

## Sustainable fabrication of organic electronics

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# organic electronics

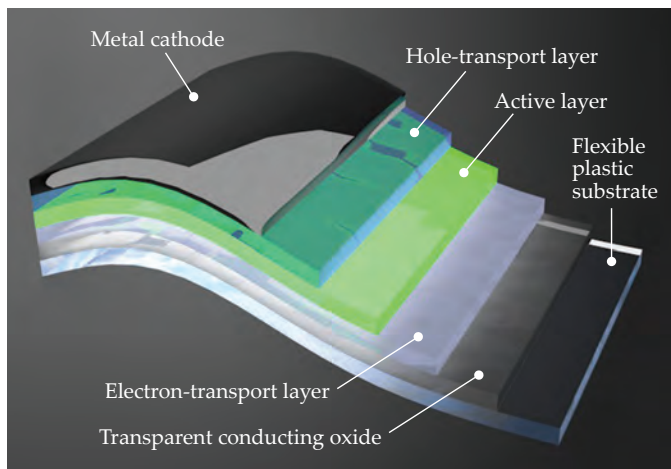
**I**ndustrial manufacturing is responsible for a great deal of harm to the environment. To help undo the damage, the United Nations has included mitigating the ongoing harm in its “industry, innovation, and infrastructure” sustainable development goal, one of 17 such goals.<sup>1</sup> Several can be tackled through innovation in materials design, engineering, and production. The deliverables are multifold: Simplified, low-cost manufacturing methods enable a more widespread, rapid, and equitable deployment of new technologies. When those technologies are themselves means to harness renewable energy, or to make better use of the energy already available, the benefits are compounded. In addition to being low cost and low energy, manufacturing should also be nimbler and easily implemented.

Manufacturers who follow tenets of green chemistry in an effort to be less wasteful and who forgo using or generating harmful chemicals are crucial.<sup>2</sup> Those tasks may seem daunting, but many of the objectives can be achieved with solution-based processing, which refrains from using high temperatures, high vacuum, and associated, complicated infrastructure and energy requirements.

Solution-based processing technologies can make a big difference in the creation of organic electronics,<sup>2</sup> including organic photovoltaics (PVs) and organic LEDs (OLEDs). As illustrated in figure 1, they are thin-film devices that contain several layers, each of which plays a key functional role.

The active layer carries out the device’s function: light absorption in a PV cell, or light emission in an OLED. On both sides of the active layer are charge-transport layers, which selectively move positive or negative charges to and from the active layer. Electrical contact is completed through conducting materials on both sides. In optoelectronic devices, at least one of the contacts, usually a conducting oxide, must be transparent. The device resides on a substrate, such as glass or a flexible plastic. In a fully organic device, all layers would be based on organic small molecules or polymers, but it is common for at least one of the layers to be an inorganic material, such as a metal oxide.





**FIGURE 1. ORGANIC LED ARCHITECTURE**, showing the multiple layers used to carry charges to the active layer responsible for light emission. The charge-transport layers are the electron-transport layer, the hole-transport layer, and the conductive transparent oxide. The layers can be made more eco-friendly by using metal oxide thin films.

In both organic PVs and OLEDs, charges must flow in a single direction. That is facilitated by the charge-transport layers, which selectively allow the transit of negative charges (electrons) or positive charges (holes). The unidirectional flow of charge is essential to device performance.

Organic semiconductors have been extensively studied as potential charge-transport layers. Organic materials, however, can become unstable when they react with moisture in the air or with the adjoining active layer. Furthermore, their thermal stability imposes a maximum temperature, or thermal budget, that must not be exceeded during device fabrication.

As an alternative, metal oxide thin films, which are touted for having a high chemical and thermal stability, can be used as charge-transport layers. For efficient layers, transition metal oxides can be used; examples include tin oxide and zinc oxide for electron-transport layers, nickel oxide and molybdenum oxide for hole-transport layers, and zinc indium tin oxide and zinc indium gallium oxide for conductive transparent oxides. To improve the commercial viability without compromising the efficiency of the finished device, room-temperature, solution-phase processing techniques to form metal oxides need to be adopted.

