CO₂-switchable materials

Michael F. Cunningham PhD

Department of Chemical Engineering, Queen's University, Kingston, Canada

Philip G. Jessop PhD

Department of Chemistry, Queen's University, Kingston, Canada

Why make a stimuli-responsive material? Designing a solvent, a surfactant, a solute, a solid surface or any other material to be stimuli responsive makes it possible for that material to meet conflicting requirements for two stages of a process. Having a light bulb emit light is useful when lighting of a room is required, while having the same bulb not emit light is preferred when lighting is not needed and instead saving energy is required. Thus, the fact that the light bulb can be switched between two states allows it to meet those seemingly contradictory requirements. A stimuli-responsive or switchable material has two (or more) states and, by switching between these two states, the material can fulfil two roles, making process design easier and saving energy and materials. In contrast, any other attempt to solve the contradictory requirements, without a switchable material, is likely to consume more energy and/or more materials. That is the green advantage of switchable or stimuli-responsive materials.

Why use CO₂ as the stimulus? Many stimuli-responsive materials, including the classic light-bulb filament, have used electrons as the stimulus for the change of states. Other stimuli that have been used include photons, redox reagents, acids/bases and temperature. CO₂ is a poor cousin of the more traditional acid/base (pH swing) stimuli. With HCl and NaOH, one can achieve very large pH changes, which are easily large enough to make many materials change their properties. However, CO₂ at 1 atm is not nearly as effective; a typical pH drop when CO₂ is bubbled through an aqueous solution is only slightly better than 2 pH units. Why, then, would one want to use CO₂ as a stimulus for a switchable material? Because CO₂ is cheap, nontoxic, noncorrosive, nonchlorinated, abundant, easily added and, most importantly, it can be removed. While acid/base stimuli cause by-products that accumulate in the system, the addition and then removal of CO₂ is clean; it does not result in the accumulation of by-products. A review of CO₂-responsive materials has been published recently.¹

This themed issue of *Green Materials* presents five papers highlighting advances in CO₂-responsive materials. Interestingly, all involve using CO₂-switchable moieties to prepare either nanoparticles or nano-scale structures such as micelles. Ethier *et al.*² demonstrate the use of CO₂-reversible silyamine systems in the controlled reduction of ionic gold salt to gold nanoparticles, and then deposition of the nanoparticles onto a solid support. Francés-Soriano *et al.*³ describe the reversible phase transfer of amine-capped, lipophilic CdSe/ZnS quantum dots from an organic phase to water phase, enabled by the presence of a CO₂-switchable surfactant. The optical properties of the quantum

dots are preserved through multiple phase-transfer cycles. The preparation of CO₂-switchable polymer nanoparticle latexes, whose colloidal stability and surface charge can be reversibly altered, is presented by Su *et al.*⁴ The effectiveness of CO₂-switchable surfactants was shown to be significantly improved by altering the design of the surfactant molecule to include a hydrophilic spacer that ensures the switchable amidine is better solvated in the aqueous phase. Liu *et al.*⁵ prepared liposoluble star copolymers via sequential Pd-catalysed chain walking followed by an atom-transfer radical polymerisation. Their star copolymers, which had hyperbranched polyethylene cores and CO₂-switchable arms, readily dissolved in aliphatic hydrocarbon solvents under air or nitrogen, but reversibly formed micelles in water with CO₂ bubbling. Zhang *et al.*⁶ report on the behaviour of CO₂-responsive wormlike micelles based on natural erucic fatty acid solutions. In the absence of CO₂, the wormlike micelles are highly viscoelastic, but when CO₂ is introduced low-viscosity solutions result. These wormlike micelles are especially attractive because they are formed simply by changing the pH of erucic acid solutions.

In each of the described systems, the responsiveness to CO₂ gives the materials extra functionality that has practical benefits, but for optimum performance, careful design of the switchable materials is required.

REFERENCES

1. Jessop, P. G.; Mercer, S. M.; Heldebrant, D. J. CO₂-triggered switching of solvents, surfactants, and other materials. *Energy & Environmental Science* **2012**, 5, 7240–7253.
2. Ethier, A. L.; Hart, E. C.; Saunders, S. R.; Biddinger, E. J.; Fadhei, A. Z.; Dilek, C.; Pollet, P.; Eckert, C. A.; Liotta, C. L. Reversible ionic surfactants for gold nanoparticle synthesis. *Green Materials* **2014**, 2(2), 54–61.
3. Francés-Soriano, L.; Pocoví-Martínez, S.; González-Béjar, M.; Pérez-Prieto, J. Reversible phase transfer of quantum dots by gas bubbling. *Green Materials* **2014**, 2(2), 62–68.
4. Su, X.; Jessop, P. G.; Cunningham, M. F. Switchable surfactants at the polystyrene–water interface: effect of molecular structure. *Green Materials* **2014**, 2(2), 69–81.
5. Liu, P.; Zhang, Y.; Wang, W.-J.; Li, B.-G.; Zhu, S. CO₂-triggered fast micellization of a liposoluble star copolymer in water. *Green Materials* **2014**, 2(2), 82–94.
6. Zhang, Y.; Yin, H.; Feng, Y. CO₂-responsive anionic wormlike micelles based on natural erucic acid. *Green Materials* **2014**, 2(2), 95–103.