Electronic Supplementary Material (ESI) for Analytical Methods.

Selective determination of trace boron based on resonance Rayleigh scattering energy transfer from nanogold aggregate to complex of boric acid-azomethine-H

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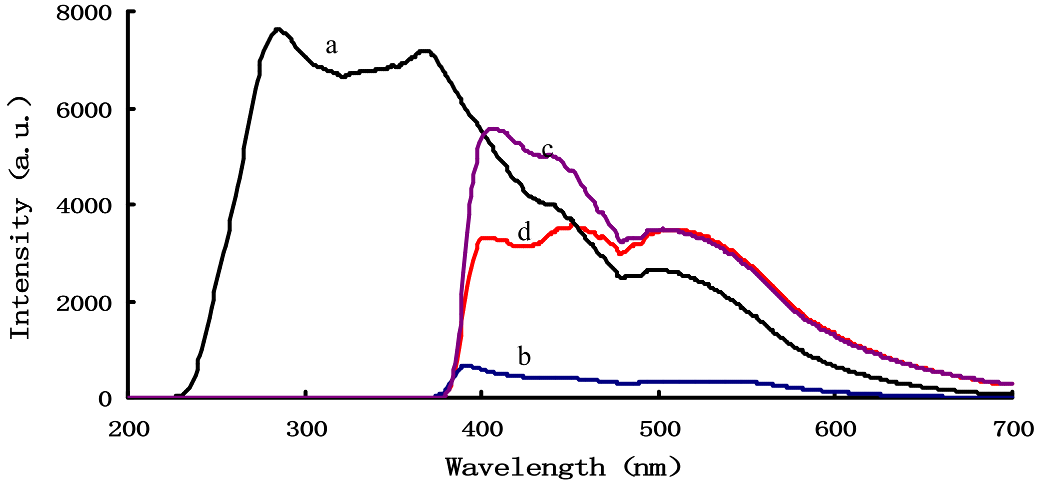


Figure 1S RRS spectra of the AMH-AuNPs-boron system

(a) 200 ng/ml B-0.17μg/m AuNPs -pH 5.6 NH_4AC-HAc; (b) 200 ng/mlB-0.17μg/ml AuNPs-7.5×10^{-4}g/ml azomethine –H; (c) pH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH -0.17μg/ml AuNPs; (d) pH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH-0.17μg/ml AuNPs-200 ng/ml B.

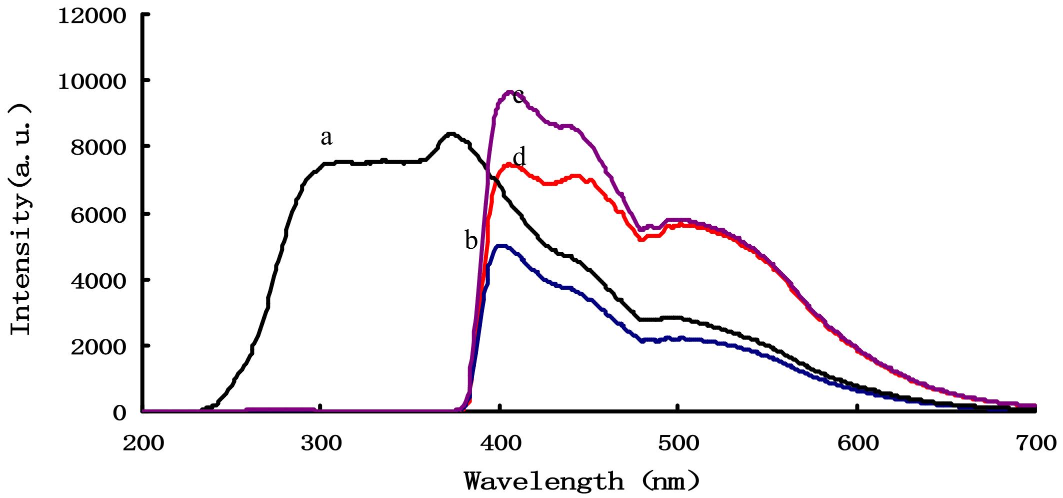


Figure 2S RRS spectra of the AMH-HAuCl$_4$-boron system

（a）200 ng/mL B-pH 5.6 NH_4AC-HAc -0.375μg/ml $HAuCl_4$; (b) 200 ng/mL B- 7.5×10^{-4}g/ml AMH - 0.375μg/ml $HAuCl_4$;（c）pH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH -0.375μg/ml $HAuCl_4$;（c）pH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH- -0.375μg/ml $HAuCl_4$-200 ng/mL B.

