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Emerging investigators in materials science 2017–2018

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The development and advancement of human civilizations are largely tied to materials science [1]. Accordingly, historians and archeologists often divide history into time periods based on the materials in manufactured tools and devices—in the three-age archaeology system, such a classification scheme divides human technological history into the Stone Age, Bronze Age, and Iron Age. In the Stone Age, natural materials such as stone, wood, and bone were used to make weapons and implements with an edge, a point, or a percussion surface, thereby enabling our ancestors to butcher animals, dig up roots, and crack hard-shelled nuts. Interestingly, separation of the genus *Homo* (man) from *Australopithecus* (southern ape) occurred about the same time as the advent of these tools, leading some to deduce that the utilization of stone, wood, and bone played a major role in our evolutionary process [1]. The Bronze Age marked the period in history when metals were regularly utilized in the manufacture of weapons and tools. The key prerequisite to the Bronze Age was the development of smelting, or the process of extracting metal from ore. The first metal to be smelted was copper, but given its limited yield strength, artisans eventually learned to dissolve tin and arsenic into the molten copper and create bronze and copper-arsenic alloys, thus strengthening the metal and lowering the smelting temperature. This increased focus on metallurgy inadvertently aided in the rise of urbanization, given that mining, smelting, and casting required labor specialization and surplus food production to support the artisans, whereas the search for raw materials motivated exploration and colonization of new territories [2]. Eventually, advances in smelting resulted in bronze being surpassed by iron, which led to the Iron Age. The advantages to the evolution were two-fold: (1) iron is the more abundant material and (2) iron can be alloyed and heat treated to create a higher-strength material in the form of steel. The iron and steel industries expanded rapidly during the Industrial Revolution, as manufacturers used coke instead of charcoal for smelting iron and steam-powered machines in place of manual hammering for rolling [3]. This rapid expansion had several consequences. On the front end of production, coal mining surged to provide fuel for iron smelting, which required significant additions to the labor force (e.g., mining and metallurgy for production) and infrastructure (e.g., railways for transportation). On the back end of production, machine building expanded rapidly, which enabled new

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inventions such as the spinning machine and steam engine to move from prototypes to mass production much faster.

There is some contention among historians about what constitutes the end of the Iron Age, with some suggesting that it never ended as iron and steel still play a substantial role in contemporary society, and others proposing that materials such as polymers, composites, and semiconductors have surpassed iron and steel as the predominant materials over the last century. In particular, the latter group points to silicon as the heir apparent to steel, and have therefore dubbed the last half century the Silicon Age. The rise of silicon is due to a unique combination of advantageous properties: its natural abundance and availability in large, defect-free single crystals provide a good feedstock, whereas its capacity to act as a variable conductor via doping or an insulator via oxidation allow for a wide range of properties in a single material. These properties have enabled the electronics industry to follow Moore's law for over five decades, which led to the advent of personal computers in the 1980s, followed by the growth of mobile devices such as laptops, tablets, and smart phones in the 2000s [4]. The success of silicon has not been limited to electronics; its optical and mechanical properties have also been the basis for seminal advances in photonics and photovoltaics [5, 6] and micro- and nanoelectromechanical systems [7, 8], respectively. However, the size of silicon components is fast approaching the limits of what can be achieved on a large-scale industrial basis, leading some to look past silicon and consider the next transformational material. Some argue that two-dimensional (2D) materials are poised for this type of impact. The discovery of freestanding graphene provided definitive evidence for the existence of 2D materials at finite temperatures [9]. Another group feels that metamaterials will be vital to the next materials evolution, given their ability to exhibit properties and functionalities not observed in conventional materials. For instance, optical, acoustic, and mechanical metamaterials have revealed optical frequency magnetism [10], negative refractive index [11], and programmable stiffness [12]. Regardless of what material will define the next 'age', *Materials Research Express* will likely play a key role in the dissemination of the underlying research, given its mission to act as the proverbial 'big tent' for the entire spectrum of materials science and engineering [13]. In this special issue on Emerging Investigators, this diversity is captured in a set of invited contributions featuring two reviews and six original research articles. This is an invitation-only issue for rising stars with independent research positions, but less than 12 years of experience beyond their doctoral degrees.

In short, *Materials Research Express* is a multidisciplinary journal devoted to publishing cutting-edge experimental and theoretical research on the processing, structure, properties, and performance of all classes of materials, with an emphasis on the following categories: nanomaterials and nanostructures, organic materials, glasses and amorphous materials, polymers, biological and biomedical materials, energy and environment materials, carbon materials, smart materials, metamaterials, semiconductors, superconductors, magnetic materials, photonic materials, electronic materials, metals and alloys, and surface, interfaces, and thin films. Interestingly, nearly half of these materials are represented in this issue, which points to the diversity of the journal, readers, and contributors. In the nanomaterials and nanostructures section, two contributions utilize low-dimensional materials to enable high-efficiency energy generation and storage solutions. The first article uses Cu dopant

