

Supplementary:

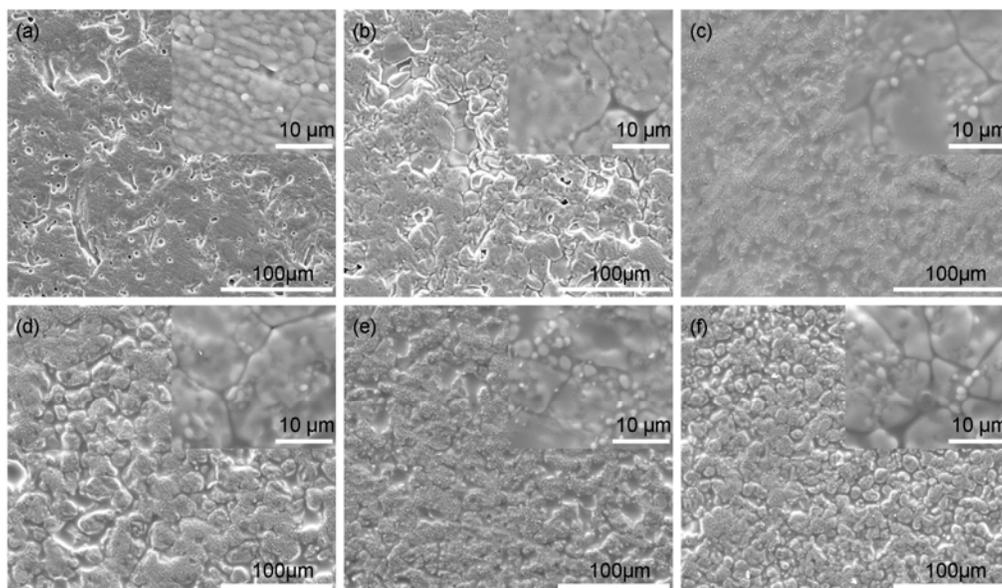


Fig.s1 SEM image for the TINO and SiO₂-TINO composite ceramics sintered at 1500°C for 10 h. The inset pictures were the enlarged view to each image.

It was obvious that the ceramics with low porosity were obtained at relative high doping concentration (>2 mol%). From the inset-enlarged view, the small globular particles were observed among the grain boundaries, which were certified to be SiO₂ by the following elemental distribution analysis. It is known that the doping ions may change the main phase structure and lattice parameters.

