A novel N/Au co-doped carbon dots probe for continuous detection of silicate and phosphate by resonance Rayleigh scattering

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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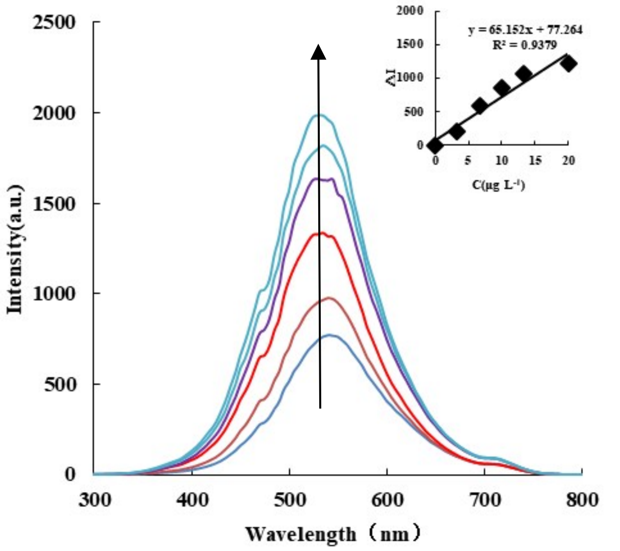

Fig. S1 RRS spectrum of CD $_{N/Au1}$-AMS-CAS-PO_4^{3-}-SiO_3^{2-} system (a):75mM H_2SO_4 +9.99μg L^{-1} PO_4^{3-}+ SiO_3^{2-}+3.33mg mL^{-1}AMS+1.13mg mL^{-1}CAS+1.6mg mL^{-1} $CD_{N/Au1}$; (b): a+3.33μg L^{-1} SiO_3^{2-}; (c): a+6.66μg L^{-1} SiO_3^{2-}; (d): a+9.99μg L^{-1} SiO_3^{2-}; (e): a+13.32μg L^{-1} SiO_3^{2-}; (f): a+16.65μg L^{-1} SiO_3^{2-}.

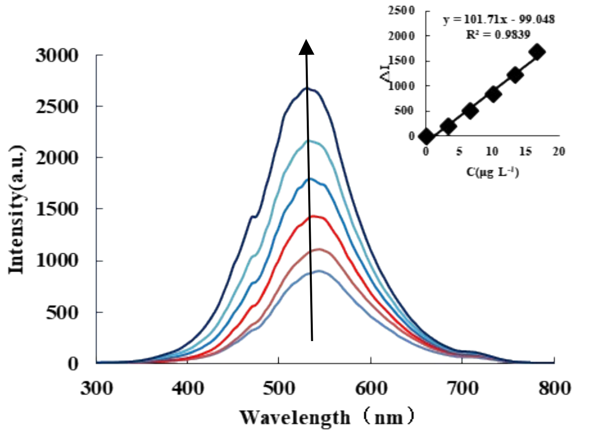

Fig. S2 RRS spectrum of CD $_{N/Au3}$-AMS-CAS-PO_4^{3-}-SiO_3^{2-} system (a): 75mM H_2SO_4 +9.99μg L^{-1} PO_4^{3-}+ SiO_3^{2-}+3.33mg mL^{-1} AMS+1.13mg mL^{-1} CAS+1.6mg mL^{-1} $CD_{N/Au3}$; (b): a+3.33μg L^{-1} SiO_3^{2-}; (c): a+6.66μg L^{-1} SiO_3^{2-}; (d): a+9.99μg L^{-1} SiO_3^{2-}; (e): a+13.32μg L^{-1} SiO_3^{2-}; (f): a+16.65μg L^{-1} SiO_3^{2-}

