

now report a unidirectional self-assembly/disassembly cycle powered by light that expands this ratchet mechanism beyond single-molecule systems³.

The researchers achieve this using a pseudo-rotaxane: a rotaxane-like system in which the stoppers are small enough to allow for threading and dethreading of a ring. Chemical recognition motifs are incorporated into the ring and axle of the system, which means that under thermal equilibrium conditions they can self-assemble into the pseudo-rotaxane. At one end of the axle, the researchers attach a bulky unit that provides a significant — but not insurmountable — barrier to threading/dethreading (Fig. 1; brown). At the other end of the axle there is an azobenzene unit that can undergo isomerization from an easily threadable *E* isomer (Fig. 1; blue) to an unthreadable *Z* form (Fig. 1; red). Thermal isomerization disfavours the *Z* isomer meaning that under thermal equilibrium conditions the *E* isomer will predominate, allowing facile threading (and dethreading) of the ring from this end of the axle.

This asymmetric axle structure means that at thermal equilibrium the macrocycle undergoes threading/dethreading predominantly through the *E* isomer (Fig. 1a). However, Credi and colleagues use light to direct the macrocycle almost exclusively through a unidirectional threading of the axle, from one end to the other end (Fig. 1b). The light reversibly photoisomerizes the azobenzene end of the

axle, so that at photostationary conditions, the unthreadable *Z* form dominates over the threadable *E* form (opposite to that at thermal equilibrium). A ring that has threaded onto one of the few axles with an *E* isomer under photostationary conditions gets trapped on the axle by conversion of the *E* isomer to its *Z* form. Dethreading of this *Z*-pseudo-rotaxane is thermodynamically favoured, but must proceed through the bulky stoppered end. This dethreading step is slow, but at photostationary conditions, it occurs before the azobenzene is isomerized back to its *E* form, either through reversible thermal or photoisomerization. Overall, while the threading and dethreading steps occur through thermal fluctuations, the fast photochemical step endows the system with unidirectionality, effectively ‘pumping’ the ring along the axle.

Credi and colleagues use UV-vis and fluorescence spectroscopy to study the kinetics and steady-state self-assembly of the pseudo-rotaxanes, determining experimental partition coefficients and rate constants. These experimental quantities were fed into a simple kinetic model of the cycle to show that the predominance of unidirectional threading corresponds to a $5.1 k_B T$ driving energy per cycle (12.6 kJ mol^{-1}), provided by light. This energy is completely dissipated in the unidirectional assembly/disassembly of the pseudo-rotaxane in solution.

One of the most noteworthy features of the system is its chemical simplicity.

Furthermore, by reliably demonstrating unidirectional cyclic operation under photostationary conditions, it provides a critical step towards creating synthetic molecular machines that are inspired by biological assemblies and can do work over some distance. However, in addition to the unidirectional and dissipative behaviour displayed by the pseudo-rotaxanes of Credi and colleagues, complex biological motors can also carry transport cargo and store energy through the establishment of a concentration gradient.

A challenging next step is to extend this pseudo-rotaxane design so as to unidirectionally thread (transport) the rings (cargo) over longer distances, that is, distances that are significantly longer than Brownian displacements of rings in solution. In that way, the unidirectional assembly/disassembly could be implemented to establish local concentration gradients without resort to a chemical reaction or an external field. □

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References

1. Boyle, M. M. *et al. Chem. Sci.* **2**, 204–210 (2011).
2. Serreli, V., Lee, C.-F., Kay, E. R. & Leigh, D. A. *Nature* **445**, 523–527 (2007).
3. Ragazzon, G., Baroncini, M., Silvi, S., Venturi, M. & Credi, A. *Nature Nanotech.* **10**, 70–75 (2015).

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PHOTOELECTROCHEMICAL WATER SPLITTING

A new use for bandgap engineering

Strontium titanate can act as a transparent protection layer for silicon photocathodes, preventing corrosion without compromising photocatalytic redox activity.

