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Full Length Article

A study on selective surface nitridation of TiO_2 nanocrystals in the afterglows of N_2 and N_2-O_2 microwave plasmas

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ABSTRACT

Surface-selective chemical modification of anatase TiO_2 nanocrystals is performed in the post-discharge region of N_2 microwave plasma and the chemical bonding states of surface nitrogen species are carefully evaluated using X-ray photoemission spectroscopy (XPS). It is found that the surface treatments in the afterglows induce the formation of stable nitrogen species at or near the surface of TiO_2. Interestingly, the detailed bonding structure varies strongly depending on the afterglow condition. In pure N_2 afterglows, various N species with a direct Ti—N bond are formed on the surface, while the use of N_2-O_2 mixtures induces the formation of additional oxidized species of NO_3^- on the surface. This is attributed to the high concentrations of O or NO in the afterglows of N_2-O_2 plasmas. The incorporation of substitutional N species in the subsurface is also achieved after a prolonged exposure in the early afterglow with a high density of N_2^+ species. Our results show that the exposure condition can be controlled for a selective chemical modification of TiO_2 surface for the control of surface properties in various applications.

1. Introduction

TiO_2 is an abundant oxide material with advantageous properties such as nontoxicity and chemical stability, which is a reason for its diverse use in various applications of photocatalysis [1,2], photovoltaics [3–6] and sensors [7,8]. In such diverse applications, the ultimate performance of TiO_2 is, in many cases, largely determined by the detailed chemical structure of the surface as is evident from the examples of enhanced photocatalytic activity of surface-modified TiO_2-based photocatalysts [9–13].

For example, the introduction of nitrogen in TiO_2 can reduce the bandgap below 3.0 eV for a photocatalytic activity in the visible range of the spectrum [14–17]. However, the detailed bonding configuration of nitrogen in TiO_2 can vary widely depending on the preparation methods [18] and may lead to an undesirable effect on photoactivity when the newly formed defects act as recombination centers [19,20]. Thus, the control of nitrogen bonding structure and distribution between the surface and the bulk may be beneficial in further enhancing the performance of TiO_2 in photocatalysis.

Recent studies indicate that plasma treatments can be quite effective in enhancing the photoresponse of TiO_2 materials [21–27]. The enhanced absorption of visible light has been generally reported after plasma treatments [23,24,26] due to the role of plasma treatments on the formation of new chemical states such as the reduced phases (e.g., TiO_{2-x}) [27] and the nitride phases [25,26]. Here, understanding on the role of different type of active species in plasma on the formation of the new phases in the oxide materials would be utmost important in getting a better insight into the process.

To achieve such a goal, the use of N_2 and N_2-O_2 plasmas can be a very promising approach [28,29] since the active nitrogen species in the plasma and the afterglows can be easily controlled by varying the process parameters such as the pressure, the flow rate and the applied power [30–37]. N_2 is an abundant inert molecule that requires a very high temperature to induce a reaction. By employing plasma, however, various excited states of N_2, N_2^+ and atomic N species are generated in the N_2 plasmas and in their afterglows under a moderate operating condition [30,31,35,36,38]. In addition, different lifetime of each active species can provide a chance of controlling the densities of the different excited states of N_2 in the afterglow region; for example, neutral active species such as N-atoms, $N_2(X,v > 13)$ and $N_2(A)$ are enriched over N_2^+ ions in the

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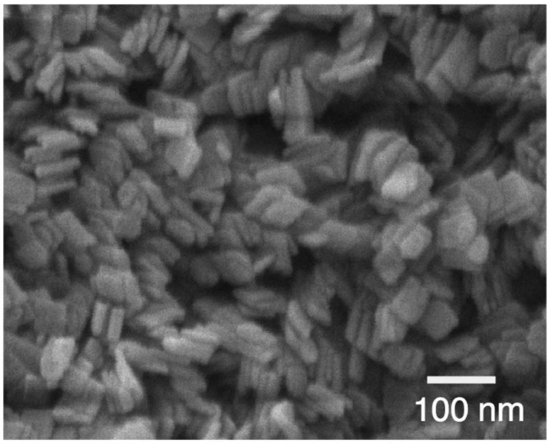

Fig. 1. A SEM image of anatase TiO_2 nanocrystals spin-coated on a Si wafer.

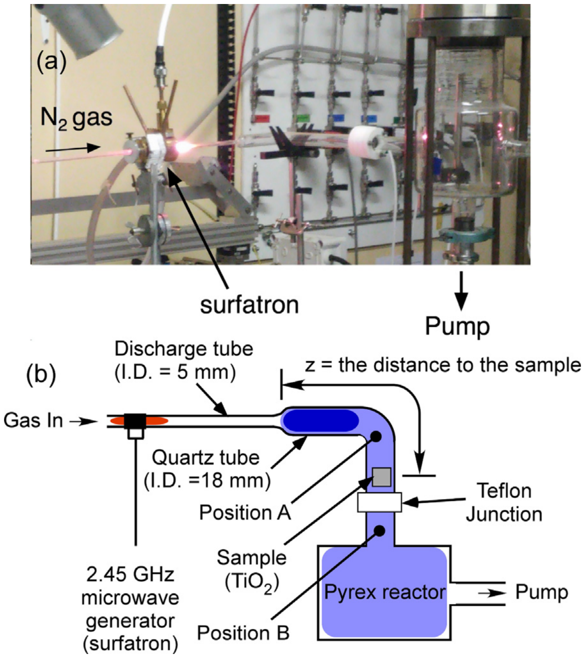

Fig. 2. (a) Experimental setup used in this experiment for the generation of the N_2 and N_2–O_2 microwave plasmas for surface treatments and (b) the corresponding schematic drawing. The sample position is varied from the position A (z = 13 cm) to the position B (z = 40 cm).

afterglows [31,36,39]. This controllability of the densities of active species in the afterglows can be useful for a damage-free selective chemical modification of oxide surfaces with nitrogen for example.

