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Supplementary information for: Fabrication of nanocrystalline λ-Ti_3O_5 with tunable terahertz wave transmission properties across a temperature induced phase transition

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Description of a heating cell used in the THz time domain spectroscopy (THz-TDS) system

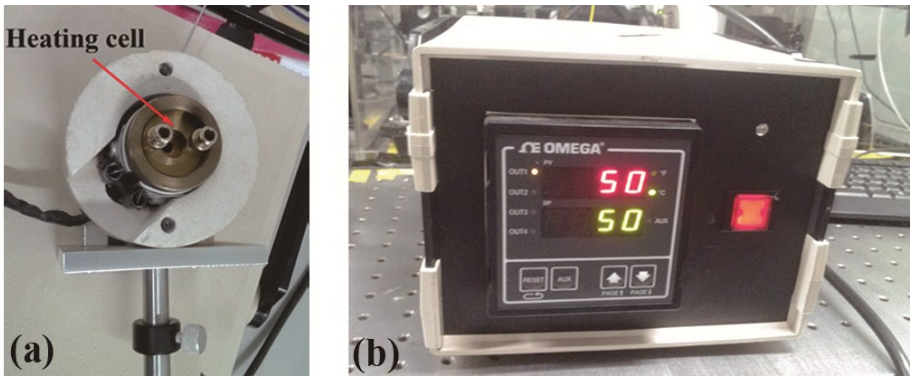

Fig. S1 A designed heating cell incorporated in the THz time-domain spectroscopy system: (a) sample holder with heating stage, and (b) temperature controller.

The THz transmission characteristics of the λ-Ti_3O_5 during the temperature induced phase transition was investigated using a THz time domain spectroscopy (THz-TDS) system. A heating cell was employed to realize the temperature controlling. It is comprised of a sample holder with heating stage (Fig. S1(a)) and a temperature controller (Fig. S1(b))

Morphology of the raw material of nano-TiO_2 powder

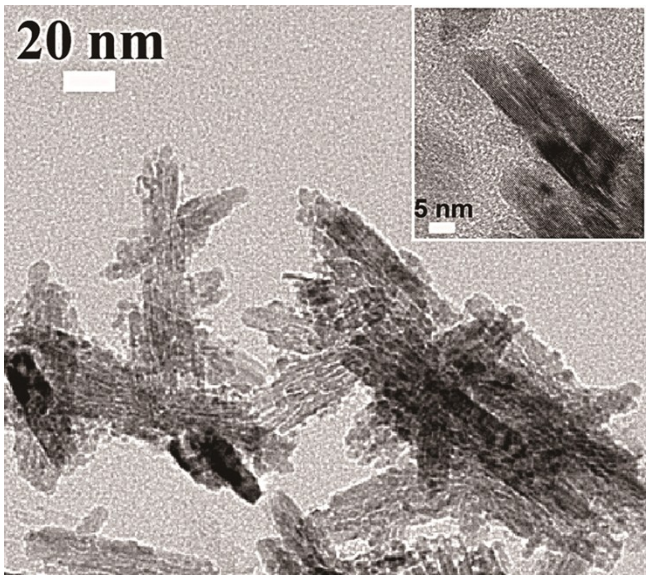

Fig. S2 TEM morphology of the unmodified nano-TiO_2. Inset: HRTEM morphology of the TiO_2.

XRD profiles of the titanium oxides annealed from unmodified nano-TiO_2 at different temperatures

