Photocatalytic removal of NO\textsubscript{x} over visible-light-responsive oxygen-deficient TiO\textsubscript{2}

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Introduction
Nitrogen oxides (NO\textsubscript{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\textsubscript{x} at ppb levels\textsuperscript{[1]}

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

In this study, a series of oxygen-deficient TiO\textsubscript{2} catalysts were prepared by a facile and low temperature method. The catalysts were utilized to remove gaseous NO\textsubscript{x} under visible light irradiation.

Materials and Methods
Oxygen-deficient TiO\textsubscript{2} 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 TiO\textsubscript{2}-150, TiO\textsubscript{2}-200, TiO\textsubscript{2}-300, TiO\textsubscript{2}-400, and TiO\textsubscript{2}-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\textsubscript{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/cm\textsuperscript{2}. The experiment conditions were: T=25 °C, m\textsubscript{cat}=50 mg, NO\textsubscript{2,initial}=400 ppb, RH=55%, F=1.2 L min\textsuperscript{-1}. The concentration of NO\textsubscript{x}, NO\textsubscript{y} and NO\textsubscript{z} was continuously measured by a chemiluminescence NO 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 \((2 \times 2 \times 2)\), energy cutoff=380 eV, convergence tolerance: energy<5.0×10\textsuperscript{-6} eV/atom, force<0.01 eV/Å, stress<0.02 GPa and displacement<5.0×10\textsuperscript{-4} Å. A 108-atom supercell made up by \(3 \times 3 \times 1\) unit cells was used to simulate a anatase bulk crystal. The oxygen vacancy was modeled by removing one oxygen atom in TiO\textsubscript{2} cells, thus forming TiO\textsubscript{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 TiO\textsubscript{2} and TiO\textsubscript{2-x}. A self-consistent Hubbard U correction of 3.3 eV for the d electrons of Ti has been calculated \textsuperscript{[4]}.

Results and Discussion
TiO\textsubscript{2}-200 is highly active for the removal of NO\textsubscript{x} under visible light. On the basis of the characterization results, the excellent catalytic activity of TiO\textsubscript{2}-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\textsubscript{y} and NO\textsubscript{z} 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) TiO\textsubscript{2} and (C) TiO\textsubscript{2-x} in a (100) plane. DOS for (B) TiO\textsubscript{2} and (D) TiO\textsubscript{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\textsubscript{2-x} is 2.27 eV, which is narrower than that of TiO\textsubscript{2} (2.44 eV). In TiO\textsubscript{2}, the valence band is dominated by the O 2p state, while the conduction band by the Ti 3d state (Figure 2B). In TiO\textsubscript{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 recombinations.

Significance
Oxygen-deficient TiO\textsubscript{2} is highly active for the removal of NO\textsubscript{x} under visible light. The excellent catalytic activity of TiO\textsubscript{2}-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