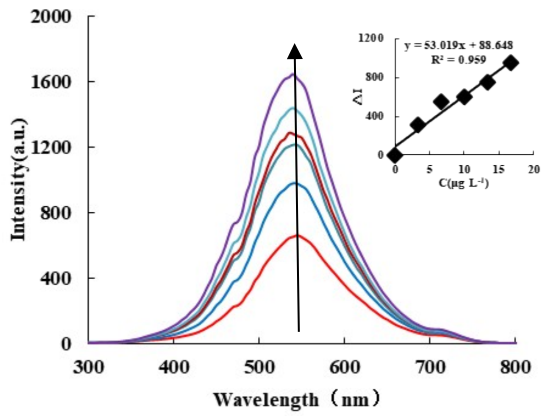

Fig. S3 RRS spectrum of CD $_{N/Au4}$-AMS-CAS-PO_4^{3-}- SiO_3^{2-} system (a): 75mM H_2SO_4 +9.99μg L^{-1} PO_4^{3-}+ SiO_3^{2-}+3.33mg mL^{-1}AMS+1.13mg mL^{-1}CAS+1.6mg mL^{-1} CD $_{N/Au4}$; (b): a+3.33μg L^{-1} SiO_3^{2-}; (c): a+6.66μg L^{-1} SiO_3^{2-}; (d): a+9.99μg L^{-1} SiO_3^{2-}; (e): a+13.32μg L^{-1} SiO_3^{2-}; (f): a+16.65μg L^{-1} SiO_3^{2-}

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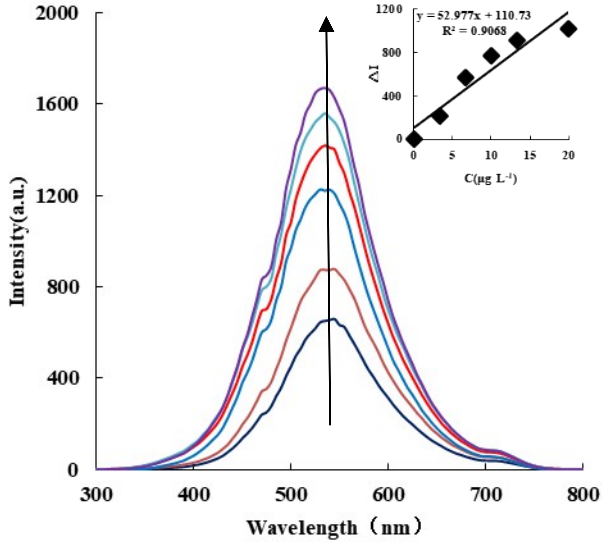

Fig. S4 RRS spectrum of CD $_{N/Au1}$-AMS-PO_4^{3-} system (a): 75mM H_2SO_4 + PO_4^{3-} +3.33mg mL^{-1}AMS+1.6mg mL^{-1} CD$_{N/Au1}$; (b): a+3.33μg L^{-1} PO_4^{3-}; (c): a+6.66μg L^{-1} PO_4^{3-}; (d): a+9.99μg L^{-1} PO_4^{3-}; (e): a+13.32μg L^{-1} PO_4^{3-}; (f): a+16.65μg L^{-1} PO_4^{3-}.