Jiming Bao

Bandgap engineering is a powerful way to design semiconductor optoelectronic devices. By stacking layers of semiconductors with precise sequences and thicknesses, the approach allows new electronic states to be created with specific energies and spatial positions. This quantum design of devices is possible because nearly defect-free interfaces can be formed using two lattice-matched semiconductors and growth methods that can be controlled at the atomic level. The

power of bandgap engineering is perhaps best illustrated by the fabrication of the first quantum cascade laser, which had more than 100 alternating layers of GaInAs and AlInAs (ref. 1). The principle of lattice matching and bandgap engineering can also be used to design tandem photovoltaic cells in which a combination of defect-free interfaces and an optimal bandgap is required to stack cells made from different materials². Writing in *Nature Nanotechnology*, Li Ji and colleagues at the

University of Texas at Austin now show that bandgap engineering can also be used to create photoelectrochemical (PEC) cells for efficient water splitting³.

Photoelectrochemical cells combine solar energy collection and water electrolysis in a single semiconductor-electrode-based device, allowing solar energy to be converted into hydrogen fuel. Silicon is often used as the photoelectrode material in such cells because of its dominance in the photovoltaics market, which is the result of

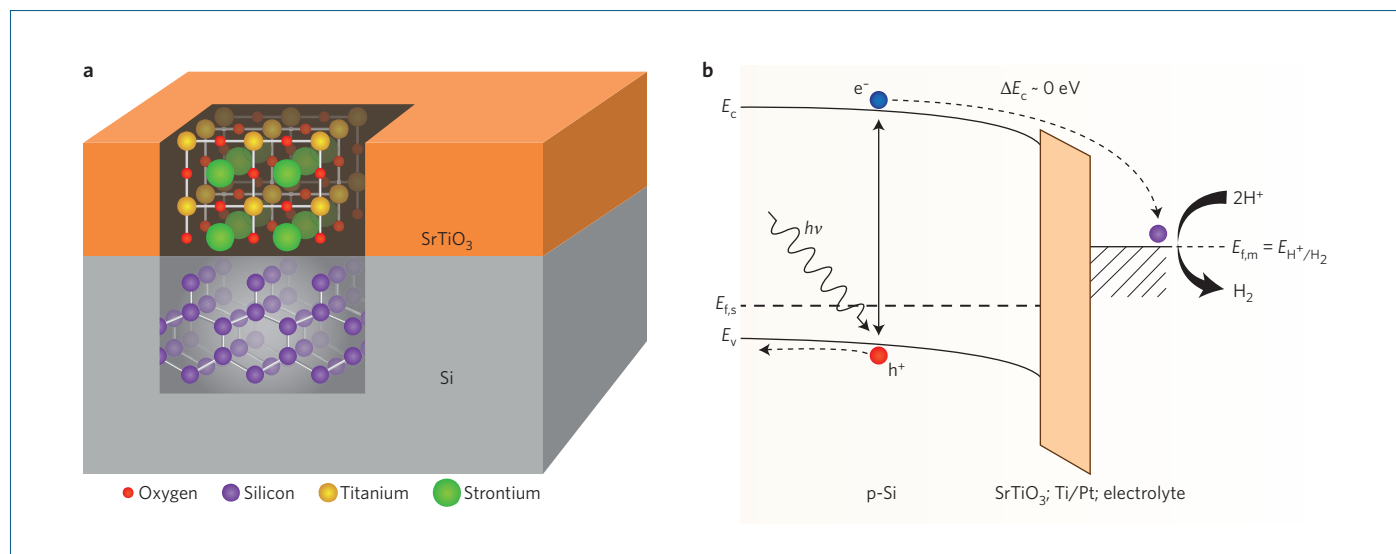


Figure 1 | Lattice-matched SrTiO₃/Si heterojunctions. **a**, Atomic structure of a SrTiO₃/Si(001) interface. **b**, Energy level schematic of the SrTiO₃-protected silicon photocathode (the bandgaps are not drawn to scale). At the photocathode, protons are reduced to hydrogen by capturing electrons. The schematic illustrates the generation and transport of the charge carriers, and highlights the minimum conduction-band offset between SrTiO₃ and silicon, which helps electrons to be transported across the protection layer. E_c , E_v , $E_{f,s}$ and $E_{f,m}$ are the conduction band, valence band, and Fermi level of silicon and metal, respectively. Figure adapted from ref. 3 by Yanan Wang.

the material's long lifetime (>30 years) and decent efficiency (>12%). However, silicon exhibits poor photostability in aqueous solution and deactivates rapidly. A simple solution to this problem is to use silicon oxide as a protection layer. (The passivating and insulating properties of silicon oxide are, in fact, two of the principal reasons why silicon beat germanium to become the material of choice for field-effect transistors and integrated circuits.) But there is a sizeable conduction-band offset between silicon oxide and silicon, and this increases the electron tunnelling barrier and limits charge transport.