Thus, in this study, we employ N_2 microwave plasma for a selective surface chemical modification of TiO_2 nanocrystals for a potential application in photocatalysis in mind. To find the effect of the different type of active species and their respective densities on the resulting surface chemical bonding states, we control the exposure conditions as follows: Pure N_2 flow is employed to obtain two different conditions for the afterglows with different active species densities such as a high N atom density (N atom condition) and a high N_2^+ density (N_2^+ condition), respectively. Also, a mixture of N_2 and O_2 is used to obtain two more conditions with high densities of active oxygen species such as a high O atom density (O atom condition) and mixed O/NO densities (O/NO condition), respectively. Photoemission studies performed after the exposure of TiO_2 to the afterglows with different densities of active species reveal that the surface chemical bonding states of nitrogen are indeed strongly dependent on the type and the densities of active species in the afterglows used for the surface treatment.

2. Experimental details

The sample employed in this study is a powder of anatase TiO_2 nanocrystals in a shape of nanosheets with a specific surface area of about 40 m^2/g. The detailed synthetic procedure involves a hydrothermal method with tetrabutyl titanate as a precursor and HF as a shape-controlling agent as described in our earlier publication [13]. The as-synthesized powder is dispersed in a deionized water:ethanol solution and then is spin-coated on a clean Si substrate. The resulting film of TiO_2 nanocrystals on the Si substrate is shown in the SEM image of Fig. 1. The top-view image of the TiO_2 film reveals that the planar square-shaped TiO_2 nanocrystals are randomly agglomerated up to a thickness of a few μm with voids between nanocrystals. Such voids would allow a plasma treatment of TiO_2 nanocrystals deep into the innermost layers of the film with the active nitrogen species in the post-discharge tube for an uniform surface chemical modification.

The detailed experimental setup for the plasma treatment is shown in Fig. 2. A 30 cm-long discharge quartz tube with the inner diameter (ID) of 5 mm is inserted to the surfatron cavity for the microwave (2.45 GHz) plasma generation, which is connected to a bent tube with the ID of 18 mm [40]. At the end of the tube (40 cm long with z = 0 at the beginning of the tube) is a 5 L-pyrex chamber (Fig. 2) with a Baratron gauge for the pressure measurement. N_2 and N_2-(1–8%) O_2 plasmas are generated from a steady gas flow at operating conditions of pressures up to 8 Torr, flow rates of 0.5–1.5 slm (standard liter per minute) and applied powers up to 150 W. Under each selected plasma generation condition, the emission characteristics of N_2, N_2^+ and atomic N species are analyzed along the tube to find the best position for the sample exposure with an optimized density of each species. The sample position for the N_2^+ condition is the position A (z = 13 cm) and that for the N atom condition (or O atom condition) is the position B (z = 40 cm). The O/NO condition is obtained at z = 35 cm. Details on the active species for each condition at each specified position are discussed in the Results and Discussion section.

For a characterization of the N_2 and N_2-(1–8%)O_2 afterglows in the post-discharge region, the optical emission spectra are obtained with an optical fiber connected to an Acton Spectra Pro 2500i spectrometer (grating 600 gr/mm) equipped with a Pixis 256E CCD detector. N_2 second positive (2nd pos), N_2^+ first negative (1 st neg) and N_2 first positive (1 st pos) and NO(β) intensities are recorded at various positions along the tube.

The X-ray photoelectron spectroscopy (XPS) measurements are carried out with a PHI5000 Versa Probe II (Ulvac-PHI) using a monochromatic Al Kα source operating at a base pressure below 4×10^{-10} Torr. The instrument work function is calibrated to give the binding energy (BE) of 83.96 eV for the Au $4f_{7/2}$ core level from a metallic gold film. The X-ray beam diameter is set to 200 μm and a charge neutralizer is used to minimize an undesirable charging effect. The charge neutralizer installed in the model is a dual type with an electron neutralizer with a pulsed Ar^+ ion beam. The analyzer pass energy is set to 58.7 eV and the binding energy scale of the analyzer is calibrated with the peak positions of Au $4f_{7/2}$, Ag $3d_{5/2}$ and Cu $2p_{3/2}$ core levels of sputter-cleaned Au, Ag and Cu films. The binding energy for all spectra is calibrated by referring the C 1 s peak from ubiquitous hydrocarbon contamination to 284.8 eV. The fitting analysis of the spectra is performed using a Shirley background subtraction and mixed Gaussian-Lorentzian peaks. The fitting parameters are set to minimize the residual standard deviation (STD) between the measured and fitted XPS spectra.

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