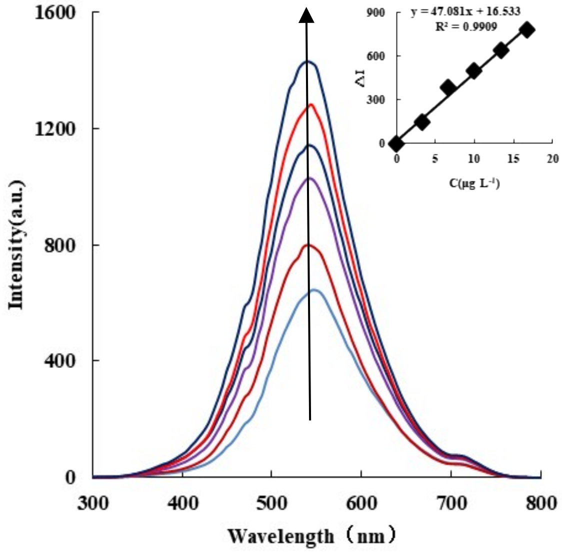

Fig. S6 RRS spectrum of CD $_{N/Au4}$-AMS-PO_4^{3-} system (a): 75mM H_2SO_4+ PO_4^{3-} +3.33mg mL^{-1}AMS+1.6mg mL^{-1} CD$_{N/Au4}$; (b): a+3.33μg L^{-1} PO_4^{3-}; (c): a+6.66μg L^{-1} PO_4^{3-}; (d): a+9.9 9μg L^{-1} PO_4^{3-}; (e): a+13.32μg L^{-1} PO_4^{3-}; (f): a+16.65μg L^{-1} PO_4^{3-}

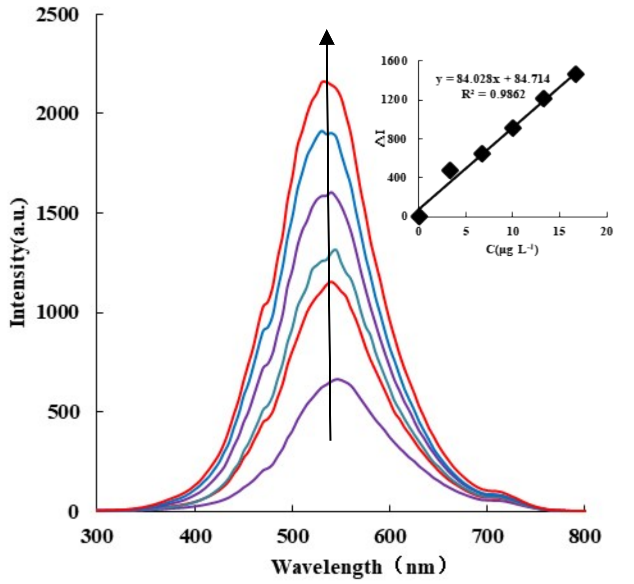

Fig. S5 RRS spectrum of CD $_{N/Au3}$-AMS-PO_4^{3-} system (a): 75mM H_2SO_4 + PO_4^{3-} +3.33mg mL^{-1} AMS+1.6mg mL^{-1} CD$_{N/Au3}$; (b): a+3.33μg L^{-1} PO_4^{3-}; (c): a+6.66μg L^{-1} PO_4^{3-}; (d): a+9.99μg L^{-1} PO_4^{3-}; (e): a+13.32μg L^{-1} PO_4^{3-}; (f): a+16.65μg L^{-1} PO_4^{3-}

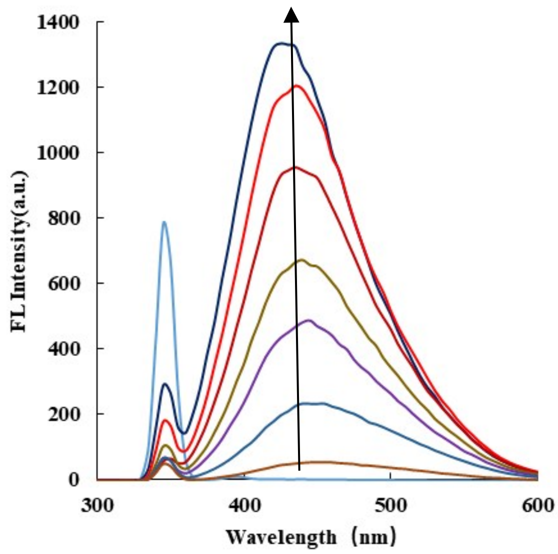

Fig. S7 Fluorescence spectrum of CD$_{N/Au2}$ system a: 0 mg mL^{-1} CD$_{N/Au2}$; b: 0.08mg mL^{-1} CD$_{N/Au2}$; c: 0.24 mg mL^{-1} CD$_{N/Au2}$; d: 0.32 mg mL^{-1} CD$_{N/Au2}$; e: 0.4 mg mL^{-1} CD$_{N/Au2}$; f: 0.48 mg mL^{-1} CD$_{N/Au2}$; g: 0.72 mg mL^{-1} CD$_{N/Au2}$; h: 0.80 mg mL^{-1} CD$_{N/Au2}$

