Electronic Supplementary Material (ESI) for RSC Advances.

Rapid on-site detection of paraquat in biologic fluids by iodide-facilitated pinhole shell-isolated nanoparticle-enhanced Raman spectroscopy

SUPPORTING INFORMATION

Yingjie Zhu,[a] Jianfeng Wu,[a] Haiyue Gao,[a] Guokun Liu, [b] Zhongqun Tian,[c] Jianlin Feng,[a] Lei Guo,*[a] and Jianwei Xie*[a]

*** Correspondence to: Lei Guo (Dr.), State Key Laboratory of Toxicology and Medical Countermeasures, and Laboratory of Toxicant Analysis, Institute of Pharmacology and Toxicology, Academy of Military Medical Sciences, Beijing 100850, China.**
E-mail: guolei@bmi.ac.cn; Tel:86-10-66931650;Fax:86-10-68225893
*** Correspondence to: Jianwei Xie (Dr.), State Key Laboratory of Toxicology and Medical Countermeasures, and Laboratory of Toxicant Analysis, Institute of Pharmacology and Toxicology, Academy of Military Medical Sciences, Beijing 100850, China.**
E-mail: xiejw@bmi.ac.cn; Tel.(Fax):86-10-68225893

[a] State Key Laboratory of Toxicology and Medical Countermeasures, and Laboratory of Toxicant Analysis, Institute of Pharmacology and Toxicology, Academy of Military Medical Sciences, Beijing 100850, China
[b] College of the Environment and Ecology, Xiamen University, Xiamen 361005, China
[c] State Key Laboratory of Physical Chemistry of Solid Surfaces, and College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

Characterization of the pinSHINs

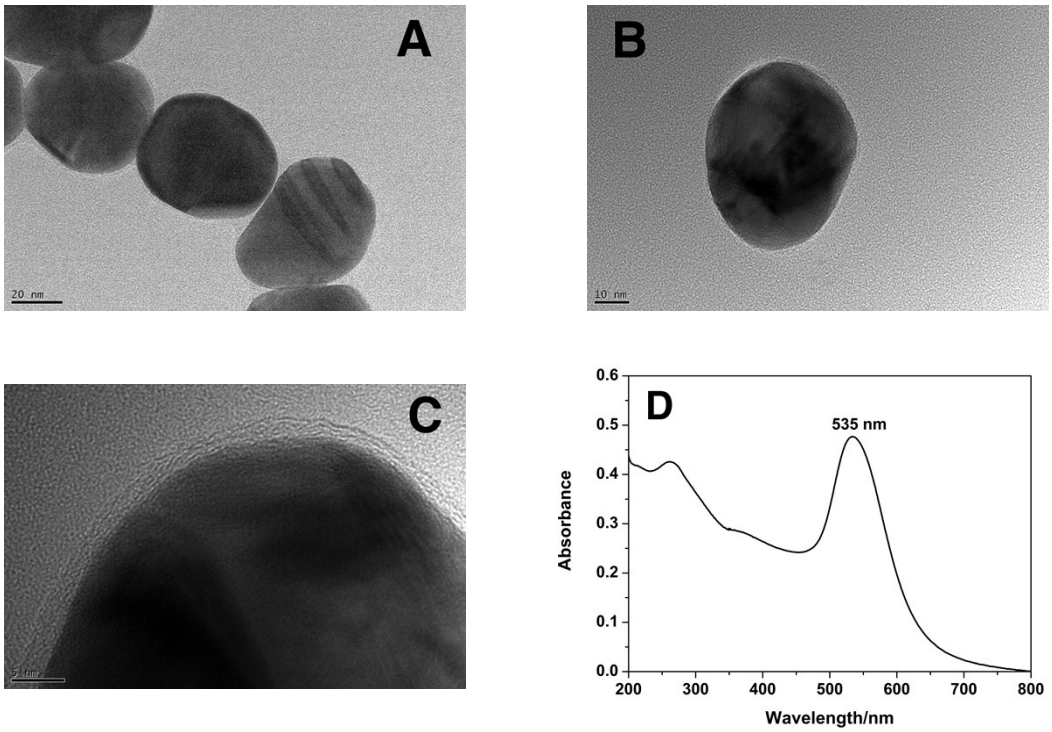


Fig. S1 HR-TEM images (A-C) and UV-Vis absorption spectra (D) of pinSHINs.

