Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Experimental Section

Synthesis of monodisperse NiCo alloy spheres and Synthesis of monodisperse NiCo@SiO_2 composite microspheres.

Materials. All of the reagents used in the experiment were of analytical grade and used without further purification. Nickel chloride hydrated ($NiCl_2 \cdot 6H_2O$), Cobalt chloride hydrated ($CoCl_2 \cdot 6H_2O$), Ruthenium chloride ($RuCl_3$), Sodium hydroxide (NaOH), Hydrazine hydrate ($N_2H_4 \cdot H_2O$), Ammonium hydroxide ($NH_3 \cdot H_2O$), Tetraethylorthosilicate (TEOS), Polyvinyl pyrrolidone (PVP), silver nitrate ($AgNO_3$), Citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) and absolute ethanol were obtained from Shanghai Chemical Reagent Company (Shanghai, China). 4-mercaptobenzoic acid (MBA) and p-aminothiophenol (p-ATP) were obtained from Sigma Company. Ultrapure water (>18.0MΩcm) was purified using a millipore milli-q gradient system throughout the experiment.

Synthesis of monodisperse NiCo alloy spheres. The monodisperse NiCo alloy spheres were prepared by a solution reaction at room temperature. In a typical procedure, 0.02 mol of $CoCl_2 \cdot 6H_2O$ and 0.01 mol of $NiCl_2 \cdot 6H_2O$ were added to 20 mL of deionized water in a three-necked flask, followed by mixing with 1mL of $RuCl_3$ (1 mM) aqueous solution. The mixture was stirred under a mechanical stirrer for 30 min. Then, the hydrazine hydrate solution containing 0.4 g NaOH were added to the above mixture drop by drop. After intense stirring for 4 h, the products were carefully collected by a magnet and washed with distilled water and absolute ethanol several times to remove impurities. Finally, the products were vacuum-dried at 50 ℃ for 6 h.

Synthesis of monodisperse NiCo@SiO_2 composite microspheres. Silica-coated NiCo composite microspheres ($NiCo@SiO_2$) were prepared via the modified Stöber method.[1,2] Typically, 50 mg of NiCo alloy spheres was ultrasonically dispersed in a solution containing 50 mL of absolute ethanol and 10 mL of distilled water for 30 min. Under vigorous stirring, $NH_3 \cdot H_2O$ (0.5 mL, 28 wt %) was added to the mixed solution, followed by the addition of TEOS (50 μL) in absolute ethanol (10 mL) 3 times within 6 h. After stirring for 6 h, the products were washed with absolute ethanol and distilled water several times. Finally, $NiCo@SiO_2$ composite microspheres with a 60 nm thick silica shell were obtained.

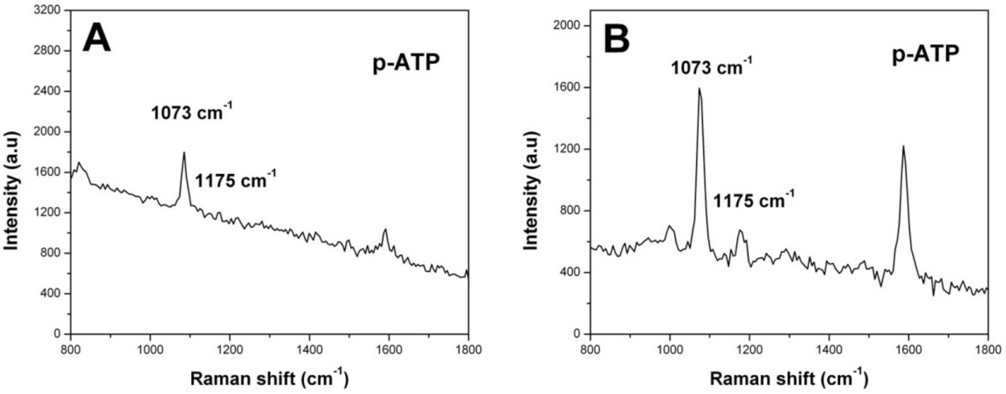

Figure.S1 (A) Raman spectrum of p-ATP in the solid state. (B) SERS spectrum of p-ATP (10^{-6} M) obtained on $NiCo@SiO_2@Ag$ composite microspheres.

For preparation of SERS substrates, the as-prepared $NiCo@SiO_2@Ag$ composite microspheres was immersed in 0.2 mL of p-ATP ethanol solutions for overnight to ensure the saturated coverage, then the samples were extracted using an external magnet and washed by ethanol and deionized water, and dried in air before the subsequent characterization. After the sample was carefully dropped onto clean glass slides, the substrates were measured using a Raman instrument. All SERS and Raman spectra were collected by a portable Raman instrument (*i*-Raman, B&W Tek Inc., USA) attached with a microscope (20 × objective). The SERS enhancement factor (EF) was calculated as follows:

$$EF = \frac{I_{SERS} / N_{SERS}}{I_{bulk} / N_{bulk}}$$

where I_{SERS} and I_{bulk} denote the Raman scattering intensities from the p-ATP adsorbed on the surface of NiCo@SiO_2@Ag composite microspheres and the p-ATP solid, respectively [1]. N_{SERS} and N_{bulk} represent the numbers of the corresponding surface and solid molecules effectively excited by the laser beam, respectively. We assumed that the p-ATP molecules were evenly scattered on the SERS substrate, N_{SERS} can be calculated according to the average surface density of p-ATP and the area of the Laser spot [2]. The NiCo@SiO_2@Ag composite microspheres adsorbed p-ATP molecules were dropped onto clean glass slide and formed a circular spot with the radius of ~ 1 mm. Thus the mean surface density of p-ATP molecules was calculated as 6.37×10^{-17} mol/μm^2. According to the diameter of Laser beam (100 μm), the area of the Laser spot was estimated to be 7.85×10^3 μm^2. Therefore, we can conclude that the value of N_{SERS} is 3.01×10^{11}. For the bulk R6G sample, the volume of Laser radiation = the area of Laser spot × the penetration depth of the Laser beam (1 mm). Referring to the density and molar mass of the bulk p-ATP (1.2 g/cm^3, 125.19 g/mol), N_{bulk} can be calculated to be 4.53×10^{16}. For the typical band at 1073 cm^{-1}, the ratio of I_{SERS} / I_{bulk} is about 2.01. Finally, the EF value is calculated to be 3.0×10^5. Accordingly, the EF value for the typical band at 1175 cm^{-1} is calculated to be 4.8×10^5.

References

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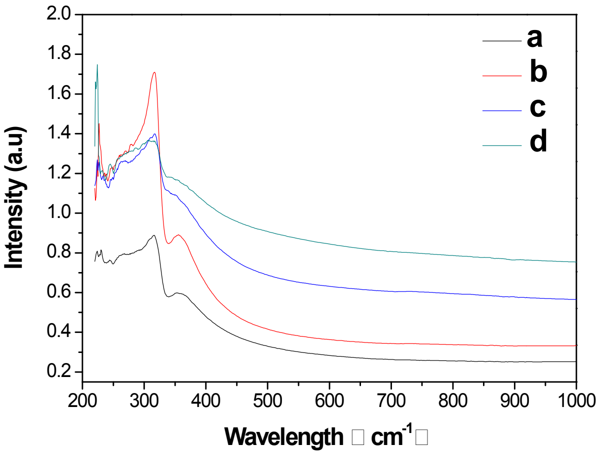

Figure.S2 UV/Vis absorption spectra of the samples with different morphologies shown in (a) Figure. 4B, (b) Figure. 4D, (c) Figure. 4F, and (d) Figure. 4H.