### Typical metal oxide synthesis

The classic recipes for synthesizing metal oxides are hardly considered sustainable. The ubiquitous shake-and-bake approach relies on mixing metal oxides or salt powders, milling those starting materials to a fine powder, and firing them at high temperatures, often as high as 1000 °C, over periods of hours to days.<sup>3</sup> That process often needs to be repeated more than once for the reaction to go to completion. The approach provides a straightforward means to produce well-crystallized, single-phase functional metal oxides in bulk quantities, but it is slow and energy-intensive. The high temperature and long reaction times are indicative of the processes involved: namely, the calcination of the starting materials to separate components and remove impurities, the solid-state diffusion of the ions that is required to form a homogeneous material, and the formation of the thermodynamic product of choice—a crystallized oxide of the desired phase. The large crystals that are formed are not amenable to integration in thin-film devices.

So how are metal oxide thin films typically formed? The

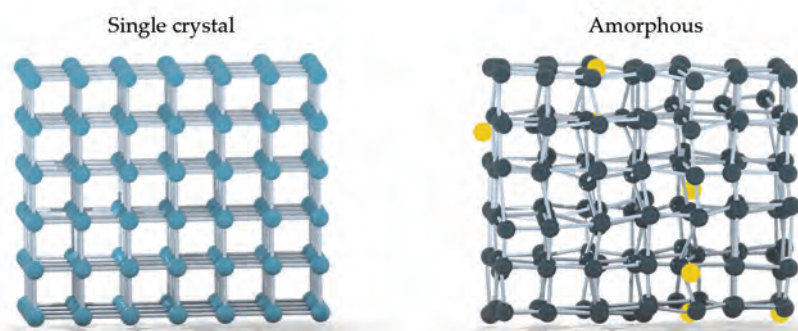
table on page 27 compares thin-film deposition methods.<sup>4</sup> One family of methods uses metal oxides as starting materials. While binary metal oxides can be procured from commercial vendors, custom complex oxides containing two or more distinct metals will typically be formed through the solid-state shake-and-bake process previously described. Those metal oxides are then vaporized and allowed to condense on the surface of a cooler substrate, thus depositing a thin film. For metal oxides with a low enough boiling point, vaporization can be achieved by simply heating the source metal oxide in a crucible. The heating is carried out in a vacuum chamber, which adds to the technical requirements of an otherwise simple approach. Such solid-state synthesis methods are used to form molybdenum oxide thin films that are used as hole-transport layers in PV devices.

Other methods, such as sputtering and pulsed laser ablation, can be used to vaporize the metal oxide. In those cases, the energy required to eject material from the source target is gained from collisions with ions, high-energy electrons, laser pulses, or a plasma. Such physical deposition methods can yield high-quality films but are rarely amenable to large-scale synthesis because of the large vacuum chambers that would be required. Metal oxide layers in thin-film devices are typically fabricated through sputtering, whose requirements pose a challenge to large-scale sustainable commercialization. For example, currently available transparent conducting oxide layers, such as tin-doped indium oxide, are prepared by high-vacuum techniques and represent a further inefficiency in device manufacturing.

To form large-scale, uniform thin films, fabricators use methods that typically rely on gas-phase chemistry, including chemical vapor deposition and atomic layer deposition. In those cases, a volatile metal-bearing precursor will be decomposed on or near the substrate's surface to yield the metal oxide. Again, the methodology relies on complex instrumentation, controlled atmospheres, elevated temperatures, and the handling of hazardous reactants. Some precursors are highly toxic and must be rigorously contained to avoid accidental release.

Researchers have developed solution-based methods to decrease both the energy and complexity of metal oxide thin-film deposition. One such method relies on sol-gel chemistry: Metal-containing precursors are mixed with chemicals that lead to the formation of the sol, a colloidal suspension that then reacts to form a gel, a semisolid material with a bonded network in three dimensions.<sup>3</sup> The solution can then be delivered onto a substrate. Subsequent heating leads to the calcination of the film, which turns into a solid metal oxide.

Technically, it is a much-simplified approach because the reaction occurs at low temperature and can happen in everyday glassware. One advantage of using solution processing rather than solid-state diffusion is that the intimate mixing of



**FIGURE 2. MATERIALS ARE ORDERED OR AMORPHOUS.** When researchers know the position of a single atom in a single-crystalline material (left), they can position the other atoms in all directions. By contrast, they cannot do that in an amorphous material (right) because it lacks a regular arrangement of the atoms. The bond distances between next nearest neighbors are not well defined, and neither is the symmetry around each atom. Several defects, such as vacancies (shown as yellow spheres), are also present.

atoms necessary for the formation of a homogenous material is greatly simplified. Such mixing ensures that the process does not spend a large portion of the device's thermal budget. Temperatures ranging from 400 °C to 600 °C are still required to convert the gel into the metal oxide.

