

Efficient Visible-Light-Induced Photocatalytic Activity on Gold-Nanoparticle-Supported Layered Titanate

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Abstract: The visible-light-induced photocatalytic conversion of aqueous benzene to phenol on Au-nanoparticle-supported layered titanate was accelerated when the reaction was conducted in the presence of aqueous phenol.

The visible light response of semiconductor photocatalysts such as TiO_2 is an important issue for environmental applications; accordingly, efforts have been focused toward designing novel photocatalysts that function under visible light by such methods as dye sensitization and heteroelement doping.¹ Recently, it has been reported that the immobilization of gold nanoparticles on TiO_2 particles led to visible-light-induced photocatalysis for the oxidation of aqueous organic substrates.^{2,3} Gold-nanoparticle-loaded titania appears to be a potential material for further nanostructure design,⁴ because of the size and morphology-dependent light absorption of gold nanoparticles from the visible to near-infrared region.⁵ In this communication, we report the preparation of a new photocatalyst composed of an ultrathin layer of titanium oxide and gold nanoparticles. A layered titanate was chosen to be supported with gold nanoparticles, since gold nanoparticles were deposited in the interlayer space of a layered titanate to possibly give a “pillared” clay-type material with molecular-sieving ability.⁶ Studies on the catalytic conversion of organic substrates using zeolites⁷ and mesoporous materials^{8,9} have demonstrated that the separation of substrates from the target products on the catalysts plays an important role in the efficient formation of the products.

The present hybrid photocatalyst was used for the direct oxidation of benzene to phenol by visible light irradiation. Since phenol is one of the most important chemicals in industry and few efficient photocatalysts for direct benzene oxidation have been developed,^{9,10} benzene oxidation was chosen as the photocatalytic reaction to be examined in the present study. During the study, we found that the reaction efficiency was substantially modified when the reaction was conducted in the presence of the product (phenol). In the field of heterogeneous photocatalysis, the reaction efficiency is also one of the most important problems requiring improvement. The present very simple approach, just adding the product in the reactant, seems to be versatile for various photocatalytic systems.

A gold-nanoparticle-pillared layered titanate (abbreviated as Au-titanate) was prepared on the basis of the reported procedure developed for the synthesis of gold nanoparticles in layered solids.^{11,12} A layered titanate, $\text{K}_{0.66}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_{3.93}$,¹³ was modified with (3-mercaptopropyl)trimethoxysilane according to the reported procedure.^{11a} The particle surface of the pristine titanate was preliminarily modified with another silane coupling reagent which does not possess a thiol group, octadecyltrimethoxysilane, to avoid the deposition of Au on the particle surface.¹¹ The thiol-modified layered titanate was mixed with HAuCl_4 followed by reduction with NaBH_4 . The increase in the basal spacing (Figure 1a) and enhanced

N_2 adsorption capacity (Figure 1b, BET surface area increased from 0 to $53 \text{ m}^2 \text{ g}^{-1}$) of the thiol-modified layered titanate after the reactions revealed that Au-titanate was nanoporous where gold nanoparticles were immobilized in the interlayer nanospace of the titanate through thiol groups bounded on the titanate sheets to create pores, which is schematically shown in the Figure 1d inset. The FE-SEM image of Au-titanate showed that Au nanoparticles did not deposit on the particle surface (Figure S1 in the Supporting Information), supporting the intercalation of Au nanoparticles. Similar results have been reported for the synthesis of a chromia-nanoparticle-pillared $\text{H}_{0.67}\text{Ti}_{1.83}\text{O}_4$, where the basal spacing and BET surface area are *ca.* 1.7 nm and $100 \text{ m}^2 \text{ g}^{-1}$, respectively.¹⁴ The gallery height of Au-titanate (*ca.* 1.3 nm if the thickness of the titanate sheet is 0.5 nm ¹⁵) is comparable to that (*ca.* 1.3 nm) of the thiol-modified titanate, which is explained by the conformational change of the attached propyl group.¹¹ The partial deintercalation of the attached silyl group is another possible reason for the result.