emission to investigate the variation in band gap and edges of CdS and CdSe quantum dots as a function of temperature and size [14], while the second demonstrates highly-oriented vertical arrays of SnS/SnS₂ p-n heterostructures with average power conversion efficiencies of 1.4% [15]. In the biological and biomedical materials section, two contributions present experimental data and molecular simulations of materials for drug delivery and protein engineering applications. The article on the thermodynamics of charging in weak linear and star polyelectrolytes indicates that the charging behavior observed in their work could be useful for tuning the coil-globule transition to various biological conditions, thus enabling targeted drug delivery to specific parts of the body [16]. Similarly, the review on lipases summarizes experimental and modeling results on engineering their activity, specificity, and stability to render them functional in environments beyond physiological conditions [17]. The final four contributions are divided over four sections and include work on carbon materials, metamaterials, electronic materials, and surfaces, interfaces, and thin films. One article addresses the energy and power density limitations of lithium-ion batteries through the development of porous graphene current collectors filled with Si, as this reduces interfacial resistance, accommodates Si volume expansion, and enables more Si per unit area [18]. Another article demonstrates the growth of smooth Al-doped ZnO thin films with tunable epsilon-near-zero frequency, which show promise as constituent materials for zero-index photonics and tunable metamaterial devices [19]. Yet another article investigates the atomistic mechanisms of resistance-switching random access memory cell operation and reliability, given its potential for combining the speed in dynamic random-access memory and the non-volatility in flash memory [20]. The final article reviews helium and hydrogen-induced surface evolution in tungsten and other plasma-facing materials, with an emphasis on the underlying mechanisms responsible for fuzz formation, helium and hydrogen transport, and electronic effects [21].

The Editorial Board of *Materials Research Express* were invited to select two of the articles from the issue for best contribution. The task of selecting the winners was challenging given the high-quality of the work, and thus, the board subsequently agreed to also identify a highly-commended article for recognition. After a lengthy deliberation process, best contribution awards were presented to Rathee *et al* [16] for their work on simulating the thermodynamics of charging in weak polyelectrolytes and Ababtain *et al* [18] for their work on three-dimensional porous graphene current collectors filled with Si for high-performance lithium battery anodes. In the first article, the authors utilize a hybrid Monte Carlo and molecular dynamics approach to examine the conformation and charging of linear and star polyelectrolytes at different ionic screening conditions and pH. The effect of topology on the charging behavior is studied via a comparison between a linear chain and star polymer; it is found that the topology of the star suppresses charging and shifts the coil-globule transition to lower Debye lengths λ_D . For the 10-arm star polymer, an increase in λ_D promotes a collapsed configuration, suppresses charging, and shifts the effective acid or base strength pK_0 in the interior of the polymer, as shown in figure 1. In the second article, the authors demonstrate a method to deposit conformal films of Si on porous graphene current collectors; as shown in figure 2, current collectors with Si thicknesses from 100 nm to 1000 nm exhibit porosity in the structure, thereby aiding electrolyte percolation to enhance Li-ion conductivity and volume expansion of the Si during lithiation and delithiation. The

deposition process is optimized to improve the Si surface area and mass distribution, which results in energy densities of 1.8 mAh cm^{-2} and current rates up to 5 C with a reversible capacity of 0.37 mAh cm^{-2} . Finally, a highly-commended award was presented to Pandey [20] for work on first-principles-based modeling of resistance-switching random access memory (ReRAM) operation and reliability. Explicitly, an atomistic description of retention, low- and high-resistance states, and intrinsic cell-level variability is presented. Under an applied voltage, the author show that metal ions or oxygen vacancies move in clusters along electric fields and form conductive paths between the electrodes. Figure 3 illustrates the phenomenon for a ReRAM cell with Cu electrodes and an SiO_2 dielectric. The simulations show Cu ions near the top electrode migrate as clusters and form a bridge to the bottom electrode. Moreover, the degree of Cu ionization is heightened at the Cu- SiO_2 interface, leading to a Cu charge distribution in the cell.

The articles highlighted above represent the second Emerging Investigators special issue in *Materials Research Express*. The research accomplishments presented herein are best characterized as showing extreme attention to critical detail, careful analytical insight, and thorough consideration of relevant factors. Moreover, the work has enabled new fundamental knowledge, accelerated industrial progress, and enriched connections between seemingly disparate branches of materials science and engineering. As such, the Editorial Board intends to continue the Emerging Investigators special issue on an annual or biennial basis. It is our hope that such issues will not only bring together emerging investigators to showcase their current research, but will also provide a forum to help identify the next paradigm shift or ‘age’ in materials science and engineering. As described above, new eras such as those presented in the three-age archaeology system can lead to considerable leaps forward in evolution, urbanization, industrialization, and technology, leaving us to ponder what the next new material system will enable.

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Figure 1.

Combined Monte Carlo-molecular dynamics simulations of 10-arm star polymers at constant charging chemical potential $\mu = 5$ and two Debye lengths $\lambda_D = 2$ and 5. The conformation, average charge distribution, and effective acid or base strength ΔpK_0 are shown for (a)–(c) $\mu = 5$ and $\lambda_D = 2$ and (d)–(f) $\mu = 5$ and $\lambda_D = 5$. Reproduced from [16]. © IOP Publishing Ltd. All rights reserved.

Figure 2.

Scanning electron microscopy images of three-dimensional porous graphene current collectors with plasma-enhanced chemical vapor deposition (PECVD) silicon coatings. The PECVD process is used to generate Si thicknesses of (a) 100 nm, (b) 200 nm, (c) 500 nm, and (d) 1000 nm. Reproduced from [18]. © IOP Publishing Ltd. All rights reserved.

Figure 3. Molecular dynamics simulations of a conductive-bridging resistive random access memory cell under an applied electric field. Atomic structure for the (a) pristine and (b) formed cell. Si, O, and Cu are yellow, red, and cyan, respectively. Charge distribution in the (c) pristine and (d) formed cell. Cu ions transition from gray to white with increasing oxidation state. Reproduced from [20]. © IOP Publishing Ltd. All rights reserved.