

ORIGINAL ARTICLE

Change in Zeta Potential with Physicochemical Treatment of Surface of Anatase-form Titania Particles

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SYNOPSIS

The zeta potential of the surface of anatase-form titania particles modified by ultraviolet (UV)-irradiation or cold-plasma O₂ treatment was investigated and compared with that of unmodified titania particles.

Zeta potential was first determined after suspension in 10 mM sodium chloride and then with exposure to various concentrations of sodium hydroxide. The charge shifted from positive with a low pH to negative and finally zero with increase in pH. The pH of the solution at which the zeta potential was zero was determined as the isoelectric point (pI). The pI of unmodified titania particles was 6.5. After UV-irradiation, the pI shifted with increase in alkalinity (pI=9.2). Cold-plasma O₂ modification of the titania particles also yielded a shift in pI with increase in alkalinity (pI=8.9). These findings showed that physicochemical surface modification of anatase-form titania particles by UV-irradiation or cold-plasma O₂ treatment resulted in a change in surface charge.

This indicates that such treatment could be used to control adsorption and desorption of specific molecules to titania surfaces. Further research is needed, however, to determine the applicability of such treatment to other metals. These findings are useful in controlling the physicochemical nature including the surface electrical charge, and in surface modification of the titanium scaffolds for tissue engineering.

Key words: *surface modification, titanium oxide, UV-irradiation, cold-plasma O₂ treatment*

INTRODUCTION

Adsorption between the surface of a material and proteins or peptides is primarily influenced by hydrophobic, electrostatic, and van der Waals interactions. The hydrophobicity of a material surface can be determined by measuring contact angle, surface roughness, and surface free energy. It is

difficult, however, to determine hydrophilicity by measuring the surface electric potential. Chemical reaction occurs through contact between molecules. Being able to determine the electric charge of a material surface based on intermolecular interactions would be beneficial in evaluating intermolecular adsorption such as between a material

surface and proteins or peptides. Changes in surface charge density can be determined by measuring zeta potentials before and after adsorption, thereby allowing calculation of adsorption capacity. Research on the behavior of material surfaces employing this method has shown great promise for application to the medical field, in evaluating adsorption of biological macromolecules and preventing adsorption by coating of surfaces, for example.

We have carried out the surface characterization of many types of material under various conditions, including substances used in dental implants¹⁻³. In an earlier study, we investigated the inhibitory effect of surface modification of titanium on oral bacterial adhesion¹. In the present study, two dry processes (solvent-free methods), cold-plasma O₂ treatment or ultraviolet (UV)-irradiation, were used to modify the surface of the targeted compound. Typically, either of these methods only modifies the outermost layer of a surface. Cold-plasma treatment, which can increase surface energy, is probably the most versatile surface treatment technique available⁴⁻⁷. Application of UV-irradiation results in a similar effect to that observed with cold-plasma treatment⁸.

On the other hand, the influence of cold-plasma O₂ treatment and/or UV-irradiation on surface electrokinetic potential remains to be fully elucidated, even though electrostatic interaction is an important characteristic in the adsorption of proteins, bacteria, and cells on biomaterials⁹.

In this report, the surface electrokinetic potential of titania particles is measured in solutions of differing pH, after which zeta potentials are calculated and quantified based on electrophoretic mobility. The pH at which electric potential vanishes, or more specifically, the isoelectric point (pI), is calcu-

lated. After processing the titania particles by UV-irradiation or cold-plasma O₂ treatment, the zeta potentials are also determined. The aim of this study was to clarify the surface properties of titania particles after physicochemical treatment. The goal of this study is to make it possible for tissue engineering to apply this surface modification method.

MATERIALS AND METHODS

1. Application of UV-irradiation or cold-plasma O₂ treatment to titania particles.

Five-mg batches of anatase-form titanium oxide particles (size < 5 μm, less than 81.1%; Wako, Osaka, Japan) were placed in 12 glass dishes. Four dishes of the particles were used as unmodified samples; 4 for continuous exposure to UV-irradiation in a UV irradiator (Bio-Force Nanosciences, Ames, IA, USA) for 2 hr; and 4 for continuous exposure to cold-plasma O₂ treatment. A commercially available plasma surface modification apparatus (VEP-1000 system, ULVAC, Kanagawa, Japan) was used for cold-plasma O₂ treatment. Chamber pressure was maintained at 1.8 Pa throughout treatment. Plasma modification was performed for 10 min at 200 W. After cold-plasma O₂ treatment, the samples were stored immediately in an appropriate solution until zeta potential assay.

