# A novel metal-semiconductor SERS self-cleaning system with synergistic effects for highly sensitive detection of pollutant

Junnan Wang<sup>1</sup>, Zeyu Wang<sup>\*2</sup>, Jindou Shi<sup>1</sup>, Chen Zhang<sup>1</sup>, Qin Yao<sup>1</sup>, Yun Zhou<sup>1</sup>, Zheyuan Da<sup>1</sup>, Arshad Saleem Bhatti<sup>3</sup>, Minqiang Wang<sup>\*1</sup>

<sup>1</sup>Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education International Center for Dielectric Research&Shannxi Engineering Research Center of Advanced Energy Materials and Devices, Xi'an Jiaotong University, 710049 Xi'an, China.

<sup>2</sup>Frontier Institute of Science and Technology (FIST), Xi' an Jiaotong University, 710049 Xi' an,

China

<sup>3</sup>Center for Micro and Nano Device, Department of Physics, COMSATS Institute of Information

Technology, Islamabad, 44500, Pakistan

\*Corresponding author

E-mail address: <u>zeyu.wang@xjtu.edu.cn</u> (Z.y. Wang), <u>mqwang@xjtu.edu.cn</u> (M.q. Wang)

## **EXPERIMENTAL SECTION**

# **Reagents and materials**

Gold chloride tetrahydrate (HAuCl<sub>4</sub>·4H<sub>2</sub>O, 99.99 %), Silver nitrate (AgNO<sub>3</sub>, 99.99%), HCl (AR, 36.0~38.0%), n-butanol (C<sub>4</sub>H<sub>10</sub>O,  $\geq$ 98%), Sodium citrate (C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>Na<sub>3</sub>, 98%), Poly(diallyldimethylammonium chloride) solution (Mw 200,000-350,000, 20 wt. % in water), Titanium butoxide (TBT, C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti,  $\geq$ 99%) were purchased from Aladdin Reagent (Shanghai) Co., Ltd. (Shanghai, China). Ascorbic acid (AA, C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>, 99.99%), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH, AR,  $\geq$ 95%), HNO<sub>3</sub> (AR, 70%), zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>, AR,  $\geq$ 99%), Sodium hydroxide (NaOH,  $\geq$ 96%), Methylene blue (MB, C<sub>16</sub>H<sub>18</sub>ClN<sub>3</sub>S·3H<sub>2</sub>O), 4-mercaptobenzoic acid (C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>S<sub>4</sub>, 4-MBA, 99%), were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized water (DI, resistance > 18.2 MΩ/cm) was used in necessary reactions. All the reagents were used without further purification.

# Synthesis of the Au seed

Au seeds were synthesized using the citric acid reduction method reported by  $Frens^1$ . 0.01 g of  $HAuCl_4 \cdot 3H_2O$  was added to 100 mL of water and heated continuously until the solution boiled. 3 mL of 1 wt. % sodium citrate solution was slowly added to the boiling solution and maintained for 40 min, resulting in a burgundy colored colloidal dispersion of Au seeds.

# Synthesis of the TiO<sub>2</sub>

TiO<sub>2</sub> was synthesized using a solvothermal method. 5 mL of TBT was first mixed with 5 mL of anhydrous ethanol. Then it was added dropwise to a mixture of 20 mL ethanol, 5 mL water and 1 mL HNO<sub>3</sub>. After continuous stirring for 2 h a light yellow sol was obtained. It was poured into a reactor and kept at 160 °C for 6 h, followed by drying at 80 °C for 6 h and finally calcined at 450 °C for 2 h to eventually obtain TiO<sub>2</sub>.

# Synthesis of the TiO<sub>2</sub>@ZnO composite

Firstly, 50 mL Zn(NO<sub>3</sub>)<sub>2</sub> (0.1M) solution was configured and 0.4 g of TiO<sub>2</sub>

prepared above was added to it. Then 20 mL, 0.5 M NaOH solution was quickly added to the above mixture. After vigorous stirring for 20 min the precipitate was calcined at 400 °C for 2 h to obtain TiO<sub>2</sub>@ZnO composite. ZnO was prepared without adding TiO<sub>2</sub> under the same experimental conditions.

# Synthesis of the Au NU/TiO<sub>2</sub>@ZnO composite self-cleaning SERS substrate

Au NU was prepared by the seed growth method. 10 mL of 0.25 mM HAuCl<sub>4</sub> solution was first prepared and 10  $\mu$ L of HCl (1 M) solution was added to it. During continuous stirring 100  $\mu$ L, 0.003 M AgNO<sub>3</sub> solution and 50  $\mu$ L, 0.1 M AA solution were added to the solution, which rapidly turned grayish blue. Next, 100  $\mu$  L of the prepared gold seeds were added to the solution. Finally, 0.5 mL of aqueous PDDA solution was added. After incubation for 30 min at room temperature, the solution was rinsed with water and dispersed in deionized water.

