

## Letter

# Generation of titanium oxide clusters of relatively large size

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### Abstract

In this letter we report the generation of titanium oxide clusters by direct laser vaporization of compound samples. Mainly  $[\text{TiO}(\text{TiO}_2)_{n-1}]^+$  and  $(\text{TiO}_2)_n^+$  cluster ions are generated in a relatively large size range with  $n = 1-50$ , and these two cluster series are presumably the most stable Ti/O cluster ions. No prominent magic numbers are found in this size range, although  $[\text{TiO}(\text{TiO}_2)_{14}]^+$  and  $[\text{TiO}(\text{TiO}_2)_{16}]^+$  are slightly protrudent steadily. The composition and the abundance distribution reveal that the clusters are formed through gas-phase recombination with a building block of  $(\text{TiO}_2)$ . (Int J Mass Spectrom 177 (1998) L1–L4) © 1998 Elsevier Science B.V.

*Keywords:* Cluster; Titanium oxide; Direct laser vaporization; TOF mass spectrometer

### 1. Introduction

Cluster science has been one of the most active research fields in recent years, which is rapidly deepening and widening. It is of great importance in both fundamental and practical aspects, and relates closely with many other disciplines such as atomic and molecular physics, condensed matter physics, chemistry, and material science. The metal oxide cluster, for example, is an important class of clusters due to its potential applications in the fields of material and catalysis. We have investigated extensively the generation of clusters [1–3] with direct laser vaporization (DLV) technique. In this

letter, we report the production of  $[\text{TiO}(\text{TiO}_2)_{n-1}]^+$  and  $(\text{TiO}_2)_n^+$  cluster ions with  $n = 1-50$  and present analysis on the basis of their relative abundance. Related study of titanium oxide clusters has been reported elsewhere [4–6], but has been limited to smaller size. However, in view of the transition of matter from atoms/molecules to condensed state, experimental study of the evolution of the structure and stability with the cluster size is one of the most important and fundamental aspects of the cluster research, which requires the presence of clusters in a relatively large size range to obtain an integrated analysis. Our results supply one answer to the basic questions as how to produce the clusters and which types can be produced, and they can also bring about information on the cluster structure. Another reason why the result attracts us is that structures of both the titanium

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oxide cluster and the corresponding bulk matter are much more complex, which are different from the most extensively studied clusters of the NaCl-type structure (see Ref. 7 and references therein). In view of that, titanium dioxide, especially in nanometer size, is one of the most technologically important oxide materials, the geometric [8] and electronic [9] structures of small titanium oxide clusters have also been studied theoretically and/or experimentally.

The DLV method employs only a single laser beam to accomplish the vaporization and ionization processes, and it utilizes no additional reaction gas, buffer gas, or carrier gas. Consequently the constituent elements in the product species all simply come from the laser target. We use chemical compounds as the laser target to produce metal oxide clusters and multiple element clusters. There is evidence that DLV can not only produce abundant cluster ions but also provide much information about the laser vaporization process [10, 11]. Small stable gaseous species existing in the laser-induced plasma were thought to play a role similar to buffer gases and facilitate the formation and stabilization of large clusters [10]. Both recombination and direct emission attribute to the production of the observed clusters [11].

## 2. Experimental

The experiments were carried out with a TOF mass spectrometer, which has been described in our previous papers [1,2]. The procedure is basically as follows. A focused YAG laser beam (532 or 355 nm, operated at 10 Hz, pulse width about 10 ns), which was perpendicular to the free flight direction of the ions, irradiated normally onto the sample surface with a spot of 1 mm in diameter, and the pulse energy is in the range of 20–100 mJ. The sample surface was vaporized into a plume in plasma state consisting of electrons and atoms, molecules and other small species, either neutral or charged. Complex reactions take place in the plasma, and cluster ions are formed therein. The plume on its own spreads into the first acceleration region, where the charged particles were pulsed out for identification by time-of-flight. In the present study, only the positive ions were detected. The target is fixed at a distance of 5 cm from the axis of the electrode plates, and neither translation nor rotation is exerted. The samples used in this study were chemi-

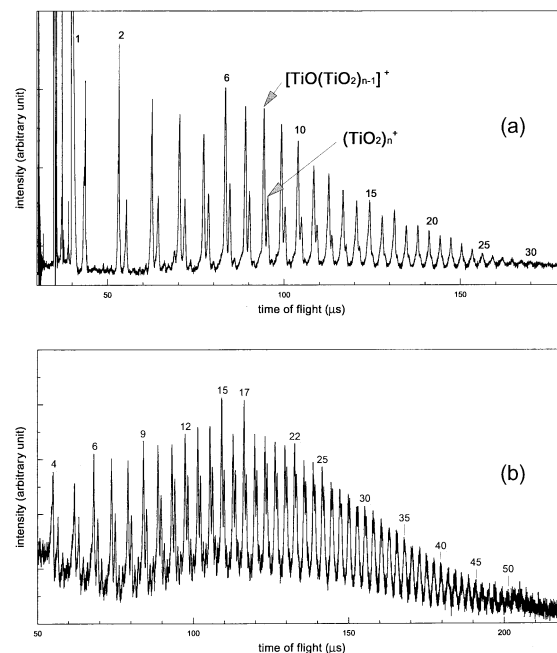


Fig. 1. TOF mass spectra obtained by direct laser vaporization of (a)  $\text{Ti}(\text{SO}_4)_2$  and (b)  $\text{TiO}_2$ . The spectra are similarly composed of two major cluster series  $[\text{TiO}(\text{TiO}_2)_{n-1}]^+$  and  $(\text{TiO}_2)_n^+$ , with the  $n$  values marked at the top of the peaks. The detecting conditions were optimized for large size for spectrum (b).