While sol-gel synthesis is a step in the right direction, the temperature range is still too high to be compatible with many organic optoelectronic devices. At those temperatures, organic functional materials are likely to melt, react, or altogether decompose. Doped indium oxide, for example, is a ubiquitous transparent conducting oxide used in myriad optoelectronic devices where light must be transmitted through a substrate. That transparency is crucial in PV devices so that the light can reach the light-absorbing layer and in LEDs so that the light is efficiently transmitted. Unfortunately, tin-doped indium oxide is unstable above temperatures of approximately 250 °C;<sup>5</sup> heating it above that temperature greatly decreases its conductivity and thus limits its use and the thermal budget of any device incorporating it.

An advantage of organic electronics is the prospect of using them on a flexible plastic substrate,

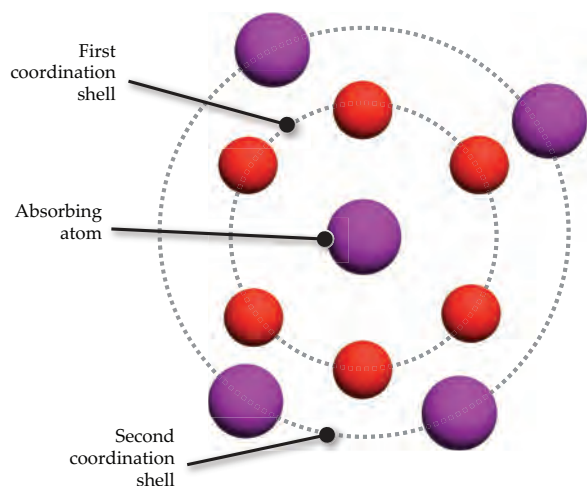
material will irreversibly crystallize into a well-ordered material when sufficient energy, such as a high temperature, is provided. Amorphous materials are notoriously difficult to characterize.<sup>3</sup> Instead of long-range atomic ordering, they have only short-range order, typically just a few shells of neighboring atoms. Even in those small regions of localized order, bond distances and angles will display discrepancies from atomic site to atomic site.

such as polyethylene terephthalate. Coincidentally, polyethylene terephthalate starts melting in the same 250–260 °C range. As such, keeping the thermal budget to below 250 °C has been a long-standing goal.

## Amorphous materials

If the thermal input during material formation is reduced, the atoms do not get to move and sample various arrangements with their nearest neighboring atoms to achieve the thermodynamically preferred configuration. As such, there is an increased probability that they form an amorphous material (see figure 2). Importantly, the amorphous state is a metastable one, meaning the atoms are frozen in a kinetically trapped arrangement.<sup>6</sup> Given the chance, an amorphous

Thin-film deposition methods					
	✗ Not a component or benefit of the method	— Sometimes a component or benefit of the method	✓ A component or benefit of the method		
Method	Solution process	Ambient atmosphere	Simple equipment	Low temperature	Large-area films
<b>Solid-state synthesis</b>	✗	✓	✗ high-T furnace	✗	✗
<b>Physical deposition</b> sputtering, pulsed laser ablation	✗	✗ vacuum chambers	✗ vacuum chambers	✗	—
<b>Chemical deposition</b> chemical vapor deposition, atomic layer deposition	✗	✗	✗	✗	✓
<b>Sol-gel</b>	✓	✓	✓	—	✓
<b>Combustion</b>	✓	✓	✓	✓	✓
<b>Photodeposition</b>	✓	✓	✓	✓	✓



## X-ray absorption spectroscopy

Deciphering structure–property relationships in disordered, amorphous materials is as challenging as it is necessary in order to drive the design of new materials with customized and optimized properties. The golden method to achieve that is based on a quantitative analysis of the absorption of x-ray photons.

In x-ray absorption spectroscopy, the energy of the incident photons is typically 1000–10 000 times as much as the energy of the photons used in UV–visible spectroscopy. Upon absorption of the high-energy x-ray photons, electrons from deep-lying energy levels (such as a 1s orbital in what's termed *K*-edge spectroscopy) are excited to vacant energy levels or, when sufficient energy is provided, photoemitted into the vacuum. That family of methods provides element-specific information about an atom's oxidation state, coordination geometry, and local structural arrangement.

