

## A SERS nanocatalytic reaction and its application to quantitative analysis of trace Hg(II) with Vitoria blue B molecular probe

Aihui Liang\*, Guangyun Shang, Lingling Ye, Guiqing Wen, Yanghe Luo, Qingye Liu, Xinghui Zhang, Zhiliang Jiang\*

(Key Laboratory of Ecology of Rare and Endangered Species and Environmental Conservation of Education Ministry; Guangxi Key Laboratory of Environmental Pollution Control Theory and Technology, Guangxi Normal University, Guilin 541004, China)

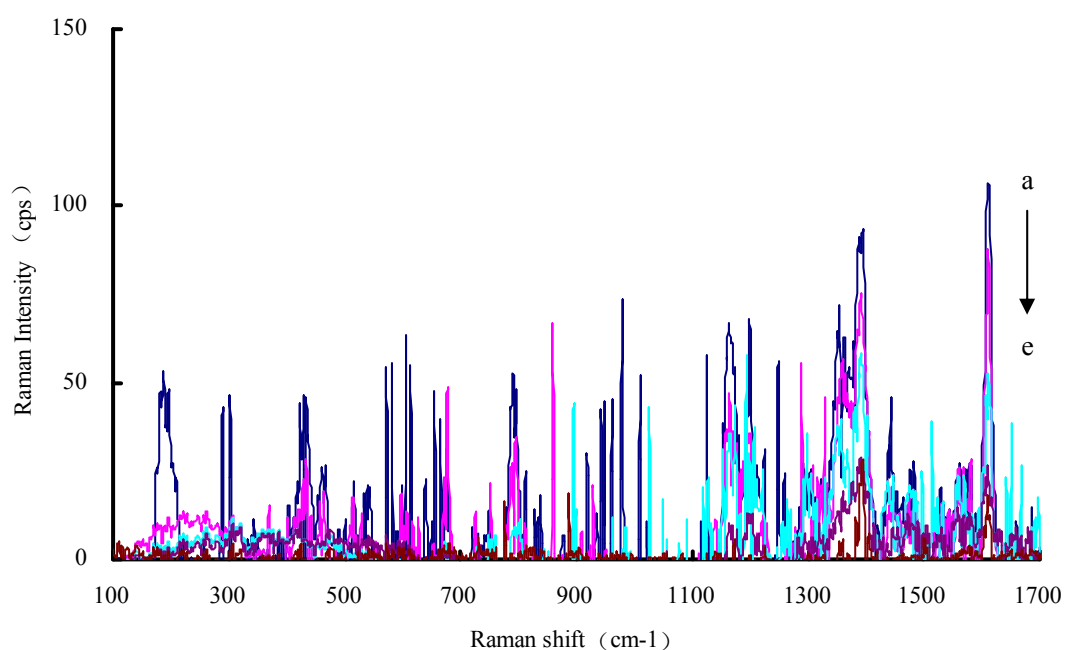
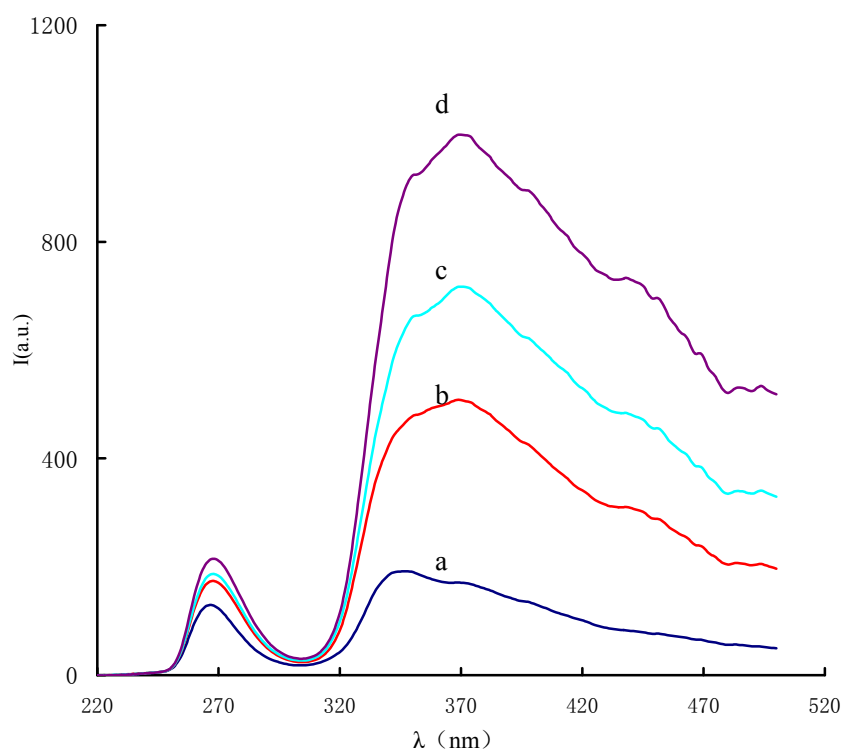


