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Materials science

Ink that mimics the colour of incoming light

Hector Lopez-Rios & Monica Olvera de la Cruz

Light-sensitive particles have been shown to stratify in solution in a way that changes the colour of the whole suspension. The system forms a colour-changing ink that could make electronic paper a viable technology. **See p.499**

As you read this, various receptors in your eyes are being activated. These receptors respond to light by sending signals to the brain, allowing you to discern different wavelengths of light through your perception of colour and brightness. On page 499, Zheng *et al.*[1] report the development of an ink that can be activated by specific colours of light, much like receptors in the eye. Instead of sending signals, however, the authors' ink particles become motile when activated, and reorganize into a configuration that reflects the activating light, thereby taking on its colour. Such a response is typically seen only in nature – for example, in a cuttlefish's ability to camouflage its entire body in a matter of seconds in the presence of a predator[2].

Many functional materials rely on the fact that their components can be reorganized through segregation or stratification. Particles that respond to external driving, such as magnetic fields, are good candidates for such components, because their responsiveness can be used to manipulate their organization[3]. And light-sensitive particles suspended in solution are particularly attractive – with uses in soft robots, for example[4] – because light propagates through liquid and offers precise control over long distances. Such particles can be made to segregate by using light to modify their velocities and interactions[5–7].

Zheng *et al.* synthesized a suspension of light-responsive microparticles, each the width of a human hair, and coated them with various dyes. They then showed that they could activate the particles selectively using light with the same wavelength as that absorbed by the particle's dye. Cyan-coloured particles, for example, were activated by red light, because their absorption of red light is what gives them their cyan hue. When this light is absorbed, it produces a chemical reaction that generates an uneven distribution of oppositely charged ions around the particle, which in turn causes nearby ions to move, creating a flow field that moves the activated particle. This process is known as diffusiophoresis[8], and it is used widely to generate flow in living systems, from cellular components to entire organisms.

In Zheng and colleagues' system, the diffusiophoretic flows caused active particles to cluster together whereas the passive particles remained dispersed in the solution (Fig. 1). This resulted in a stratification of the particles, because the flow moved the active clusters downwards, shifting the passive particles above them and effectively shielding the active particles. The configuration was stable long enough for the light source to be removed. The colour of light reflected by the suspension was then determined entirely by the passive particles. And the strength of the attraction between active particles could be controlled by the intensity of the light source.

The segregation resembled that of systems comprising two types of passive particle, which can separate into two phases of different composition that coexist for a long time. However, the way that the authors' clusters grew in size does not reflect the growth predicted and observed in these passive two-component mixtures, even when the fully passive systems are driven by flow at the interface between the two phases[9]. The dynamics of phase separation are not the same in all active systems: in some cases, segregation can be induced only by the particles' motility[10], whereas in others, cluster size can be limited[11]. Systems that are driven by diffusiophoresis can be highly dynamic and have average cluster sizes that are controlled by the particles' self-propelling velocity[12]. In Zheng and colleagues' system, the size of the active-particle clusters grew over time as a power law with an exponent determined by the intensity of the light source.

To show that their light-responsive particles could form a kind of colour-changing ink, Zheng *et al.* used a mixture of cyan, magenta and yellow particles to create images. They projected an image onto the surface of a solution containing the three types of particle. The researchers found that the segregation

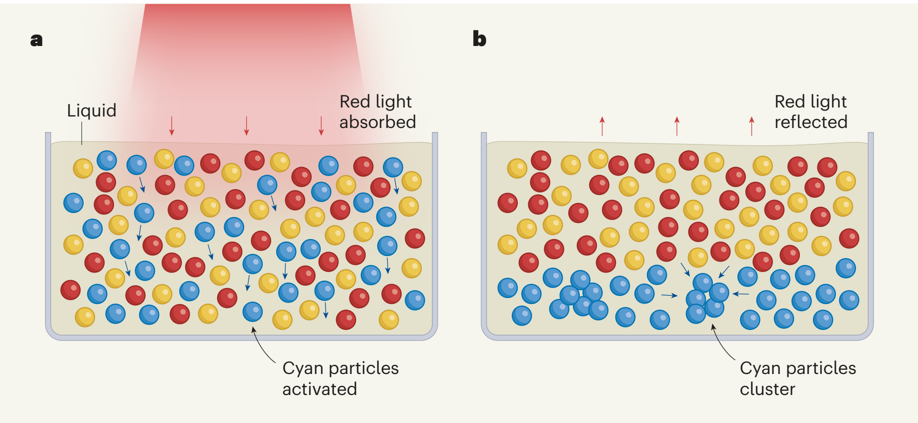

Figure 1 | Phase separation of light-sensitive particles creates colour-changing ink. Zheng *et al.*[1] synthesized a suspension of light-responsive particles, each coated with a different dye. **a**, The particles were activated by light with the same wavelength as that absorbed by the particle's dye (red light is shown here activating cyan particles). **b**, This activation caused the particles to become motile and form clusters that were pushed downwards and shielded by particles coated in other colours. The subsequent stratification meant that, when the light source was removed, the non-activated particles determined the colour of the suspension. The authors showed that the particles could be used to generate coloured images. With further development, these particles could even be used to make colour-changing ink for electronic paper.

and subsequent sedimentation of the active particles resulted in the images appearing on the surface of the solution (see Fig. 5 of the paper). This layered segregation of active and passive particles enabled the authors to embed a series of images one after the other, because each image was generated solely in response to the reorganization of particles activated by the projection.