Influence of pH and different ions on paraquat measurement

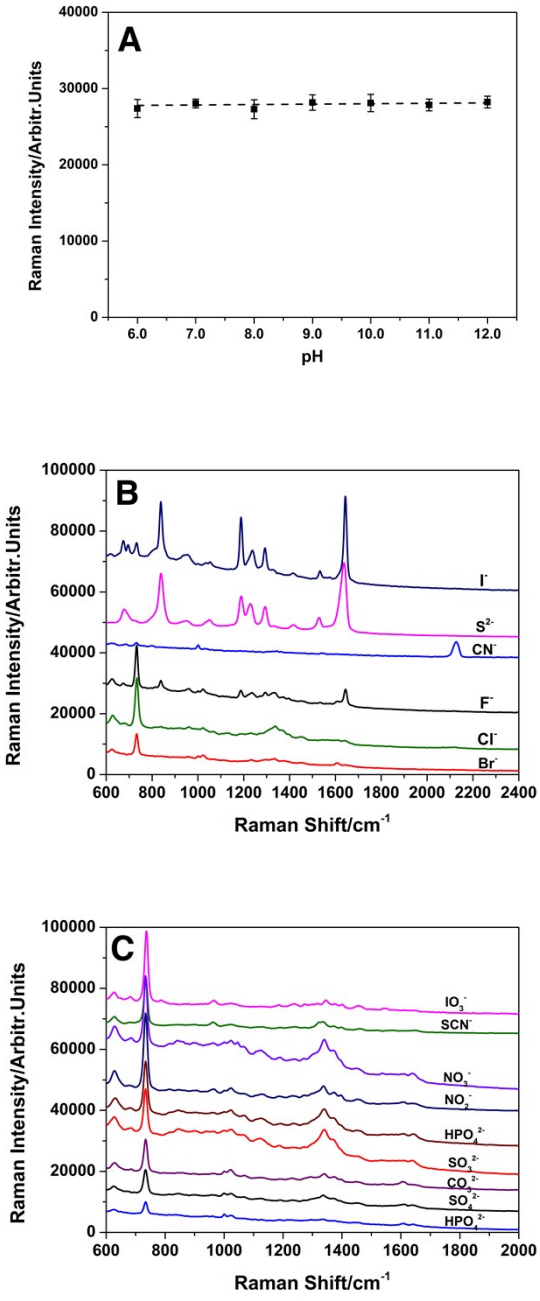


Fig. S2 *The plot of SERS intensity of paraquat (50 μg L^{-1}) at 1643 cm^{-1} versus pH from 6.0 to 12.0. Each data point represents the average value of three SERS measurements (A).* SERS spectra of paraquat in plasma (50 μg L^{-1}) with the addition of different kind of anions at 100 mM *(B and C)*.

