

TiO₂ compact layer induced charge transfer enhancement in three-dimensional TiO₂-Ag array SERS substrate for quantitative and multiplex analysis

Zhuang Ding,^a Yaru Wang,^a Wanpeng Zhou,^a Yanna Shui,^a Zhengdong Zhu,^a Maofeng Zhang,
*^a Youju Huang,^{*c} Changlong Jiang,^{*d} Jianhua Li,^e Yucheng Wu^b

^a School of Chemistry and Chemical Engineering, Hefei University of Technology, 193 Tunxi Road, Hefei, 230009, China

^b School of Materials Science and Engineering, Hefei University of Technology, 193 Tunxi Road, Hefei, 230009, China

^c College of Materials, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 311121, China

^d Institute of Solid State Physics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, Anhui, 230031, China

^e Anhui Topway Testing Services Co. Ltd., 18 Rixin Road, Xuancheng Economic and Technological Development Zone, 242000, China

*Corresponding Authors E-mail: mfzhang@hfut.edu.cn , yjhuang@hznu.edu.cn, cljiang@iim.ac.c

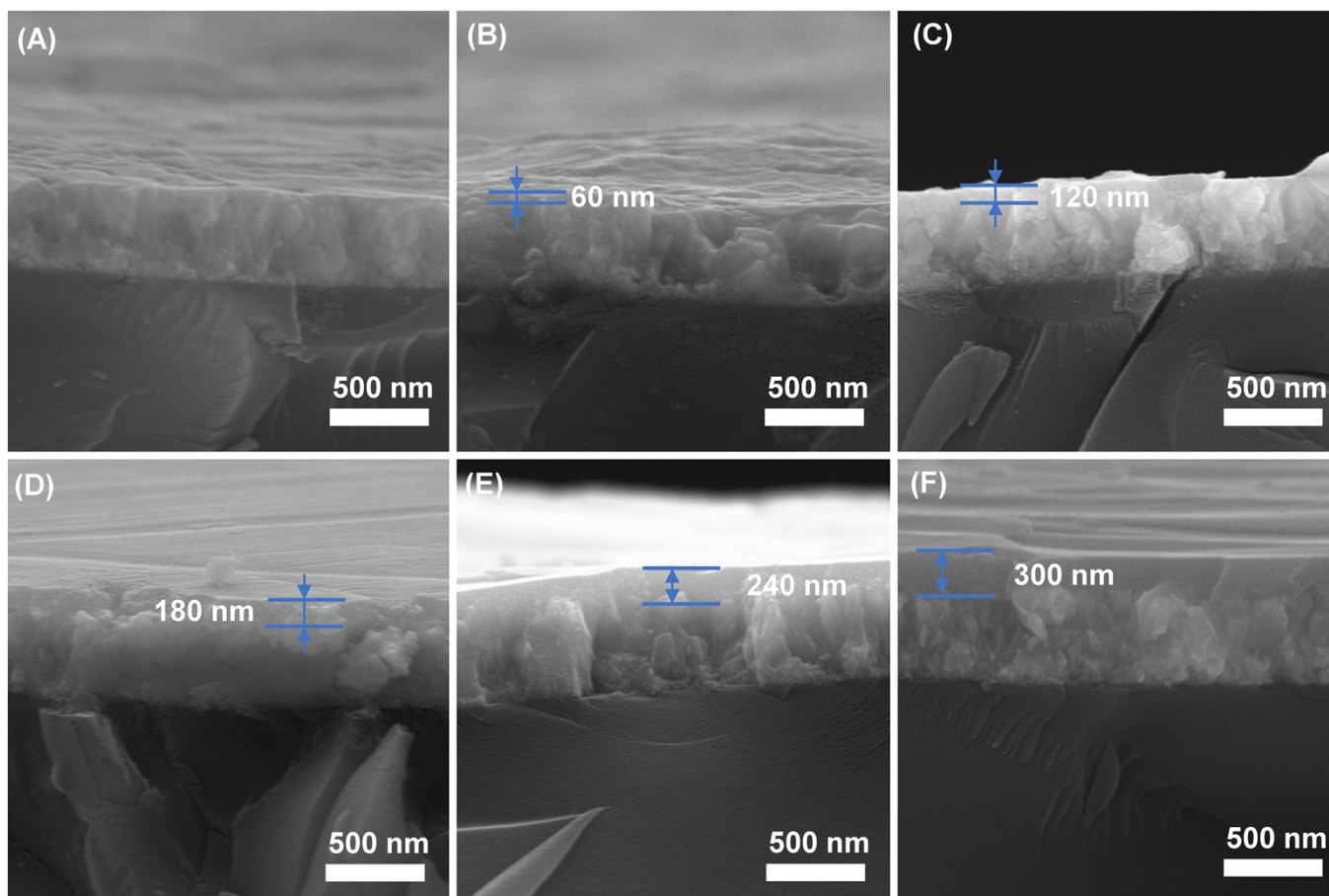


Figure S1. Cross-sectional SEM images of (A) FTO substrate, TiO₂ compact layers prepared by different spin-coating cycles (B) once, (C) twice, (D) 3 times, (E) 4 times, (F) 5 times.