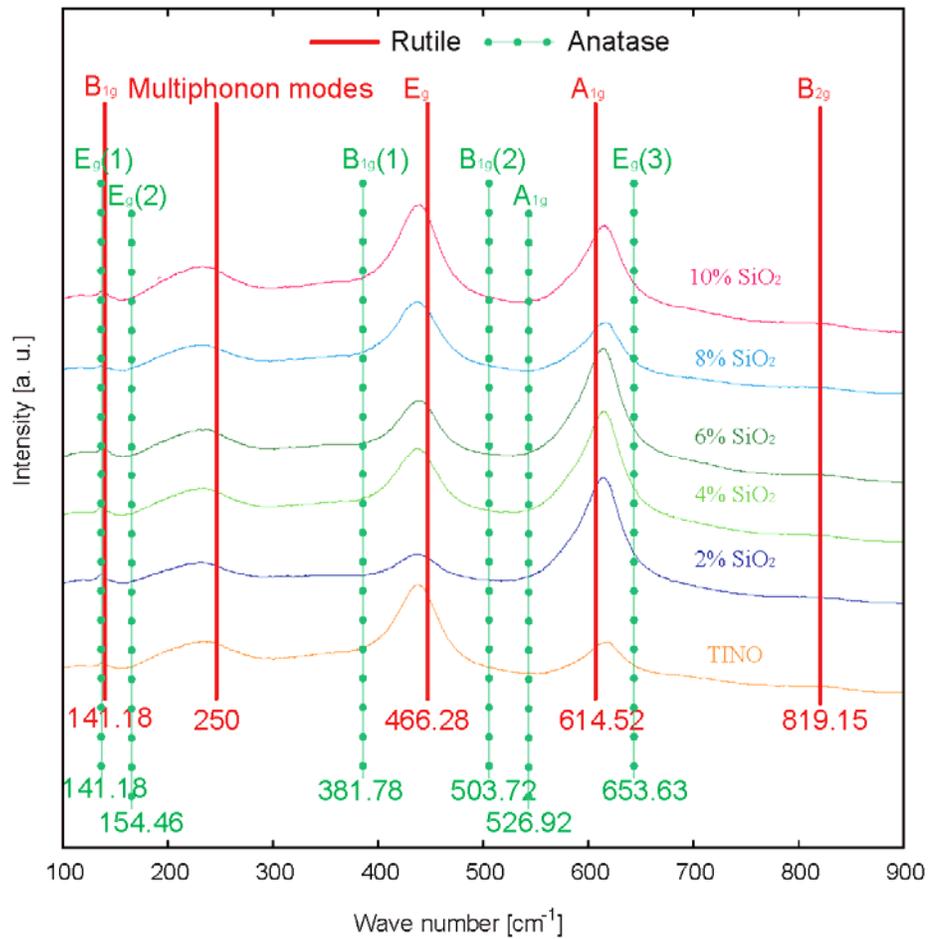


Fig.s2 Raman spectrum for TINO and SiO₂-TINO composite ceramics obtained in the range of 100-1000 cm⁻¹.

There were four Raman active fundamental modes in rutile TiO₂ compared with anatase structure : B_{1g} (143 cm⁻¹), E_g (447 cm⁻¹), A_{1g} (613 cm⁻¹), and B_{2g} (819 cm⁻¹).¹ The 143 cm⁻¹ (B_{1g}) Raman peak was an O-Ti-O bond bending mode, the 613 cm⁻¹(A_{1g}) relates to Ti-O stretch mode while the 447 cm⁻¹ (E_g) mode was due to oxygen atom liberation along the c-axis out of phase.² The peak around 250 cm⁻¹ was multi-phonon peak, which was thought to be associated with second-order Raman scattering in the rutile structure.³

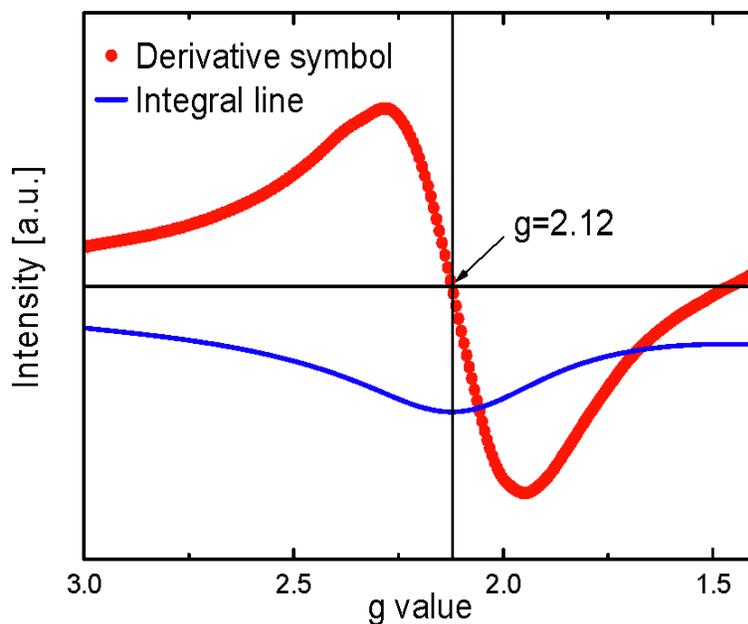


Fig.S3 ESR curves (red solid circle line) and corresponding fittings (blue lines) measured at room temperature. The red solid circle and the blue line were the derivative symbol and the integral line, respectively.

