Supporting Information

Ultrasensitive detection of Trinitrotoluene by

Fe₃O₄@mTiO₂/P-ATP-TNT/Au@Ag SERS sensor via synergetic effect

Mei Sun^{‡a,b,c,d}, Ping Chen^{‡a,b,d}, Aiwu Zhao^{a,b,d*}, Fangtao Zuo^{a,b,d}.

^a Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei, 230031, P. R. China.

^b University of Science and Technology of China, Hefei, 230026, Anhui, P. R. China

^c School of Materials and Chemical Engineering of Anhui Jianzhu University, Hefei, 230601, P. R. China.

^d State Key Laboratory of Transducer Technology, Chinese Academy of Sciences, Hefei, 230031, P. R. China

E-mail: awzhao@iim.ac.cn

‡ These authors contributed equally to this work.

Materials

Ferric (III) chloride hexahydrate (FeCl₃·6H₂O), tetrachloroauric acid tetrahydrate (HAuCl₄·4H₂O), silver nitrate (AgNO₃), trisodium citrate dihydrate (C₆H₅Na₃O₇) polyethylene glycol (PEG), sodium acetate anhydrous (NaAc) and ethylene glycoethanol (EG) were obtained from Shanghai Chemical Reagents Company (Shanghai, China). P-aminothiophenol (P-ATP) was purchased from Aladdin. 2,4,6-Trinitrotoluene (TNT) was supplied by National Security Department of China. The deionized (DI) water with aelectrical resistivity of 18.25 MΩ·cm was purified using a Millipore Milli-Q gradient system.

Instrumentation and Characterization

The characterization of the products were analyzed by using a Quanta 200 FEG field

emission scanning electronic microscope (FESEM), a JEOL JEM-2010 high-resolution transmission electron microscope (HRTEM), a Philips X-Pert Pro X-ray diffractometer (XRD) with Cu K α radiation ($\lambda = 1.5418$ A), The SERS substrates of the P-ATP by using a portable-Raman spectrometer (B&W TEK, i-Raman) equipped with a diode laser emitting at 785 nm, the laser power was 30 mW and the integration time was 5 s.

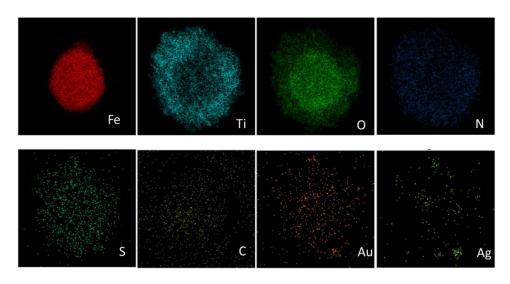


Fig. S1 elemental distribution mappings of Fe₃O₄@mTiO₂/P-ATP/Au@Ag NPs

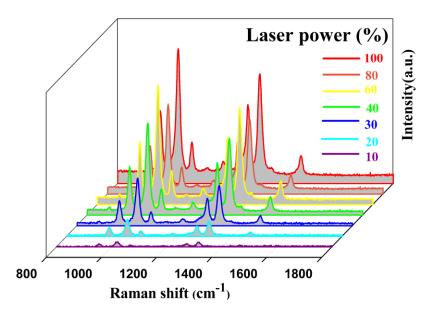


Fig. S2 SERS spectra of P-ATP at various laser powers in Fe₃O₄@mTiO₂/P-ATP/Au@Ag assemblies

| P-ATP | | DMAB | |
|--------------------------|------------------------|--------------------------------|-----------------------------------|
| wavenumber (cm $^{-1}$) | assignment | wavenumber (cm ⁻¹) | assignment |
| 1078 | V _{CS} | 1078 | V _{CS} |
| 1181 | v _{сн} | 1141 | $\beta_{CH} + \nu_{CN}$ |
| 1595 | v _{cc} | 1181 | ν _{cн} |
| | | 1388 | $v_{NN} + v_{CN}$ |
| | | 1429 | ν _{nn} + β _{ch} |
| | | 1595 | V _{CC} |

 Table S1. Wavenumbers and assignments of Raman band of P-ATP and DMAB.

Abbreviations: v, stretching; β , in-plane bending.