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Noble metal-modified octahedral anatase titania particles with enhanced activity for decomposition of chemical and microbiological pollutants

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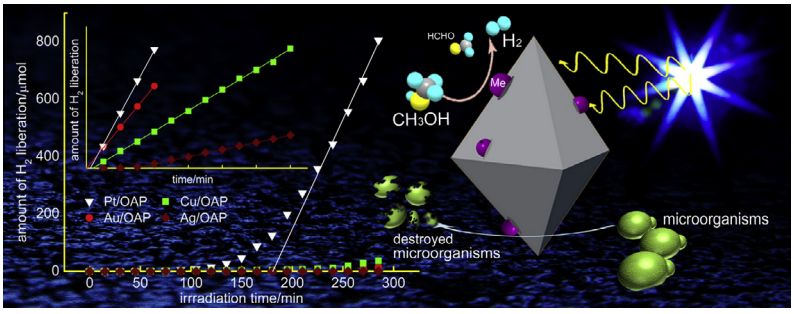
HIGHLIGHTS

- Enhancement of titania activity by modification with Au, Pt, Ag and Cu.
- Significant change of properties by metal photodeposition in the presence of oxygen.
- Correlation of antimicrobial and photocatalytic properties for octahedral anatase.
- Zero-valent Pt and Au and positively charged Cu and Ag in the ambient environment.
- Visible activity of Au/OAPs and Ag/OAPs, due to activation of plasmon resonance.

GRAPHICAL ABSTRACT



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ABSTRACT

Octahedral anatase particles (OAPs) were prepared by hydrothermal (HT) reaction of titanate nanowires (TNWs). OAPs were modified with noble metals (Au, Ag, Cu and Pt) by two photodeposition methods: in the absence and in the initial presence of oxygen in the system. Photocatalytic activities for oxidative decomposition of acetic acid and anaerobic dehydrogenation of methanol under UV/vis irradiation and for oxidation of 2-propanol under visible light irradiation were investigated. Antibacterial activities for bacteria (*Escherichia coli*) and fungi (*Candida albicans*) were investigated in the dark and under UV irradiation and/or visible light irradiation. It was found that the kind of metal deposition significantly influenced the properties of photocatalysts obtained and thus their photocatalytic and antimicrobial activities. Modification of OAPs with metallic deposits resulted in enhanced photocatalytic activities for all tested systems. Pt-modified OAPs showed the highest activity for dehydrogenation of methanol due to their highest work function and lowest activation overpotential of hydrogen evolution. Cu-modified OAPs exhibited the highest activity for oxidative decomposition of acetic acid under UV/vis irradiation, probably due to the heterojunction between Cu oxides and TiO_2. On the other hand, Au-modified OAPs showed the highest photocatalytic activity under visible light irradiation due to their plasmonic properties. Bare OAPs, prepared with various durations of the HT reaction, did not have any antibacterial properties in the dark, while their activity under UV/vis irradiation was correlated with their photocatalytic activities for dehydrogenation of methanol and decomposition of acetic acid. Antimicrobial activity of modified OAPs in the dark and under visible light irradiation was the highest for Ag-modified OAPs. Under UV irradiation, Cu-modified OAPs showed the highest activity for inactivation of both bacteria and fungi.

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1. Introduction

An enormous amount and various kinds of indoor and outdoor pollutants (both chemical and microbiological) that have adverse effects on health are released into environment every day. Although environmental contamination by chemical pollutants is usually well-monitored and controlled [1–3], microbiological pollution is often accidental and results in uncontrolled spread of microorganisms. Microorganisms can grow rapidly without continuous release into the environment. For example, some bacteria and fungi can rapidly reproduce on the surfaces of building materials such as wood, paper, gypsum, ceramics, minerals, paints and plastics [4]. Moreover, positive, negative or neutral interactions between various bacteria and fungi *via* infochemicals produced by them [5,6], as well as between microorganisms and chemical pollutants, may have a crucial impact on the environment. Interactions between microorganisms, chemical compounds and the environment are complex and unpredictable. Therefore, the development of environmentally friendly techniques that can efficiently degrade pollutants is needed.

Photocatalysis is considered to be one of the best methods for environmental purification since additional chemical compounds such as oxidants (ozone, hydrogen peroxide and chlorine) [7–14] are not introduced into the environment [15,16]. Energy consumption is also much less than that in other advanced oxidation processes (AOPs) such as wet air oxidation [17], supercritical water oxidation [18] and H_2O_2/UV-C [19] because UV-A lamps and even free solar radiation can be used for photocatalyst activation [20].

