Photocatalysis

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A rationale for charge carrier lifetimes in transition metal semiconductors

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Long-lived charge carriers in semiconductors are essential for effective sunlight-to-energy conversion. Still, few studies have fundamentally rationalized the charge carrier lifetimes. Now, metal-centred ligand field states of transition metal oxides have been suggested to control carrier lifetimes, akin to those for molecular photosensitizers.

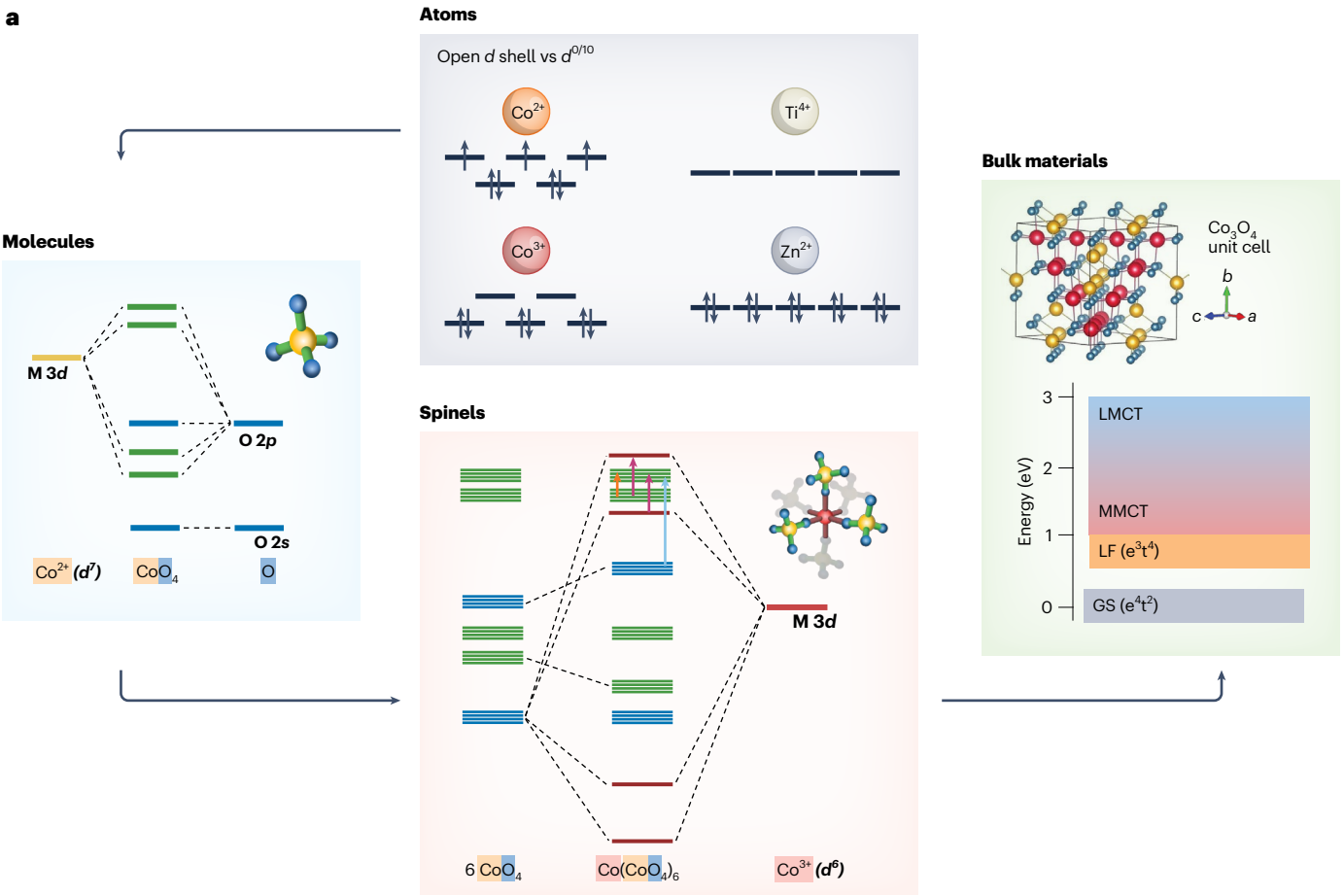
Our society relies heavily on fossil-fuel-derived energy and materials, which in due time, and with sufficient political and societal commitments, will be replaced by renewable energy and chemical feedstocks. Energy based on solar, wind and tides is rapidly expanding; however, a renewable energy transition requires cost-efficient and competitive technologies, such as photoelectrochemical cells[1]. The conversion of solar energy into electricity, or 'solar fuels,' depends on the efficient and ideally permanent separation of photogenerated holes and electrons, that is, charge carriers. In typical photocatalytic water-splitting devices, holes oxidize water into oxygen, whereas electrons reduce protons to form hydrogen. However, to carry out such reactions, holes and electrons must escape the deleterious and competing charge recombination process. Hence, a longer charge carrier lifetime implies higher reactivity. Developing semiconductors with long-lived charge carriers represents one of the biggest challenges of the 21st century.

