A pestle and mortar approach for room temperature defect engineering in metal oxides

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Impurity doping and defect engineering represent common strategies for tailoring the electronic properties of solid-state materials, for example, controlling the carrier type and carrier concentration in semiconductor materials. More recently, it has been shown that by the introduction of certain impurities the electronic band structure of TiO_2 can be greatly modified, resulting in substantially different electronic and optical properties. For example, Chen *et al.* [1] reported the discovery of a

defective “black” TiO_2 fabricated by annealing pristine powders in H_2 atmosphere (20 bar) at 200°C for 5 days. Unlike typical white TiO_2 that does not absorb visible light, “black” TiO_2 strongly absorbs visible photons and shows extraordinary photocatalytic activity in the visible range, which has generated considerable excitement among the photocatalysis community. Similarly, Nakajima *et al.* [2] used pulsed laser-induced oxygen release process to produce defective black TiO_2 with enhanced

Figure 1 (a) Schematic diagram for defect engineering of oxides by lithium reduction strategy. (b and c) High angle annular dark field (HAADF) images of pristine and 5% lithium-reduced TiO_2 . (d) Photograph of TiO_2 . (e) Photograph of ZnO , SnO_2 , and CeO_2 , respectively. Reprinted with permission from Ref. [5], Copyright 2018, Springer Nature.

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solar water splitting efficiency. In parallel, reductive metals, such as Mg and Al, have also been introduced to tailor the defects in TiO_2 for the production of black TiO_2 for visible light-assisted hydrogen production [3,4].

These studies have highlighted the exciting potential in defect engineering of metal oxide for tailoring their electronic, optical and catalytic properties. However, the approaches used to engineer such defects to date usually require some rather complicated procedures involving high-temperature, high pressure and long-duration and highly specialized laser ablation, which are costly and can lead to undesired crystal structural and morphological changes of nanomaterials. Additionally, it remains a significant challenge to precisely control the defects concentration to generate tunable properties.

To these challenges, Wu and Li *et al.* [5] from Tsinghua University and their collaborators including Li-Min Liu from Beihang University reported a new lithium reduction strategy to generate defects in TiO_2 nanoparticles to produce black TiO_2 at room temperature. With their approach, defective oxide can be readily produced by grinding oxides with Li powders in a mortar (Fig. 1a). Thanks to the high reducibility of Li, it can readily extract oxygen from TiO_2 , resulting in defects and disorder and producing black TiO_2 (Fig. 1b, c). This approach is easy to control, fast, versatile and readily scalable. Notably, the defects in the oxides can be tuned by adjusting the ratio of Li to oxides, producing TiO_2 with different levels of defects and hence different colors (Fig. 1d, e). Their study further shows that these colored TiO_2 exhibit excellent photocatalytic activities and stability.

This study defines a facile, rapid and controllable way to engineer the defects in TiO_2 for scalable production of

“black” TiO_2 at room temperature, and may open up exciting opportunities for photocatalyst applications. More broadly, the lithium reduction approach may offer a general pathway for defect engineering and for tailoring the electronic structures of a wide range of metal oxides. According to Ellingham diagrams, most oxides can be reduced by lithium metal at room temperature. Indeed, the authors have shown that their method can be readily extended to implant defects into a series of oxide materials, including ZnO , SnO_2 and CeO_2 (Fig. 1e). This approach may be further extended for defect engineering in diverse material systems beyond metal oxides, including sulfides and selenides, opening up a new pathway to tailor and tame the electronic and optical properties of the relevant materials for broad applications in electronics, photonics and catalysis.

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