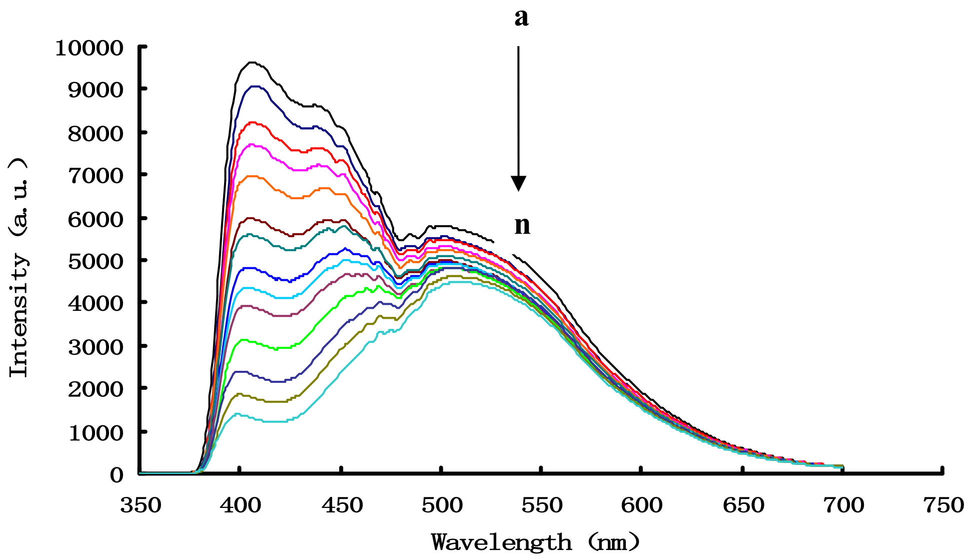


Figure 3S RRS spectra of the B-AMH-HAuCl$_4$ system

（a）2.5×10^{-2}g/mlpH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH -0.375μg/ml $HAuCl_4$; (b)a+5 ng/ml B; (c) a+40 ng/ml B; (d) a+80 ng/ml B; (e) a+100 ng/ml B; (f) a+150 ng/ml B; (g) a+200 ng/mlB; (h) a+250 ng/mlB;（i）a+300 ng/mlB;（j）a+350 ng/ml B;（k）a+400 ng/ml B;（l）a+450 ng/ml B;（m）a+500 ng/ml B; (n）a+600 ng/ml B.

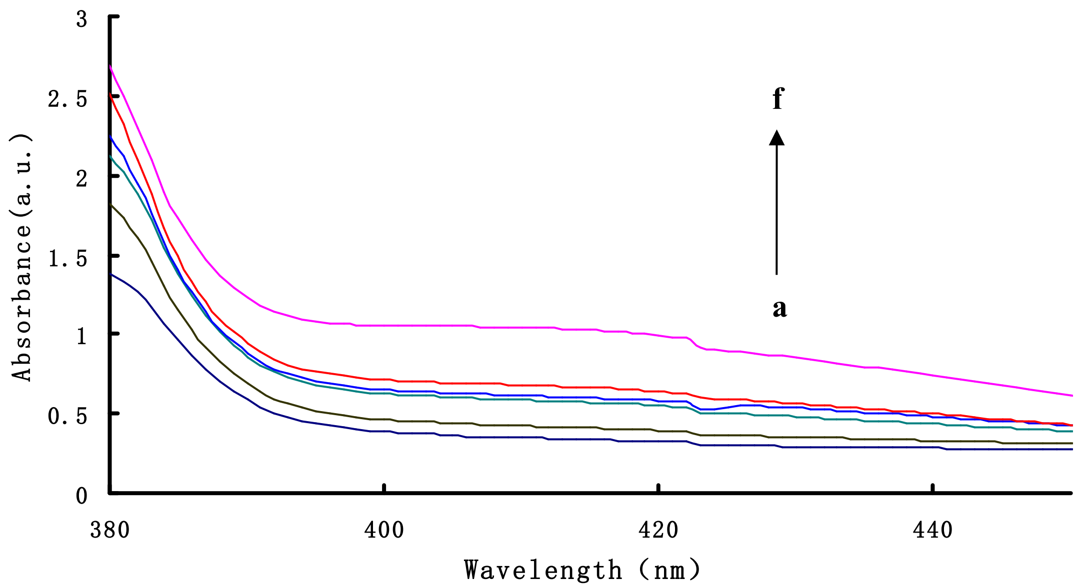


Figure 4SA Absorption spectra of the B-AMH-AuNP system

(a)pH 5.6 NH_4Ac-HAc -7.5×10^{-4}g/mL AMH-0.17μg/mL AuNPs; (b)a+100 ng/mL B; (c) a+200 ng/mL B; (d) a+250 ng/mL B; (e) a+600 ng/mL B; (f) a+650 ng/mL B.

