Shape-Dependent Photocatalysis

Shape-Dependent Acidity and Photocatalytic Activity of Nb$_2$O$_5$ Nanocrystals with an Active TT (001) Surface

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The search for new low carbon and clean energy technologies is prominent on the research agendas of many governments, universities, and industrial sectors. In particular, the possibility of using solar energy for hydrogen production, fine chemicals manufacture, and water cleansing is currently under intense research. The use of semiconducting oxides, such as TiO$_2$ and ZnO, as photoactive materials has been receiving much attention. Recent work indicates that nanoparticles of these compounds show strong shape-dependent (surface-dependent) photocatalytic properties.$^{[1,2]}$ Spherical nanoparticles with high specific surface area to volume ratios are generally preferred. However, the high electron–hole recombination rate sometimes seen on their defect-rich nonplanar surfaces can be problematic.$^{[1]}$ As an n-type transition metal oxide semiconductor, Nb$_2$O$_5$ has attracted a great deal of interest owing to remarkable applications in gas sensing, acid catalysis, electrochromics, field emission displays, and microelectronics.$^{[3–7]}$ Despite having high photocatalytic activity and well-documented water-tolerant acidic surfaces, at present there are few studies concerning the use of Nb$_2$O$_5$-based materials for photocatalytic applications.$^{[8,9]}$

Herein we report that the (100) surface lying along the axis of pseudo-hexagonal TT Nb$_2$O$_5$ nanorod crystals offers enhanced photocatalytic activity over nanospheres for methylene blue decomposition in aqueous solution. We also reveal for the first time that the strong acidic sites on the exposed crystallographic planes of the nanorods readily bind methylene blue molecules from solution. In the presence of a typical radical scavenger (DMSO), Nb$_2$O$_5$ nanorods show only a marginal decrease in decomposition rate. This is in contrast to ZnO, which adopts the classical mechanism of hole-induced hydroxyl radical attack on organic molecules in solution. The unique combination of adsorption and pre-concentration of organic contaminants followed by direct surface decomposition driven by photocarriers gives rise to improved efficiency in this nonclassical mechanism for photomineralization on a Nb$_2$O$_5$ surface.

Details on materials synthesis, testing, and characterization can be found in the Supporting Information. As seen from the TEM image in Figure 1a, Nb$_2$O$_5$ nanospheres of 20–50 nm diameter were obtained by our precipitation method. Selected area electron diffraction (SAED) (see the Supporting Information) gave ring patterns indicative of the poor long-range crystallinity of the Nb$_2$O$_5$ nanospheres. This is not surprising given the fact that the rapid non-equilibrium precipitation conditions do not allow for the extended growth of a particular phase. Thus, spherically shaped particles that offer a decrease in overall surface energy are anticipated. However, in the case of Nb$_2$O$_5$ nanorod synthesis, we employed the solvothermal technique over a lengthy growth period in the presence of a structure-directing agent, oleic acid in trioctylamine. The TEM image in Figure 1b clearly shows the formation of rod structures (stacked bundles) with sharp edges indicative of small single crystals. As shown, the rod length ranges from 100 to 500 nm with a diameter of 5–20 nm. Indeed, the SAED (see the Supporting Information) shows a single diffraction pattern. The lattice parameters, calculated with the camera constant of the microscope taken into account, matched with the pseudo-hexagonal TT structure of the Nb$_2$O$_5$ phase. A HRTEM study of many randomly selected Nb$_2$O$_5$ nanorod bundles clearly showed lattice fringes perpendicular to the rod axis, and the fringe separation of 3.9 ± 0.3 Å corresponds closely to the (001) crystal plane with the predominant (001) exposed on the bundle surfaces (Figure 1c). Thus, the crystal growth of the nanorod appears to follow the [001] zone axis with a (001) fringe separation of 3.9 ± 0.3 Å along the rod surface.

Figure 1. Analysis of Nb$_2$O$_5$ nanostructures. a) TEM image of Nb$_2$O$_5$ nanospheres; b) TEM image of Nb$_2$O$_5$ nanorods; c) HRTEM image and electron diffraction of Nb$_2$O$_5$ nanorods showing the [001] zone axis with a (001) fringe separation of 3.9 Å along the rod surface.
single crystals. XRD suggests that both the nanospheres and nanorods adopt the pseudohexagonal TT phase, however a poorer crystallinity (short-range order) with lower intensity of peaks for the Nb$_2$O$_5$ nanospheres is evident (see the Supporting Information). The enhancement in (001) peak intensity relative to the typical powder diffraction pattern is caused by the preferred orientation of Nb$_2$O$_5$ rod crystals.

