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## Improving surface-enhanced Raman scattering properties of TiO<sub>2</sub> nanoparticles by metal Co doping

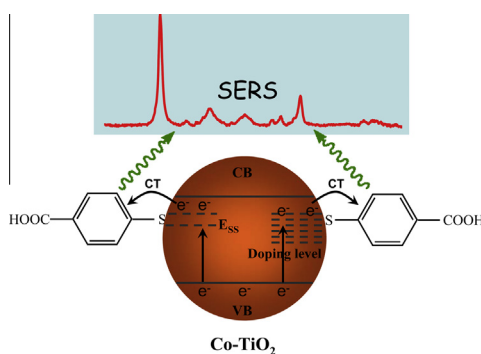
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### HIGHLIGHTS

- Co doped TiO<sub>2</sub> nanoparticles were synthesized and served as SERS-active substrate.
- Co<sup>2+</sup> ions doping can remarkably improve the SERS properties of TiO<sub>2</sub> nanoparticles.
- Abundant metal doping energy levels can be formed in TiO<sub>2</sub> energy gap by Co doping.
- Doping levels promote TiO<sub>2</sub>-to-molecule CT and additional SERS of adsorbed molecules.

### GRAPHICAL ABSTRACT



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### ABSTRACT

In this paper, pure and different amount Co ions doped TiO<sub>2</sub> nanoparticles were synthesized by a sol-hydrothermal method and were served as SERS-active substrate. The effect of metal Co doping on SERS properties of TiO<sub>2</sub> nanoparticles was mostly investigated. The results indicate that abundant metal doping energy levels can be formed in the energy gap of TiO<sub>2</sub> by an appropriate amount Co ions doping, which can promote the charge transfer from TiO<sub>2</sub> to molecule, and subsequently enhance SERS signal of adsorbed molecule on TiO<sub>2</sub> substrate, and improve remarkably SERS properties of TiO<sub>2</sub> nanoparticles.

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### Introduction

In the past 40 years, surface-enhanced Raman scattering (SERS) has attracted considerable attention not only in spectroscopy field but also in material field due to its broad application prospects. Researches on preparation of new style SERS-active substrate and enhancement mechanism of SERS have been hot themes.

At present, SERS-active substrate material has been extended into semiconductor material field (Fe<sub>2</sub>O<sub>3</sub>, Cu<sub>2</sub>O, TiO<sub>2</sub>, ZnO, ZnS, CdTe, etc.) [1–6], which previously has been restricted to studies

on noble metals (Ag, Au, Cu) and the transition metals (Pt, Pd, Ru, Rh, Fe, Co and Ni) [7–11]. Especially, SERS research on wide band gap semiconductor has attracted increasing attention recently [3–5,12–15], this is not only because the wide band gap semiconductor materials have a very wide application prospect in many fields such as environmental cleanup, photocatalysis, and solar cells, but also because the high sensitivity and resolution of SERS make it ideal for extracting detailed information as to the nature of molecular interaction with semiconductor particles. This extracted information is very important for further understanding the photochemical and photophysical phenomena on the surface of semiconductor material and optimizing the performance of the materials. In recent years, our group has been concentrating on

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the semiconductor-based SERS research; we have successfully detected strong SERS signals of adsorbed molecules on some semiconductor substrate materials (such as  $\text{TiO}_2$ , ZnO, ZnS,  $\text{Pb}_3\text{O}_4$ , CuO and CdTe). In particular for the wide band gap semiconductor nanoparticles (NPs) substrates ( $\text{TiO}_2$  and ZnO), we firstly proposed a semiconductor ( $\text{TiO}_2$ )-to-molecule charge-transfer (CT) mechanism for explaining the extraordinarily large SERS enhancement of the molecules adsorbed on  $\text{TiO}_2$  NPs substrate [3]. The charge transfer mechanism is related to the surface state energy level ( $E_{\text{SS}}$ ) of  $\text{TiO}_2$  NPs, which serves as a necessary intermediate state in the process of  $\text{TiO}_2$ -to-molecule charge transfer, the abundant and various surface states of  $\text{TiO}_2$  NPs are favorable to  $\text{TiO}_2$ -to-molecule CT and SERS for the molecules adsorbed on  $\text{TiO}_2$ . The metal ions doping can enrich the surface states (surface defects) of semiconductor nanometer materials and improve their surface performances. The study of  $\text{Zn}^{2+}$  doped  $\text{TiO}_2$  NPs system [16] shows that an appropriate amount  $\text{Zn}^{2+}$  doping could enrich the surface states (surface defects) of  $\text{TiO}_2$  NPs and improve separation efficiency of photogenerated charge carriers related to surface states in  $\text{TiO}_2$ , and subsequently promote the  $\text{TiO}_2$ -to-molecule CT and SERS for the adsorbed molecules. However, the doped  $\text{Zn}^{2+}$  ions could not enter into crystal lattice of  $\text{TiO}_2$  to replace Ti ions because of the larger radius of  $\text{Zn}^{2+}$  than that of  $\text{Ti}^{4+}$ . In fact, the doped  $\text{Zn}^{2+}$  ions were dispersed among  $\text{TiO}_2$  crystallites in the form of ZnO clusters. It means that the doping energy level was not formed in the energy gap of  $\text{TiO}_2$ .

In this paper, the metal Co ions is considered to use as dopants for improving SERS properties of  $\text{TiO}_2$  NPs, and deeply understanding the mechanism of semiconductor ( $\text{TiO}_2$ )-to-molecule CT and its contributing/controlling factors. The study shows that the doped Co ions can enter into crystal lattice of  $\text{TiO}_2$  to replace Ti ions, and then the abundant metal doping energy levels can be formed in the energy gap of  $\text{TiO}_2$ , which can obviously enhance SERS properties of  $\text{TiO}_2$  NPs.