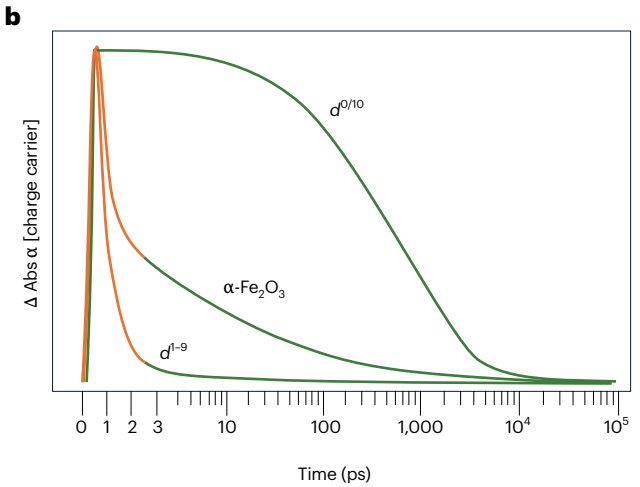
Now, writing in *Nature Chemistry*, Sachs, Pastor, Walsh, Durrant and co-workers rationalize factors that control the charge carrier lifetime of transition metal oxide (TMO) semiconductors and reveal that, in an analogous manner to transition-metal-based photosensitizers, metal-centred ligand field states control charge carrier lifetimes[2]. TMOs are attractive candidates for solar energy conversion as they are chemically stable, non-toxic, abundant and fulfil the requirements for low-cost manufacturing methods under ambient conditions. Some of them, with either open (d^0) or closed (d^{10}) *d* shells have already achieved quantum efficiencies approaching unity[3]. Though a significant limitation of these d^0 or d^{10} TMOs is their insufficient absorption in the visible region of the solar spectrum, restricting the overall maximal efficiency that could be achieved. In contrast, TMOs with an open *d* shell (d^{1-9}) generally exhibit enhanced visible light absorption, but also a significant decrease in photocatalytic activity owing to the markedly shorter charge carrier lifetimes. To assess correlations between charge carrier lifetime and electronic structure, Sachs, Pastor, Walsh, Durrant and co-workers examined the excited-state behaviour of TMOs via steady-state and time-resolved optical spectroscopic techniques. They complemented this approach with theoretical computations to elucidate the corresponding band structure and, therefore, the resulting absorption features.

