Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

A High reproducible SERS sensor based on Au nanoparticles /Graphene Oxide hybrid nanocomposite for label-free quantitative detection of antibiotics

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In order to study the layer number of GO, we added the AFM diagram of GO material, as shown in Fig. S1. The height of the red line in the AFM morphology was 1.245 nm, indicating that the GO was monolayer.

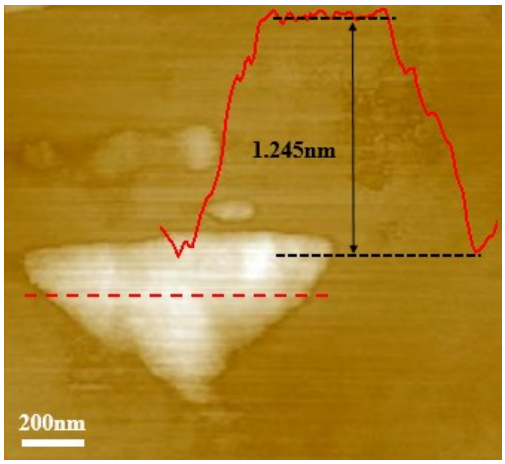

Fig. S1. AFM image of GO. Inset is the height profile of the red dashed line in AFM image.

In order to evaluate the performance of the substrate, the Raman spectra of Au NPs/GO and GO were detected. Fig. S2 shows that GO has a strong D peak at 1349 cm^{-1} and a G peak at 1580 cm^{-1}. The D peak of GO at 1349 cm^{-1} is a disordered vibration peak due to the presence of defects in the GO layer, which are usually attributed to the oxidation of graphite and doping effects in the hexagonal lattice. The G peak at 1580 cm^{-1} is composed of sp^2 carbon. The symmetry and order of the reaction materials confirm the origin of the layered GO in the graphite structure. The characteristic peak D and peak G of GO appeared at 1334 cm^{-1} and 1604 cm^{-1} respectively in the Raman spectra of the Au NPs/GO feeding. Comparing the positions of the G peaks of the g Au NPs/GO and GO. The G peak of the Au NPs/GO

is clearly moving towards the high wave band, and the shift in the position of the G peak indicates that the carbon atoms on the base plane are replaced, or that electrons (hole doping) are replaced by other atoms.

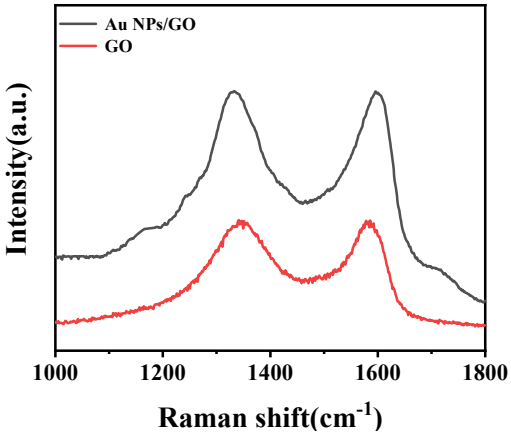

Fig. S2. Raman spectra of Au NPs/GO materials and GO

In order to assess the ability of the substrate for rapid detection of antibiotics, the same batch of substrate test substrates were mixed with antibiotics and directly transferred to a silicon substrate and soaked overnight in the treated antibiotics, and antibiotic solids were tested at the same parameters under test conditions. Fig. S3A shows the SERS spectra of the substrate mixed with ampicillin and directly transferred to the silicon substrate and soaked overnight. It can be seen from the figure that the relative spectral intensity of the SERS spectra of ampicillin soaked overnight was significantly higher than that of the same kind. This is because overnight immersion can promote the contact between the substrate and the sample molecules, thus enhancing the role of Raman signal. Although the enhanced effect of SERS spectrum of ampicillin directly transferred to silicon substrate after mixing with the substrate was not as good as the effect of soaking overnight, its relative intensity was significantly higher than the Raman spectrum of solid ampicillin. Meanwhile, we also studied the influence of soaking overnight on the detection of nitrofurantoin. Fig. S3B shows the SERS spectra of substrate mixed with nitrofurantoin (10 μg/ mL) and directly transferred to silicon substrate and soaked overnight. The experimental results show that the enhancement effect of nitrofurantoin soaked overnight is the best. In summary, although the detection efficiency of the SERS spectrum of antibiotics

directly transferred to the silicon substrate after ampicillin was mixed with the substrate was improved, its enhanced effect was not as good as that of the SERS spectrum of antibiotics soaked overnight. In order to improve the detection efficiency of antibiotics, we can make the detection intensity higher by adjusting the soaking time and other factors.. In this respect, we need to make further improvement.

