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Interfacial electronic structure and ion beam induced effect of anatase TiO_2 surface modified by Pd nanoparticles

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ABSTRACT

Anatase TiO_2 surface could be modified by Pd nanoparticles using an electrochemical deposition method. Surface morphology, light absorption and interfacial electronic structures were studied by field emission scanning electron microscopy (FE-SEM), UV–visible reflectance absorption, X-ray diffraction (XRD) crystallography, and depth-profiling X-ray photoelectron spectroscopy (XPS). On the basis of XRD patterns, Pd 3d XPS and valance band spectra, the as-deposited overlayer Pd is metallic, with no detectable Pd oxides. The optical band gap of TiO_2 decreases from 3.25 to 3.14 eV upon Pd deposition. The XPS spectra with Ar^+ ion sputtering show that 4+ oxidation state of Ti dramatically changes to lower (3+ and 2+) oxidation states. As a result of this, oxygen defects are created in the bulk while the oxygen diffuses outward to likely form hydroxyl group on the surface. The Pd 3d XPS peak shifts by +0.6 eV to a higher BE position, and the density of state at the Fermi level is more or less reduced. It appears that the overlayer Pd becomes less metallic, plausibly due to TiO_2 support and/or size effect. No critical interfacial interaction between Pd and TiO_2 was observed by XPS.

1. Introduction

Ever since the discovery of water splitting on TiO_2 under the illumination of UV light in 1972 by Fujishima and Honda [1], TiO_2 has become one of the most actively studied metal oxides, and played very important roles in many fields including green energy (e.g., solar cell and hydrogen fuel cell) and environments (e.g., photodecomposition of pollutants, and air cleaner) [2–6]. For solar cell energy industry and research, dye-sensitized TiO_2 solar cells have become a promising alternative to other photovoltaic devices [7,8]. The dye absorbs photons and creates electrons in the conduction band, and then the electrons are injected into the conduction band of TiO_2. For this reason, the creation efficiency of electrons in the conduction band is dramatically enhanced, compared to the direct photon absorption process of TiO_2. TiO_2 has also importantly been used as a catalyst support. Enache et al. observed that Au/Pd bimetal supported on TiO_2 exhibits very high turnover frequencies for the oxidation of primary alcohols [9]. Zhang and He showed that Pt on TiO_2 catalysts could completely oxidize HCHO into CO_2 and H_2O, even at room temperature [10]. Methane could completely be oxidized over Pd supported on TiO_2/Al_2O_3 [11]. Gold supported on TiO_2 (and on some other metal oxides) is known to be active for CO oxidation [12]. It was shown that the reduction of NO_x under oxygen-rich conditions could be achieved by using $Pd/TiO_2/Al_2O_3$ catalyst [13]. Additionally, it has been found that Au–TiO_2 is an efficient catalyst for water–gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) [14].

TiO_2 has been modified in various ways to enhance visible light absorption and catalytic activities [15,16]. Asahi et al. improved a photocatalytic activity of TiO_2 even under illumination of visible light by doping with nitrogen [15]. Doping methods have commonly been employed to make that TiO_2 absorbs a large portion of solar radiation [15,17]. Khan et al. synthesized TiO_2 by flame pyrolysis of Ti metal, and improved visible light absorption and water splitting efficiency [16].

Palladium has commonly been deposited on TiO_2 by a metal evaporation method [18–24]. Other methods include a wet impregnation technique from Pd solution [25,26], and a hydrothermal method [17] from mixed Pd and TiO_2-precusor solution. In this paper, TiO_2 and Pd were used as a catalytic support and an overlayer material, respectively. I employed a simple electrochemical deposition method. To my knowledge, detailed studies of Pd directly electrodeposited on TiO_2 have not yet been reported, and this is the first detailed study dealing with the interfacial electronic structures.

2. Experimental section

Anatase TiO_2 nanopowder (99.7%, <25 nm in size) was purchased from Aldrich, and dispersed in acidic water (HCl, pH 1).

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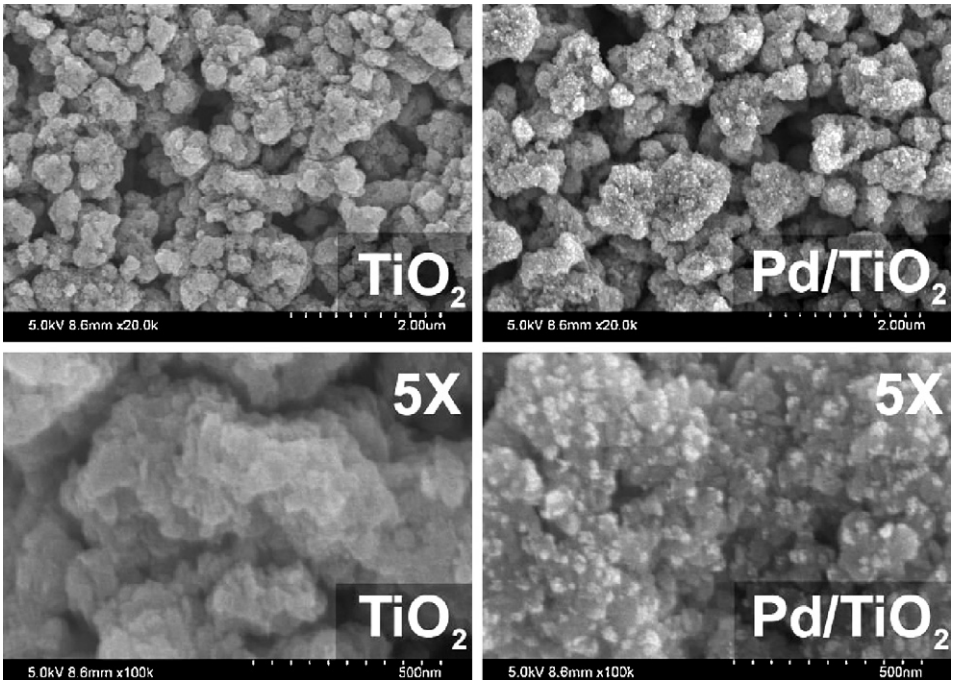

