Electronic supplementary information

Ag-nanoparticles-decorated NiO-nanoflakes grafted Ninanorod arrays stuck out of porous AAO as effective SERS substrates

Qitao Zhou,[†] Guowen Meng,^{*,†,‡} Qing Huang,[§] Chuhong Zhu,[†] Haibin Tang,[†] Yiwu Qian,[†] Bin Chen,[†] and Bensong Chen[†]

[†]Key Laboratory of Materials Physics, and Anhui Key Laboratory of Nanomaterials and Nanostructures, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of

China

[‡]University of Science and Technology of China, Hefei 230026, P. R. China

[§]Key Laboratory of Ion Beam Bioengineering, Institute of Technical Biology and Agriculture Engineering, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, 230031, China

*To whom correspondence should be addressed.

Tel: (86) 0551-65592749, Fax: (86) 0551-65591434, E-mail: gwmeng@issp.ac.cn.

Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics This journal is The Owner Societies 2013

The Supporting Information includes:

Part S1. Uniformity of SERS sensitivity of the SERS substrates

Part S2. Calculation of the average enhancement factor (EF)

Part S3. The morphology of Ag-NPs@Ni-NR arrays

Part S4. The absorption spectra of the products at each step

Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics This journal is © The Owner Societies 2013





Fig. S1 SERS spectra of 10^{-7} M R6G aqueous solution on five randomly chosen spots of (a) Ag-NPs@NiO-NFs@Ni-NR arrays, (b) Ag-NPs@Ni(OH)₂-NFs@Ni-NR arrays with NH₃·H₂O treatment for 30 min, (c) Ag-NPs@Ni(OH)₂-NFs@Ni-NR arrays with NH₃·H₂O treatment for 60 min and (d) Ag-NPs@Ni-NR arrays. The integration time was 10 s for each spot with a 532 nm laser line. For all the substrates, the Ag-sputtering duration was 5 min.

Part S2. Calculation of the average enhancement factor (EF)

We calculate the average EF from the SERS substrate point of view under plausible assumption that all the probe molecules within the laser spot are illuminated and contribute to the SERS spectra and the Raman spectra. The EF can be calculated by

$$EF = \frac{I_{SERS} / N_{SERS}}{I_{RS} / N_{RS}}$$
(1)

where I_{SERS} and I_{RS} represent the intensities of the same band of the SERS spectra and the Raman spectra (non-SERS) respectively, and N_{SERS} and N_{RS} represent the number of molecules on the substrates within the laser spot. Herein for SERS examination, a certain volume V_{SERS} R6G aqueous

solution was dispersed to an area of S_{SERS} at a concentration of C_{SERS} on the Ag-NPs@NiO-NFs@Ni-NR arrays, Ag-NPs@Ni(OH)₂-NFs@Ni-NR arrays and Ag-NPs@Ni-NR arrays. For non-SERS Raman spectra, a certain volume V_{RS} R6G ethanol solution was dispersed to an area of S_{RS} at a concentration of C_{RS} on a clean silicon wafer. Both the substrates were dried in the air. The foregoing equation thus becomes

$$EF = \frac{I_{SERS}}{I_{RS}} \cdot \frac{S_{SERS}V_{RS}C_{RS}}{S_{RS}V_{SERS}C_{SERS}}$$
(2)

Raman measurements were conducted under identical experimental conditions (laser wavelength, laser power, microscope objective/lenses, spectrometer, etc.). In our experiment, 1 μ L of 10⁻¹⁰ M R6G aqueous solution was dispersed to an area of 6mm² for the Ag-NPs@NiO-NFs@Ni-NR arrays and Ag-NPs@Ni(OH)₂-NFs@Ni-NR arrays substrates and 1 μ L of 10⁻³ M R6G ethanol solution was dispersed to an area of 9 mm² for the silicon wafer. For the 6 mm² Ag-NPs@Ni-NR arrays, 1 μ L of 10⁻⁸ M R6G aqueous solution was used. Fig. S2 shows the SERS spectra and the Raman spectra of R6G from the asprepared substrates. The intensities for the C–C–C ring in-plane vibration mode at 612 cm⁻¹ are 487 units for Ag-NPs@Ni-NR arrays substrates, 156 units for the Ag-NPs@Ni(OH)₂-NFs@Ni-NR arrays, 397 units for the Ag-NPs@NiO-NFs@Ni-NR arrays and 1247 units for the silicon wafer substrate, respectively. The average EFs are calculated to be 2.1×10⁶ for the Ag-NPs@NiO-NFs@Ni-NR arrays, 8.3×10⁵ for the Ag-NPs@Ni(OH)₂-NFs@Ni-NR arrays and 2.6×10⁴ for the Ag-NPs@Ni-NR arrays. Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics This journal is © The Owner Societies 2013



Fig. S2 (a) SERS spectra of 1 μ L 10⁻⁸ M R6G aqueous solution on 6 mm² Ag-NPs@Ni-NR arrays. (b) SERS spectra of 1 μ L 10⁻¹⁰ M R6G aqueous solution on 6 mm² Ag-NPs@Ni(OH)₂-NFs@Ni-NR arrays with NH₃·H₂O treatment for 30 min, the spectra intensity has been multiplied by 5 for clarity. (c) SERS spectra of 1 μ L 10⁻¹⁰ M R6G aqueous solution on 6 mm² Ag-NPs@NiO-NFs@Ni-NR arrays. (d) Raman spectra of 1 μ L 10⁻³ M R6G ethanol solution on 9 mm² silicon wafer. The laser line was 532 nm for all the three samples.

Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics This journal is O The Owner Societies 2013

Part S3. The morphology of Ag-NPs@Ni-NR arrays



Fig. S3 SEM oblique view of Ag-NPs@Ni-NR arrays after Ag sputtering for 5 min.

Part S4. The absorption spectra of the products at each step

There is no obvious absorption before decoration of Ag-NPs. The new obvious band appears at around 410 nm due to the SPR absorption of the Ag-NPs.



Fig. S4 The absorption spectra of the products at each step.