Photocatalytic decomposition of methylene blue in an aqueous solution was evaluated in the presence of Nb$_2$O$_5$ spheres or rods and compared to ZnO plates under ultraviolet irradiation. As seen from Figure 2 (see also the Supporting Information), the reaction, monitored at 664.5 nm (corresponding to monomer absorption), followed pseudo-first order reaction kinetics for the two forms of Nb$_2$O$_5$. The apparent rate constant was calculated to be $k = 0.0733$ min$^{-1}$ for the rods and 0.0074 min$^{-1}$ for the spheres (see the Supporting Information). Thus, the rate constant for the rods was almost 10 times higher than that of the spheres as well as being more active than the ZnO plates (see the Supporting Information). Saito and Kudo reported enhanced photocatalytic activities for H$_2$ evolution from water by photocatalytic decomposition using TT Nb$_2$O$_5$ nanowires (vs. spherical particles) with a similar morphology to our rods.[13] They suggested that one possibility is the difference in the surface area of the wires versus the spheres. However, the measured N$_2$ BET surface areas for our spheres and rods were 77.27 and 102.99 m$^2$ g$^{-1}$, respectively. The small difference in the specific surface area between them implies that surface structure and electronic properties, rather than surface area, are the key factors for the observed high decomposition rates.

Diffuse reflectance UV–visible spectra showed different absorption edges for Nb$_2$O$_5$ rods and spheres (see the Supporting Information) compared to the bulk band gap ($E_g$), which is size dependent.[12] The apparently higher $E_g$ of the spheres may be accounted for by the lower number of interconnected Nb–O polyhedra,[12] which was also reflected in the poor crystallinity shown by SAED and XRD analysis. It is important to note the longer absorption tail stretching to the visible region for the spheres (see the Supporting Information), which indicates a significant absorption range adjacent to the interband transition because of the presence of defects. XPS confirmed that the rods gave a surface stoichiometric Nb/O ratio and binding energy (BE) comparable to bulk Nb$_2$O$_5$ crystals. However, there were significant BE shifts for Nb 3d5/2 and O 1s peaks for the spheres. These variations are ascribed to the formation of oxygen vacancies V$_{O}^{-1}$ with reduction of Nb$^{5+}$ to Nb$^{4+}$ on the surface.

The surface of Nb$_2$O$_5$ is known to be covered with acidic sites[8–10,12,13] comparable to the strength of 70% sulphuric acid ($H_a = -5.6$). Thus, the difference in the nature of these Lewis acid sites may account for the observed photocatalytic differences between spheres and rods. Infrared spectra of Nb$_2$O$_5$ spheres and rods were recorded using adsorbed pyridine at different desorption temperatures.[14] IR bands at 1450 cm$^{-1}$ and 1550 cm$^{-1}$ can be attributed to pyridine coordinated to a Lewis acid site and pyridinium on Brønsted acid sites, respectively.[14] There was only one peak at 1450 cm$^{-1}$, indicating that both spheres and rods contained only Lewis acid sites after calcination. Based on the temperature programmed desorption peak areas, we estimated that there were nearly three times as many Lewis acid sites on the rods as on the spheres. The surface hydrolysis of Nb$^{5+}$–O may also contribute to strong Brønsted acidity, thus rendering the rod surfaces much more acidic. The nucleophilic moieties of methylene blue, such as lone pair electrons in nitrogen and sulfur may adsorb on these strongly Lewis acid Nb$^{5+}$ sites before irradiation. To test this, the degree of adsorption on the nanorods was assessed in the absence of a light source. The nanorods indeed exhibited a strong affinity for the dye molecules, particularly binding methylene blue monomers (absorption at 664.5 nm; uptake of $4.11 \times 10^{18}$ molecules per gram of rods) from solution in preference to the dimers (absorption at 620 nm), with absorption profiles similar to Figure 2a in the presence of light. However, fewer dye molecules were observed to adsorb on ZnO. IR spectra were collected for adsorbed dye species on the surface of Nb$_2$O$_5$ nanorods after a gentle rinse with water (see the Supporting Information). Without discussing in detail the assignment of individual peaks, it was seen that the number of peaks of adsorbed methylene blue compared to the free molecules decreased. This observation can be attributed to the disruption of flexional degrees of freedom when the molecule is in an adsorbed state, which suggests a strong chemical interaction.

