Introduction

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One contribution of 8 to a Theo Murphy Meeting Issue 'Theo Murphy International Scientific Meeting between the UK and China on the chemistry and physics of functional materials'.

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Single crystals of elemental or simple binary or ternary materials, such as Si, GaN or Nb₃Sn, have been the basis of many past and current electronic, optoelectronic and energy technologies. However, there has been a recognition that in order to meet demanding future performance requirements and to enable realization of multiple functionalities in new application environments we need to explore more complex functional materials that can be synthesized by the rich methods of organic or inorganic chemistry and designed to exhibit defined functional properties. Examples include mesoporous metal–organic frameworks with well-defined channels for ion transport and storage [1], complex transition metal oxides with highly correlated d-electrons [2] and emerging applications from batteries to superconductors and conjugated molecular/polymer semiconductors [3] and carbon allotropes [4], which allow realization of a broad range of electronic or optoelectronic functions through molecular design at low process temperatures.

These functional materials have a broad range of potential applications in electronics, optoelectronics, energy storage, energy conversion and more generally in the context of materials for sustainable development [5]. Examples include organic semiconductor-based displays, such as organic light-emitting diodes (OLEDs) and
flexible displays or energy-efficient flat panel OLED lighting, and organic solar cells [3]. The latter have the potential to reduce the cost of electricity for photovoltaic energy to levels competitive with those of coal or gas but require further improvement in their efficiencies and lifetime. Other examples are batteries with transition metal-based cathodes, which need to be improved in order to achieve higher capacity and lower cost. Metal–organic frameworks have wide, potential applications as membranes for separation or ion transport [1]. Many of these materials are designed to comprise only Earth-abundant elements and to be energy-efficient by combining high levels of performance with low-temperature, CO₂-avoiding manufacturing processes.

Many of these materials acquire their unique functional properties through tailored nanostructuring, complex elemental composition and/or lack of long-range crystalline order. This renders their experimental investigation by conventional techniques and their modelling by electronic structure calculations challenging. As a result, the scientific understanding of their structure–property relationships is often still phenomenological and incomplete at an atomic/molecular level. It does not help that there is often little scientific exchange between the individual scientific communities working with these materials, although many of the challenges appear to be common. These include the need for methods for characterizing microstructure and structure–property relationships of a nanostructured material without long-range structural order or the need to perform theoretical modelling on multiple length scales from the ab initio atomistic level to the mesoscopic level that can be probed by experiments. There are also opportunities for using different materials in combination to achieve novel functions. This requires a detailed scientific understanding of the electronic structure of the interfaces formed in such hybrid structures.

The general aim of the Theo Murphy International Scientific Meeting between UK and China on the chemistry and physics of functional materials was to explore these common themes and to discuss recent progress in the development of controlled synthesis methods for functional materials, experimental characterization of their structure–property relationships as well as theoretical modelling of their properties. Both China and the UK have internationally leading and vibrant scientific communities in the field of functional materials. China has a very strong materials development programme in functional materials and Chinese groups are currently leading many of the breakthroughs in the discovery of new materials in the field. In the UK, there are similarly leading groups in the materials chemistry of functional materials, but also a particularly strong competence in physical characterization, device physics and electronic structure calculations/modelling. A specific objective of the workshop was to engage the diverse communities in a close scientific dialogue that bridges the boundaries between materials chemistry and physics as well as those between the individual fields and to explore common scientific challenges at the level of structural control, experimental characterization, scientific understanding and theoretical modelling of the relevant physical processes. The meeting was held with generous financial support from the Royal Society on 28 and 29 January 2013 in Chicheley Hall and brought together leading scientists from diverse communities of the UK and China in functional materials. Topics of discussion included recent advances in materials design, understanding of device physics and theoretical simulation of organic semiconductors, materials design, physics and simulation of transition metal oxide correlated electron systems, growth and transport physics of graphene and other two-dimensional materials, the realization by self-assembly of mesoporous frameworks for optoelectronic applications as well as experimental techniques for understanding the physics of Li-ion batteries. With such a diverse range of topics it is difficult for the proceedings to fully reflect the sense of common themes that was at the heart of discussions at the meeting. However, we hope that the selection of papers that are contained in this issue provides at least a glimpse of some of the common challenges and issues encountered by the diverse communities investigating this wide range of functional materials. The workshop was scientifically stimulating and helped to build new relationships between groups in China and the UK. A second China–UK workshop will be held in Beijing in September 2014.
A long-standing theme in the field of organic semiconductors is the understanding of molecular structure–property relationships that guides the choice of target molecules from among the incredible richness of conjugated molecular structures that can be synthesized by organic chemistry. Two articles in this issue illustrate this process. Zhang et al. [6] report on a new class of small-molecule organic semiconductors and their use as electron donor materials in organic solar cells. While traditionally organic solar cells have been fabricated mostly based on combining conjugated polymer donors with fullerene acceptors there has recently been a growing interest in small-molecule materials, stimulated by the demonstration in 2011 of a relatively high power conversion efficiency (6.7%) in cells with a solution-processible, small-molecule donor [7].