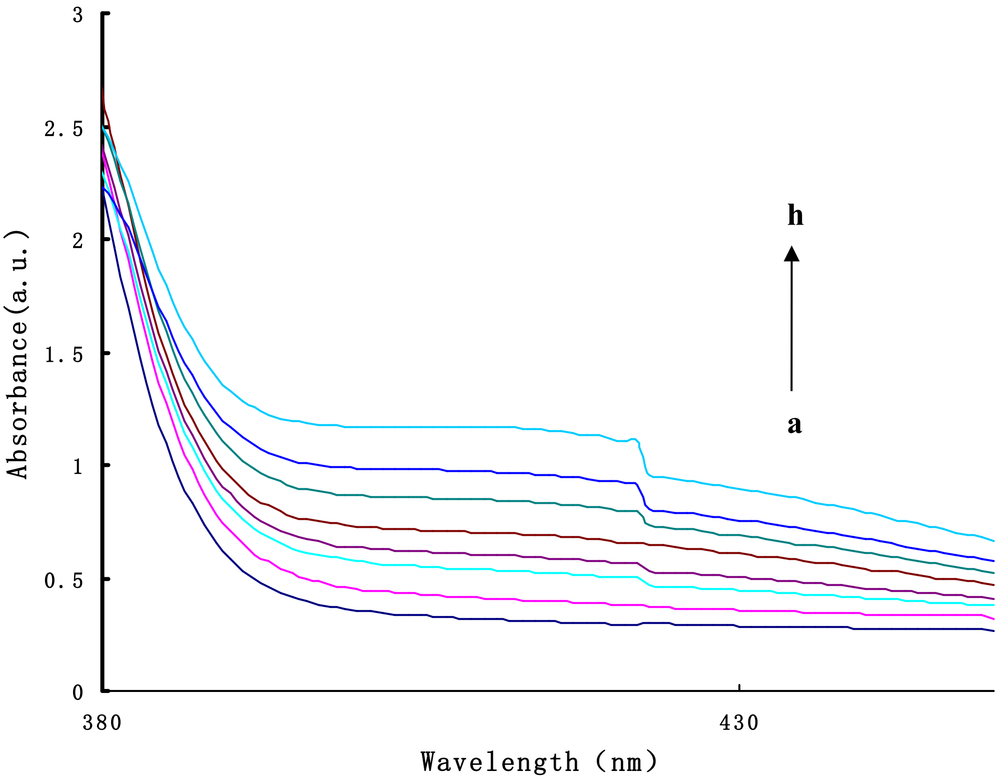


Figure 4SB Absorption spectra of the B-AMH- $HAuCl_4$ system

（a）pH 5.6 NH_4AC-HAc -7.5×10^{-4}g/mL AMH -0.375μg/mL $HAuCl_4$; (b)a+50 ng/mL B; (c) a+75 ng/mL B; (d) a+200 ng/mL B; (e) a+300 ng/mL B; (f) a+400 ng/ml B; (g) a+600 ng/mL B; (h) a+7500 ng/mL B.

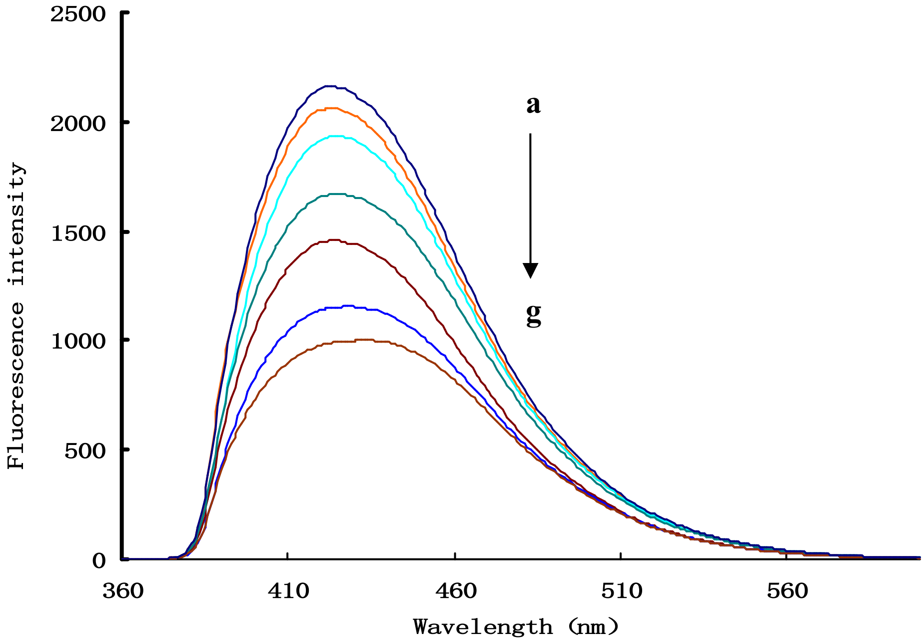


Figure 5S Fluorescence spectra of the B-AMH system

（a）2.5×10^{-2}g/mlpH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH; (b)a+10 ng/ml B; (c) a+25 ng/ml B; (d) a+100 ng/ml B; (e) a+200 ng/ml B; (f) a+240 ng/ml B; (g) a+300 ng/ml B.

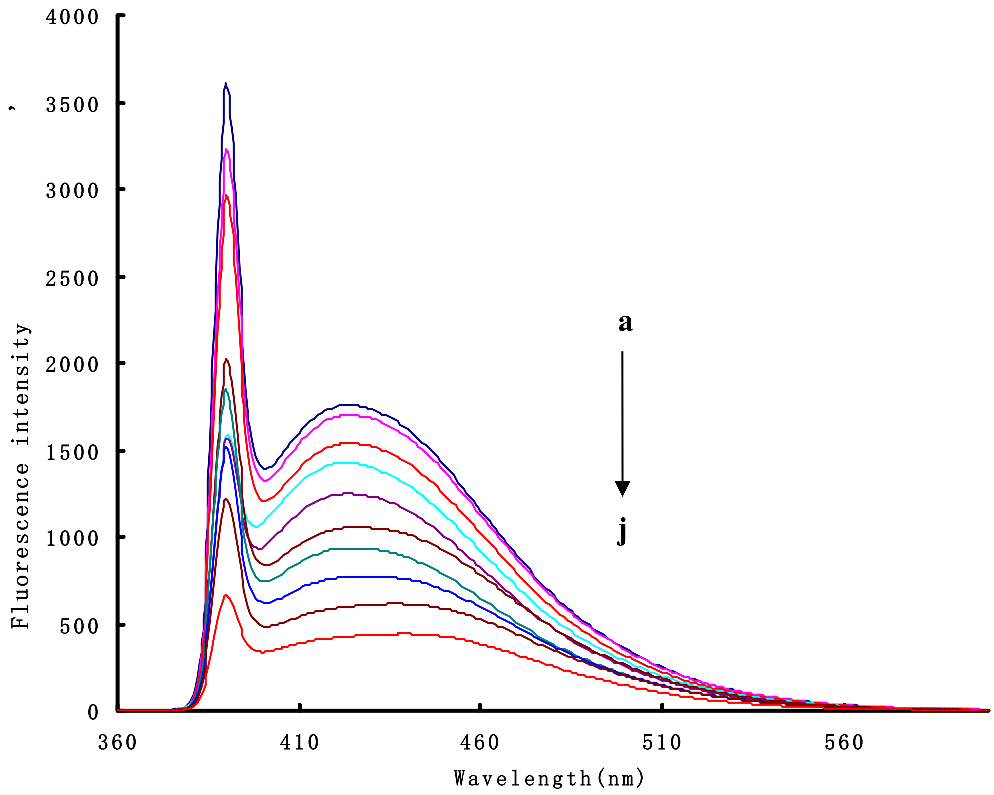
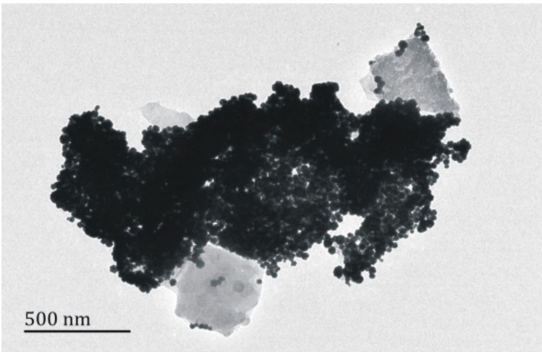