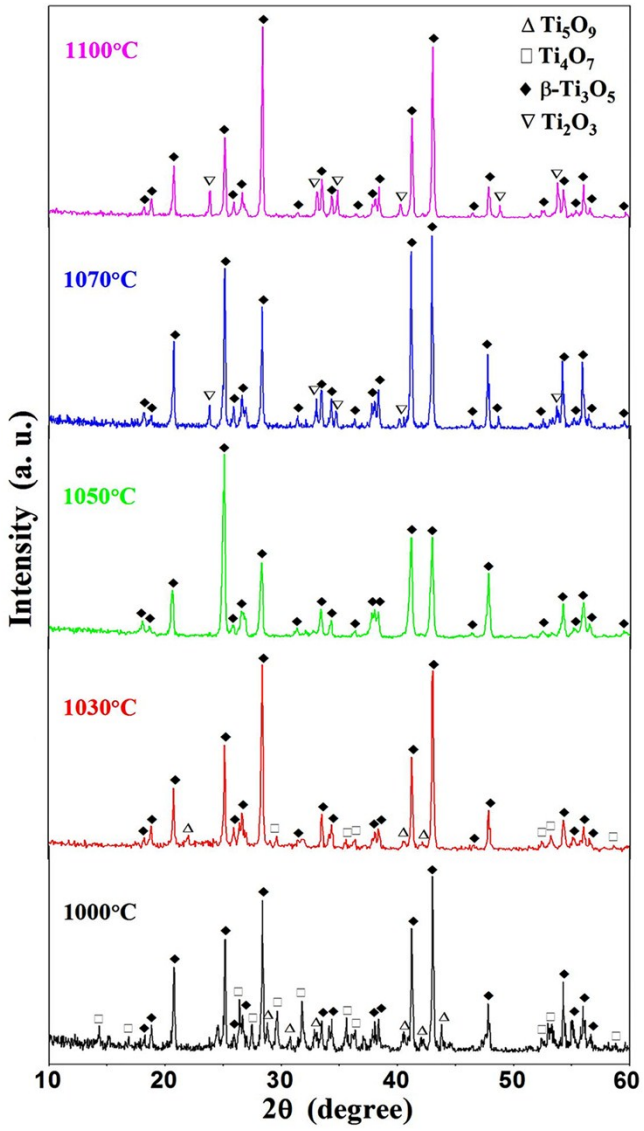

Fig. S3 XRD profiles of the samples annealed from unmodified nano-TiO_2 at temperature ranging from 1000 °C to 1100 °C.

Morphology of the β-Ti_3O_5 obtained by carbothermal reduction of nano-TiO_2 at annealing temperature of 1050 °C

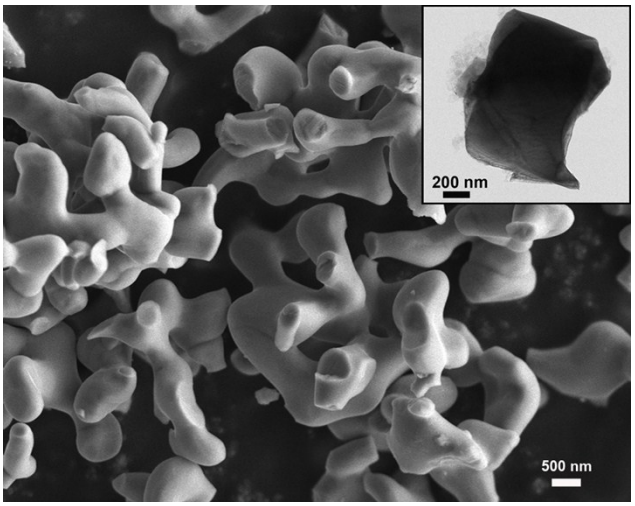

Fig. S4 FE-SEM and TEM (inset) morphology of the β-Ti_3O_5.

Change of resistance for the λ-Ti_3O_5 during the temperature induced phase transition

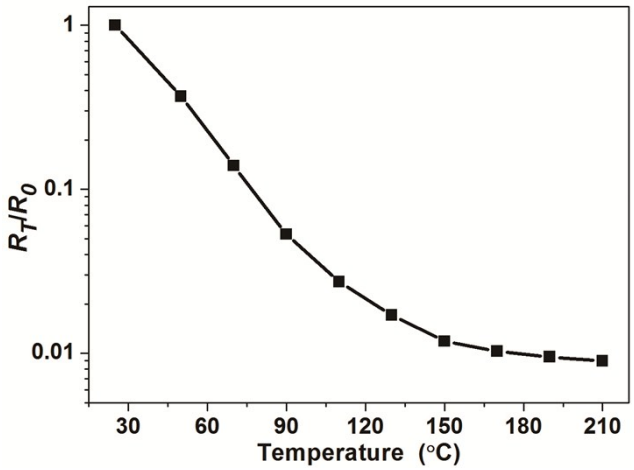

Fig. S5 R/R_0 versus temperature for the λ-Ti_3O_5 in the temperature ranging from 25 °C to 210 °C

The λ-Ti_3O_5 powder was pressed at 200 MPa for 5 minutes to form a compact disk with diameter of 12 mm and thickness of 3 mm. Then the resistance of the sample was measured using the conventional four-point probe method, combined with an electrically heated substrate

holder. R/R_0 was recorded to determine the change of resistance during the temperature induced phase transition, where R_0 represents the resistance of the sample at room temperature (25 °C) and R_T represents the measured resistance upon heating. Fig. S5 shows that the R/R_0 decreases continuously in the temperature ranging from 25 °C to 210 °C. It corresponds to the λ-Ti_3O_5 to α-Ti_3O_5 transition. And it indicates that the resistance of the λ-Ti_3O_5 decreased around two orders of magnitude during this phase transition.

