment can be contained within the casing of the warhead and will function after the warhead penetrates the target.[173]

4.7.3. Micro Power Generation. A patent documented a method to generate power by combustion of nanoenergetic composite. The nanocomposite was deposited onto a substrate. An igniter was then placed on the nanocomposite. When power was needed, the nanocomposite was ignited. Then, various forms of energy, mainly including thermal, mechanical, magnetic, and optic energy, could be exploited and converted to electrical energy via corresponding transducers.[142]

4.7.4. Energy Storage and Transfer. Nanoparticle mixtures exhibit enhanced thermal properties (including thermal capacity) compared with their micrometer-sized counterparts, which enable the nanocomposites to uniformly distribute the absorbed energy and maintain this energy for an extended duration. Therefore, sufficient energy can be applied first (just below the activation energy threshold) to the nanocomposites, and the nanocomposites can store the energy for an extended period. The nanocomposites can produce this extra energy apart from intrinsic chemical energy once the reaction is triggered. Preliminary experiments on nano-Al/Fe_2O_3 and micro-Al/Fe_2O_3 proved the higher specific thermal capacity of nanocomposites and the subsequent increased energy storage. However, the increment seems negligible compared with the large heat release from chemical reaction.[162]

5. CONCLUSIONS AND OUTLOOK

The term "nanostructured energetic composites" is preliminary coined in this review. Comprehensive discussions on the various synthesis strategies and research achievements obtained thus far are presented. Specific chapters discuss the developments of ignition/combustion modeling work and broad promising applications. The safety and health issues of personnel must be given significant attention. Researchers must be cautious throughout the experimental procedures, particularly in the sample preparation process, because of the possible high sensitivity of nanoenergetic materials to various types of stimuli. Some reactants and reaction products can be hazardous to human beings and the environment, particularly when the particle diameter reaches nanometer range. Thus, researchers must carefully refer to the material safety data sheet to follow adequate precautions and arrange appropriate disposal.[174,175]

The superiorities of nanostructured energetic composites are already revealed in various forms; however, the control that can be exerted on nanocomposites is insufficient until now. Apart from the layered vapor deposition, most of the above-mentioned methods can hardly and effectively modulate the delicate structure of nanocomposites. The geometries obtained from these techniques are usually not well-defined compared with those of multilayer foils. This condition explains why the reaction wave propagation models, which are developed thus far, are exclusively based on multilayer foils. The efforts until the present are mainly limited in enhancing the intimate contact and uniform distribution of reactants. In future research, continuous attention must be given to the improvement of existing techniques and exploration of new strategies in preparing nanostructured energetic composites. Improving current techniques and exploring novel strategies can ensure good energetic performance, and more importantly, can upgrade the manipulation of the structural adjustment. Moreover, various possible added values, e.g., mechanical properties, sensitivity, and wettability, based on nanostructured energetic composites should be investigated further. The subject of this paper is a young and fascinating research area and significant work can be done to expand its scope.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was supported by the NSAF (Grant No. U1330132) and Hong Kong Research Grants Council (Project No. CityU 125412). The authors are grateful for the useful comments provided by Professor Timothy Weihs of Johns Hopkins University, particularly those on reactive multilayer foils.

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