Figure 6S Fluorescence spectra of the B-AMH–$HAuCl_4$ system

（a）0.375μg/ml $HAuCl_4$-2.5×10^{-2}g/mlpH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH;　(b)a+1 ng/ml B; (c) a+2.5 ng/ml B; (d) a+5 ng/ml B; (e) a+50 ng/ml B; (f) a+100 ng/ml B; (g) a+200 ng/ml B; (h) a+300 ng/ml B;（i） a+400 ng/ml B; (j)a+500 ng/ml B.



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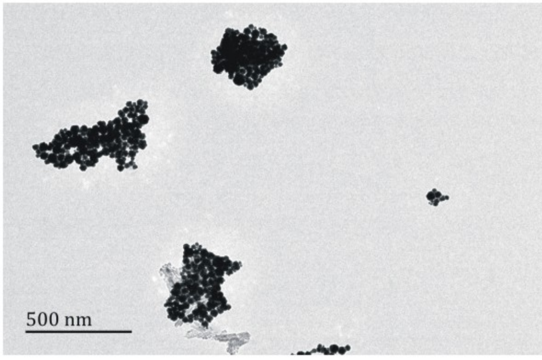

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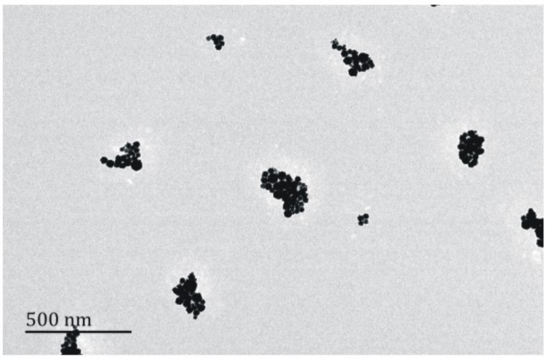
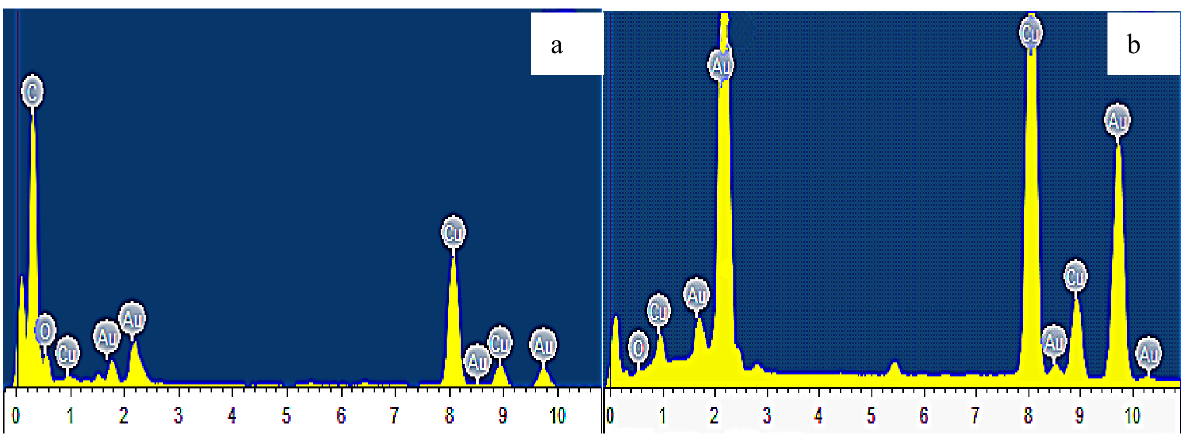


c

Figure 7S TEM of the boron-AMH- AuNPs system

a: pH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH-0.375μg/ml $HAuCl_4$; b: a+250ng/mlH_3BO_3; c: a+500ng/mlH_3BO_3.



