CHAPTER 1

# Introduction to $CO_2$-switchable Materials

Switchable materials are so common in our everyday lives that we rarely appreciate how green they are. We switch on the lights when we enter a room because we need the illumination, but we switch off the lights when we exit in order to save energy. The switchability of lights makes them greener and less energy-consuming than nonswitchable lights. Cars, ovens, computers, cellphones, doors – we are surrounded by switchable items that save energy and reduce environmental impact by their switchability. But should we not demand the same from our solvents, surfactants, drying agents, and coatings? A switchable solvent, one that dissolves a solute when needed and later releases the product when dissolution is no longer wanted, could make processes more efficient and less environmentally harmful. Switching the solvent ‘‘off’’ would precipitate the product without the solvent needing to be removed by energy-intensive distillation. Perhaps such a solvent could also be more easily recycled? Similar arguments can be made for the expectation that many switchable materials would, *other factors being equal*, be greener than their nonswitchable predecessors.

Unfortunately, other factors are rarely equal. If a switchable material is far more complex to make, more toxic, more depleting, or in any other way significantly more harmful than the material it could replace, then the potential for environmental benefit is reduced. Harm reduction can best be achieved by adding the extra functionality of switching with little, if any, increase in the environmental impact of the material itself. Switchable materials belong in the field of green chemistry because of their great potential for reductions in energy and materials usage, but like any chemicals they have the potential for environmental harm if they are not designed and used wisely. Starting with the choice of the trigger, and continuing with the design

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of the switchable molecules and the processes and products in which they will perform, the principles of green chemistry must govern their design. The metrics of green chemistry, such as life cycle assessment, must also be used to evaluate whether the switchable technology reduces environmental harm.

What triggers can be used for stimuli-responsive or ''switchable'' materials? Until recently, $CO_2$ has rarely been considered a possibility and is generally ignored in books and reviews on the topic. Instead, the most frequently studied triggers have been light, voltage, oxidants/reductants, and acids/bases. Heat, too, can be a trigger but it differs from the others in generally causing physical rather than chemical changes, such as raising or lowering the temperature of a mixture through a phase transition, although exceptions include heat-induced chemical changes like isomerizations or changes in spin state.[1] Less commonly used triggers include applied magnetic fields and ultrasound.[2–4] All triggers have advantages and disadvantages (Table 1.1), and each is likely to be appropriate in some applications and entirely inappropriate in others. Reviews and books about stimuli-responsive[5–7] and smart materials[8–10] are available.

Why, then, should we use $CO_2$ as a trigger? As summarized in Table 1.1, the key advantages are:

- it does not require a transparent system, as light-responsive materials require,
- it does not require a conductive system, as voltage-responsive materials require,
- $CO_2$ addition and removal do not cause the accumulation of materials in the system, as occurs when acid/base or redox-responsive materials are switched,
- the functional groups that respond to $CO_2$ as a trigger (amines and carboxylate anions) are typically inexpensive compared to light- or voltage-responsive functional groups, and less toxic than most voltage-responsive functional groups, although amines and carboxylic acids can be harmful to skin and eyes, and
- $CO_2$ is far more benign to health, environment, and equipment than most of the acids, bases, oxidants, and reductants used in acid/base or redox-responsive materials.

A comment on the environmental impact of using $CO_2$ is warranted. While it is the molecule most responsible for the biggest environmental threat of our time, global warming, the use of $CO_2$ as a trigger, even if the $CO_2$ is released afterwards, can be beneficial for the environment compared to the technologies it could replace. First, the $CO_2$ is recycled waste material; in almost all of the technologies described in this volume, the $CO_2$ is obtained from an external source, mostly as a byproduct of ammonia production but sometimes also from power production or fermentation processes. Therefore, use of $CO_2$ as a trigger does not *generate* $CO_2$. Second, commercialized $CO_2$-switchable materials will almost always be replacements for incumbent

**Table 1.1** Advantages and disadvantages of the various triggers or stimuli that can be used to reversibly switch materials.

| Trigger | Advantages | Disadvantages |
|---|---|---|
| Light | • Nontoxic trigger<br>• Trigger will not accumulate in the sample | • Requires the material to be transparent or translucent<br>• Requires thin material due to absorption of light<br>• Light-responsive groups are typically expensive |
| Voltage | • Nontoxic trigger<br>• Trigger will not accumulate in the system | • Requires system to be conductive<br>• Some redox-active groups are expensive, toxic, and ecotoxic |
| Oxidants/ reductants | • Does not require a transparent or conductive material | • Potentially toxic trigger<br>• Trigger will accumulate in the system<br>• Some redox-active groups are expensive, toxic, and ecotoxic |
| Temperature | • Does not require a transparent or conductive material<br>• Innocuous trigger<br>• Relatively innocuous trigger-responsive functional groups<br>• Trigger will not accumulate in the system | • Typically induces a phase change rather than a chemical change<br>• Separations triggered by temperature change may be poor unless a polymer is used<br>• Nonbiodegradable polymer often used<br>• May not be practical for large volume applications |
| Acids/bases | • Does not require a transparent or conductive system<br>• Inexpensive and relatively innocuous trigger-responsive functional groups | • Trigger will accumulate in the system<br>• Standard acids/bases are caustic or corrosive.<br>• Requires acidic/basic functional groups, which may cause health or environmental impacts |
| $CO_2$ | • Does not require a transparent or conductive system<br>• Trigger will not accumulate in the system<br>• Innocuous trigger<br>• Inexpensive trigger-responsive functional groups | • Mass transfer of $CO_2$ into and out of the system may be slow for large volumes or viscous media<br>• Acidic/basic functional groups may cause harm |

technologies that lack the energy- and materials-saving advantages possessed by switchable materials. Those energy and materials savings will inherently reduce environmental impact, including $CO_2$ emissions. This is one of the ironies of $CO_2$ utilization – the environmental benefit is not directly from the use of $CO_2$ itself but rather from the avoided harm associated with energy and materials that are no longer needed. For that reason, permanent chemical conversion of $CO_2$ into a product is not necessary for $CO_2$ utilization to be beneficial for the environment.