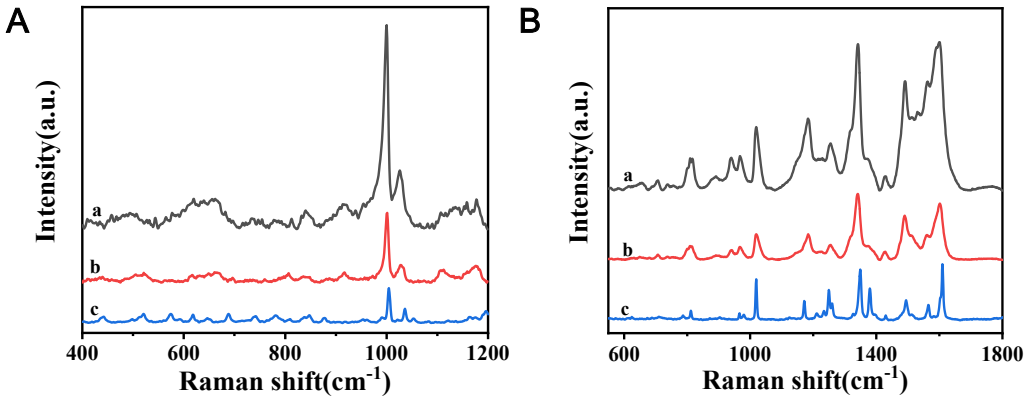

Fig. S3.(A) SERS spectrum of ampicillin soaked overnight (a), SERS spectrum of ampicillin mixed with substrate and transferred directly to silicon substrate (b) and solid Raman spectrum (c); (B) SERS spectrum of nitrofurantoin soaked overnight (a), SERS spectrum of nitrofurantoin mixed with substrate and transferred directly to silicon substrate (b) and solid Raman spectrum of nitrofurantoin (c).

Antibiotics are mainly residual in food and water environment. In order to further study the practical application of the substrate, we used the prepared Au NPs /GO substrate to detect ampicillin and nitrofurantoin in tap water. Fig. S4 in the support message. Fig. S4A shows the SERS spectra of Au NPs/GO substrates added with different concentrations of ampicillin in tap water. As can be seen from the figure, as the concentration of ampicillin decreases, the spectral intensity of all characteristic peaks of ampicillin gradually decreases. Taking the characteristic peak at 1001 cm^{-1} as an example, when the concentration is reduced to 0.01 ng/mL, the characteristic peak here can still be observed. To further observe this change, we compared the relative Raman strength of ampicillin at 1001 cm^{-1} with the concentration $\log_{10}C$ (C is ampicillin concentration in g/mL) (Fig. S4B in the supporting information). The results showed that the relative spectral intensity of ampicillin increased with the increase of the concentration. In the range of 1 ng/mL to 0.01 ng/mL, the calibration curve showed a good linear relationship with a linear

coefficient of 0.93 and a detection limit of 0.01 ng/mL. Fig. S4C shows the SERS spectrum of Au NPs/GO substrate after adding different concentrations of nitrofurantoin in tap water. As can be seen from the figure, as the concentration of nitrofurantoin decreases, the spectral intensity of all characteristic peaks of nitrofurantoin gradually decreases. Taking the characteristic peak at 1341 cm^{-1} as an example, when the concentration is reduced to 5 ng/mL, the characteristic peak here can still be observed. To further observe this change, we compared the relative Raman intensity of nitrofurantoin at 1341 cm^{-1} with the concentration $log_{10}C$ (C is the concentration of nitrofurantoin in g/ mL) (Fig. S4D in the supporting information). The results showed that the relative spectral intensity of nitrofurantoin increased with the increase of the concentration. In the range of 500 ng/mL to 5 ng/mL, the calibration curve showed a good linear relationship with a linear coefficient of 0.99 and a detection limit of 5 ng/mL. The SERS sensor platform established in this paper has great application potential in the high sensitivity quantitative detection of antibiotics.