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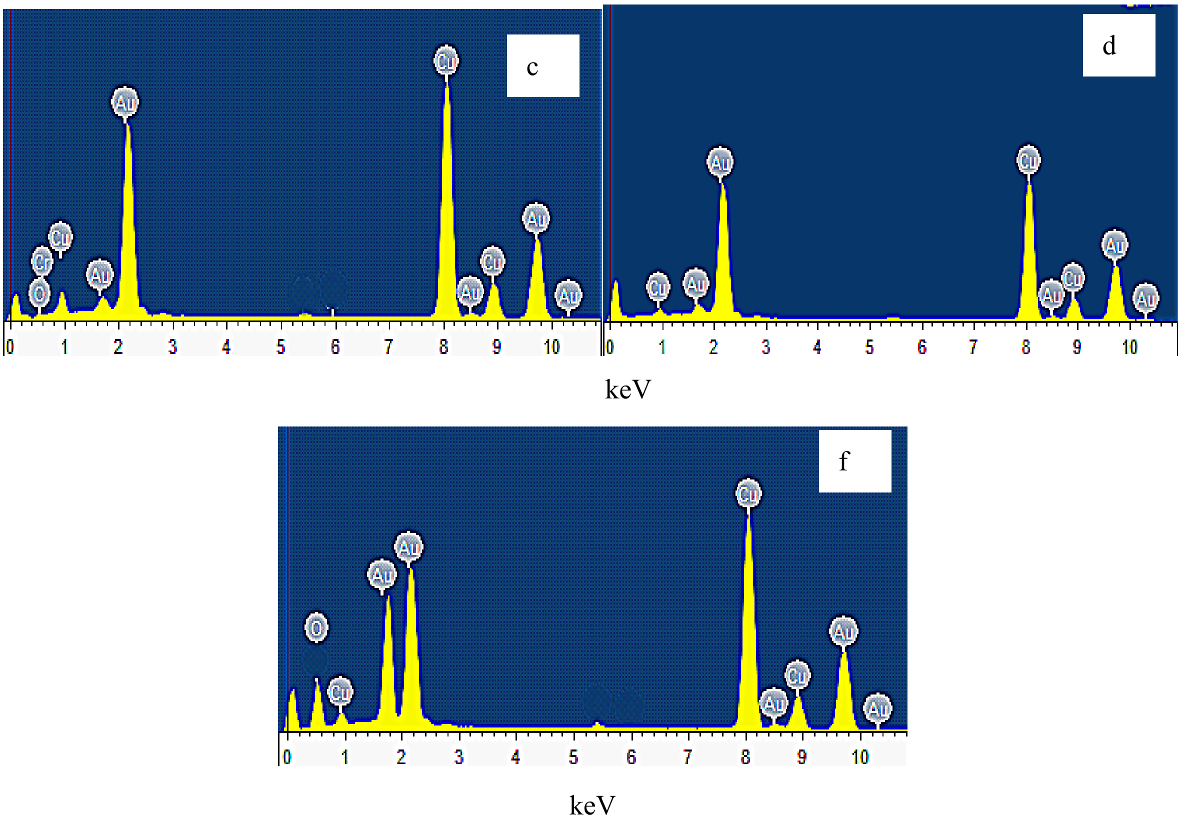

Figure 8S Energy spectra of the boron-AMH- AuNPs system

a: 0.17μg/ml AuNPs; b: pH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH -0.17μg/ml AuNPs; c: b+500ng/ml B; d: pH 5.6 NH_4AC-HAc-7.5×10^{-4}g/ml AMH -0.375μg/ml $HAuCl_4$; e: d+500ng/ml B.

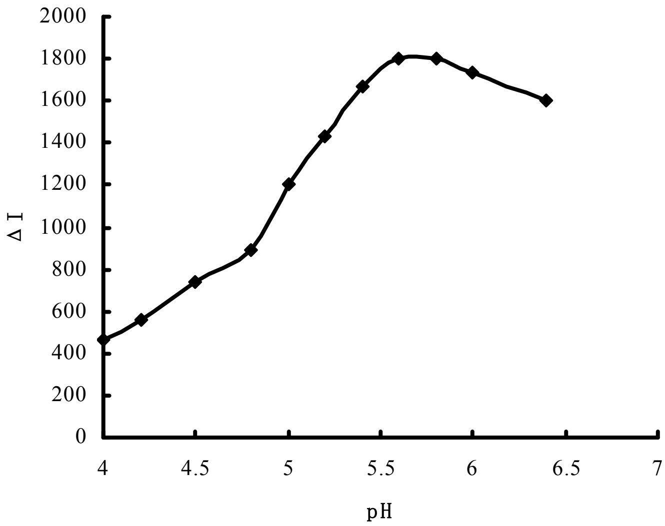

Figure 9S Effect of pH of buffer solution

200 ng/ml B -2.5×10^{-2}g/ml NH_4AC-HAc -7.5×10^{-4}g/ml AMH -0.17μg/ml AuNPs

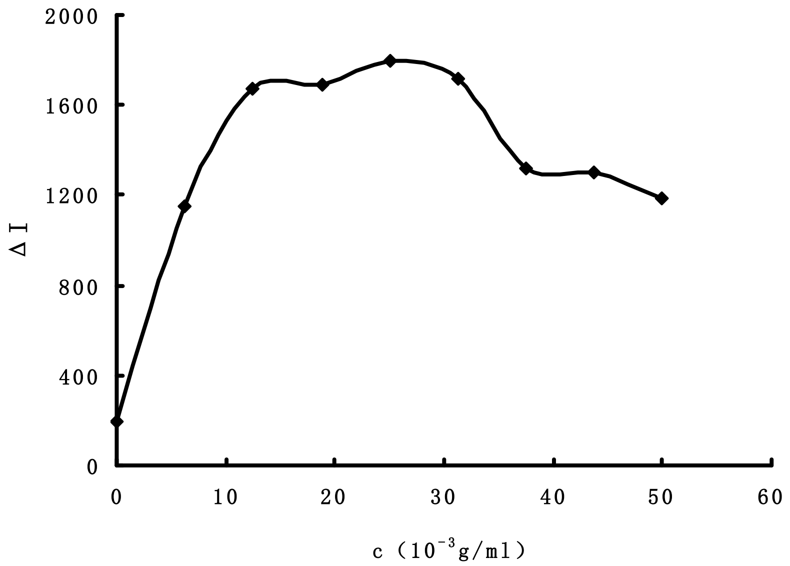

Figure 10S Effect of concentration of buffer solution

200 ng/ml B–pH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH -0.17μg/ml AuNPs