Among the various heterogeneous photocatalysts, titanium(IV) oxide (titania, TiO_2) is one of the most widely used due to its advantages such as good stability, strong redox ability, relative nontoxicity, low cost and high availability [21–24]. However, recombination of charge carriers (a typical phenomenon for all semiconducting materials) and inability to absorb visible light due to its wide band-gap (ca. 3.0 eV for rutile and 3.2 eV for anatase) limit its application to regions of the world with high intensity of solar radiation. Many studies have therefore been carried out to improve the performance of titania by its surface modification, doping and preparation of coupled nanostructures [25–34]. Modification with metals (metallic nanoparticles (NPs) and clusters [35–39], metal complexes [40,41]) has been one of the most frequently used methods for both enhancement of activity under UV light and activation of titania by visible light irradiation. Metallic deposits under UV irradiation work as an electron sink that inhibits the recombination of charge carriers. Under visible light irradiation, either narrowing of the band-gap [42–44] or energy/electron transfer from the modifier to titania [45–47] causes a visible light response. Recently, modification of titania with NPs of noble metals that have a visible light absorption property due to localized surface plasmon resonance (LSPR) has been extensively studied, and such materials obtained are called plasmonic photocatalysts. Although there have been controversial results of studies regarding the mechanism of their action, i.e., transfer of energy [48], transfer of charge carriers [49,50] and plasmonic heating [51], their photocatalytic activity in a broad range of irradiation conditions makes them promising materials for environmental purification and energy conversion. In addition, antibacterial properties of silver and copper extend their possible application to dark conditions. It is thought that the mechanism of action of these photocatalysts depends on their surface properties and morphology, i.e., on the properties of the semiconductor and noble metal and the interaction between them.

Titania with different morphologies such as NPs, nanotubes (TNT), nanowires, and nanospheres has been fabricated by various methods, e.g., hydrothermal reaction (HT), solvothermal, sol-gel, electrosynthesis and gas-phase methods [32,52–54]. Octahedral anatase particles (OAPs), which expose eight equivalent and thermodynamically stable (1 0 1) facets, exhibit a very high level of photocatalytic activity, probably due to the preferential distribution of shallow electron traps (ETs) rather than deep ETs that results in a low rate of recombination of charge carriers [55,56]. Although OAPs have a high level of photocatalytic activity, they are inactive under visible light (as is bare titania). Therefore, their surface modification with NPs of plasmonic metals, i.e., gold (Au), silver (Ag), platinum (Pt) and copper (Cu), has been investigated for decomposition of both chemical and microbiological pollutants under a broad range of irradiation conditions.

2. Experimental

2.1. Preparation of bare and metal-modified OAPs

Potassium titanate nanowires (TNWs; Earthclean Tohoku Co. Ltd), prepared by hydrothermal reaction (HT) of Evonik P25 titania (Nippon Aerosil) and potassium hydroxide solution (17 mol L^{-1}) at 383 K for 20 h [57], were used for fabrication of titania samples containing OAPs. The TNWs (267 mg) were ultrasonically dispersed in Milli-Q water (40 mL) for 1 h, and then the obtained suspension was put into a 100-mL Teflon bottle into which an additional 40 mL of Milli-Q water was added. The bottle was sealed and placed in the outer sleeve of a stainless autoclave and then heated in an oven for 3–24 h (OAP sample heated for 6 h was used for further metal deposition.) at 433 K. The obtained suspension was dispersed by ultrasonication for 10 min and then centrifugally separated (12,000 rpm, 20 min). The white precipitates were collected and dried overnight under vacuum (353 K, 12 h).

For preparation of metal-modified OAPs, aqueous (MiliQ water) solutions of chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, 99.9%, Wako Pure Chemical Industries, Ltd.), chloroauric acid ($HAuCl_4{\cdot}6H_2O$, 99.9%, Wako Pure Chemical Industries, Ltd.), copper sulfate ($CuSO_4{\cdot}5H_2O$, 99.9%, Wako Pure Chemical Industries, Ltd.) and silver nitrate ($AgNO_3$, 99.8%, Wako Pure Chemical Industries, Ltd.) were used as metal precursors. The codes of metal-modified OAP samples were defined as Pt/OAP, Au/OAP, Cu/OAP and Ag/OAP, respectively. Five hundred mg of an OAP product that had been heated for 6 h was used for each photodeposition, and the amount of each metal was calculated to be 0.5 wt% of titania. The weighed OAP powder was put into a Pyrex glass tube equipped with a magnetic stirrer, to which 25 mL of methanol (99.5%, Wako Pure Chemical Industries, Ltd.) aqueous solution (50 vol%, MiliQ water) was added. Then, the aqueous solution of metal salt was slowly dropped while being stirred. The suspension was gas-sparged (argon or oxygen) for 15 min. The tube was sealed with a rubber septum and photoirradiated with magnetic stirring (500 rpm) by a 400-W high-pressure mercury lamp (Eiko-sha) under thermostatic control at 298 K (details presented elsewhere [58]). The thus-obtained photocatalyst was centrifuged (15,000 rpm for 30 min), washed three times with methanol and three times with MiliQ water, and freeze-dried, and then the product was collected for further study.

Metal deposition on OAPs was carried out by two methods: under anaerobic conditions, i.e., proceeded by 15-min bubbling with argon (deaerated system) to remove oxygen from the tubes (Pt/OAP/Ar, Au/OAP/Ar, Cu/OAP/Ar and Ag/OAP/Ar), and under aerobic conditions, i.e., proceeded by 15-min bubbling with oxygen (aerated system) for efficient oxygen adsorption on OAPs (Pt/OAP/O_2, Au/OAP/O_2, Cu/OAP/O_2 and Ag/OAP/O_2). At the beginning of this photodeposition, photogenerated electrons are mainly

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