Estimation method of TiO₂ compact layer thickness

Since there is no obvious boundary between the TiO₂ compact layer and the SnO₂ coating of FTO, we estimated the thickness of the dense layer by comparing with the surface of FTO. For example, Figure S1A shows the thickness of SnO₂ coating, and Figure S1B shows the sum of the thickness of SnO₂ coating and TiO₂ compact layer by once of spin-coating. The thickness of TiO₂ compact layer can be obtained by the difference. The data of TiO₂ compact layer thickness in the figure is the approximate value obtained by comparison.

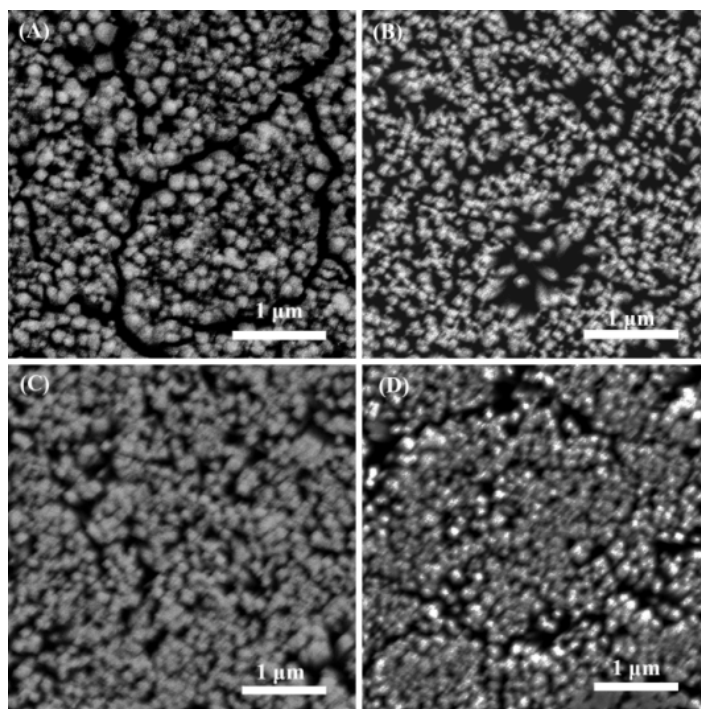


Figure S2. Images of TiO_2 nanorod arrays grown under (A) 17.5 mL deionized water, 12.5 mL hydrochloric acid and 388 μL tetra-butyl titanate at 150°C for 5h; (B) 15 mL deionized water, 15 mL hydrochloric acid and 388 μL tetra-butyl titanate at 150°C for 5h; (C) 15 mL deionized water, 15 mL hydrochloric acid and 388 μL tetrabutyl titanate at 150°C for 7.5h; (D) 15 mL deionized water, 15 mL hydrochloric acid and 388 μL tetrabutyl titanate at 150°C for 10h.