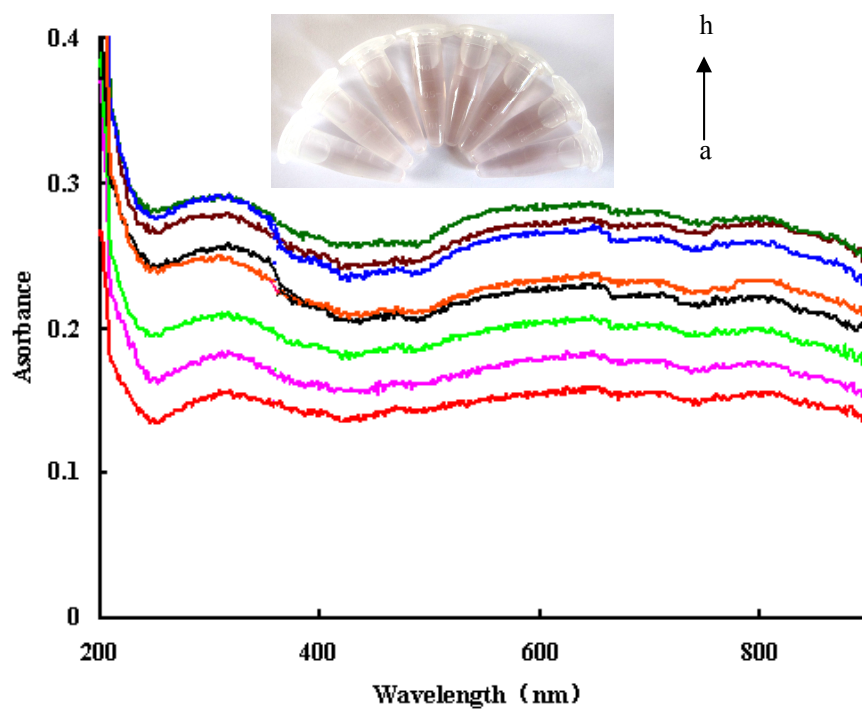
Figure S1 SERS spectra of the Hg<sup>2+</sup>-AuNPs-NaH<sub>2</sub>PO<sub>2</sub>-VBB system

a: 5.7 μg/ml AuNPs + 67.5 mmol/L CH<sub>3</sub>COOH + 50 mmol/L NaH<sub>2</sub>PO<sub>2</sub>, reaction time 15 min at 60 °C, + 1.0 μmol/L VBB; b: a + 50 nmol/L HgCl<sub>2</sub>; c: a + 125 nmol/L HgCl<sub>2</sub>; d: a + 250 nmol/L HgCl<sub>2</sub>; e: a + 375 nmol/L HgCl<sub>2</sub>.



**Figure S2** RRS spectra of the  $\text{Hg}^{2+}$ - $\text{NaH}_2\text{PO}_2$  system

a: 0.225 mol/L HCl+0.188mol/L  $\text{NaH}_2\text{PO}_2$ ; b: a+1000nmol/L  $\text{Hg}^{2+}$ ; c: a+2000nmol/L  $\text{Hg}^{2+}$ ; d: a+3000 nmol/L  $\text{Hg}^{2+}$ .



**Figure S3** Absorption spectra of the  $\text{Hg}^{2+}$ - $\text{HAuCl}_4$ - $\text{NaH}_2\text{PO}_2$  system

a: 120 $\mu\text{mol/L}$   $\text{HAuCl}_4$ +0.225mol/L HCl + 0.188mol/L  $\text{NaH}_2\text{PO}_2$ ; b:a+25nmol/L  $\text{HgCl}_2$ ;

c:a+50nmol/L HgCl<sub>2</sub>; d:a+125nmol/L HgCl<sub>2</sub>; e:a+150nmol/L HgCl<sub>2</sub>; f:a+250nmol/L HgCl<sub>2</sub> g:a+300nmol/L HgCl<sub>2</sub>; h:a+350nmol/L HgCl<sub>2</sub>.