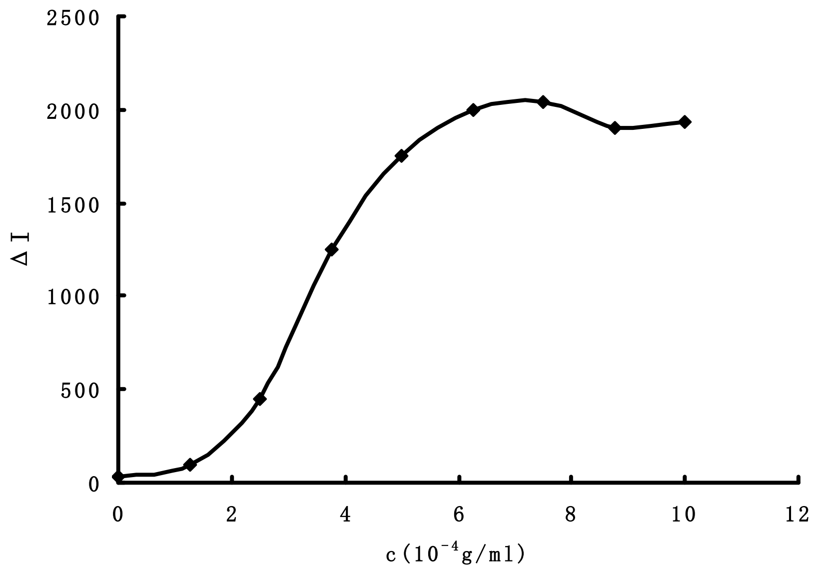

Figure 11S Effect of AMH concentration

200 ng/ml B –2.5×10^{-2}g/ml pH 5.6 NH_4AC-HAc - AMH -0.17μg/ml AuNPs;

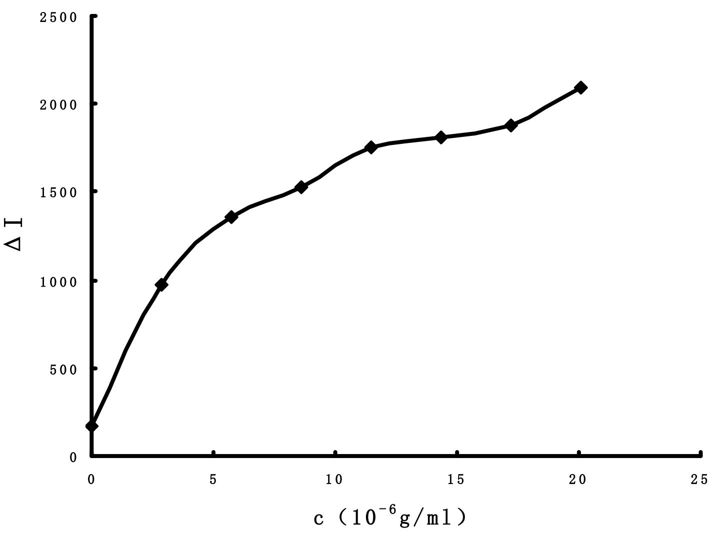

Figure 12S Effect of AuNPs- concentration

200 ng/mlB–pH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH - AuNPs

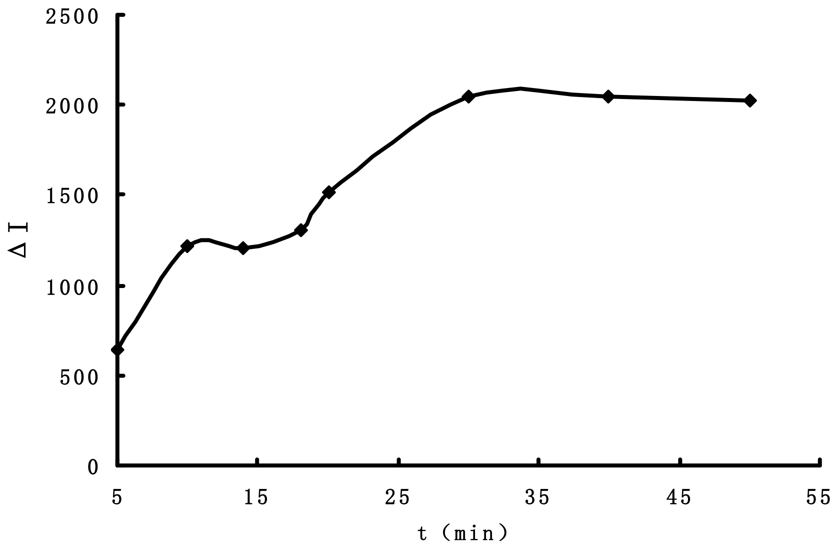

Figure 13S Effect of AMH and boron reaction time

200 ng/mlB –pH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH -0.17μg/ml AuNPs

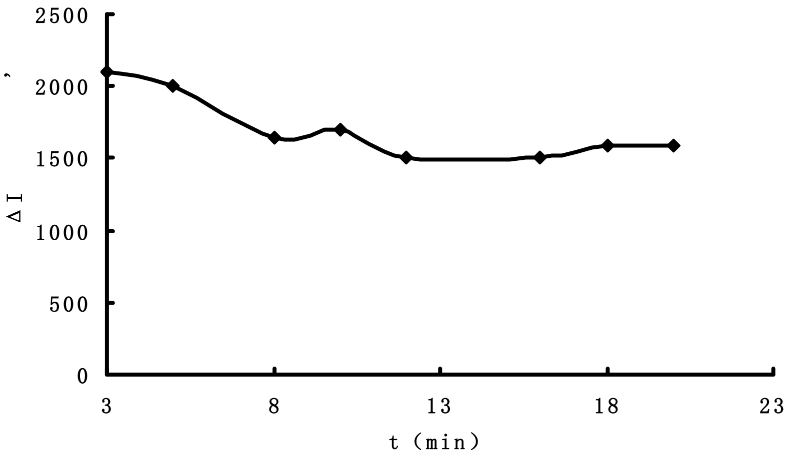

Figure 14S Effect of the time complexes react with AuNPs

200 ng/mlB –pH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH -0.17μg/ml AuNPs