The prepared Au NU was concentrated and dispersed in 50  $\mu$ L of ethanol and then 1 mL of n-butanol was added. After sonication for 15 min, it was added dropwise to the surface of water in a 5 mL beaker. 2 mL of ethanol was rapidly added dropwise to the surface of water after 8 h. The aggregated Au NU was collected with a silicon wafer and dried to obtain the Au NU substrate. 20  $\mu$ L of the prepared TiO<sub>2</sub>@ZnO dispersion was spin-coated on the Au NU substrate at 2000 rpm for 25 s to obtain the Au NU/TiO<sub>2</sub>@ZnO composite self-cleaning SERS substrate.

# **Characterization**

The X-ray diffraction (XRD) patterns were obtained using the XRD diffractometer (D8-ADVANCE, Brooke (Beijing) Technology Co., LTD, China). The morphology and micro-structure of the as-synthesized samples were analyzed using a field emission scanning electron microscopy (SEM, FEI Quatan FEG 250, America). Energy dispersive spectrometer (EDS) spectra of film were investigated by SEM equipped with an EDS. The Uv-Vis diffuse reflectance spectra (DRS) was recorded by PE Lambda 950 (Perkin Elmer Instruments Co. LTD., America). Transmission electron microscopy (TEM) images were taken from a transmission electron microscope (FEI Tecnai F20, FEI Company, America). X-ray photoelectron

spectroscopy (XPS) were performed using a X-ray photoelectron spectroscopy (K-Alpha+, Thermo Scientific, America). The Raman spectra were recorded by Laser Raman Spectrometer under laser light of 633 nm or 785 nm and 50× objective lens (LabRAM HR Evolution, HORIBA Scientific, Japan). A 250 W high pressure Hg Lamp used as the light source for performing photocatalytic activity.

# SERS detection and self-cleaning of dye on the Au NU/TiO<sub>2</sub>@ZnO composite selfcleaning SERS substrate

SERS detection was performed on the Au NU/TiO<sub>2</sub>@ZnO composite selfcleaning SERS substrate with MB ethanol solution  $(10^{-5}-10^{-12} \text{ M})$ . 10 µL of the solution were dropped on the surface of the Au NU/TiO<sub>2</sub>@ZnO composite selfcleaning SERS substrate to dry naturally before each assay. The excitation laser wavelength used was 633 nm and the exposure time set to 5 s. The spectroscope equipped with a high-speed encoding stage, could be shifted in x, y, and z directions and had a spatial resolution of 100 nm steps. All the Raman test results were the average spectra of five different locations and baseline corrected.

In photocatalytic-self-cleaning experiments, the Au NU/TiO<sub>2</sub>@ZnO composite self-cleaning SERS substrate were placed in 10<sup>-5</sup> M MB solution and a parallel light source (250 W high pressure Hg Lamp) was placed above the solution. After each interval, the UV light source was switched off and the Raman signal was collected until no Raman signal could be detected. In a cyclic experiment, the Au NU/TiO<sub>2</sub>@ZnO composite self-cleaning SERS substrate was removed after each photocatalytic process and washed with ethanol before being transferred to a new solution and the experiment was repeated.

# FDTD simulation

In this paper, we have used FDTD to calculate the electric field distribution of nanostructures. In the calculation process, we apply the perfect matching layer condition to both x,y and z directions, which can effectively prevent unphysical scattering. In addition, in order to obtain accurate calculation results, we divided the mesh of the whole simulation area into  $1 \text{ nm} \times 1 \text{ nm} \times 1 \text{ nm}$ . Importantly, we adopted the total-field scattering field plane wave as the excitation light source incident

vertically along the z-direction to the surface of the nanostructures. We set the simulation convergence time to  $1 \times 10^{-5}$  fs to ensure the convergence of the computational results. Finally, an electric field monitor was employed to obtain the electric field distribution of the nanostructures.



Figure S1. XRD standard card



Figure S2. Localized enlargement of the XRD pattern of Au NU/TiO2@ZnO, $TiO_2@ZnO$ andZnO.



Figure S3. SEM of a)  $TiO_2$ , b) ZnO. c) SEM and d-f) EDS mapping of  $TiO_2@ZnO$  composite



**Figure S4**. a) SERS spectra of MB solutions  $(10^{-5} \text{ M})$  on the TiO<sub>2</sub>@ZnO composite substrate under different UV light irradiation times (0-36 min) with an interval of 3 min. b) Raman diffraction peak intensity ratios at 1620 cm<sup>-1</sup> of MB solutions  $(10^{-5} \text{ M})$  on the TiO<sub>2</sub>@ZnO composite substrate under different UV light irradiation times.



**Figure S5**. The corresponding relative SERS variation intensity at 1620 cm<sup>-1</sup> for 25 cycles.



**Figure S6**. The normalized relative intensities of MB molecules detected at the 1620 cm<sup>-1</sup> Raman characteristic peak under different light powers.