The report by Zhang et al. focuses on molecules with a donor–acceptor–donor triad structure and provides interesting insight into the molecular structure–photovoltaic property relationships of such systems. An emerging application of conjugated polymers that has recently acquired wider interest is in thermoelectrics. This was stimulated by the observation of relatively high thermoelectric performance with ZT values of 0.25–0.42 in the conducting polymer poly(3,4-ethylenedioxythiophene)–polystyrenesulfonate [8,9]. Here, Jiao et al. [10] report on the realization of inkjet printed thermoelectric modules using composites of p- and n-type metal coordination polymers in a polymer binder. The paper reports a careful study of the Seebeck coefficient and power factor depending on composition and provides insights into how the performance of such systems might be improved.

In inorganic materials understanding of structure–property relationships is equally important. Rather than synthesizing a family of molecules with different molecular units or side chains, as commonly done for organic semiconductors, a powerful method for understanding structure–property relationships of complex inorganic materials is to tune continuously the crystal structure and properties by substituting a fraction of atoms on a particular site with atoms of larger or smaller ionic radius. This is particularly powerful for applications where several properties need to be optimized simultaneously, such as for multiferroic applications. Thomas et al. [11] investigate here the structure and magnetic properties of a novel A site scandium perovskite, \((\text{Sc}_{0.94}\text{Mn}_{0.06})\text{Mn}_{0.65}\text{Ni}_{0.35}\text{O}_3\) synthesized at high pressure.

Controlled growth and processing techniques are key to achieving optimum materials properties, to study physical properties in a controlled and reproducible manner and to enable real-world applications. Since the discovery of two-dimensional transport properties of graphene [12,13], graphene has experienced an explosion of interest in its fascinating electronic, optoelectronic and mechanical properties. However, a fully scalable and controlled large-area technique for growing graphene is not yet available. One promising approach is to grow graphene epitaxially on a suitable inorganic single crystalline substrate. In this issue, Li et al. [14] study the growth of graphene on Ru(0001), where a significant lattice mismatch gives rise to a moiré-type surface charge redistribution which can be used to guide the further deposition of small organic molecules onto the graphene/Ru surface. An alternative approach is to form a thin film from a dispersion of graphene oxide in a suitable solvent followed by chemical reduction to graphene. Chen et al. [15] report a novel filtration-based technique that allows the fabrication of free-standing graphene oxide and graphene films of up to 40 mm in diameter.

Theoretical simulation and modelling is a vital part of understanding structure–property relationships in functional materials. As theoretical methods have become more accurate and predictive they provide an increasingly powerful and predictive guidance for materials design. Two articles in this issue illustrate this. Interfaces are a critical part of many devices and an important tool to control, in particular, hybrid interfaces between a covalent/ionic material, such as an inorganic metal, and a van der Waals bonded organic material, is to modify the interface with a self-assembled monolayer (SAM). Zhang et al. [16] report here electronic structure calculations of a specific class of SAMs with two so-called double docking functional groups at the ends of the molecule and show how the surface workfunction and interface dipole depend on the molecular structure of the SAM. Maggio & Troisi [17] discuss the general process of electron transfer between a semiconductor and a redox centre that are separated by a molecular bridge, as
is relevant, for example, in dye-sensitized solar cells. They derive an expression for the electron transfer rate that can be used in density functional theory for electronic structure and charge recombination calculations of such systems.

References

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