Influence of iodide concentration on paraquat measurement

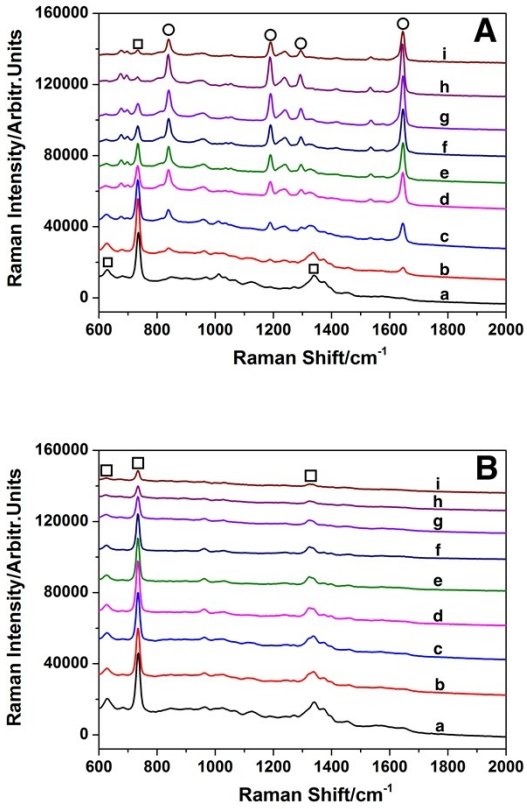


Fig. S3 SERS spectra of paraquat in plasma (50 μg L^{-1}) (A) and SERS spectra of blank plasma (B) with KI at concentration of 0, 0.1, 0.5, 1, 5, 10,50, 100, 200 mM (a-i). (○) represents the characteristic peaks, and (□) represents inherit, nonspecific peaks induced by plasma.

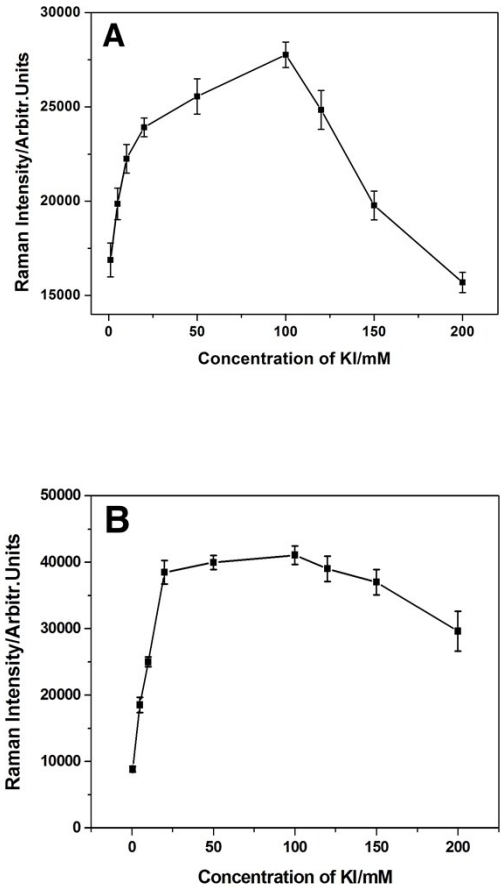


Fig. S4 Influence of KI concentration (0.5, 5, 10, 20, 50, 100, 120, 150, 200 mM) on SERS intensity of paraquat (50 μg L^{-1}) in plasma (A) and urine (B) at 1643 cm^{-1}.