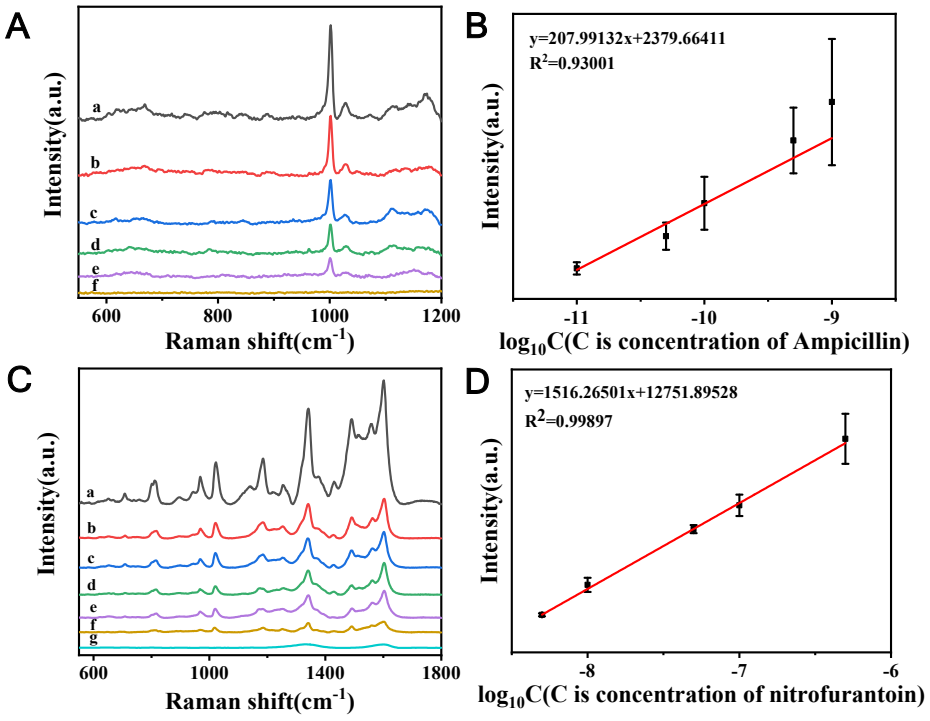

Fig. S4.（A）SERS spectra of Au NPs/GO substrates after adding different concentrations of nitrofurantoin: a) 100 ng/ml, b) 10 ng/ml, c) 1 ng/ml, d) 0.1 ng/ml, e) 0.01 ng/ml, f) 0 ng/ml. (B) nitrofurantoin with a concentration of 1 to 0.01 ng/mL is used for line ar fitting, with R2 = 0.93.

(C) SERS spectra of Au NPs/GO substrates after adding different concentrations of nitrofurantoin: a) 1000 ng/ml, b) 500 ng/ml, c) 100 ng/ml, d) 50 ng/ml, e) 10 ng/ml, f) 5 ng/ml, g) 0 ng/ml. (C) nitrofurantoin with a concentration of 500 to 5 ng/mL is used for linear fitting, with $R^2 = 0.99$

There are many methods for detecting antibiotics. In order to compare the detection limits of this method with those of HPLC, LC, LCMS, GC-MS and other methods, Table S1 is drawn.

Table. S1: HPLC, LC, LCMS and GC-MS were used to detect ampicillin and nitrofurantoin.

Analytical method	Class of antibiotics	Samples	LOD	Linear range	Year
MSPE	ampicillin	milk	0.29 mg/L	1~5000 μg/L	2020
HPLC	ampicillin	milk and meat	0.05 μg/L	0.1~25 μg/L	2019
HPLC-ESI/MS/MS	ampicillin	muscle, Liver and Kidney	muscle:0.1 μg/Kg; liver :0.2 μg/Kg; kidney: 0.3 μg/Kg	muscle:0.3~1000 μg/Kg; Liver :0.6~1000 μg/Kg; kidney: 0.9~1000 μg/Kg	2019
MIP sorbent/HPLC-UV	ampicillin	milk	10.7 μg/L	100~500 μg/L	2017
HPLC-UV	ampicillin	milk and blood	0.05 μg/L	5.0~200 μg/L	2016
SERS	ampicillin and nitrofurantoin	tap water	ampicillin: 0.01 ng/mL nitrofurantoin: 5 ng/mL	ampicillin: 0.01~1 ng/mL; nitrofurantoin: 5~500 ng/mL	This work