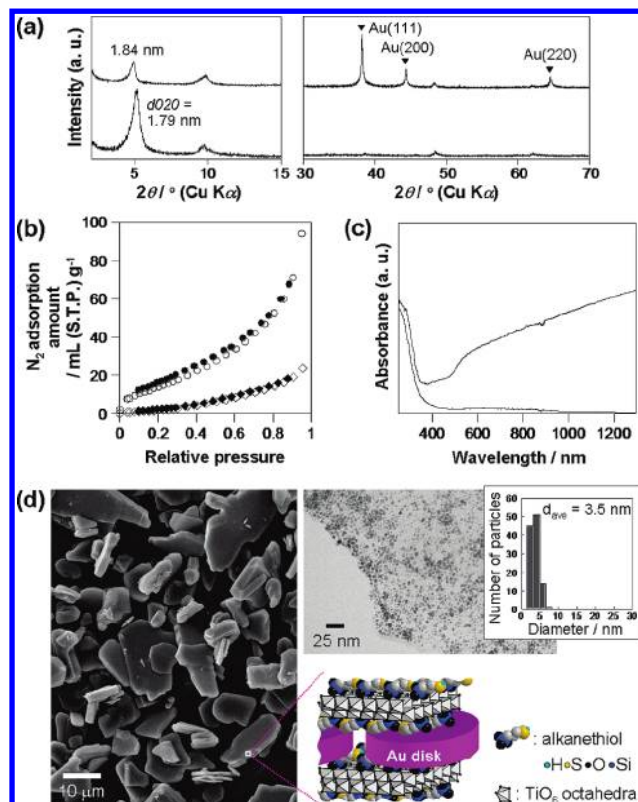


Figure 1. (a) Powder X-ray diffraction patterns, (b) N_2 adsorption (open symbol)/desorption (filled symbol) isotherms, and (c) ultraviolet–visible–near-infrared spectra recorded in diffused reflectance mode of the alkanethiol-modified layered titanate (bottom) before and (top) after gold deposition. (d) TEM and SEM images of Au-titanate. Insets show the size distribution of Au particles and schematic structure of Au-titanate.

As depicted in Figure 1c, Au-titanate exhibits absorption (≥ 520 nm) due to the surface plasmon resonance of nanometer-scale gold particles, in addition to the absorption edge at around 380 nm due to the titanate framework. The absorption from visible to near-infrared light is characteristic of the anisotropic-shaped gold nanoparticles.⁵ Figure 1d shows the TEM image of Au-titanate observed from a direction perpendicular to the basal plane. With the FE-SEM result taken into account, almost all Au particles seen in the TEM image are located in the interlayer space. From the gallery height of Au-titanate and the particle size of Au (Figure 1d inset), the morphology of the intercalated Au is considered to be a disk with a thickness of less than 1 nm and diameter of *ca.* 3.5 nm.

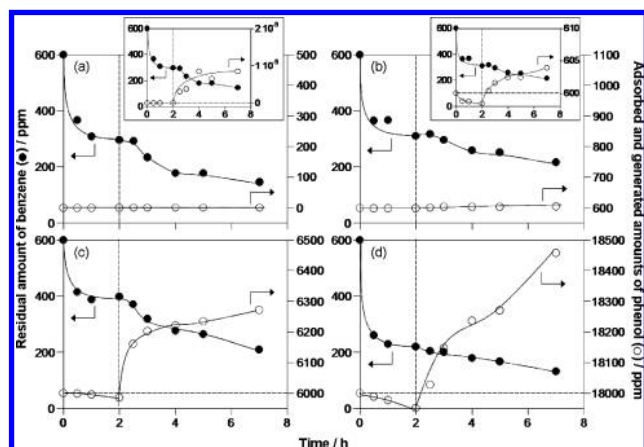


Figure 2. Visible-light-induced catalytic oxidation of benzene in water with Au-titanate in the absence and presence of aqueous phenol. The amounts of benzene and phenol in aqueous mixtures were denoted as (●) and (○), respectively. The light irradiation started after 2 h. The amounts of the initially added phenol are (a) 0, (b) 600, (c) 6000, and (d) 18 000 ppm. Inset shows the expanded version of the figures.

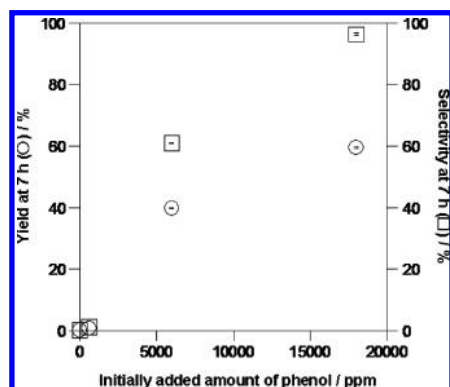


Figure 3. Variation in (○) yield and (□) selectivity of phenol formation as a function of the amount of the initially added phenol. Yield and selectivity were calculated as formed phenol (mol)/added benzene (mol) and formed phenol (mol)/reacted benzene (mol), respectively.

The photocatalytic oxidation of benzene in water was investigated using Au-titanate as the photocatalyst, which was activated by visible light (≥ 420 nm).¹⁶ After the adsorption of the substrate onto the catalyst had reached an equilibrium, the irradiation was started. Figure 2a demonstrates the variation in the amounts of the residual benzene and generated phenol during adsorption (the left side against dashed line) and photocatalytic reactions (the right side against dashed line). As clearly shown in the Figure 2a inset, Au-titanate effectively adsorbed benzene from water and subsequently oxidized benzene to phenol to some extent upon visible light

irradiation (almost all the reacted benzene was mineralized to CO_2 on the basis of the HPLC result). Unexpectedly, the catalytic efficiency for phenol formation was trace though Au-titanate was able to recognize benzene in the aqueous mixture with phenol, which was shown on the left side against dashed lines in Figure 2b–d. For example, *ca.* 42% of benzene adsorbed while only *ca.* 3% of phenol adsorbed when Au-titanate was reacted with an aqueous mixture of benzene and phenol (600 ppm for each compound) under dark conditions (Figure 2b inset).