Comparison of the stability between pinSHINs and bare AuNPs

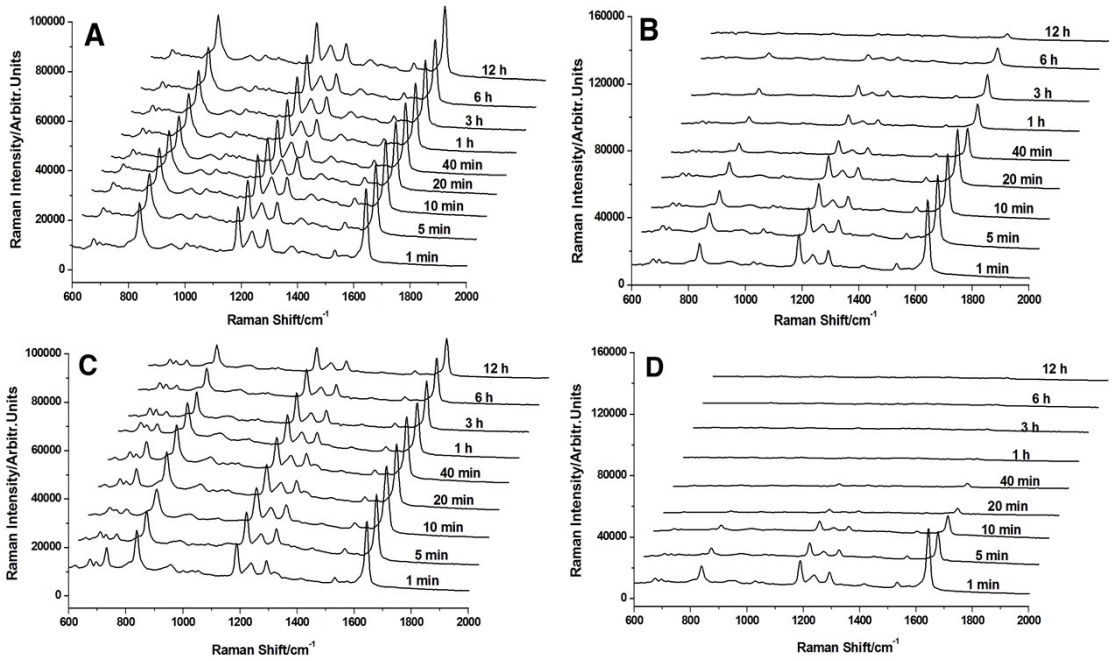


Fig. S5 Time-dependent SERS spectra of pinSHINs in plasma (A) and urine (B). Time-dependent SERS spectra of bare AuNPs in plasma (C) and urine (D). The concentration of paraquat is 50 μg L^{-1}.

Recovery in plasma and urine samples

Table S1 Measurement of paraquat in plasma and urine (n=3)

Sample	Added paraquat (μg L^{-1})	Measured paraquat (μg L^{-1})	Recovery (%)	RSD (%)
Plasma	2	2.3	115	8.2
	20	21.7	109	6.6
	30	33.0	110	2.7
Urine	2	2.2	110	7.6
	10	10.5	105	3.7
	16	14.9	93	5.5

Serial dilution of real plasma sample

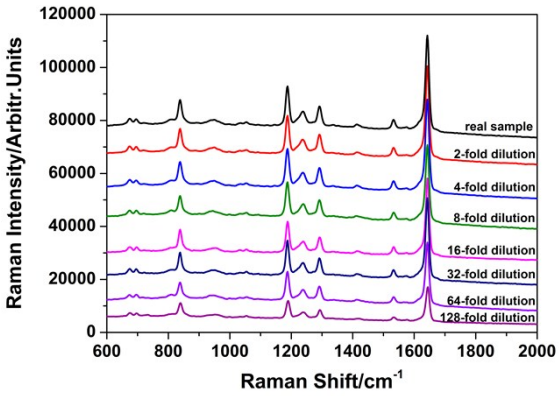


Fig. S6 SERS spectra of real plasma sample and serial diluted samples.

Applicability on other matrices

To demonstrate the wide applicability of this method, we also examined on plasma and bronchoalveolar lavage fluid (BALF) of paraquat poisoned SD rats as well as food matrices including spiked milk and orange juice samples. Plasma and bronchoalveolar lavage fluid (BALF) of paraquat poisoned SD rats were kindly provided by Dr. Jian Zhao (Institute of Pharmacology and Toxicology, Academy of Military Medical Sciences). Briefly, the male SD rats were administered by the intraperitoneal injection of paraquat at a dose of 50 mg/kg and received bronchoalveolar lavage treatment with normal saline at 6 h, 12 h and 24 h. Plasma and BALF were collected after each lavage, and measured by this method. The male SD rats were purchased from Charles River Co. Ltd. (Beijing, China). All the animal experiments were performed under the guidelines of the Association of Laboratory Animal Care International (AAALAC).

Orange juice and milk were purchased from a local supermarket. Spiked food samples were prepared by the addition of standard solutions and serially diluted to obtain a final concentration ranged from 2 to 200 μg L^{-1}.

As shown in Fig. S7, the amount of paraquat in plasma and BALF decreased largely after the third

lavage, indicating that this method could be readily applied to on-site detection of paraquat poisoning and even the evaluation of the treatment effects. This developed method is also applicable in orange juice and milk samples, reaching an LOD of 2 μg L^{-1} level for both (Figure. S8). A linear relationship between the SERS intensity and paraquat concentration was observed in the range from 5 to 50 μg L^{-1} for each kind of sample, with a recovery of paraquat between 92 and 115% (Table S2).

The results above show general applicability of this developed method in various matrices, meeting the on-site demand for paraquat measurement in biosamples and also other complex matrices.