2. Determination of zeta potential of particles.

An electrophoretic light-scattering spectrophotometer (ELS-800™, Otsuka Electronics Co., Ltd., Hirakata, Japan) was used to measure the zeta potential of the titania particles. First, standard particles (Monitor particles, Otsuka Electronics Co., Ltd.) with a zeta potential of almost zero were measured to confirm no problem with the equipment used. As buffer solution and pH influence zeta potential, the particles were

suspended in 10 mM sodium chloride solution (NaCl, pH 5.6). After being left to stand, the resulting supernatant was placed in the machine for measurement of electrokinetic potential. To measure

zeta potential in several solutions of differing pH, the suspension was first adjusted to pH 4.0 by addition of 83 mM hydrogen chloride (HCl). The surface potential of the suspension, in which pH

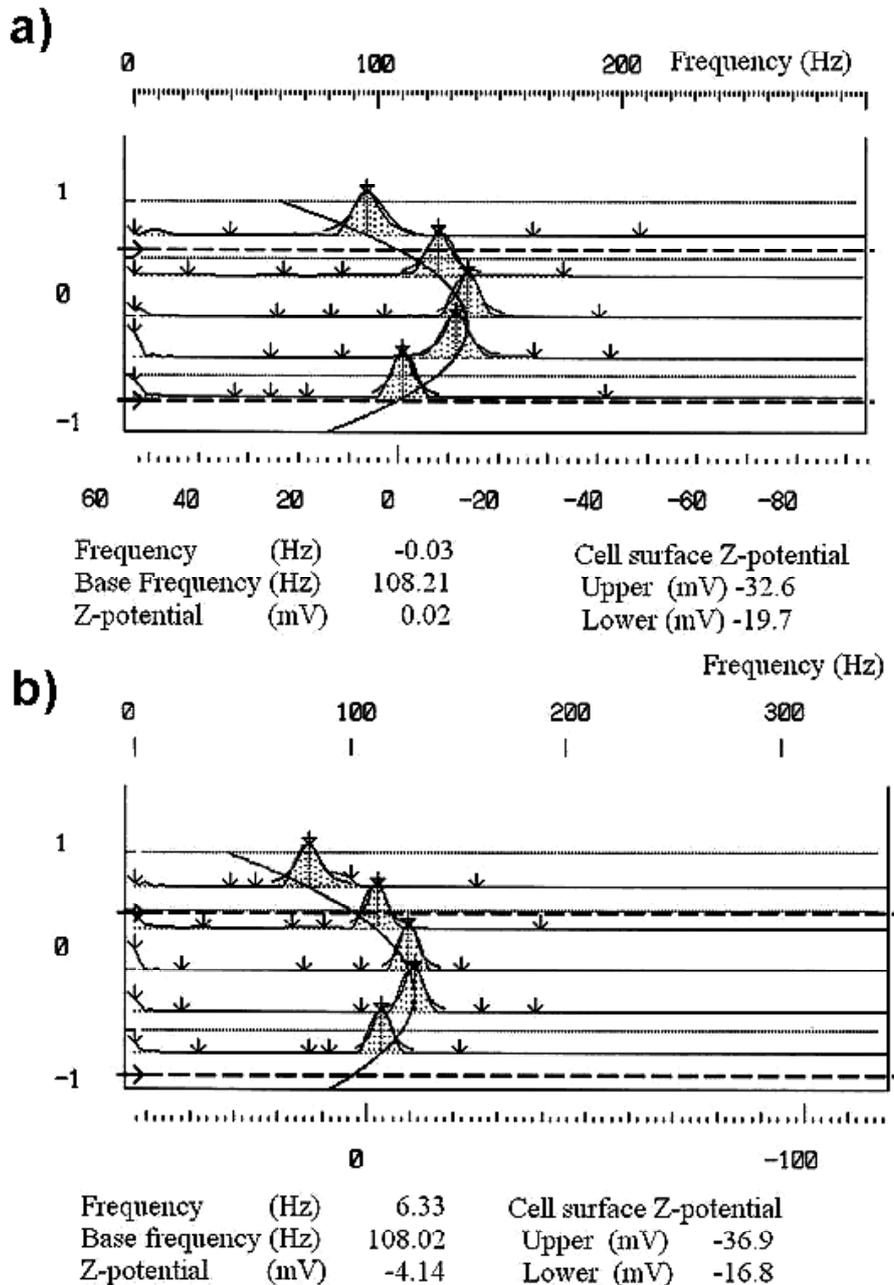


Figure 1. Comparison of charge between standard particles (a), and titania particles at pH 7.0 (b)

was stabilized at 4.0 according to a pH meter, was then immediately measured. The pH of the suspension was then raised gradually by addition of 15-mM increments of sodium hydroxide (NaOH). The potential of each suspension was similarly measured. The zeta potential of the titania particle samples was also determined after UV-irradiation or cold-plasma O₂ treatment by the same method described above.

3. Statistical Analysis

Data were analyzed for statistical significance using a two-way analysis of variance (ANOVA) followed by the Scheffe test for multiple comparisons.