Thanks to advancements in density functional theory, the band edge electronic structures of numerous oxides have been extensively investigated. Already in 2011, researchers had raised concerns about the nature of open *d*-shell TMO band edges as a limitation for photoelectrochemical applications[4]. A significant distinction is evident between the valence band edge nature of $d^{0/10}$ TMOs, which is predominantly attributed to the 2*p* orbitals of oxygen (O 2*p*), whereas the open-shell configurations consist of a mixture of the O 2*p* and 3*d* orbitals of the metal (M 3*d*). In all instances, the conduction band edge is composed of M 3*d* states, thereby classifying TMOs as Mott–Hubbard insulators for most open *d*-shell configurations, where transition arises from strong coulombic repulsion within the same orbital, and as charge transfer insulators for $d^{0/10}$ TMOs, defined by a transition occurring through the transfer of charge from neighbouring lattice atoms. However, this insight alone is not sufficient to explain the short lifetime of the active charge carriers in open *d*-shell TMOs.

The researchers —similar to a diligent chemistry student examining Tanabe–Sugano diagrams to reveal energy states that may participate in photoinduced processes — identified a missing piece to complete the puzzle of TMO photochemical behaviour. By considering these TMOs as transition metal complexes, one can consider bandgap excitation as ligand-to-metal charge transfer (LMCT) but, most importantly, a ligand field (LF) state lies between the ground state and the LMCT state (Fig. 1a, green box presenting Co_3O_4 as a case study[5,6]). This LF transition results from the electron density rearrangement within the *d* orbitals on photoexcitation and is intrinsically present in d^1 to d^9 TMOs optical features.

To investigate whether the LF states are responsible for charge carrier relaxation/recombination pathways, similar to intragap trap states originating from impurities, the research team employed ultrafast transient absorption spectroscopy to study the spectral properties and dynamics of photogenerated charge carriers. The team observed two distinct processes following photoexcitation (Fig. 1b). They attributed the first, decaying on a sub-picosecond timescale, to the non-radiative relaxation through LF states (orange traces). The researchers related the second, which occurred on the nanosecond timescale, to the recombination of the charge-separated holes and electrons (green traces). The amplitude of the signal is proportional to the concentration of charge carriers, according to the Beer–Lambert law, and consequently, the magnitude of the first relaxation pathway dictates the final population of holes and electrons. Importantly, TMOs with empty and closed *d* shells only show the second deactivation pathway, as illustrated in Fig. 1b, since LF states are absent. Although the LF state is responsible for the visible-light absorption expansion, it also results in a deactivation pathway, which lowers the yield of reactive charges. Thus, the fate of the active charge carriers is determined within the first picosecond after photoexcitation, and competition between deactivation pathways determines the photocatalytic performance.





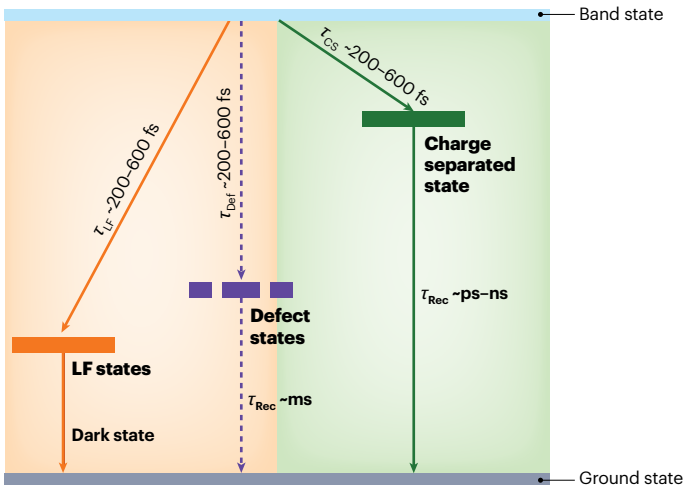


Fig. 1 | Connecting molecular ligand field states to bulk material properties. **a**, Open and closed *d*-shell electronic configuration of selected atoms along with a case study of Co_3O_4 transitions, which are elucidated using the spinel molecular orbital diagram as a fundamental building block of bulk materials. **b**, Representative dynamics of photogenerated charges in TMOS with $d^{0/10}$ and d^{1-9} electronic configuration. The intermediate case of α-Fe_2O_3, in which the LMCT–LF transition is spin-forbidden, is also represented. **c**, Electronic state diagram representing the main deactivation pathways following bandgap photoexcitation.