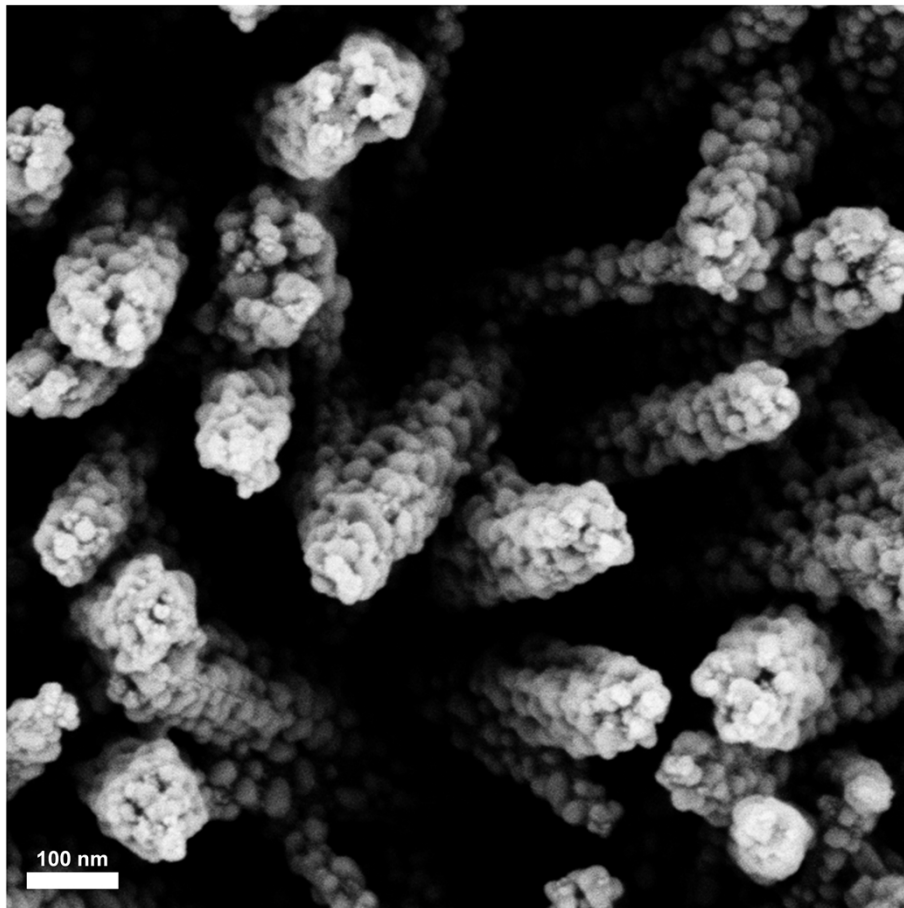


Figure S3. The locally enlarged view of the TiO₂-Ag composite structure.

