Reversible and irreversible metal oxide nanoparticle photodoping

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The photodoping is an attractive approach to readily tune the optical and electrical properties of metal oxide nanoparticles and have found the extensive applications in optoelectronics, light harvesting and smart window devices for energy management. A key advantage of photodoping is that the optical and electronic properties can be easily tuned just by irradiating by light. We have demonstrated recently the TiO_2 nanoparticle colloids in hole scavenging media that exhibit a stark response to UV light and enable to take control over the transmittance of window materials in the visible, near-infrared and even the thermal black body radiation part of the spectrum [Chem.Mater.2018,30,8968]. This is due to the combined effects of localized surface plasmon resonance (LSPR) of photodoped electrons and absorption through the introduction of mid-bandgap states from Ti^{3+}. The TiO_2 nanoparticles can be reversibly bleached by withdrawing the electron by exposing to oxygen or by external bias in electrochromic smart window devices.

The photochromic response of oxide nanoparticles can be further enhanced by aliovalent donor doping. However, the donor-doped nanoparticles exhibit permanent irreversible photodoping. As one may consider the permanent photodoping is not the desired property for the smart window, but it is a promising way to enhance the electric conductivity or to modulate the infrared absorption of metal oxides. In fact, a large number of donor dopants in transparent conductive oxides don't serve electron but are compensated by other point defects. We show that the photodoping can be a straightforward method to increase charge carrier concentration in various donor doped oxides. The photogenerated electrons are stable in the air even after storing for months. The observed behavior is explained by changing the dominating point defects contributing to extra positive charge compensation from a donor. This stabilizes the photogenerated electrons and produces LSPR absorption in the infrared region.