cal  $\text{TiO}_2$  and  $\text{Ti}(\text{SO}_4)_2$  from commercial sources. The chemical powder was pressed into pellet to form the laser target.

## 3. Results and discussion

Shown in Fig. 1 are two typical mass spectra acquired by laser ablation of  $\text{TiO}_2$  and  $\text{Ti}(\text{SO}_4)_2$  samples, respectively, and the detecting conditions were optimized for large size for spectrum (b). The mass spectra exhibit two main characteristics. One is the relatively large size, with the number  $n$  of constituent building blocks covering from 1–50, whereas the size reported in literature is generally smaller than  $n = 10$ . The intensity distribution is relatively flat through the range, in contrast with the exponential intensity decrease with increasing size for clusters produced by ion/atom beam sputtering [6]. The other point is that the spectra are regular and can be assigned clearly. They are composed of two major

cluster series,  $[\text{TiO}(\text{TiO}_2)_{n-1}]^+$  and  $(\text{TiO}_2)_n^+$ , with the former being more abundant. In each series, the mass spacing between two neighboring members is even and equals the mass of  $(\text{TiO}_2)$ . Obviously, the stoichiometry of these clusters is either the same as or close to that of the corresponding bulk matter. The distinct abundance in the large size range makes it available to obtain integral information of the formation and stability of the cluster ions on the basis of the abundance distribution. It is also declared that the present method could be useful as a cluster ion source for further study, for example, of size-selected cluster ions. The intensity distribution of the two series is obviously different from each other. The  $[\text{TiO}(\text{TiO}_2)_{n-2}]^+$  series is stronger and covers a wider size range. From the distribution characteristics [12], we can infer that the two classes of clusters each develop mainly within its own series by the stepwise attachment of  $(\text{TiO}_2)$ . So by the notation of  $[\text{TiO}(\text{TiO}_2)_{n-1}]^+$  and  $(\text{TiO}_2)_n^+$ , we think that  $(\text{TiO}_2)$  serves as the building block of the clusters. The following three facts concerning the  $\text{Ti}(\text{SO}_4)_2$  sample further manifest that the clusters are formed mainly through gas-phase growth processes. (i) No  $(\text{TiO}_2)_n$  units are contained in the sample; (ii) the product cluster does not contain S atoms; (iii) the mass spectra are generally similar to those produced by the  $\text{TiO}_2$  sample. Because clusters during formation are subjected to frequent collisions with various energetic species in the laser-induced plasma, which can lead them to associate and fragment, the finally observed cluster types are presumably the most stable ones.

The emergence of some magic numbers in a mass spectrum would be very useful for the analysis of the evolution of cluster structure and stability with the increasing cluster size. In the relatively large size range produced, however, our result shows that no prominent magic numbers appear. Nevertheless, there are two points worthy of mentioning. First, the peaks corresponding to  $n = 15$  and  $17$  are slightly protrudent steadily in the  $[\text{TiO}(\text{TiO}_2)_{n-1}]^+$  series. Because a certain stoichiometric structure consisting of many atoms generally corresponds to many local energy minimum isomers [6,8], it is probable that, for these special sizes, there is one (or more) of the isomers having special stability. Second, for clusters smaller than  $n = 6$ , the

relative intensity fluctuates obviously and depends heavily on the laser vaporization condition. On the contrary, for clusters larger than  $n = 6$ , the intensity varies gradually and follows a general tendency with increasing  $n$  value. This suggests that the cluster stability no longer varies strongly with the addition of a building block  $(\text{TiO}_2)$  once  $n$  surpasses 6, which appears as a critical point and is possibly the starting point of the tridimensional growth. It is interesting to think about the question whether these mass spectrometric features are typical for a rutile lattice structure system and to seek a satisfying explanation for them, but it must call for further experimental and theoretical studies and will not be included in this letter.

For small clusters, one could not expect their structures corresponding to the bulk matter. Freas et al. [6] have calculated the geometric structures of  $\text{Ti}_n\text{O}_{2n-\delta}$  clusters by ionic model and gave in Ref. 6 the results for  $n = 2-4$  and  $\delta = 0-2$ , which showed that each series with a certain  $\delta$  retains some structural similarities. In this cluster size, however, no regular pattern in the geometry development with the addition of a  $(\text{TiO}_2)$  unit emerges. Hagfeldt et al. [8] performed ab initio geometry optimization on  $\text{Ti}_n\text{O}_{2n-\delta}$  clusters with  $n = 1-3$  and  $\delta = 0, 1$ . According to their results, the lowest energy structures of  $(\text{TiO}_2)_2$ ,  $(\text{TiO}_2)_3$ , and  $\text{Ti}_2\text{O}_3$  are all planar. For  $(\text{TiO}_2)_3$ , the largest one, the largest coordination numbers of Ti and O are 4 and 2, respectively, within a planar structure, whereas in solid rutile  $(\text{TiO}_2)$  structure the coordination numbers are 6 and 3, respectively. We surmise that the largest coordination numbers in  $[\text{TiO}(\text{TiO}_2)_{n-1}]^+$  and  $(\text{TiO}_2)_n^+$  clusters reach those in solid rutile once the cluster size surpasses  $n = 6$ .