Figure S7. SERS spectra of MO and R6G solutions  $(10^{-5} \text{ M})$  on the Au NU/TiO<sub>2</sub>@ZnO composite self-cleaning SERS substrate under different UV light irradiation times.



**Figure S8.** FDTD simulation of the electromagnetic field distributions of the Au NU (x-z view). The excitation wavelength is 633 nm. Scale bars: 50 nm.



Figure S9. The SERS spectra of Au NU, TiO2@ZnO and Au NU/TiO2@ZnO for 4-MBA(10-3M)withdifferentexcitedlaser.

# Calculation of the enhancement factor

Enhancement factor (EF) was an important parameter of SERS substrate, which could directly reflect the performance of SERS substrate. The average enhancement factor of the Au NT/TiO<sub>2</sub>@ZnO composite self-cleaning SERS substrate could be calculated using the following formula:

$$EF = \frac{I_{surface}/N_{surface}}{I_{solution}/N_{solution}} = \frac{I_{surface} \times N_{solution}}{I_{solution} \times N_{surfac}}$$
(1)

where  $I_{surface}$  and  $I_{solution}$  correspond to the intensity of a Raman characteristic peak of the signaling molecule measured from the Au NT/TiO<sub>2</sub>@ZnO composite self-cleaning SERS substrate and that of the same peak measured from the solution, respectively.  $N_{surface}$  and  $N_{solution}$  were the average number of molecules in the detection fields of the Au NT/TiO<sub>2</sub>@ZnO composite self-cleaning SERS substrate and the solution, respectively. According to the Raman spectra of the 10<sup>-2</sup> M MB solution measured in Figure S10:

$$I_{solution} = 475 (counts) \tag{2}$$

$$N_{solution} = 6.02 \times 10^{23} \, mol/L \times 10^{-2} \, mol/L \times \left[\pi \left(\frac{d}{2}\right)^2 \times H\right] = 1.21 \times 10^9$$
(3)

where d was the laser spot diameter (about 0.8  $\mu$ m) and H was the effective laser aggregation depth (about 400  $\mu$ m).

$$N_{surface} = D_{MB} \times S_{spot} = \frac{N_{MB}}{S_{total}} \times S_{spot}$$
(5)

Where  $S_{spot}$  was the area of the region of the laser spot. The diameter of the laser spot has already been mentioned in the previous section, was 0.4 µm.  $S_{spot}$  could be calculated as:

$$S_{spot} = \pi \times \left(\frac{d}{2}\right)^2 = \pi \times 0.4^2 \approx 0.5 \,\mu m^2 \tag{6}$$

 $D_{MB}$  was the density of MB molecules on the SERS substrate. The number of MB molecules on the surface of SERS substrate,  $N_{MB}$ , needs to be calculated firstly. 10 µm of MB solution at 10<sup>-5</sup> concentration was added drop-wise to the substrate surface. After natural drying, most of the MB molecules stayed on the substrate surface. Consequently  $N_{MB}$  can be calculated as:

$$N_{MB} = 6.02 \times 10^{23} \times 10 \times 10^{-6} \times 10^{-5} = 6.02 \times 10^{13}$$
(7)

After dropping on the 10  $\mu$ m MB solution to the SERS substrate, it could form a circular area of about 2 mm in diameter.  $S_{total}$ , the total area of the region formed by the MB solution on the substrate, can be calculated as:

$$S_{total} = \pi \times 1000^2 = 3.14 \times 10^6 \,\mu m^2 \tag{14}$$

Based on the above results,  $D_{R6G}$  and  $N_{SERS}$  can be calculated separately as:

$$D_{MB} = \frac{N_{MB}}{S_{total}} = \frac{6.02 \times 10^{13}}{3.14 \times 10^6} = 1.917 \times 10^7 \,\mu m^{-2} \tag{15}$$

$$N_{surface} = D_{R6G} \times S_{spot} = 9.59 \times 10^6 \tag{16}$$

The enhancement factor of the Au NU/TiO<sub>2</sub>@ZnO composite self-cleaning SERS substrate can be calculated based on the  $I_{surface}$  intensities from the Figure 3a:

$$EF_{composite} = \frac{I_{surface} \times N_{solution}}{I_{solution} \times N_{surfaces}} = \frac{26318}{1.917 \times 10^7} \times \frac{1.21 \times 10^9}{475} = 3.5 \times 10^3$$
(17)

Similarly, the EF of the Au NU substrate was  $1.65 \times 10^3$ , and the EF of the TiO<sub>2</sub>@ZnO substrate was  $7.07 \times 10^2$ . Therefore, it can be judged that electromagnetic enhancement dominated in the Au NU/TiO<sub>2</sub>@ZnO composite self-cleaning SERS substrate.



Figure S10. The Raman spectrum of the MB solution of 10<sup>-2</sup> M

# Reference

1. Y. Zheng, X. Zhong, Z. Li and Y. Xia, Part. Part. Syst. Charact. 2014, 31, 266-

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