

Photocatalytic removal of NO_x over visible-light-responsive oxygen-deficient TiO₂

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Introduction

Nitrogen oxides (NO_x), mainly produced from combustion of fossil fuels and vehicle exhaust, are responsible for atmospheric environmental problems such as haze, photochemical smog, acid rain and so on. Semiconductor photocatalysis, as a “green” technology, has been used to remove NO_x at ppb levels^[1].

TiO₂ has long been a promising candidate for photocatalysis applications owing to its strong photocatalytic oxidation performance, photostability, natural abundance, and nontoxicity^[2]. However, the relatively large band gap of TiO₂ (3.0-3.2 eV) limits its application in the visible light region (400 nm < λ < 750 nm), which accounts for 43% of the incoming solar energy. Oxygen vacancies are the most important defects in TiO₂ for photocatalysis^[3]. It has been shown that the photocatalytically important properties of TiO₂, including the electronic structure, charge transport and surface properties, are closely related to oxygen vacancies.

In this study, a series of oxygen-deficient TiO₂ catalysts was prepared by a facile and low temperature method. The catalysts were utilized to remove gaseous NO_x under visible light irradiation.

Materials and Methods

Oxygen-deficient TiO₂ was synthesized using a sol-gel method. After drying at 110 °C, the powder samples were calcined in air at 150, 200, 300, 400 and 500 °C for 5 h and were labeled as TiO₂-150, TiO₂-200, TiO₂-300, TiO₂-400, and TiO₂-500, respectively. The catalysts were characterized by SEM, XRD, Raman, physisorption analysis, UV-vis diffuse reflection spectra and photoluminescence (PL) emission spectra.

The photocatalytic experiments for the removal of NO_x were performed in a home-made continuous flow reactor. A 500-W commercial Xenon arc lamp was used as the simulated solar light source. Two optical filters were used to obtain light in the 420-700 nm range and the integrated light intensity was 35.8 mW/cm². The experiment conditions were: T=25 °C, m_{cat}=50 mg, NO_{initial}=400 ppb, RH=55%, F=1.2 L min⁻¹. The concentration of NO, NO₂ and NO_x was continuously measured by a chemiluminescence NO_x analyzer.

DFT calculations were performed using the CASTEP package. The generalized gradient approximation (GGA) with the PBE exchange–correlation functional was adopted. The parameters were: ultrasoft pseudo-potential, *k*-point mesh of (2×2×2), energy cutoff=380 eV, convergence tolerance: energy<5.0×10⁻⁶ eV/atom, force<0.01 eV/Å, stress<0.02 GPa and displacement<5.0×10⁻⁴ Å. A 108-atom supercell made up by 3×3×1 unit cells was used to simulate an anatase bulk crystal. The oxygen vacancy was modeled by removing one oxygen atom in TiO₂ cells, thus forming TiO_{2-x} with x=0.028. After finishing the geometry optimizations, the DFT+U method was used to calculate the band structures and the projected density of states (PDOS) of TiO₂ and TiO_{2-x}. A self-consistent Hubbard U correction of 3.3 eV for the d electrons of Ti has been calculated^[4].

Results and Discussion

TiO₂-200 is highly active for the removal of NO_x under visible light. On the basis of the characterization results, the excellent catalytic activity of TiO₂-200 was attributed to its larger surface area, greater light absorption in the visible region and more effective charge transport and separation than catalysts prepared at other temperatures, which was caused by the formation of oxygen vacancies in the presence of carbonaceous species.

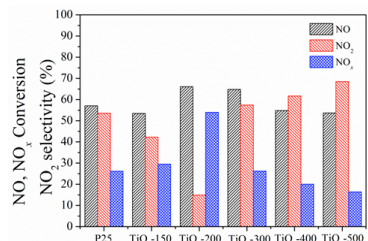


Figure 1. NO, NO_x conversion and NO₂ selectivity at 0.5 h for various catalysts

Figure 2 (A) and (C) show the geometry of Ti and O atoms located on a (100) plane of anatase formation, respectively. The removal of an O atom induces a dramatic change in the local geometry around the vacancy site. The significant lattice distortion changes the dipole moments and an internal field is introduced, which can promote the separation of photogenerated electron-hole pairs and improve the photocatalytic activity.

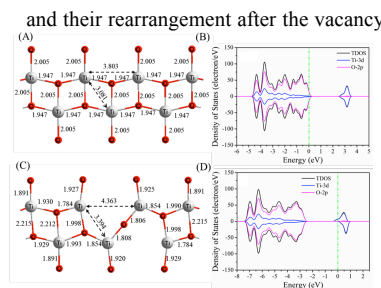


Figure 2. Optimized geometries of (A) TiO₂ and (C) TiO_{2-x} in a (100) plane. DOS for (B) TiO₂ and (D) TiO_{2-x}. O (red spheres) and Ti (blue spheres), the energy zero is taken as the Fermi level (green dashed line). Atomic distances are given in angstroms.

The calculated band gap of TiO_{2-x} is 2.27 eV, which is narrower than that of TiO₂ (2.44 eV). In TiO₂, the valence band is dominated by the O 2p state, while the conduction band by the Ti 3d state (Figure 2B). In TiO_{2-x}, the Fermi level is located at the bottom of the conduction band, which is a typical n-type doping (Figure 2D). The oxygen vacancy does not induce impurity levels within the band gap, but splits the Ti-3d states near the Fermi level. The calculated results give a good explanation for the experimentally observed band gap narrowing and decreased electron-hole recombination.

Significance

Oxygen-deficient TiO₂ is highly active for the removal of NO_x under visible light. The excellent catalytic activity of TiO₂-200 was attributed to its larger surface area, greater light absorption in the visible region and more effective charge transport and separation than catalysts calcined at other temperatures, which was caused by the formation of oxygen vacancies. DFT calculation confirms that the oxygen vacancies lead to light absorption in the visible region and effective separation of photogenerated electron-hole pairs

References

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