Beyond merely indicating a trend based on the TMOs' *d*-shell occupancy, this conceptualization of molecular levels as applied to the solid state offers a different photophysical model (Fig. 1c). Within this model, after direct bandgap photoexcitation, there are three distinct pathways to return to the ground state. The first is the relaxation into LF states (orange path), present in the case of open *d* shells, which will dominate if the LMCT–LF energy gap is small and if the transition is spin- and parity-allowed. The second illustrates charge carrier trapping (purple path), which occurs in spatial proximity to physical defects, also predominantly on the sub-picosecond timescale. Although these deactivation pathways have not been discussed here, extensive studies have explored these trap states, and this process occurs regardless of the *d* configuration of the metal[7]. The third and most crucial pathway is the non-radiative formation of the charge-separated state with a nanosecond-scale lifetime (green path), competent for photocatalysis and solar fuels formation.

Additionally, the presence of an applied electrical bias can further slow recombination, allowing the semiconductor to drive chemical reactions through long-lived reactive holes[8]. Importantly, this model shines light on the poor photocatalytic performance of open *d*-shell TMOs and enables rationalization of the improved photocatalytic behaviour of α-Fe_2O_3, a well-known water-splitting photoanode. Here, the spin-forbidden LMCT–LF transition favours the formation of charged-separated species (Fig. 1b), akin to the cage escape process in bimolecular electron transfer reactivity[9].

In addition to oxides, the observed correlation aligns with high-performance non-oxides, such as lead halide perovskites and chalcogenide semiconductors. These materials are based on *d* metals that do not experience ultrafast deactivation after photoexcitation, as the ligand field state is absent from the bandgap. Thus, the improved understanding gleaned from TMOs not only facilitates the development of novel enhancement strategies, but also elucidates previously encountered experimental limitations. Consequently, a winning strategy to tackle the 21st-century challenges may be to enhance the ligand field through well-established concepts from the study of transition-metal-based molecular complexes[10].

In conclusion, real gains can be reached through the synergy between molecular and solid-state chemists by leveraging fundamental principles to advance the development of photocatalytic materials. This work demonstrates how applying molecular-level concepts to solid-state systems can provide crucial insights into the photophysical behaviour of transition metal oxides. These findings provide a rational framework for designing more effective photocatalytic materials by manipulating the ligand field and electronic structure and will undoubtedly guide future research in renewable energy technologies.

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References

1. Walter, M. G. et al. *Chem. Rev.* **110**, 6446–6473 (2010).
2. Sachs, M. et al. *Nat. Chem.* https://doi.org/10.1038/s41557-025-01868-y (2025).
3. Rühle, S. & Zaban, A. in *Advanced Concepts in Photovoltaics* 11th edn (eds Nozik, A. J. et al.) 258–286 (RSC, 2014).
4. Huda, M. N., Al-Jassim, M. M. & Turner, J. *J. Renew. Sustain. Ener.* **3**, 053101 (2011).
5. Miedzinska, K. M. E., Hollebone, B. R. & Cook, J. G. *J. Phys. Chem. Solids* **48**, 649–656 (1987).
6. The Materials Project. *Materials Data on Co_3O_4* (Lawrence Berkeley National Laboratory, USA, 2020); https://doi.org/10.17188/1193429
7. Barroso, M., Pendlebury, S. R., Cowan, A. J. & Durrant, J. R. *Chem. Sci.* **4**, 2724 (2013).
8. Cowan, A. J., Leng, W., Barnes, P. R. F., Klug, D. R. & Durrant, J. R. *J. Phys. Chem. Chem. Phys.* **15**, 8772 (2013).
9. Goodwin, M. J. et al. *Chem. Rev.* **124**, 7379–7464 (2024).
10. Morselli, G., Reber, C. & Wenger, O. S. *J. Am. Chem. Soc.* **147**, 11608–11624 (2025).

Competing interests

The authors declare no competing interests.