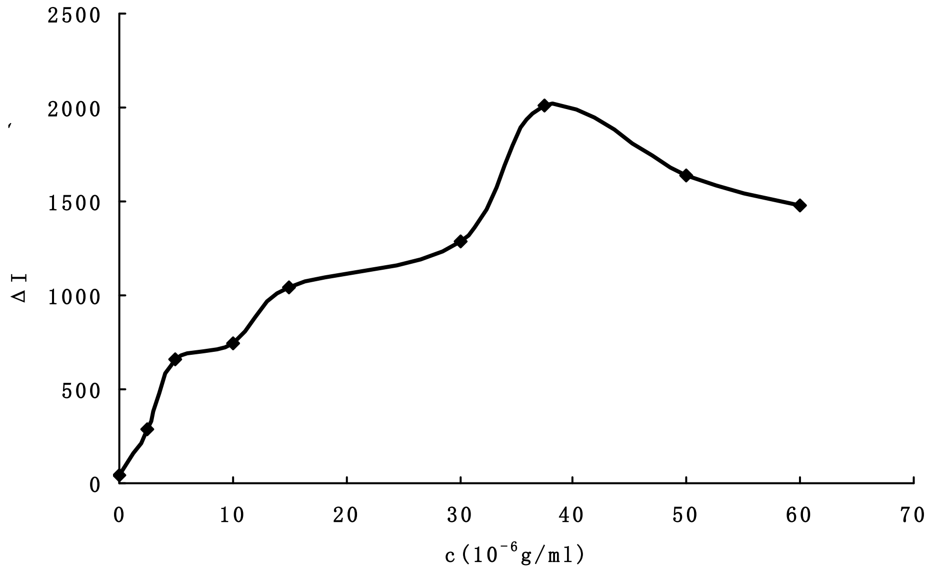

Figure 15S Effect of $HAuCl_4$ concentration

200 ng/mlB - pH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH

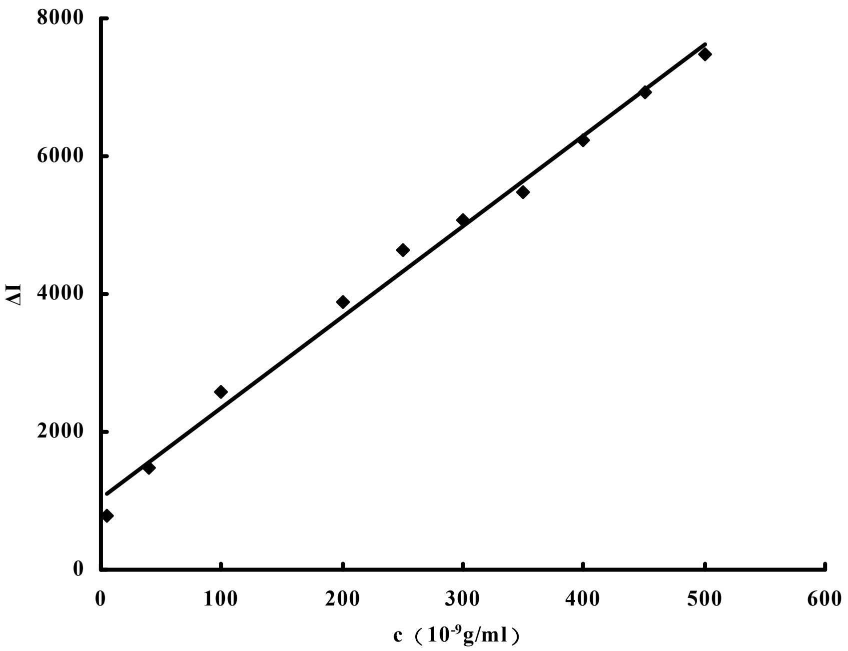

Fig. 16S Working curve of the boron-AMH- AuNPs Rayleigh scattering system
pH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH -0.375μg/mL $HAuCl_4$

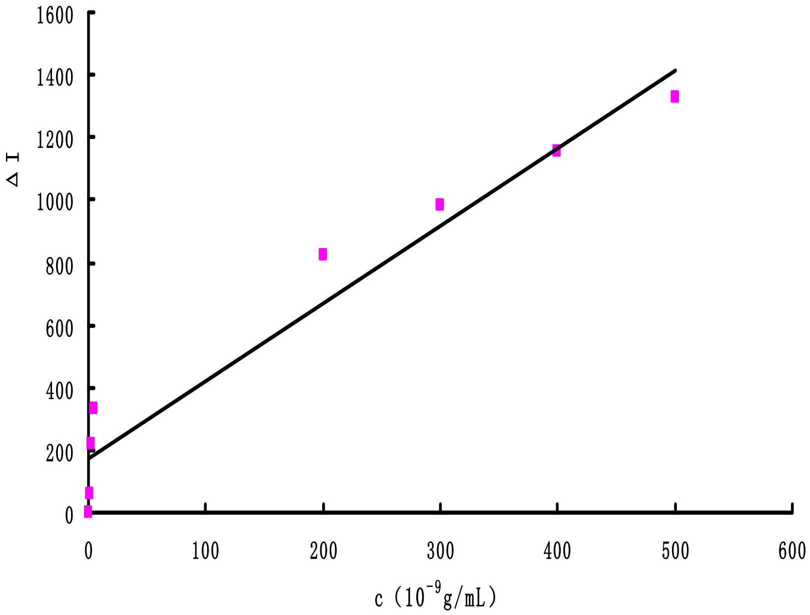

Fig. 17S curve of AMH- AuNPs-boron fluorescence system
pH 5.6 NH_4AC-HAc -7.5×10^{-4}g/ml AMH -0.375μg/ml $HAuCl_4$.