$CO_2$-switchable materials were first invented by nature, not humans. The opening and closing of stomata, the mouth-shaped pores on plant leaves that allow gases and moisture to enter and exit the leaf (Figure 1.1), are controlled by $CO_2$-switchable guard cells. The stomatal pore opens when $CO_2$ concentration is low and closes when $CO_2$ concentration is high. This makes it possible for the plants to exchange gases with the surrounding atmosphere without losing too much moisture. While the system is elegant, the biochemistry is complex.[11] Plants developed this advanced technology by the Silurian era, over 400 million years ago.[12]

Humans started to explore $CO_2$-switchable materials somewhat more recently. Early examples were the $CO_2$-switchable catalysts developed by researchers at the Montedison company in Milan in 1978[13] and the $CO_2$-switchable latex resins invented at Dow Chemical in Michigan in 1985.[14] Academic research in the area was pioneered from 1999 onwards by researchers such as Joseph Lakowicz at the University of Maryland,[15] Richard Weiss at Georgetown,[16] Dmitry Rudkevich at the University of Texas, Austin,[17] and then the authors of this volume.[18,19]

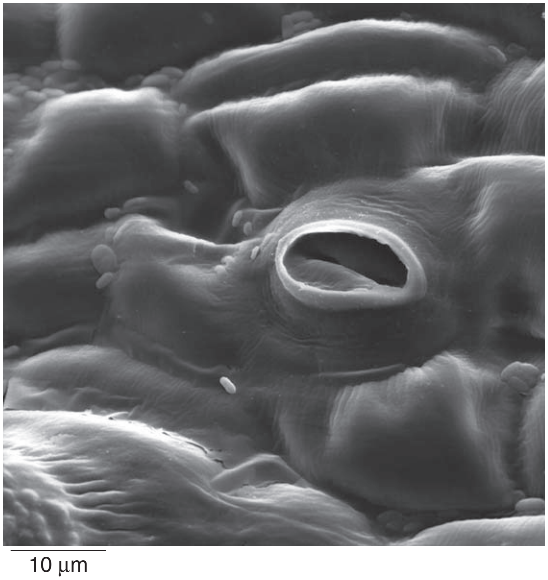

**Figure 1.1** A tomato leaf stomatal pore. The scale bar at the lower left is 10 μm. Reproduced from https://en.wikipedia.org/wiki/Stoma.

Terminology in the field is rather mixed. The terms "switchable" and "stimuli-responsive" are largely interchangeable, but the term "smart" when used to describe chemicals or materials usually has the added connotation that the material is designed to respond to changes in its environment that are *not* directly caused by the user. Examples include a smart catalyst that stops an exothermic reaction if the temperature starts to rise dangerously[20] or a smart insulin-delivery system that only releases the insulin inside the patient when blood glucose levels rise.[21] Another related term, "tunable", describes materials that can have their properties adjusted along a continuum rather than switched from one state to a second state. An example is a supercritical fluid, the polarity of which can be continuously varied by changes in pressure. Many switchable materials could, theoretically, be adjusted to intermediate states and are therefore technically also "tunable", but they are rarely used that way because the improvements in efficiency can best be achieved by accessing only the two extremes in properties and not the intermediate states.

This book is intended for a broad audience, suitable for academic, government and industrial researchers, industrial practitioners, and graduate students. While we have delved deeply into the details of the principles fundamental to the science of $CO_2$ switching, design, properties, and behaviour of $CO_2$-switchable materials, we have also provided general introductions to each topic to make the book accessible to nonspecialists. A scientific or engineering background will make the content more comprehensible.

After this brief introduction, the book starts with a chapter (Chapter 2) describing the basic concepts, reactions, and principles of $CO_2$ switching, laying the scientific foundation for understanding and appreciating the properties and behaviour of the wide range of $CO_2$-switchable materials described in the subsequent chapters. A similar format is maintained in each of the later chapters – the basic physical chemistry followed by properties, applications, and environmental considerations.

- Switching of the properties of aqueous solutions is presented in Chapter 3.
- Chapter 4 discusses cases where switching the properties of solutes, rather than solutions, can be useful.
- An extensive discussion of $CO_2$-switchable organic solvents details the properties and use of solvents whose polarity (Chapter 5) or hydrophilicity (Chapter 6) can be readily switched simply by $CO_2$ addition or removal.
- Presentation of the design and selection principles of $CO_2$-switchable surfactants (Chapter 7) illustrates how many novel material and process applications may be enabled using this new class of surfactant.
- Chapter 8 presents an extensive overview of the numerous new types of $CO_2$-switchable particles, many of them nano-scale, including a diverse range of self-assembled structures and morphologies, and various nanoparticles (inorganic and organic) that can be made $CO_2$-switchable.

- Recent discoveries in $CO_2$-switchable surfaces and coatings are described in Chapter 9.
- The use of cross-linked $CO_2$-switchable polymers yields $CO_2$-switchable gels, microgels, and adhesives which are presented in Chapter 10.

We conclude with an outlook (Chapter 11), a personal perspective on what we believe are the greatest opportunities and challenges for $CO_2$-switchable materials.

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