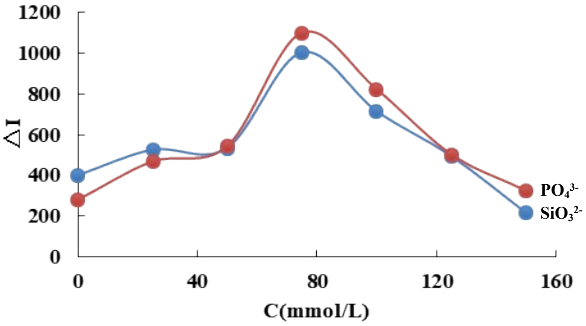

Fig. S8a Effect of H_2SO_4 concentration on ΔI H_2SO_4+10μg L^{-1} SiO_3^{2-}(10μg L^{-1} PO_4^{3-})+3.33mg mL^{-1} AMS+1.6mg mL^{-1} $CD_{N/Au2}$

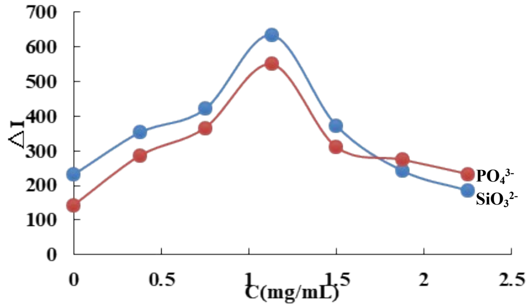

Fig. S8c Effect of CAS concentration on ΔI 75mM H_2SO_4+10μg L^{-1} SiO_3^{2-}(10μg L^{-1} PO_4^{3-})+3.33mg mL^{-1} AMS+CAS+1.6mg mL^{-1} $CD_{N/Au2}$

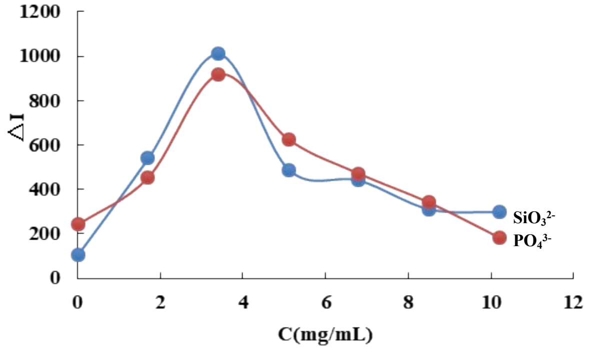

Fig. S8b Effect of AMS concentration on ΔI 75mM H_2SO_4+10μg L^{-1} SiO_3^{2-}(10μg L^{-1} PO_4^{3-})+AMS+1.6mg mL^{-1} $CD_{N/Au2}$

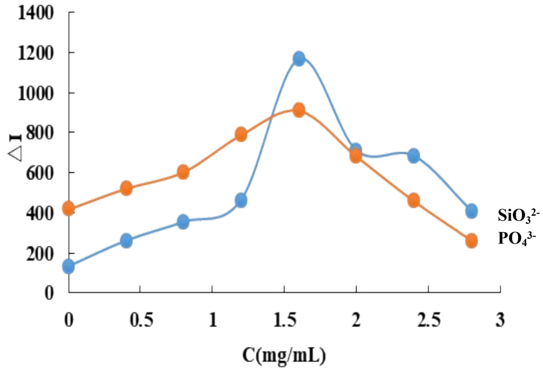

Fig. S8d Effect of $CD_{N/Au2}$ concentration on ΔI 75mM H_2SO_4+10μg L^{-1} SiO_3^{2-}(10μg L^{-1} PO_4^{3-})+3.33mg mL^{-1}AMS