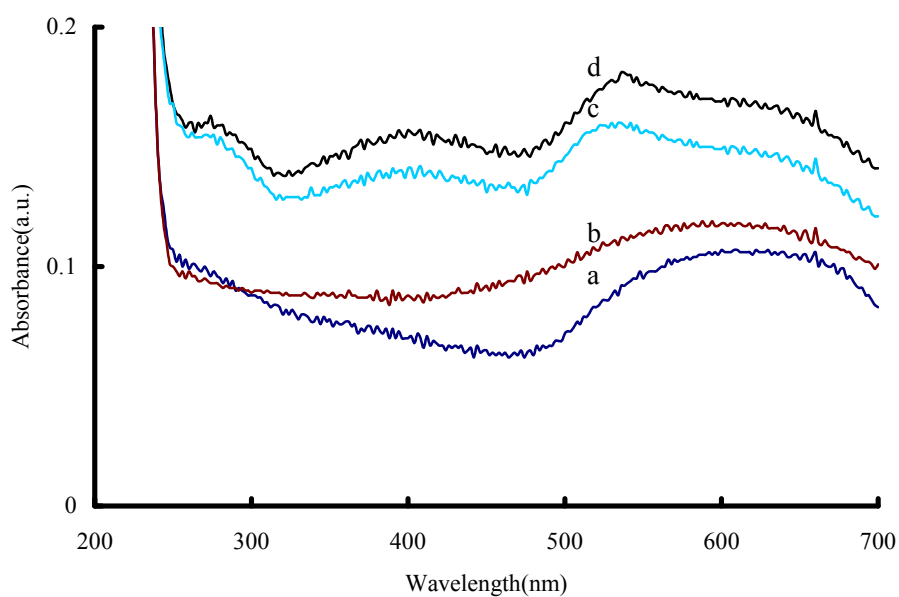


Figure S4 Absorption spectra of the Hg<sup>2+</sup>-AuNPs-NaH<sub>2</sub>PO<sub>2</sub> system

a: 5.7μg/ml AuNPs + 67.5mmol/L CH<sub>3</sub>COOH + 25mmol/L NaH<sub>2</sub>PO<sub>2</sub>, reaction time 15min at 60 °C; b:a+0.25μmol/L HgCl<sub>2</sub>; c:a+0.5 μmol/L HgCl<sub>2</sub>; d: a+0.75μmol/L HgCl<sub>2</sub>; e:a+1μmol/L HgCl<sub>2</sub>.

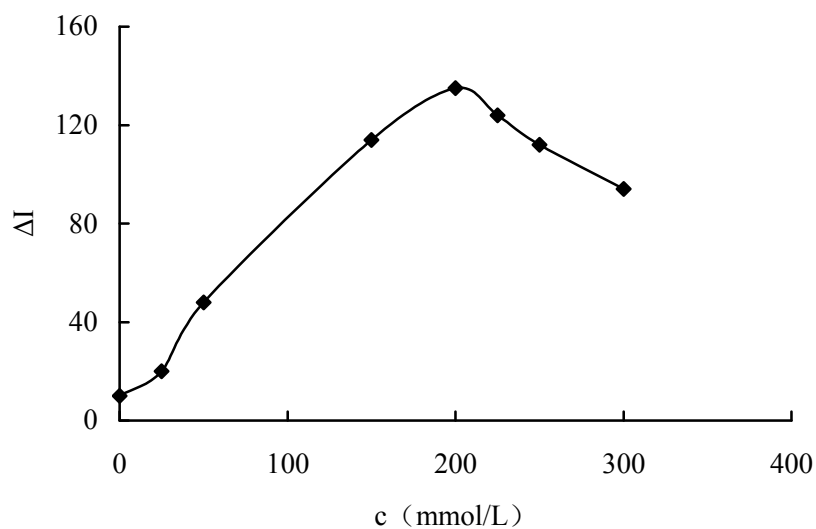
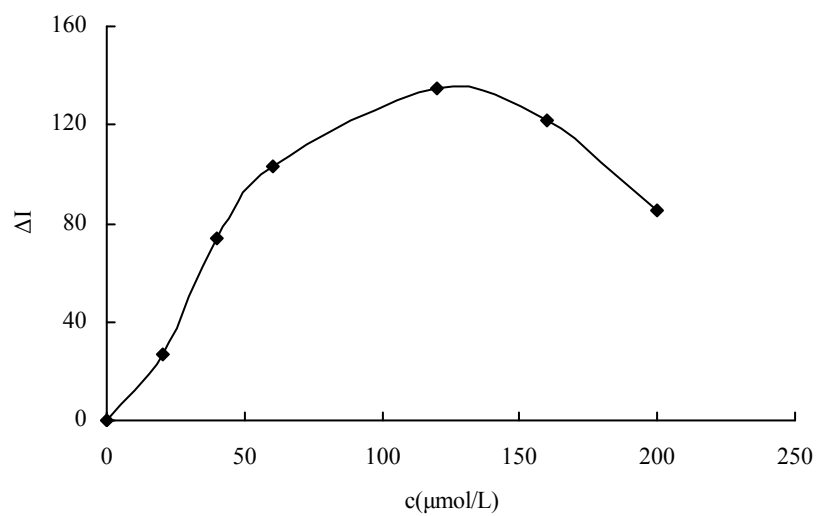