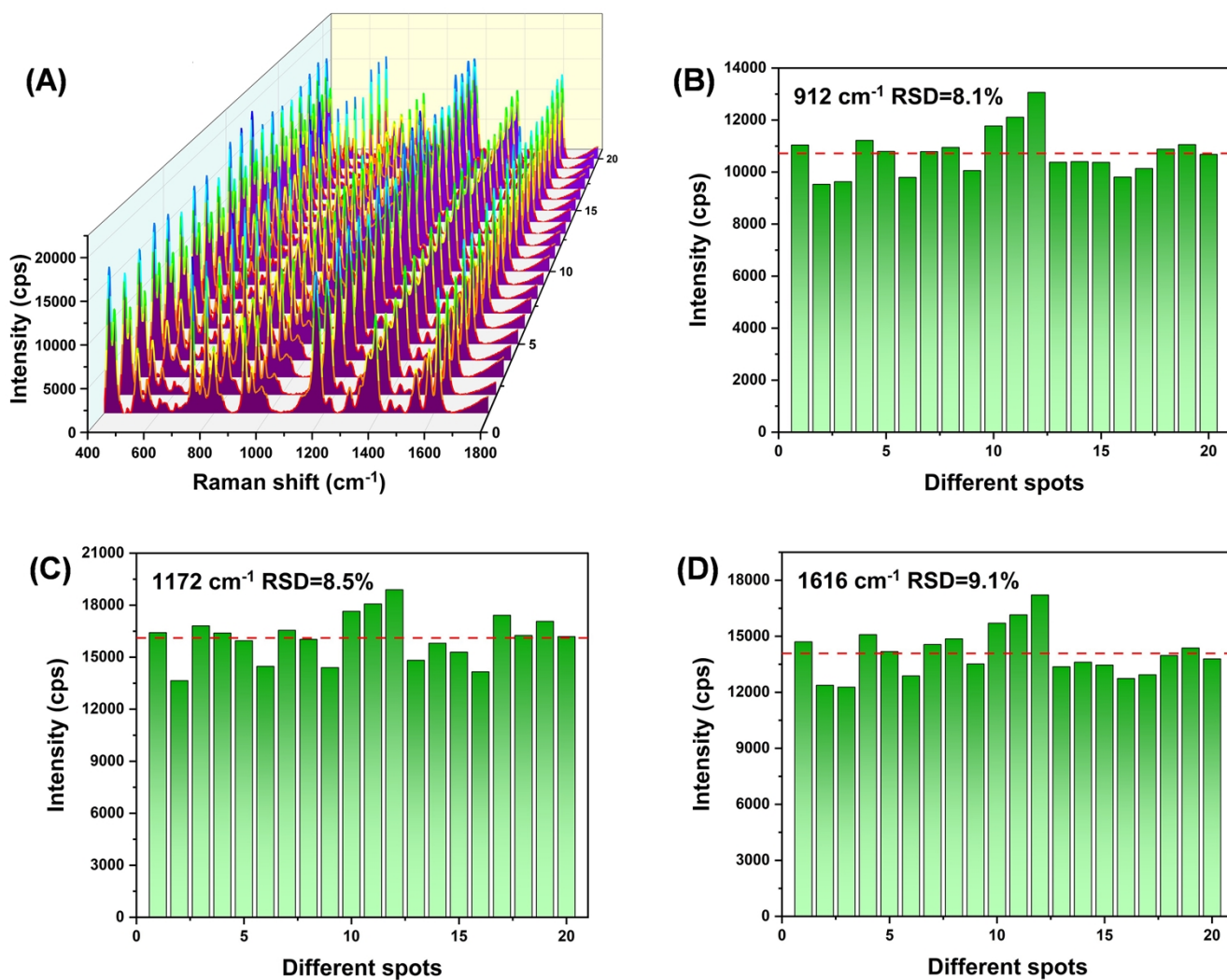


Figure S4. (A) SERS spectra of CV (10^{-6} M) at 20 different points on $\text{TiO}_2\text{-Ag}$ composite structure; the RSD values of different peaks (B) 912 cm^{-1} , (C) 1172 cm^{-1} and (D) 1619 cm^{-1}

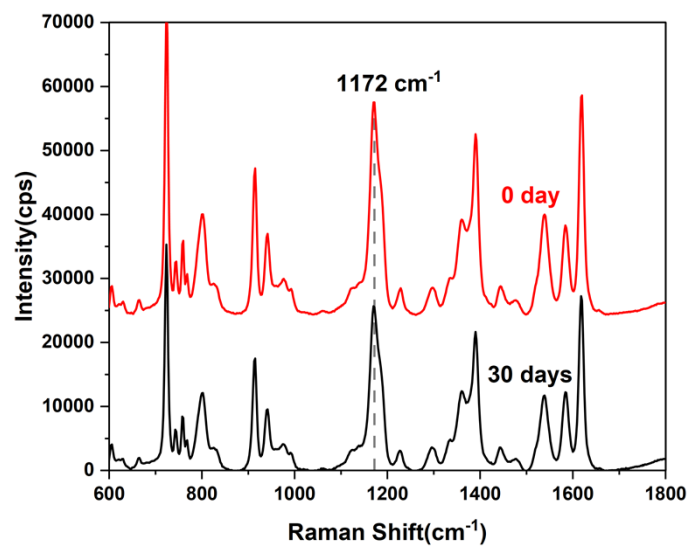


Figure S5. SERS spectra of newly prepared substrate and that stored for 30 days.