Ji and colleagues created photocathodes that can carry out the water reduction reaction step of a PEC cell by growing a 4-nm-thick layer of strontium titanate (SrTiO₃), a wide-bandgap oxide, on a p-type silicon substrate using molecular beam epitaxy. The SrTiO₃ acts as a protection layer for the silicon, as well as a tunnelling junction for charge transport: two roles that silicon oxide has provided in previous devices. However, SrTiO₃ is lattice matched with silicon, so a perfect interface with very low density of defect states can be established (Fig. 1a). Furthermore, SrTiO₃ provides a favourable band alignment: that is, there is only a minimum conduction-band offset, which allows a large tunnelling current (Fig. 1b). Thanks to this, under broad-spectrum illumination at 100 mW cm⁻², the silicon photocathode exhibits a maximum photocurrent density

of 35 mA cm⁻², which is the highest reported photocurrent for a silicon-based photocathode to date. Furthermore, by combining the photoelectrode with a Ti/Pt nanostructured catalyst, a photon-to-hydrogen energy conversion efficiency of 4.9% can be achieved with the device.

The SrTiO₃/Si heterojunction has attracted a lot of attention in recent years because of the interesting ferroelectric properties of the interface⁴. Moreover, SrTiO₃ has been used as a buffer layer to grow other oxides on silicon, so that the unique functionalities of oxides can be directly integrated with silicon devices⁵. In the past, SrTiO₃ was also considered as a potential gate material for field-effect transistors and integrated circuits⁶, because it could potentially provide a perfect interface with silicon and a higher dielectric constant than silicon oxide. However, SrTiO₃ turned out to be problematic for such applications because a SrTiO₃ transistor will exhibit a large leakage current through the gate due to the small conduction-band offset. Such a large tunnelling current is though exactly what a protection layer should offer for a PEC photoelectrode.

A silicon photocathode alone is not a complete PEC cell: a photoanode is required to carry out the water oxidation step of the water splitting process. Analysis has shown that photoanode–photocathode tandem structures, in which silicon is integrated with a semiconductor that has a bandgap of 1.6–1.8 eV, could generate

solar hydrogen with an efficiency greater than 25%⁷. Furthermore, a maximum efficiency of 31.1% can be achieved if we have the freedom to choose two semiconductors with an optimal bandgap combination. Here though it is assumed that the two photoabsorbing semiconductors are also perfect catalysts that do not exhibit photocorrosion. In reality, such semiconductors rarely exist. One way to get around this problem is to add the transparent protection layers to photoelectrodes, as Ji and colleagues have clearly illustrated by growing SrTiO₃ on silicon photocathodes. However, a suitable protection layer for the photoanode of such silicon-based PEC cells still needs to be identified, and this will be a challenging task. □

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References

1. Faist, J. *et al.* *Science* **264**, 553–556 (1994).
2. Cotal, H. *et al.* *Energy Environ. Sci.* **2**, 174–192 (2009).
3. Ji, L. *et al.* *Nature Nanotech.* **10**, 84–90 (2015).
4. Warusawithana, M. P. *et al.* *Science* **324**, 367–370 (2009).
5. Reiner, J. W. *et al.* *Adv. Mater.* **22**, 2919–2938 (2010).
6. McKee, R. A., Walker, F. J. & Chisholm, M. F. *Phys. Rev. Lett.* **81**, 3014–3017 (1998).
7. Hu, S., Xiang, C., Haussener, S., Berger, A. D. & Lewis, N. S. *Energy Environ. Sci.* **6**, 2984–2993 (2013).