RESULTS

Figure 1 shows an example of the charge aspects of standard particles (a) and those of the titania particles (b) around the pI. This chart shows that at a pH of 7.0, the surface was negatively charged, with a zeta potential of -4.14

mV. Normal titania particles exhibited an uncharged state at a pH of lower than 7.0.

When the titania suspension was acidulated by addition of 83 mM HCl before measuring zeta potential, the particles showed a positive charge. For example, at pH 4.0, a value of +10 mV was obtained. Each addition of 15 mM NaOH resulted in a gradual decrease in zeta potential. At pH 11.0, zeta potential showed a value of -10.0 mV.

Figure 2 shows typical transition in zeta potential of the surface-treated titania particles with gradual change in pH. Curves were drawn by extrapolating the number of points. All particles tested showed a downward-sloping curve with rising pH. Zeta potential ranged from near +30.0 mV in the acidic region to near -30.0 mV in the basic region. With unmodified titania particles, the pI was 6.5. Relative to unmodified particles, both UV-irradiated and cold-plasma O₂-treated particles showed different

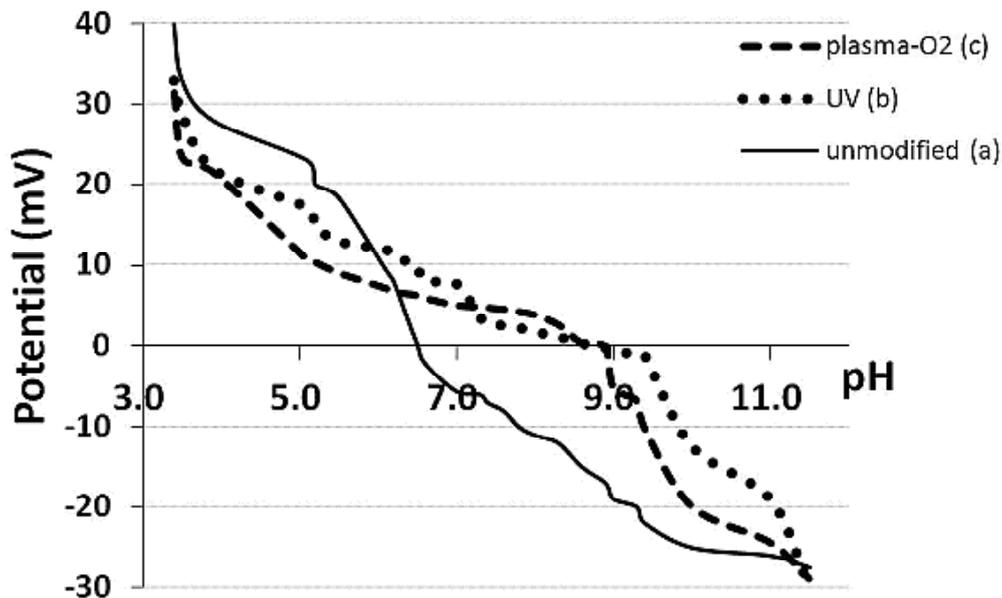


Figure 2. Change in pI of various particles of titania: unmodified (a), UV-irradiated (b), cold-plasma O₂-treated (c).

values, with their zeta potential curves shifting to the right of the graph. Surface-treated particles showed a high pI. The pI value of the cold-plasma O₂-treated and UV-irradiated particles was 8.9 and 9.2, respectively. This indicates that pH influences the distribution of the surface charge of the particles. For example, as shown in Fig.2, at around pH 7.0, the surface charge of the particles was negative, because the pI of the titania particles was 6.5. On the other hand, the surface charges of the physicochemically-modified titania particles by UV or cold-plasma O₂ treatment were both positive.

Zeta potential values were determined at 3 or 4 pH levels above and below the pI. The average values obtained and their standard deviation are shown in Figure 3.

Apparent differences were observed between unmodified (Fig.3 a) and UV-irradiated (Fig.3 b), and between unmodified (Fig.3 a) and cold-plasma O₂-treated particles (Fig.3 c). This indicates a clear shift in the pI with UV irradiation or cold-plasma O₂ treatment compared with unmodified particles. These shifts in pI with cold-plasma O₂ treatment or UV irradiation were similar. The difference in mobility between the two treatments as a result of transition to an alkaline region was close.

DISCUSSION

In this report, we measured the zeta potentials and calculated the pI of titania particles after processing the titania particles by UV-irradiation or cold-plasma O₂ treatment for the purpose of clarifying the surface properties of titania particles.