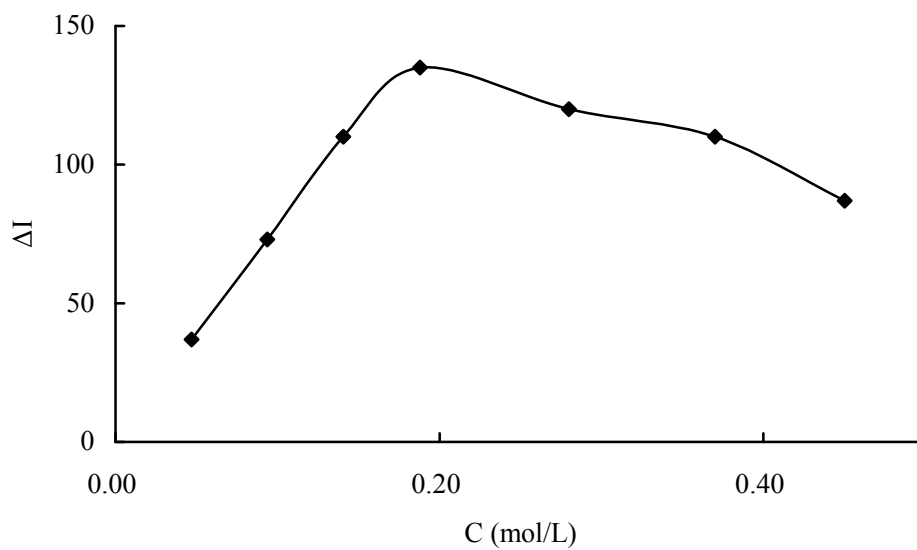
Figure S5 Effect of HCl concentration on the ΔI

120μmol/L HAuCl<sub>4</sub>+0.188mol/L NaH<sub>2</sub>PO<sub>2</sub>+20nmol/L HgCl<sub>2</sub>+ 1μmol/L VBB



**Fig. S6** Effect of  $\text{HAuCl}_4$  concentration on the  $\Delta I$

0.225mmol/L HCl + 20nmol/L  $\text{HgCl}_2$  + 0.188mol/L  $\text{NaH}_2\text{PO}_2$  + 1μmol/L VBB



**Fig. S7** Effect of  $\text{NaH}_2\text{PO}_2$  concentration on the  $\Delta I$

0.225mmol/L HCl + 20nmol/L  $\text{HgCl}_2$  + 120μmol/L  $\text{HAuCl}_4$  + 1μmol/L VBB