Photoelectrons created from the absorption of x-ray photons will propagate as an outgoing wave. As that wave travels through the material, it will scatter off neighboring atoms. Scattering will produce interference in that outgoing wave, resulting in an absorption spectrum that varies with the energy of the incident x rays. The oscillations observed in the absorption spectrum are called the extended x-ray absorption fine structure.

By analyzing that pattern, one can determine the type, occurrence, and distance of atoms around the atom that initially absorbed the x-ray photon. Although the analysis does not provide a direct atomic structure of the material, it does give the distances between the absorbing atom and its neighboring atoms, from which details about the atoms' coordination and bonding can be inferred. That information is available irrespective of the crystallinity of the material, making x-ray absorption spectroscopy a tool of choice to study amorphous materials, for which diffraction-based methods are ineffective.<sup>7</sup> Until recently, x-ray absorption spectroscopy experiments were possible at only synchrotron light sources. Newly available commercial, lab-scaled instruments will accelerate the use of the method in materials science.

Diffraction methods, such as x-ray and electron diffraction, that rely on well-ordered periodic arrangements of atoms will return featureless patterns for amorphous materials. That makes identifying the local structure in amorphous materials challenging. Given the localized regions of order, methods that can probe the short-range atomic arrangement are necessary to elucidate that structure. A prominent family of methods uses synchrotron-based analysis, such as extended x-ray absorption spectroscopy<sup>7</sup> (see the box at left) and the atomic pair distribution function technique. The latter method analyzes the diffuse scattering of x rays that occurs in disordered materials. Such an analysis yields the likelihood that a pair of atoms are separated by a given distance. Although the methods are quite different, both ultimately yield insight into the structure in disordered materials.

Nanobeam electron diffraction, carried out in a transmission electron microscope, is another approach to structurally characterize amorphous materials.<sup>6</sup> A highly focused electron beam is directed toward a suitably thin (less than 100 nm) sample. The microscope focuses the beam to an approximately 0.1 nm spot size to ensure that the beam interacts and scatters from only a few atoms at a time. The scattered electron beam forms a diffraction pattern on the detector. Instead of sharp diffraction spots characteristic of crystals, amorphous materials typically produce ring-like diffraction patterns in nanobeam diffraction. The radius and intensity of the rings can be analyzed by pair distribution function analysis to reveal information about nearest-neighbor distances, coordination numbers, and short-range order in the amorphous structure.

The difficulties involved in characterizing disordered materials lead to conflicting reports of their physical properties. Unlike crystalline materials with well-defined structural features that can be easily identified and cataloged, not all amorphous materials are created equal. That idea, called “polyamorphism,” proposes that multiple structural instances of a given composition may exist in amorphous states. For example, a material may be densified through annealing but remain amorphous.

In addition to the inherent challenge in elucidating their structural characteristics, the electronic properties of amorphous materials can be difficult to understand. The lack of well-defined, or well-characterized, structure restricts the utility of computational methods. The myriad atomic configurations present in amorphous materials are difficult to capture in simulations, which typically rely on so-called melt-and-quench molecular dynamics methods. Because the properties of amorphous materials are known to be highly dependent on the preparation method, it is difficult to ensure that a simulated amorphous structure bears relevance to the laboratory sample.<sup>8</sup> The same diversity of atomic configurations leads to a smearing of the electronic energy levels and the creation of new electronic bands and defect sites.<sup>6</sup> Those defect sites tend to be deeper in amorphous materials, meaning that charge carriers that get trapped in such defects will require more energy to be able to escape from them.



Despite the paucity of information available in the literature, amorphous materials have found important applications in many technological devices. Two contemporary examples of preparation methods for amorphous materials are combustion<sup>9,10</sup> and photochemical deposition.<sup>11</sup>

## Combustion method

The combustion method remains a thermal decomposition approach, with the exception that the temperature is locally delivered through a highly exothermic reaction. Combustion requires three elements: an oxidizer, a fuel, and an ignition source. Combining an oxidizer, such as a metal nitrate, and a fuel, such as urea or acetylacetone, provides two of the elements needed to form metal oxides; myriad fuels and oxidizer combinations have been demonstrated. Under ideal conditions, the combustion reaction could reach temperatures of up to 700 °C and be ignited at temperatures as low as 200 °C. The process is efficient: Not only does the reaction occur rapidly, it runs cleanly, removing any impurities in the process. The temperatures are compatible with organic materials on flexible plastic substrates.