As shown in Figure 3, a clear shift in the pI by UV irradiation or cold-plasma O₂ treatment was observed in comparison with unmodified titania particles, indicating that these surface

modifications were allowed to turn a negative charge of the unmodified titania into a positive charge at neutral pH. The possible mechanism of causing a positive charge on the surface might be due to the increase in terminal hydroxyl radicals on the titania surfaces by cold-plasma O₂ treatment¹⁰. Likewise, Murakami et al. proposed that hydroxylation of titania by cold-plasma O₂ exposure is similar to that of titania by UV irradiation¹¹.

Describing the clinical aspects, generation of positive charge on the titania surface facilitates to adsorb to cellular adhesive proteins, such as fibronectin for example, which normally charged negatively *in vivo*. Subsequent to the direct adsorption of proteins to titania surface, it takes advantage of the cell adhesion. In clinical application, in the field of regenerative medicine using a tissue engineering, it is important to process physicochemical modification such as wettability and electric charge on the titanium scaffolds.

In conclusion, the results of the present study demonstrate that physicochemical modification of anatase-form titania such as by exposure to UV irradiation or cold-plasma O₂ treatment yields a shift in zeta potential, and that, as a result, the pI shifts toward the basic side. This indicates that the adsorption or desorption of specific molecules on titania surfaces could be controlled by physicochemical modification. Further investigation is needed, however, to clarify these properties in dental implant materials.

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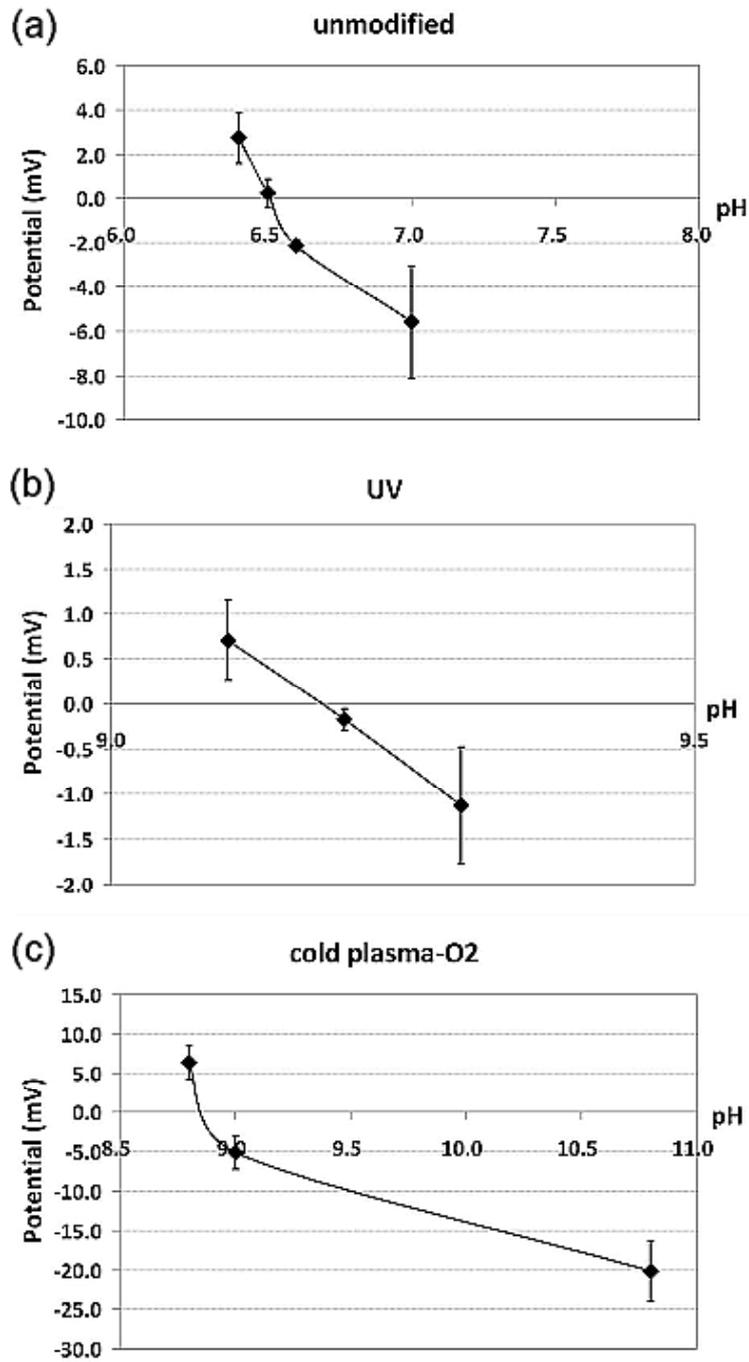


Figure 3. Zeta potential around pI of anatase-form titania particles: unmodified (a), UV-irradiated (b), and cold-plasma O₂ treated (c). Values are expressed as mean of 3 or 4 experiments. Standard deviations are shown in the bar.

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