Fig. 1. SEM images of bare TiO_2 and TiO_2 modified by Pd nanoparticles. The lower two images are 5× amplified.

The TiO_2 solution was then drop-coated on a Si substrate, and completely dried at 100 °C. Electrochemical Pd deposition on the TiO_2 substrate (as the working electrode) was carried out in a conventional three-electrode cell with a Ag/AgCl reference and a Pt wire counter electrodes using an electrochemical workstation (CH Instruments 660A: a courtesy of professor K.T. Leung, University of Waterloo, Canada). The electrolyte solution was 1 mM palladium (II) sulfate (98% purity, Aldrich) and 30 mM HCl. After the deposition, the sample was gently rinsed with Millipore water (18.2 MΩ cm resistivity), and was fully dried in a N_2 condition before further experiments.

The surface morphology of Pd/TiO_2 was characterized by FE-SEM (Hitachi, SE-4800) combined with energy dispersive X-ray elemental analysis (EDX). Diffuse reflectance spectra were taken using a UV-vis spectrophotometer (Cary 500) equipped with Lapshere integrating sphere optics. The XRD patterns of Pd/TiO_2 were obtained using a PANalytical X'Pert Pro MPD diffractometer with Cu Kα radiation. The XPS experiments with Ar^+ ion sputtering depth were performed using a Thermo-VG Scientific MultiLab 2000 with a monochromatic Al Kα X-ray source (1486.6 eV), a pass energy of 20.0 eV and a hemispherical energy analyzer. During the XPS, no surface charging of the Pd/TiO_2 sample was observed.

3. Results and discussion

Fig. 1 shows typical FE-SEM images of bare TiO_2, and Pd nanoparticles on TiO_2 electrochemically prepared at −1.0 V for 120 s. For the image of Pd/TiO_2, unlike that of bare TiO_2 two different contrasts are clearly seen in the image. The whiter spots (contrast to TiO_2 gray background) are attributed to Pd nanoparticles which are smaller than 50 nm. Generally, the element with a higher atomic number produces the more electrons, and appears brighter in the image. That is, Pd exhibits whiter spots because Pd has a higher atomic number than Ti and O. The Pd nanoparticles were confirmed by an EDX analysis. The EDX spectrum (not shown) between 0 and 6.0 keV shows the major signals of Ti (Lα, Kα and Kβ), Si(Kα) and Pd(Lα). No other elements were notably detected in the spectrum. A Si peak was very weakly observed because a Si substrate was used for supporting TiO_2 film.

The Pd/TiO2 was further characterized by XRD shown in Fig. 2. It was found that the XRD patterns are due to two different species, and in good accord with the reference XRD patterns of tetragonal anatase TiO_2 (JCPDS 21-1272) and face-centered cubic metallic Pd (JCPDS 01-087-0639). The (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4) and (2 2 0) planes of TiO_2, and (1 1 1), (2 0 0) and (2 2 0) planes of Pd are assigned on the peaks. Because a commercial anatase TiO_2 was used it is not surprising that the XRD pattern of TiO_2 is of anatase. The electrochemically deposited Pd is metallic evidenced by the XRD, and no XRD peak was found for Pd oxides. For PdO, the strongest XRD peak (JCPDS 21-1272) is expected to be seen at ~34°, but this is absent in Fig. 2.

Fig. 3 shows $[\alpha h\nu]^{1/2}$ versus photon energy ($h\nu$) plots of TiO_2 and Pd/TiO_2, where α is an absorbance, h is the Planck constant, and ν is a frequency of light. The photo images shown in inset clearly show a high contrast between the two samples: white and dark. Intuitively, the white TiO_2 reflects all the wavelengths of visible light while the black absorbs visible light. For Pt with the same outermost electron configuration as Pd, Vorontsov et al. showed that Pt deposition on

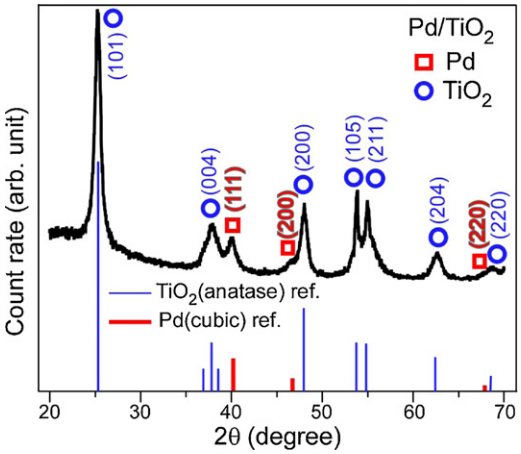

Fig. 2. XRD patterns of electrodeposited Pd on TiO_2. The reference XRD patterns of anatase TiO_2 and metallic Pd are also displayed.