The oxidizer and fuel mixture can be delivered by various methods, including spin coating, inkjet printing, and blade coating. That makes the combustion method amenable to large-scale area deposition.

As expected, the low temperatures can lead to amorphous materials. A particularly successful family of amorphous oxide semiconductors is based on post-transition metal oxides.<sup>9</sup> (The post-transition metals, which include aluminum, indium, and tin, are located between the transition metals on the left and nonmetals on the right in the periodic table.) For example, amorphous indium gallium zinc oxide<sup>12</sup> has been successfully commercialized in displays, where they are part of thin-film transistors.<sup>9</sup> The success of post-transition metal oxides lies in their electronic structure. The conduction path in covalent semiconductors such as silicon relies on highly directional  $sp^3$  orbitals responsible for the tetrahedral geometry around the atoms. In the amorphous state, the fluctuation in bond distances and angles between atoms disrupts the bonding overlap, thus reducing conductivity. Indeed, the electron mobility in amorphous silicon is

approximately 1/200 that in single-crystal silicon. In post-transition metal oxide semiconductors, the electrons can travel through diffuse and spherical  $s$  orbitals.

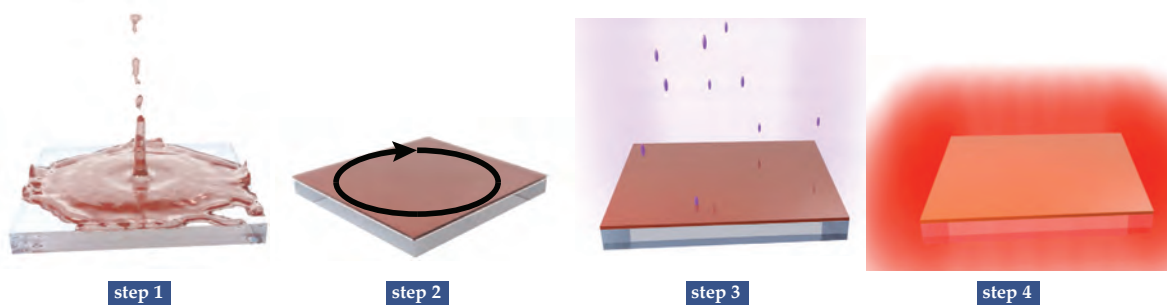
The lack of strong directionality means that bonding and conductivity are not as sensitive to structural disorder.<sup>13</sup> As such, the electron mobility in amorphous indium gallium zinc oxide exceeds that of amorphous silicon by an order of magnitude, making the oxide a useful semiconductor in consumer devices.

## Photochemical deposition

A different means of delivering the required energy to convert a precursor to the desired metal oxide is to use photons rather than heat. That method is called photodeposition, depicted in figure 3. One way a light-sensitive precursor is applied as a solid-state thin film is by spin-coating a solution containing the precursor. A suitable metal-containing precursor first needs to be identified. To be solution-processable, the precursor must be soluble, which is accomplished by choosing an appropriate molecular group, called a ligand, that binds to the metal center. For example, metal centers that are bound to carboxylate and  $\beta$ -diketonate ligands become light-sensitive precursors.

The film is then exposed to UV light, which triggers a ligand-to-metal charge-transfer excitation and ultimately leads to precursor decomposition and the formation of a metal oxide. The process is conducted entirely in air. The precursors are soluble in various organic solvents and can be delivered onto the substrate by a wide complement of methods, including spin coating, dip coating, spray coating, and printing. Photodeposition has been shown to be extremely versatile, compatible with essentially all the transition metals, the alkali and alkaline-earth metals, and the lanthanides and several elements from groups 13 and 14 as well as post-transition metals.

Additionally, the composition of the metal oxide obtained through photodeposition is easily controlled through the ratio of metal precursors in the initial precursor solution; that control allows easy access to binary, ternary, and more complex oxides. Because there is no thermal input, the atoms in the formed film do not have the necessary thermal motion required to sample various configurations and form a stabilized



**FIGURE 3. THE PROCESS OF PHOTODEPOSITION**, which includes coating a substrate with a light-sensitive, metal-containing precursor, involves three primary steps and one optional treatment. It begins with spin coating: the precursor material is applied (step 1) and the sample spun quickly (step 2) to spread a thin film across the material evenly. Next, the precursor thin film is irradiated with UV photons (step 3) to trigger charge-transfer excitation. Annealing (step 4) is an optional low-temperature step to further tune the material. Photodeposition does not require the high temperature of other methods and can be applied across a large area.

crystalline material; instead, they form a kinetically trapped amorphous material. The metal oxides can be further tuned via an optional low-temperature annealing step.

