Time-resolved optical spectroscopy: A versatile, complementary tool for advancing cutting-edge materials technologies

By Christopher Grieco

With the rapid expansion of technology comes an increasing demand for new and improved functional materials. Developing materials for a wide variety of applications, such as solar cells, transistors, light-emitting devices (LEDs), fuel cells, energy storage, and drug delivery is crucial for advancing our everyday life. One overlooked tool for measurements of materials is time-resolved optical spectroscopy, which is mainly used by physical chemists today. Time-resolved optical spectroscopy offers materials researchers and engineers powerful methods for analyzing materials in action. A stimulus, which is often (but not limited to) a pulse of light, initiates a dynamical process in a material that is tracked over time by meas-uring its interaction either with or through the emission of light (**Figure 1**).

But what do spectroscopists actually do, and how can they contribute to materials science? A spectroscopist studies how molecules and materials interact with light. Measuring their specific interactions yields information about the material. Often, a spectroscopist is interested in solving fundamental problems; however, time-resolved optical spectroscopy can also be applied to measure materials functionality over time. For example, it can be used to watch electrons migrate in a solar cell or energy flow within an LED before it produces light. It can be used to watch chemical bonds break or form, or monitor structural organization of polymers in thin films. Such information is particularly useful for designing and testing a new material and can help solve contemporary problems in materials science and engineering.

For instance, transient absorption spectroscopy (TAS) is a time-resolved method that is used to monitor excited species that form and decay in a material following light absorption. A particularly appealing application of TAS is to study charge generation and recombination in solar-energy-conversion materials, such as organic semiconducting polymers and inorganic perovskites. TAS measurements of charge-carrier recombination were used in combination with x-ray scattering to explain how the chemical structure in conjugated block-copolymer materials can be tailored to optimize thin-film nanomorphology and enhance their performance in solar cells.[1] **Figure 2** illustrates how more charges survive in the block-copolymer material compared to a polymer mixture, because the latter is able to undergo nanoscale self-assembly. This process limits phase separation, enabling light-generated, bound charges to transfer and separate at the interfaces between the polymer domains.

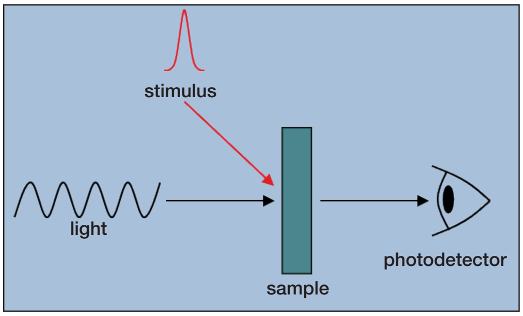

Figure 1. Simplified illustration of a time-resolved optical spectroscopy experiment. A stimulus induces a change in the sample that is monitored by measuring its interaction with light.

Other exciting opportunities include multidimensional spectroscopy techniques, such as two-dimensional infrared (2D IR) spectroscopy, which have become significantly more accessible because of continually improving technological advances. The 2D IR technique probes molecular-level vibrational motion to obtain structural and dynamical information about a material, which is useful for making connections between materials design and performance. In the past, instrumentation required rigorous maintenance, and measurements were very time-consuming. Now 2D IR meas-urements are applied more routinely, leading to an acceleration in our understanding of materials with functions ranging from biology to energy conversion and storage.[2]

Previous challenges to implementing time-resolved optical spectroscopy included limited awareness and practicality. In particular, the language of spectroscopists is different from that of materials scientists and engineers, so the benefits of spectroscopic tools are not readily discerned by the latter. In addition, time-resolved spectroscopy was traditionally difficult to carry out. But now with improved laser, optical, and detector technologies, it is becoming a much more accessible, standardized, and affordable tool. New technologies are emerging and continuing to improve, such as fully integrated transient absorption instruments like a UV–vis or Fourier transform infrared spectroscopy, which are becoming easier to use.

What remains is to merge spectroscopy with engineering and materials research and to expand time-resolved optical spectroscopy into a versatile tool for analyzing and guiding materials development. This would also foster multidisciplinary approaches for solving problems. But how can we facilitate this? We can start by providing additional multidisciplinary sessions at professional scientific conferences for exposing problems faced in a

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variety of scientific fields; contemporary research is commonly exposed in sessions segregated by discipline. Physical chemists can also publish more perspective or tutorial articles on applying spectroscopy to materials systems.