We have also studied the effect of the delay time (between the acceleration electric pulse and the laser pulse) and the laser intensity on the mass spectrum. With a longer delay, the relative intensity of  $(\text{TiO}_2)_n^+$  cluster series is increased. It is a general phenomenon that the relative intensity of a series with a higher oxygen/metal ratio increases with moderately increasing delay time [3]. Many others [13-15] have already mentioned the strong effect of the laser intensity on the mass spectra and it has also been observed in the present study. But the condition is not critical for producing mass spectra composed of the two major series. It can be realized in a range of laser intensity (30-80 mJ/pulse).

It is intriguing to compare the present results with those of Freas et al. [6] and Castleman et al. [4, 5], which shows that the types of clusters are affected strongly by the production method. By using an energetic xenon atom beam, Freas et al. produced mainly  $[\text{Ti}_n\text{O}_{2n-\delta}]^+$  (the  $\delta$ 's in the following text have the same meaning as in this notation), where  $n$  equals 1–8 and  $\delta$  ranges from 0 to 4, whereas sputtering titanium foil in a high-pressure fast-atom bombardment (HPFAB) ion source with  $\text{O}_2$  produced  $[\text{Ti}_n\text{O}_{2n-1}]^+$  as the only abundant cluster species, which were also the predominant product from reactions of the  $[\text{Ti}_n\text{O}_{2n-\delta}]^+$  ( $\delta = 2-4$ ) ions with  $\text{O}_2$ . Studies of Castleman et al. [5] on the reaction with oxygen of size-selected titanium oxide cluster cations indicate that the inert clusters belong to  $(\text{TiO}_2)_n^+$  ( $n \geq 3$ ) and  $[\text{TiO}_3(\text{TiO}_2)_n]^+$  ( $n \geq 1$ ) (i.e.  $\delta = 0, -1$ ). Castleman et al. [5] have also studied the formation of titanium oxide clusters in a laser-induced plasma source (24-Torr water, 60-psi He, titanium rod), which produced clusters in the form  $[(\text{TiO})_n(\text{TiO}_2)_m]^+$  ( $m + n$  equals 1 to 13 and  $n$  equals typically 0 to 5 (i.e.  $\delta = 0$  to 5), among which the  $n = 1$  series is obviously the strongest. In the present study, we detected cluster ions formed directly in the plasma produced by laser vaporization of the  $\text{TiO}_2/\text{Ti}(\text{SO}_4)_2$  sample. It is interesting that our result is distinct from both of the previous ones [4,6] and is just in between. The  $[\text{TiO}(\text{TiO}_2)_{n-1}]^+$  (i.e.  $\delta = 1$ ) series is predominant with the  $(\text{TiO}_2)_n^+$  (i.e.  $\delta = 0$ ) series also processing a comparative abundance. In sum, it is common that  $[\text{TiO}(\text{TiO}_2)_{n-1}]^+$  series is predominant. This is attributed to the low ionization energy of  $\text{TiO}(\text{TiO}_2)_{n-1}$  than  $(\text{TiO}_2)_n$  and the easy fragments of  $(\text{TiO}_2)_n^+$  to  $[\text{TiO}(\text{TiO}_2)_{n-1}]^+$  [8]. It can also be explained by considering the most stable oxidation states of the elements. With stoichiometry  $[\text{TiO}(\text{TiO}_2)_{n-1}]^+$  (i.e.  $\delta = 1$ ), all atoms are in their most stable oxidation states except one Ti atom in its second most stable oxidation state (all atoms in most stable oxidation states would make a doubly charged cluster). Obviously, the elements are near their most stable oxidation states for series with  $\delta = 0$ , and are less near for series with  $\delta = -1, 2, 3$ , etc. The significant differences, of course, come from the different experimental conditions. Comparison reveals that whether there is enough oxygen in

the formation atmosphere is essential for determining which types of Ti/O clusters are generated.

## Conclusions

In summary, we produced the titanium oxide clusters of relatively large size by direct laser vaporization. The stoichiometry of the clusters is similar to that of the corresponding bulk matter, which indicates that the composition of the clusters is principally determined by the most stable oxidation states of the constituent elements. No prominent magic numbers were found in the mass spectra in the range of  $n = 1-50$ , while the  $[\text{TiO}(\text{TiO}_2)_{n-1}]^+$  clusters with  $n = 15$  and 17 appear with slightly protrudent relative abundance. The size  $n = 6$  seems to be the starting point of the tridimensional growth.

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