Visible Light Photochemistry in Epitaxial N-doped TiO_2 Anatase

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Much effort has been devoted to heterogeneous photocatalysis using oxide semiconductors. TiO_2 has been widely used since its utility for photoelectrolysis of water was first reported [1]. TiO_2 has also attracted much attention for use in dye-sensitized solar cells [2, 3] and the photodecomposition of organic pollutants [4,5]. However, with a 3 eV bandgap, TiO_2 absorbs relatively little of the solar spectrum. Asahi *et al.* [6] first suggested that nitrogen doping reduces the bandgap. There have since been a plethora of publications describing enhanced visible-light photochemical activity in N-doped TiO_2 nano-particles. While intriguing, these studies lack the in-depth materials understanding required to establish defensible cause-and-effect relationships between composition/structure and electronic structure/ photochemical properties. Such determinations are difficult in light of the heterogeneous, multiple-orientation, and defective nature of nano-particle assemblies. Electronic structure calculations predict that N 2*p*-derived states are localized about substitional N at O sites, and fall at midgap or close to the valence band maximum. The absence of band formation at typical doping levels (≤ ~1 at. % substitution for O) suggests that holes created by light absorption should become trapped at N sites, precluding surface photoactivity.

Indeed, we have found this to be the case for epitaxial films of N-doped rutile grown by molecular beam epitaxy (MBE) in three different orientations. In contrast, epitaxial N-doped anatase TiO_2(001) *is* photoactive in the visible [7]. We have used hole-mediated photodecomposition of trimethyl acetate (TMA) as a probe of photochemical activity. We find the (001)-oriented surface of epitaxial $TiO_{2-x}N_x$ anatase (x = ~0.02) grown on Nb-doped $SrTiO_3$(001) by MBE is nearly as active at TMA photo-decomposition with visible light as it is using broad-band (visible + UV) light from a Hg arc lamp. These results reveal that at least for this particular orientation, holes are not trapped at N sites, but can freely migrate to the surface, despite the relatively long distances between substitutional N dopants. An intensive search for the mechanism behind this unusual and potentially useful result is underway.

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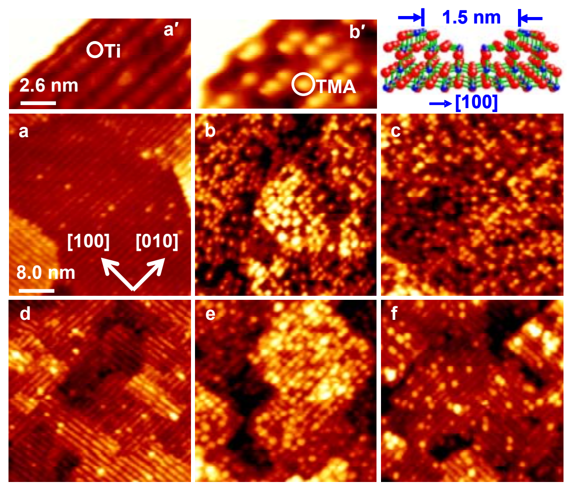

STM images of epitaxial $TiO_{2-x}N_x$ anatase/*n*-$SrTiO_3$ (001) with and without saturation doses of TMA, and before and after visible light irradiation: (a, a′) x=0, clean; (b, b′) x=0, TMA, no irradiation, where a′ and b′ are higher magnification images of a and b; (c) x=0, TMA, after visible light exposure (5.64×10^{20} photons/cm^2); (d) x=0.02, clean; (e) x=0.02, TMA, no irradiation; (f) x=0.02, TMA, after visible light exposure (5.64×10^{20} photons/ cm^2). The individual TMA anions appear as bright lobes, separated by ~1.2 nm and ~1.5 nm along [010] and [100], respectively. Also shown is a structural diagram for the clean, (1×4) reconstructed surface.

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