Normalized THz frequency-domain spectra of the hybrid material containing λ-Ti_3O_5 upon heating and cooling

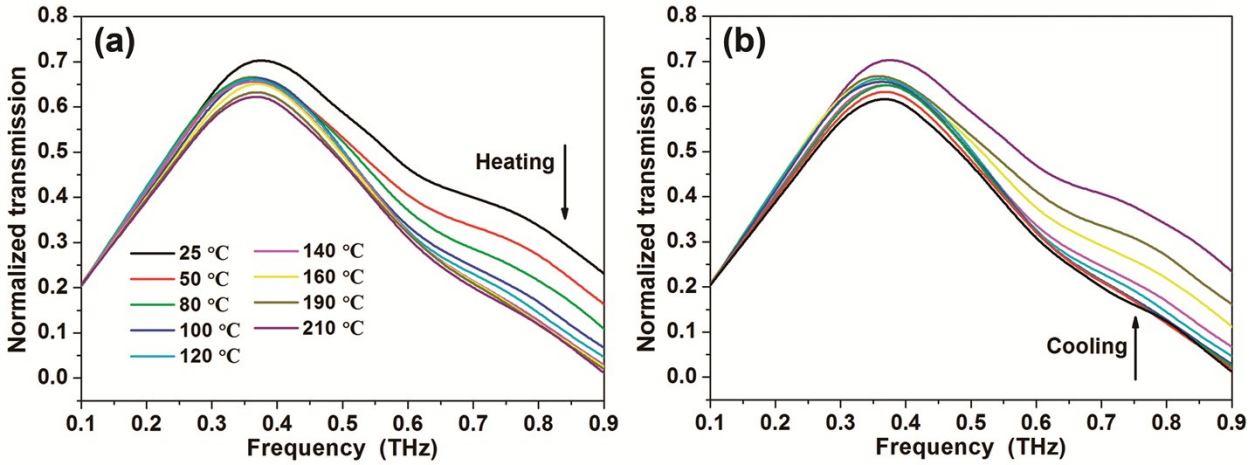

Fig. S6 Normalized THz frequency-domain transmission spectra of the sample (a) heating from 25 °C to 210 °C and (b) cooling from 210 °C to 25 °C.

The THz frequency-domain spectra of the sample were obtained from fast Fourier transforming time-domain signals. And the transmission amplitude was normalized by comparing the THz transmission of the sample to the air. As shown in Fig. S6(a), the THz transmission amplitude decreases gradually during the heating process, corresponding to a temperature induced phase transition from λ-Ti_3O_5 to α-Ti_3O_5. And Fig. S6(b) shows that the THz transmission amplitude increases and recovers to the initial state during the cooling process, which corresponds to the phase recovery from α-Ti_3O_5 to λ-Ti_3O_5.

Temperature induced phase transition characteristic of λ-Ti_3O_5 studied using Differential scanning calorimetry (DSC)

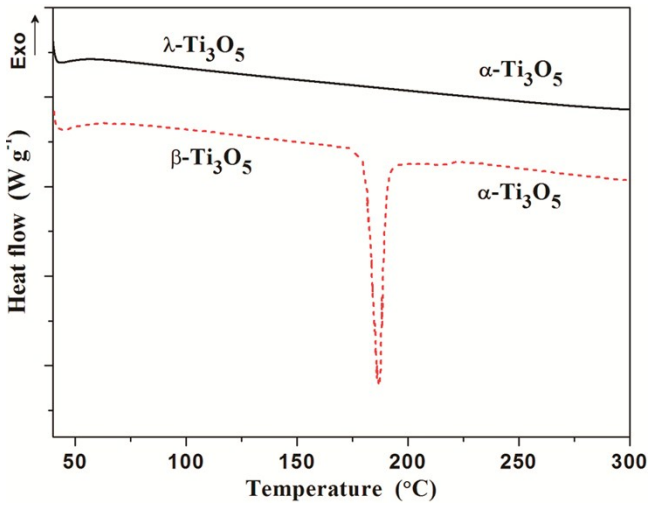

Fig. S7 DSC curves of the λ-Ti_3O_5 and β-Ti_3O_5 with increasing temperature.

As shown in Fig. S7, DSC curve of the β-Ti_3O_5 with increasing temperature exhibits an obvious exothermal peak. It has been demonstrated that this exothermal peak corresponded to the first-order phase transition from β-Ti_3O_5 to α-Ti_3O_5.[1] By contrast, there is not any exothermal peak emerged for the λ-Ti_3O_5 with increasing temperature. Our results are consistent with precious report. It was proposed that the temperature induced phase transition from λ-Ti_3O_5 to α-Ti_3O_5 was a typical second-order phase transition.

REFERENCES

(1) Ohkoshi, S.; Tsunobuchi, Y.; Matsuda, T.; Hashimoto, K.; Namai, A.; Hakoe, F.; Tokoro, H. Synthesis of a metal oxide with a room-temperature photoreversible phase transition. *Nat. Chem.* **2010**, *2*, 539-545.