We then decided to conduct the photocatalytic reaction in the presence of the product, “phenol”, to utilize the benzene/phenol recognition ability of the presently designed photocatalyst. Surprisingly, benzene was oxidized to phenol substantially when the reaction was conducted in the presence of phenol (the right side against dashed lines in Figure 2b–d). The turnover number of phenol formation was much larger than 1 (see Supporting Information for details). Higher reaction efficiency was attained when a larger quantity of light was used (Figure S2 in the Supporting Information). Moreover, the XRD pattern and absorption spectrum of Au-titanate did not change upon reaction, indicating the material remained unchanged after the reaction. These facts support the phenol formation results from the photocatalysis of Au-titanate. As shown apparently in Figure 3, the yield and selectivity of phenol formation depended on the amount of the initially added phenol in the water. When using 18 000 ppm of phenol, benzene was oxidized to phenol in 62% yield and 96% selectivity (it should be noted here that the ratio of the formed phenol to the initially added phenol is much larger than the experimental error for two runs; for example, 3% > 0.7% and 5% > 0.7% for the initially added phenol of 18 000 and 6000 ppm, respectively). These values were superior or comparable to those reported in other direct oxidations using catalysts or photocatalysts (Table S1 in the Supporting Information): for example, 34% yield and 81% selectivity were attained by a UV-light-activated catalytic system using mesoporous titania as the catalyst and water as the oxidant,⁹ or 34% yield and >98% selectivity were obtained by a thermally activated catalytic system using a titanium-containing molecular sieve as the catalyst and H_2O_2 as the oxidant.⁸ If compared with other systems for the direct oxidation of benzene previously reported,^{17–24} the present system exhibits two advantages: (i) mild reaction conditions (visible light and room temperature), (ii) cheap source of oxidant (water). Dissolved oxygen in water acted as an acceptor of the electron injected to the titanate from Au nanoparticles (active center).^{3a,b}

A similar reaction was conducted using other visible-light-responsive photocatalysts which did not efficiently adsorb both benzene and phenol from water, a layered titanate where gold nanoparticles are deposited only at the particle surface (abbreviated as Au(external)-titanate) and a ruthenium complex-sensitized titania particulate (abbreviated as dye-P25).²⁵ As shown in Table S1, only a trace amount of phenol formed when the two materials were reacted with an aqueous benzene and phenol mixture under the same reaction conditions. There are several reasons for the low photocatalytic abilities of Au(external)-titanate and dye-P25 compared to that of Au-titanate, such as the variation in the oxidation power.^{3b,26} We consider that the molecular recognition ability for benzene of Au-titanate (the left side against dashed lines in Figure 2b–d) plays an important role in the unique photocatalytic ability.

The modification of the photocatalysis of semiconductor particles for visible light response and substrate selective reaction has been reported so far. For example, visible-light-induced water splitting and the oxidation of organic substrates have been achieved by the complexation of semiconductors with photosensitizing complex ions²⁷ and noble metal^{2,3} or metal sulfide nanoparticles²⁸ and by

doping with metal or nonmetal elements.⁴ Visible-light-induced water splitting has also been achieved on polymeric semiconductors²⁹ and systems involving two photoexcitation processes (so-called Z-scheme-type systems).³⁰ Substrate-selective photocatalysis has been attained on molecular recognitive layer-coated titanium dioxide particles,³¹ nanoporous titania-based compounds,^{9,32} and layered titanates with controlled swelling ability.³³ On the other hand, to the best of our knowledge, this is the first report on the modification of photocatalysis to a higher yield and product selectivity by the addition of the product in the starting mixture. In addition to the versatility, the idea is economically and environmentally favorable; therefore, it is potentially applicable for improving the efficiency and selectivity of existing photocatalytic processes.

In summary, a layered titanate containing immobilized gold nanoparticles in the interlayer space was found to catalyze the oxidation of aqueous benzene to phenol by visible light irradiation. In addition, we have unexpectedly found that the photocatalytic reaction was substantially modified to a higher yield and selectivity of phenol formation when the reaction was conducted in the presence of aqueous phenol. Under visible light irradiation at room temperature using water as the oxidant, the direct benzene oxidation was accelerated to attain 62% yield and 96% selectivity for phenol formation by simply adding phenol in the starting mixture.

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Supporting Information Available: Turnover number of the present photocatalysis, examples of catalytic oxidation of benzene to phenol (Table S1), FE-SEM image of Au-titanate (Figure S1), effect of quantity of light on the photocatalysis of Au-titanate (Figure S2), and chromatographs of aqueous benzene/phenol mixture before and after the reaction with Au-titanate (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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