Table 1S Comparison of different analytical methods for B

Method	Principle	Linear range	Detection limit	Comments	Ref.
Fluorescence method	Base on the borate ion and alizarin red S using flow injection analysis of aqueous phase reaction	4 -40μgml^{-1}	0.34μgml^{-1}	Stability, suitable for the determination of ultra trace boron in environmental water samples, but the sensitivity is low	11
Quartz crystal resonator	Polymers with boron complexes, polymer film deposited on quartz crystal, the oscillation frequency is directly proportional to the change the concentration of boron .	0.3-80μmol/L	0.3μmol/L	complicated operation	44
Ion chromatography	Tetrafluoroborate ions change to boron	0.0667–1.0 M	----	Simple, stable. But the sensitivity was very low	29
voltammetry	Boron complexes with alizarin red S (ARS) complexes and the free ligands, adsorbed on the hanging mercury drop electrode	0–500μg L^{-1}	15μg L^{-1}	Stability, good selectivity, simple	12
ET-AAS	Determination of boron in shrimp by electrothermal atomic absorption spectrometry	-	-	Stability, good selectivity, and applied to real life	9
ICP-AES	digestion and matrix (flux) separation approach for the determination of boron in high-purity graphite powder using ICP-OES.	-	90 ng g^{-1}	The content of boron in graphite powder can be detected in less than 1 ppm level	45
Spectrophotometry	In alkaline solution, lysine with and 1,2 -naphthoquinone	2.16–43.24μgmL^{-1}	2μgmL^{-1}	Fast, low cost, but the sensitivity is low	6

HPLC	sulfonic acid and the -4-reaction of boron, charge transfer occurs Boron, at sub-ppm levels, in U_3O_8 powder and aluminum metal, was determined using complex formation and dynamically modified reversedphase high-performance liquid chromatography	0.02-0.5μg	-	Simple, expensive instrument	47
SRET	Rayleigh scattering resonance energy of nanogold transfer to the complex form by boric acid and AMH	5-1000ng/mL		The method is simple, rapid, high sensitivity, stability, selectivity	This assay
SRET	The Rayleigh scattering resonance energy of $HAuCl_4$ transfer to the complex form by boric acid and AMH	5-600ng/mL		The method is simple, rapid, high sensitivity, stability, selectivity	This assay
Fluorescence method	AMH with fluorescence, and after react with boric acid fluorescence quenching, gold nanoparticles can enhance the fluorescence quenching efficiency	9-1000 ng/mL		The method is simple, rapid, high sensitivity	This assay
Fluorescence method	AMH with fluorescence, and after react with boric acid fluorescence quenching, $HAuCl_4$ can enhance the fluorescence quenching efficiency	9-500 ng/mL		The method is simple, rapid, high sensitivity	This assay

Table 2S Accuracy of the different boron systems

System	B concentration (ng/mL)	I	Average	RSD (%)
AMH-AuNPs	150	4293, 4087, 4155, 4400, 4044	4196	3.5
	180	3254, 3043, 3200, 3058, 3124	3156	2.9
AMH-$HAuCl_4$	200	5623, 5824, 5577, 5702, 5500	5645	2.2
	500	3255, 2977, 2999, 3052, 3122	3081	3.6

Table 3S Effect of foreign substances

Coexistent substances	Tolerance (μmol/L)	Relative error(%)	Coexistent substances	Tolerance (μmol/L)	Relative error(%)
Mn^{2+}	400	0.36	F□	400	-6.9
Cd^{2+}	400	5.1	IO_3^-	400	-8.7
Zn^{2+}	400	-1.14	SO_4^{2-}	400	0.5
Na^+	400	0.2	NO_3^-	400	5.8
Glucose	400	-7.5	ClO_4^-	400	2.1
Hg^{2+}	400	-3.9	Bi^{3+}	400	-0.3
Al^{3+}	400	0.4	SiO_3^{2-}	400	-4.6
Mannitol	400	6.7	H_2O_2	400	-6.7
Glycerol	400	4.6	Glycol	400	-3.8
Salicylic acid	200	6.9	Mandelic acid	400	4.1
L-tyrosine	40	4.4	L-glutamic acid	200	-0.1

Table 4S Results for the determination of boron in water samples (n=5)

Sample	Single value (ng/mL)	Average (ng/mL)	B content (ng/mL)	Spiked B（ng/mL）	Found B (ng/mL)	Recovery (%)	RSD (%)
Sample 1	81.1, 85.3, 90.6, 75.7, 92.0	84.9	420	150	229.1	97.57	2.4
				200	324.1	96.8	2.7
Sample 2	58.7, 60.8, 57.6, 44.3, 73.8	59.0	300	150	199.8	95.6	1.7
				200	304.2	98.8	3.0
Sample 3	108.4, 103.3, 92.0, 107.3, 114.4	105.1	530	200	328.3	102.6	1.6
				400	461.7	99.7	4.1
Sample 4	23.7, 27.6, 22.2, 23.8, 27.3	24.9	120	200	301.4	109.6	2.6
				400	445.6	104.9	3.4
Sample 5	30.5, 23.1, 30.4, 30.5, 31.8	29.3	150	200	300.7	107.6	2.7
				400	446.3	103.9	4.1
Sample 6	56.4, 62.9, 73.1, 47.1, 50.0	57.9	290	200	310.7	100.9	3.7
				400	448.5	97.9	2.3