When it comes to device fabrication, photodeposition can be used to directly pattern the metal oxide without the need for photoresists, thus streamlining the process and reducing waste. The precursor thin film is exposed through a photomask, which provides a template for which areas of the film are converted to the metal oxide. So-called negative- and positive-tone direct-write photolithography and electron-beam lithography have all been shown to work in a breadth of applications compatible with most semiconductor manufacturing techniques.

Photodeposition has been used to fabricate both organic PV cells and LEDs.<sup>13,14</sup> Previous work demonstrated that photodeposited metal oxides could supplant PEDOT:PSS—an organic polymer often used as a hole-transport layer in organic devices. That polymer benefits from being easily processed in solution, but its strong acidity can lead to the degradation of adjoining organic layers and of semiconductor device performance, so researchers are currently looking for an alternative to the polymer.<sup>15</sup>

One replacement candidate being explored for the hole-transport layer is copper oxide. In one set of experiments, a series of copper oxide thin films were photodeposited and then annealed in air to moderate temperatures (below 250 °C, constrained by the stability of indium tin oxide described above).<sup>14</sup> An initial x-ray diffraction study showed that all samples were amorphous—their diffractograms didn't show any features. Organic PV device performance told a different story. The as-prepared copper oxide thin films rendered barely functional devices. The behavior was maintained until an annealing temperature of 150 °C was reached. A drastic change in performance occurred at 200 °C and above, where the devices became fully functional.

Based on the drastic changes in the copper *K*-edge x-ray absorption spectra, the change in behavior was ascribed to a rarely observed amorphous-to-amorphous phase transition. Those spectra are characteristic of both the local atomic geometry and the oxidation state of the copper atoms. The low-temperature nonfunctional copper oxide was identified as Cu<sub>2</sub>O, which oxidizes to CuO between 150 °C and 200 °C. Identifying such amorphous-to-amorphous phase transitions is challenging without the use of x-ray absorption spectra.

While the photodeposited amorphous copper oxide is a good step in the direction of identifying a replacement for PEDOT:PSS, it still requires a thermal treatment, albeit at temperatures that are fairly low. To decrease—or even completely remove—the thermal input, vanadium oxide thin films were used as hole-transport layers.<sup>15</sup> The as-deposited films were amorphous; they crystallized to form nanocrystalline V<sub>2</sub>O<sub>5</sub> at 250 °C. No significant benefit was found for thin films created with annealed vanadium oxide instead of the unheated, room-temperature material.

## Scaling up

In 2007, OLEDs were commercialized in Sony televisions.<sup>16</sup> With a market size of up to \$25 billion, organic electronics are poised to see an ever-increasing share of day-to-day devices.

Yet the organic PV market is still facing challenges toward successful commercialization.<sup>17</sup>

Of the materials and methods discussed here, both the combustion and photodeposition methods are rapid, scalable, and compatible with current thin-film fabrication and printing methods. As such, they offer enormous advantages over conventional oxide deposition techniques. Manufacturing opportunities can arise as new amorphous, metastable materials, which may not be thermodynamically stable, are formed. Amorphous materials open up a new parameter space for material discovery, and they are well suited to high-throughput screening. In particular, high-entropy oxides, which contain several (typically five) metals, present a new emerging field of highly tunable materials properties.<sup>18</sup> With their demonstrated ability to form multimetallic oxides, both combustion and photodeposition are poised to change the future of the field.

Several necessary steps are available to sustainably implement those fabrication methods. Full life-cycle analyses would likely shed light on areas where improvements need to be made. While reducing the thermal input is a step in the right direction, other aspects must be critically analyzed, such as the use of green solvents. The speed of the process should also be improved. That is especially important for making processes high-throughput, particularly when such approaches as roll-to-roll manufacturing are considered. The slowest step will dictate the speed of the process. Reducing the exposure time in photodeposition will have a huge impact on its commercial applicability.

The observation of amorphous-to-amorphous phase transition poses a new challenge. Researchers need to recognize that those transitions can have a determining influence on the functional properties while also presenting new opportunities and avenues for research. The advent of commercial turnkey x-ray absorption spectroscopy will catalyze such research and remove the need for synchrotron facilities to elucidate structure–property relationships in amorphous materials.

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