Calculation of SERS enhancement factor (EF)

To quantify the enhancement contribution from TiO₂-Ag composite structure and TiO₂ compact layer, we calculated their enhancement factor (EF) based on the following formula:

$$EF = (I_{\text{SERS}} / I_{\text{BULK}}) \times (N_{\text{BULK}} / N_{\text{SERS}})$$

where I_{SERS} and I_{BULK} represent the intensities of SERS and normal Raman scattering, whereas N_{SERS} and N_{BULK} , respectively, denote the numbers of corresponding CV molecules effectively excited by a laser beam. According to the above formula, the EF for the TiO₂-Ag composite structure without TiO₂ compact layer is calculated to be 2.70×10^4 . The EF is calculated to be 4.02×10^5 for the TiO₂-Ag composite structure. As a result, the EF for the TiO₂-Ag composite structure shows a 10-fold enhancement compared to the composite structure without TiO₂ compact layer.

$$N_{\text{BULK}} = (\text{Laser spot area} / \text{Diffusion area}) \times (N_A \times \text{Volume}_{\text{BULK}} \times \text{Concentration}_{\text{BULK}})$$

$$N_{\text{SERS}} = (\text{Laser spot area} / \text{Substrate area}) \times (N_A \times \text{Volume}_{\text{SERS}} \times \text{Concentration}_{\text{SERS}})$$

$$\text{Diffusion area} = \pi(d/2)^2 = 0.5027 \text{ cm}^2$$

$$\text{Substrate area} = 0.25 \text{ cm}^2$$

$$\text{Volume}_{\text{BULK}} = \text{Volume}_{\text{SERS}}$$

$$\text{Concentration}_{\text{BULK}} = 10^5 \times \text{Concentration}_{\text{SERS}}$$

$$N_{\text{BULK}} / N_{\text{SERS}} = (0.25 / 0.5027) \times 10^4 = 5 \times 10^3$$

I = intensity of the 1172 cm⁻¹ peak

$$I_{\text{BULK}} = 14989$$

$$I_{\text{SERS, TiO}_2/\text{Ag}} = 80855$$

$$I_{\text{SERS, TiO}_2/\text{Ag}} / I_{\text{BULK}} = 5.39$$

$$EF_{\text{TiO}_2/\text{Ag}} = (I_{\text{SERS}} / I_{\text{BULK}}) \times (N_{\text{BULK}} / N_{\text{SERS}}) = 2.70 \times 10^4$$

$$I_{\text{SERS, c-TiO}_2/\text{TiO}_2/\text{Ag}} = 847235$$

$$I_{\text{SERS, c-TiO}_2/\text{TiO}_2/\text{Ag}} / I_{\text{BULK}} = 56.52$$

$$EF_{\text{c-TiO}_2/\text{TiO}_2/\text{Ag}} = (I_{\text{SERS}} / I_{\text{BULK}}) \times (N_{\text{BULK}} / N_{\text{SERS}}) = 2.83 \times 10^5$$

$$EF_{\text{c-TiO}_2/\text{TiO}_2/\text{Ag}} / EF_{\text{TiO}_2/\text{Ag}} = 2.83 \times 10^5 / 2.70 \times 10^4 = 10.48$$

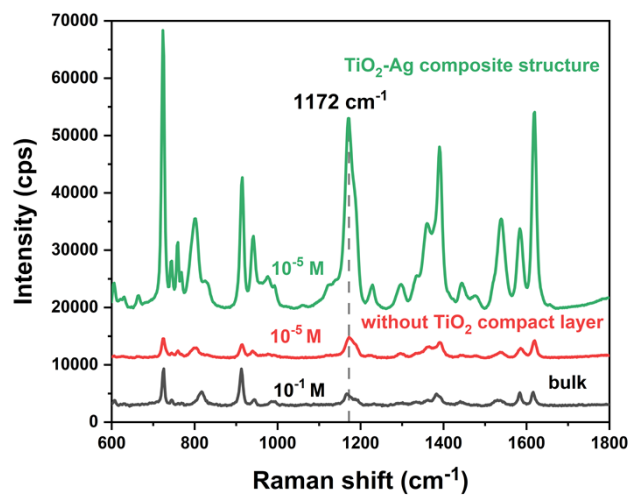


Figure S6. Raman spectrum of CV solution and SERS spectra of CV absorbed on TiO₂-Ag composite structure with or without TiO₂ compact layer