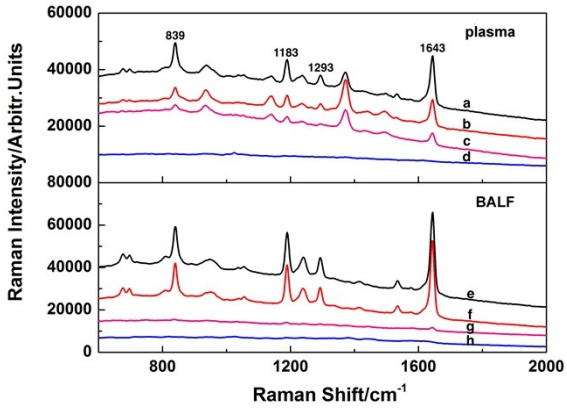
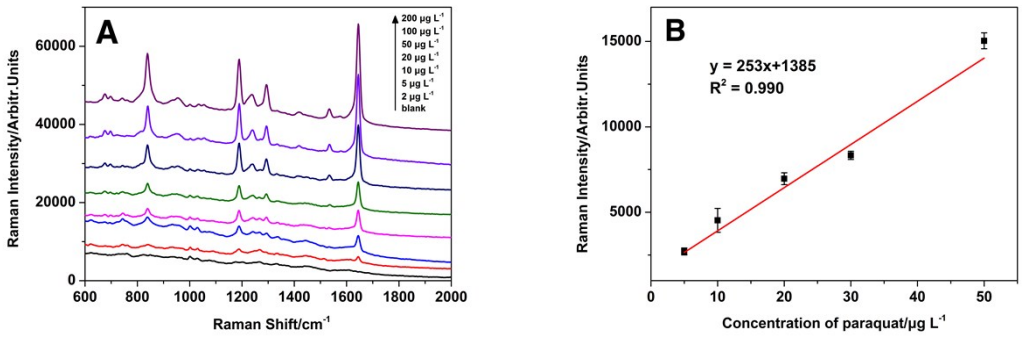


Fig. S7 SERS spectra of the plasma of paraquat poisoned rats after bronchoalveolar lavage at 6 h (a), 12 h (b), 24 h (c), and blank rat (d); SERS spectra of the BALF of paraquat poisoned rats after lavage at 6 h (e), 12 h (f) and 24 h (g), and of blank rat (h).



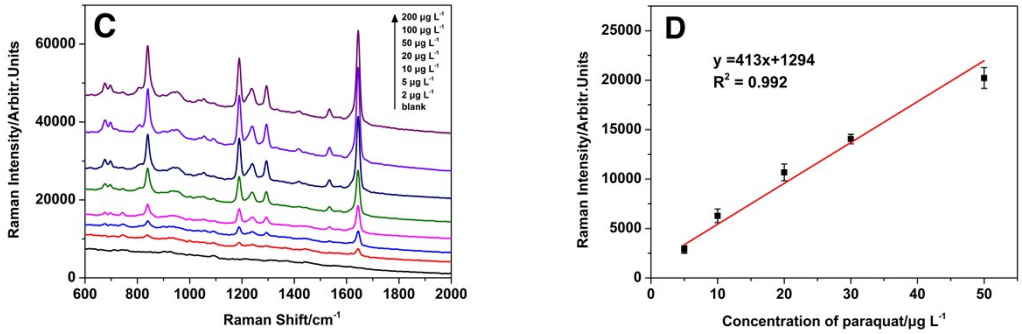


Fig. S8 SERS spectra of paraquat in orange juice (A) and milk (C) at concentration from 2 to 200 μg L^{-1} with 100 mM of KI; Calibration curves of SERS intensity at 1643 cm^{-1} versus concentration of paraquat in orange juice (C) and milk (D) from 5 to 50 μg L^{-1}.

Table S2 Measurement of paraquat in orange juice and milk (n=3)

Sample	Added paraquat (μg L^{-1})	Measured paraquat (μg L^{-1})	Recovery (%)	RSD (%)
Orange juice	10	9.5	95	9.1
	25	24.4	98	7.1
	40	43.5	109	9.2
Milk	10	11.4	114	5.8
	25	22.9	92	10.2
	40	45.8	115	4.4