## Materials and methods

### Chemicals

4-Mercaptobenzoic acid (4-MBA) was purchased from Acros Organics Chemical Co. and used without further purification. The other chemicals were all analytical grade without further purification too. Triply distilled water was used in all experiments.

### Sample preparation

The synthesis of pure  $\text{TiO}_2$  and Co ions doped  $\text{TiO}_2$  (Co- $\text{TiO}_2$ ) NPs in this work is similar to that described in previous papers [3,16], employing a sol-hydrothermal method. First, a mixed solution of 5 mL of tetrabutyl titanate and 5 mL of anhydrous ethanol was added dropwise into another mixed solution, consisting of 20 mL of anhydrous ethanol, 5 mL of water, 1 mL of 70% nitric acid and an appropriate amount of cobalt nitrate, at room temperature under roughly stirring to carry out hydrolysis. Subsequently, the yellowish transparent sol was obtained by continuously stirring for 1 h. The as-prepared sol was kept at 160 °C for 6 h in a stainless-steel vessel, and then cooled to room temperature. The sol-hydrothermal production was dried at 60 °C for 24 h. Finally,  $\text{TiO}_2$  and Co- $\text{TiO}_2$  NPs were obtained by calcining the sol-hydrothermal production at 450 °C for 2 h.

$\text{TiO}_2$  and Co- $\text{TiO}_2$  NPs surface-modified by 4-MBA molecules were obtained as follows: 20 mg of  $\text{TiO}_2$  or Co- $\text{TiO}_2$  NPs were dissolved in 10 mL of 4-MBA ( $1 \times 10^{-3}$  M) ethanol solution respectively, and the mixture was stirred for 2 h. Then, the precipitate

was centrifuged and rinsed with purified water once more. In this way,  $\text{TiO}_2$  and Co- $\text{TiO}_2$  NPs modified by 4-MBA were obtained.

### Sample characterization

The crystal structure of  $\text{TiO}_2$  and Co- $\text{TiO}_2$  samples was determined by X-ray diffraction (XRD) using a Siemens D5005 X-ray powder diffractometer with a Cu  $K\alpha$  radiation source at 40 kV and 30 mA. The surface morphology of the sample was measured on a Hitachi H-800 transmission electron microscope (TEM) operated at an acceleration voltage of 200 kV. The element composition and chemical state of samples were analyzed by X-ray photoelectron spectroscopy (XPS) with a VG ESCALAB MK II X-ray photoelectron energy spectrometer. The UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded on a Shimadzu UV-3600 UV-vis spectrophotometer. Raman spectra were obtained by using a Renishaw Raman system model 1000 spectrometer with the resolution of ca.  $4 \text{ cm}^{-1}$ . The 514.5 nm radiation from a 20 mw air-cooled argon ion laser was used as exciting source. Data acquisition was the result of three 30s accumulations for 4-MBA molecules adsorbed on  $\text{TiO}_2$  and Co- $\text{TiO}_2$  NPs at room temperature. Replicate measurements of each sample were made at least three times to verify the spectra reproducible.

## Results and discussion

### Measurements of XRD, TEM and XPS

XRD is usually used for identification of the crystal phase structure and estimation of crystallite size for NPs. The XRD peaks at  $2\theta = 25.4^\circ$  (101) and  $48^\circ$  (200) are generally identified as the characteristic diffraction peaks of the anatase crystal phase of  $\text{TiO}_2$  [17]. Fig. 1 shows the XRD patterns of pure and 0.5–5 mol% Co- $\text{TiO}_2$  NPs. All Co- $\text{TiO}_2$  samples, as well as undoped  $\text{TiO}_2$ , exhibit an anatase phase. Even at the highest Co ions dopant concentration (5 mol%) there are no new diffraction peaks related to cobalt oxides appearing. It can be seen from Fig. 1 (the inset) that the diffraction peak (101) of Co- $\text{TiO}_2$  samples shifts to higher  $2\theta$  diffraction angle compared with the pure  $\text{TiO}_2$  NPs and the shift degree decrease gradually with the increase of doped Co amount, indicating that doped Co ions enter into the crystal lattice of  $\text{TiO}_2$  to substitute for Ti ions, which leads to lattice distortion of  $\text{TiO}_2$  NPs and subsequent diffraction peak shift. The peak shift toward higher  $2\theta$  diffraction angle for Co- $\text{TiO}_2$  samples should be ascribed to the decrease in the interplanar distance induced by doped Co ions (lesser radius of Co ion than that of Ti ion) according to the Bragg equation ( $2d$

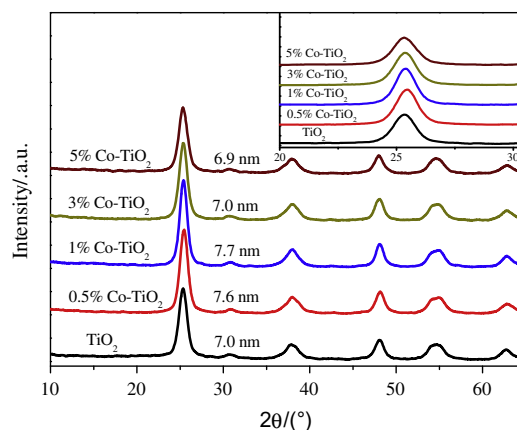


Fig. 1. XRD patterns of  $\text{TiO}_2$  and Co- $\text{TiO}_2$  nanoparticles (The inset is the magnified XRD patterns between  $20^\circ$  and  $30^\circ$ ).

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