With their innovative use of light-sensitive particles, Zheng *et al.* might well have laid the foundations for future technologies such as electronic paper and camouflage materials. But the timescale on which the particles segregate is around one to two minutes, which makes their application to electronic paper possible, but not yet feasible. Similarly, electronic camouflage materials need to be made from components that respond to light intensities that are much lower than that required to activate these particles. However, Zheng and colleagues say they think that the segregation times and sensitivity of their light-responsive ink can be improved, so these exciting applications might soon be realized.

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Structural biology

Clues to how water splits during photosynthesis

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The tools of crystallography, spectroscopy and quantum chemistry are pulling back the curtain on photosynthesis, probing previously elusive catalytic intermediates that arise when water splits to form oxygen. **See p.623 & p.629**

The step during photosynthesis in which water is split through a light-driven reaction to generate oxygen (O_2) is a fundamental process for life on Earth. Grasping how this occurs might offer inspiration for the development of water-splitting technologies to produce solar fuels. Bhowmick *et al.*[1] (page 629) and Greife *et al.*[2] (page 623) now shed light on this process, paving the way for a more complete understanding of the underlying mechanism.

Research efforts over the past four decades have refined our understanding of crucial catalytic steps that occur in a cluster of four manganese ions and one calcium ion that are connected by bridging oxygens (Mn_4CaO_5). This cluster of ions is known as the oxygen-evolving complex (OEC), and it is embedded in an enzyme called photosystem II. To oxidize water, the OEC first needs to lose up to four electrons from its manganese ions, generating a series of intermediate states that are termed S-states (Fig. 1). During the transitions between S-states, the removal of electrons from the OEC is coupled with the removal of hydrogen ions (H^+, a single proton) from the water, and with the binding of water to the OEC, all of which is regulated by the functionally important protein that surrounds the OEC.

> **“This tremendous achievement comes as close as possible to real-time observation of the oxygen-evolving complex at work.”**

The first four S-states in the catalytic cycle (S_0, S_1, S_2 and S_3) can be captured and studied, and scientists have a reasonably advanced, but incomplete, understanding of their nature. By contrast, it has been exceedingly difficult to resolve the complex cascade of events in the final part of the cycle, the $S_3 \rightarrow S_4 \rightarrow S_0$ transition that involves: the formation of a reactive S_4 intermediate through the loss of an electron; the formation and release of O_2; the release of two protons; and the binding of one water molecule to return the OEC to the starting position (S_0) for the next catalytic cycle.

Bhowmick *et al.* used a technique called serial femtosecond crystallography using X-ray free electron lasers (XFELs) to probe structural changes at the enzyme’s active site during the $S_3 \rightarrow S_4 \rightarrow S_0$ transition. In contrast to conventional protein crystallography methods, this technique allows rapid collection of time-resolved structural data at room temperature. Snapshots obtained at different microsecond-to-millisecond intervals after light activation of the S_3 state document time-dependent structural changes at the tetramanganese cluster of the OEC and its protein environment.

Bhowmick and colleagues measured changes in the electron density indicating that after light exposure of the S_3 state, oxidation (electron loss) of a nearby tyrosine amino-acid residue, termed Y_Z, occurs within 50 microseconds (µs). Y_Z mediates electron transfer from the OEC to a special pair of chlorophyll molecules. Formation of the resulting tyrosine radical triggers an early deprotonation event (at 200–500 µs) that involves a manganese-bound water ligand and two amino-acid residues, Asp61 and Glu65. This is a remarkable observation that points directly to a specific hydrogen-bond network as the preferred route for proton removal.

The Y_Z radical subsequently extracts an electron from the manganese cluster, which then progresses to the transient S_4 state. This process begins after approximately 500 µs; by about 700 µs, the signal for an oxygen atom that was incorporated in the OEC during the previous catalytic step ($S_2 \rightarrow S_3$) begins to disappear. This is interpreted to be one of the two O_2-forming atoms. The source of the other oxygen atom is not clear, but it might be an adjacent oxygen in the manganese-containing cluster of atoms.

The subsequent data do not enable the generation of well-defined structural models until the S_0 state begins to be reconstituted (at about 2 milliseconds; ms), but the shortening (at approximately 1.2 ms) of the distance between the two manganese ions that are farthest apart is suggested to signify the presence of a partially formed O_2 molecule. This is presumably a bound peroxide ion (O_2^{2-}), and hence the shortening coincides with the onset of O_2 formation and release. This tremendous scientific achievement comes as close as possible to real-time observation of the OEC at work.

Greife *et al.* used an approach known as time-resolved microsecond Fourier-transform