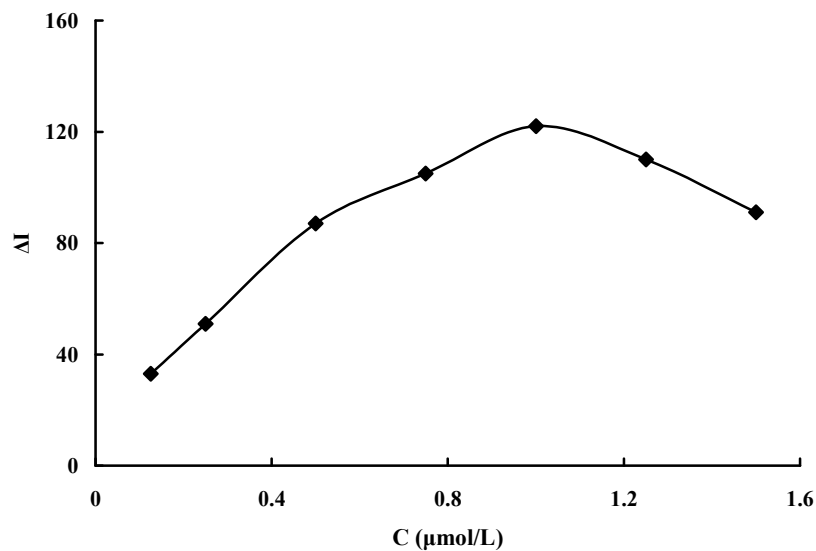
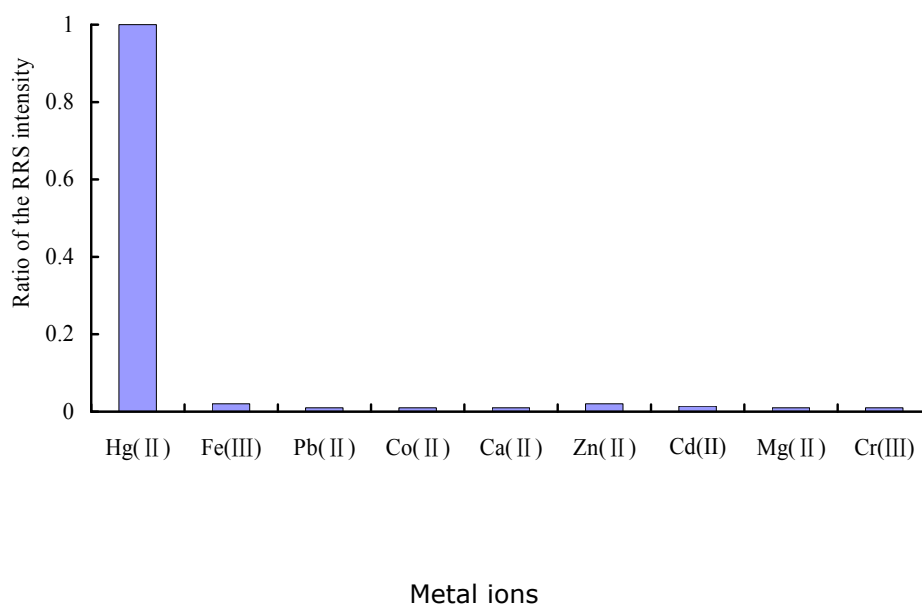


Figure S8 Effect of VBB concentration on the  $\Delta I$

0.225 mmol/L HCl + 120 μmol/L H<sub>AuCl<sub>4</sub></sub>+0.188mol/L NaH<sub>2</sub>PO<sub>2</sub>+20 nmol/L HgCl<sub>2</sub>



**Figure S9** Metal ion catalytic enhancement on the AuNP particle reaction

0.225 mol/L HCl+50nmol/L HgCl<sub>2</sub>+120 μmol/L H<sub>AuCl<sub>4</sub></sub>+0.188 NaH<sub>2</sub>PO<sub>2</sub>+ 1.0 μmol/L VBB. Ratio =  $[(I)_{\text{Hg}} - (I)_{\text{Hg+MI}}] / (I)_{\text{Hg}}$ , the MI represents metal ion.

Table S1 Catalysis of AuNPs on the particle reaction

Size (nm)	Regress equation	Linear range ( $\mu\text{mol/L}$ )	Coefficient
10	$\Delta I = 19.1 C_{\text{AuNP}} + 12.5$	0.1-10	0.9849
30	$\Delta I = 17.5 C_{\text{AuNP}} + 51.5$	0.2-15	0.9739
50	$\Delta I = 13.8 C_{\text{AuNP}} + 40.7$	0.4-15	0.9876
70	$\Delta I = 9.7 C_{\text{AuNP}} + 75.6$	0.5-15	0.8974

Table S2 The comparing of analytical features for Hg(II)

System	Method	Regress equation	LR (nmol/L)	Coefficient	DL (nmol/L)
Au(III)-NaH <sub>2</sub> PO <sub>2</sub> -VBB	SERS	$\Delta I = 5.18C + 9.2$	3.0-150	0.9890	0.8
Au(III)-NaH <sub>2</sub> PO <sub>2</sub>	RRS	$\Delta I = 13.9C + 34.2$	10-100	0.9925	5.0
AuNP-NaH <sub>2</sub> PO <sub>2</sub> -VBB	SERS	$\Delta I = 0.66C + 2.8$	25-125	0.9832	10
AuNP-NaH <sub>2</sub> PO <sub>2</sub>	RRS	$\Delta I = 2.21C - 247$	250-2000	0.9932	150