Fig. S3 showed the ESR curve (red solid circle line) and corresponding integral curve (blue lines) for 2 mol% SiO₂-TiNO sample, where ESR centred at $g=2.12$. The g value of 2.12 indicated the existence of lone pair electrons in ceramics. Mozzati, et al⁴ and Pires, et al⁵ reported the ESR value $g=2.15$ in CCTO and CdCu₃Ti₄O₁₂ material system, which is higher than that of our material system. Ceresa⁶ studied on TiO₂ pigments and found ESR value $g=2.006$, which is lower than that of our material system. Nakaoka, et al⁷ investigated the effects of heat treatment over TiO₂ powder and found the g value vary from 1.99 to 2.06. Based on the previous experience, the $g=2.12$ in this experiment could be assigned to paramagnetic resonances of Ti³⁺ with 3d¹ electrons trapped on the lattice⁸.

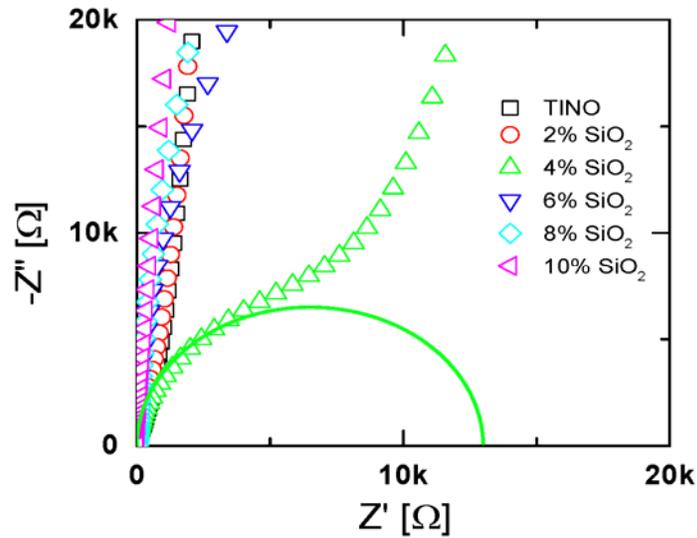


Fig.s4 Impedance analysis of various doping concentration measured at room temperature in the high frequency range. The solid symbols were the experimental results. The solid lines corresponding to each solid symbol were the best fitting results according to Eq. (1) and (2) in the paper.

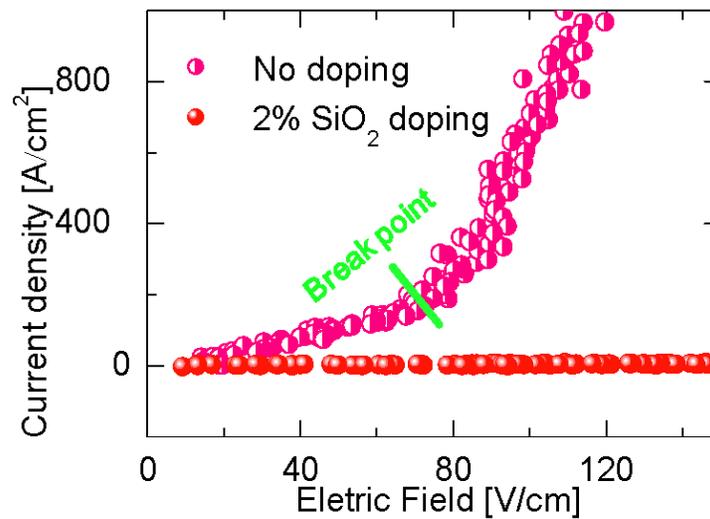


Fig. s5 The enlarged view of the Fig. 9a at low electric field

The green solid line in Fig. s5 indicated the change of resistance, which was thought to be the break point of sample. It was clearly that the TINO ceramic have much lower break down voltage than that of SiO₂-TINO ceramic.

References:

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