In the classical mechanism for photoirradiation of n-type semiconductor oxides, excitons and unbound charge carriers are generated. Hydroxyl radicals can be produced when these excitations migrate to the surface and react with adsorbed water molecules or hydroxide ions. When released, these
radicals cause decomposition of organic molecules, such as dye molecules, in the solution phase. Thus, the photoactivity of ZnO is known to be reduced in the presence of a radical scavenger, such as dimethyl sulfoxide (DMSO). Figure 3a shows about a two-fold rate attenuation when DMSO is added to a methylene blue solution containing the ZnO nanoparticles (see the Supporting Information). On the other hand, Figure 3b shows an unexpected increase in the concentration of the dye molecules in solution with the Nb$_2$O$_5$ nanorods during the first 10 mins. It was thought that the added DMSO might change the dielectric constant of the solution, thus altering the partition and releasing some adsorbed species into the solution under irradiation conditions. There is also the possibility that some DMSO molecules may selectively bind to the acidic sites, thus causing dye displacement in a dynamic equilibria with their free forms in solution. After the initial increase in the dye concentration in solution, the rate of decomposition (slope of the curve) was almost comparable to that of Nb$_2$O$_5$ rods in the absence of DMSO, indicating that the radical scavenger had only a marginal effect on photocatalysis (see the Supporting Information). With regards to the strong adsorption of the dye molecules (UV/Vis and IR results) it appears that the dye species is immobilized by the solid acid sites where the photoinduced electrons and holes on the surface can attack them without recourse to the classical radical mechanism. The rate of attack for the monomers is clearly higher than that of the dimers, as can be seen in Figure 2a and b, where the 664.5 nm peak decreases much faster than the 620 nm peak, as the surface affinity for the monomer on the rods is stronger than the monomer–monomer (dimer) interaction. This is in sharp contrast to the indiscriminate attack by radicals on both monomers and dimers in solution with the ZnO plates (Figure 2c). Related observations describing the preferential adsorption of methylene blue monomers over dimers using acidic clays have been made. Thus, the purely surface events in the non-classical mechanism over the acidic Nb$_2$O$_5$ rod-shaped crystals can account for the insensitivity towards radical scavengers added to the solution (see Figure 4).

To summarize, the strong Lewis acid sites on the TT Nb$_2$O$_5$ (001) surface can bind organic molecules from solution at locally high concentrations to provide a reservoir for more efficient photomineralization during irradiation, which accounts for the highest rate of photodecomposition observed in the present study. The shape-dependent acidic and photocatalytic properties are hereby described. These findings will further increase interest in the unique catalytic and photocatalytic properties of Nb$_2$O$_5$.

**Experimental Section**

A precipitation reaction followed by calcination at 853 K was used to synthesize Nb$_2$O$_5$ nanospheres. Ammonium niobate oxalate hydrate (2.0 g; 99.99%, Aldrich) precursor was dissolved in distilled water (20 mL). The pH value of the solution was then adjusted to 9.0 by adding an ammonia solution with vigorous stirring. The white precipitate was separated by centrifugation and washed thoroughly with distilled water. Nb$_2$O$_5$ nanospheres were obtained by calcination of the dried precipitate at 853 K for 1 h. In a typical synthesis of
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Nb$_2$O$_5$-Nanostäbe und -kugeln wurden als Photokatalysatoren der Zersetzung von Methylenblau in Wasser verglichen. Trotz ähnlicher Oberfläche waren die Nanostäbe eindeutig aktiver. Mit ihrer formabhängigen Oberflächenacidität, hydrothermalen Stabilität und hohen Photaktivität sind diese Nb$_2$O$_5$-Nanostäbe ein einzigartiges und faszinierendes Nanomaterial für die nichtklassische photokatalytische Mineralisierung organischer Verbindungen in Wasser.