Developing new functional materials is becoming increasingly important. The fusion of materials synthesis, fabrication, and characterization with time-resolved optical spectroscopy would be a huge step toward advancing the technologies of our everyday world.

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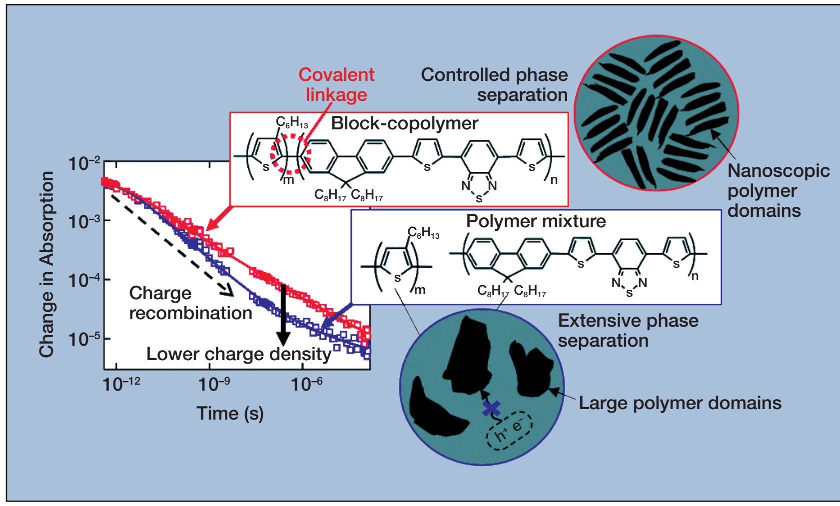

Figure 2. Transient absorption kinetic decays of charge carriers that form in polymer films upon light absorption. Charge recombination is tracked over time, revealing a lower charge density for the polymer mixture at later times. The cartoons illustrate phase separation of the polymer domains that occurs in the films.

Chemical potential and Gibbs free energy

By **Long-Qing Chen**

Chemical potential is a thermodynamics concept familiar to many, not only in materials science but also in physics, chemistry, chemical engineering, and biology. It is a central concept in thermodynamics of materials because all of the thermodynamic properties of a material at a given temperature and pressure can be obtained from knowledge of its chemical potential. Under the most common thermodynamic condition of constant temperature and pressure, chemical potential determines the stability of substances, such as chemical species, compounds, and solutions, and their tendency to chemically react to form new substances, to transform to new physical states, or to migrate from one spatial location to another.

Chemical potential is considered by many to be one of the most confusing and difficult concepts to grasp, although there appears to be no confusion about temperature, pressure, and electric potential. Chemical potential has been underappreciated and underutilized in applications of thermodynamics to materials science and engineering. One of the reasons for this is the widespread use of molar Gibbs free energy, partial molar Gibbs free energy, or simply Gibbs energy or Gibbs free energy but with the unit of J/mol. Adding to the confusion is the occasional use of Gibbs potential in place of Gibbs energy or Gibbs free energy, even when it refers to the Gibbs free energy of an entire system rather than on a per mole basis. Another reason why chemical potential is underappreciated is the surprising lack of a unique unit associated with such a quantity of central importance in the thermodynamics of materials.

The two main objectives of this article are to share the author's understanding and interpretation of chemical potential and to make a case that it is the chemical potential, not the Gibbs free energy, that should be employed in the majority of applications of thermodynamics in materials science and engineering.

Definition of potentials

We start with the definitions of different forms of potentials in contrast to their corresponding energies. A potential in physics is defined as the energy stored per unit of matter (i.e., a potential describes the corresponding potential energy intensity). A potential is an intensive property independent of system size. For example, the familiar electric potential, ϕ, is the electrostatic potential energy, U_E, with one unit (e.g., one Coulomb) of charge, q. In its simplest mathematical form, the electrical potential is defined as

$$\phi = \frac{U_E}{q}. \qquad (1)$$

Therefore, electrical potential represents the electrical energy intensity. Conceptually, it is fundamentally different from electrical energy, which is proportional to the system size and is an extensive quantity.

Another familiar example for potential is the gravitational potential or gravitational energy intensity, which is

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