Table S1 The RRS analytical properties of SiO_3^{2-}/PO_4^{3-} with CD probes

System	LR (μg L^{-1})	Regression equation	Coefficient	DL (μg L^{-1})
SiO_3^{2-}-CD_N	3.33-19.98	ΔI= 36.8 C_{Si}-10.8	0.9533	1
SiO_3^{2-}-$CD_{N/Au1}$	3.33-19.98	ΔI = 65.2 C_{Si}+77.3	0.9379	1
SiO_3^{2-}-$CD_{N/Au2}$	1.11-19.98	ΔI= 144.6 C_{Si}-191	0.9687	0.3
SiO_3^{2-}-$CD_{N/Au3}$	3.33-16.65	ΔI = 101.7 C_{Si}-99.0	0.9839	1
SiO_3^{2-}-$CD_{N/Au4}$	3.33-16 .65	ΔI= 53.0 C_{Si}+88.6	0.959	1
PO_4^{3-}-CD_N	3.33-19.98	ΔI= 35.0 C_P-49.2	0.9596	1
PO_4^{3-}-$CD_{N/Au1}$	3.33-19.98	Δ= 53.0 C_P+110.7	0.9068	1

PO_4^{3-}-$CD_{N/Au2}$	1.11-19.98	Δ*I*= 134.9 C_P-162	0.9859	0.3
PO_4^{3-}-$CD_{N/Au3}$	3.33-16.65	Δ*I*= 84.0 C_P+84.7	0.9862	1
PO_4^{3-}-$CD_{N/Au4}$	3.33-16.65	Δ*I*= 47.1 C_P+16.5	0.9909	1

Table S2 Comparison of some of the reported analytical methods for continuous determination of SiO_3^{2-} and PO_4^{3-}

Method	Principle	Linear range	Detection limit	Comments	RSD	Ref.
Flow injection analysis	The analyte was reacted with AMS to form molybdenum phosphate and molybdenum silicic acid, and the oxalic acid solution was injected and combined with the sample stream containing the heteropolyacid mixture. The area and the absorbance measured at the peak can be used to measure phosphates and silicates.	0.20-15.00 mg L^{-1} PO_4^{3} 0.20-20.00 mg L^{-1} SiO_3^{2-}	PO_4^{3-}:0.054mg L^{-} SiO_3^{2-}:0.092mg L^{-1}	Complicated operation	PO_4^{3-}:2.7% SiO_3^{2-}:0.9%	[29]
Ion Exclusion Chromatography (IEC) and Inductively Coupled Plasma Mass Spectrometry (SF-ICPM)	The dissolved silicate was determined by double isotope dilution using Si spikes, while the phosphate was quantified using a one point weight standard addition with an internal standard of the same Si spike.	0-1.670μM PO_4^{3-} 0-30.20μM SiO_3^{2-}	PO_4^{3-}:0.18ng g^{-1} SiO_3^{2-}:0.11 ng g^{-1}	Complicated operation	PO_4^{3-}:0.47% SiO_3^{2-}:0.31%	[28]
Electrochemical method	Based on the electroactive properties of molybdenum silicate and molybdate phosphate complexes, silicates and phosphates were determined using microdisk electrodes.	1-100μM	—	Low sensitivity	—	[30]
Cross-injection analysis（CIA）-spectrophotometry	PMo blue and SiMo blue products were produced in the presence of stannous chloride, and phosphate and silicate were simultaneously analyzed by spectrophotometry.	0.1-6 mg L^{-1} PO_4^{3-} 5-100 mg L^{-1} SiO_3^{2-}	—	No need to use any reagents to modify and add selective masking agents	PO_4^{3-}:1.76% SiO_3^{2-}:1.53%	[31]
Chemical sensor	The coordination between the carboxyl group of polyacrylic acid and the Cd atom on the surface of QDs quenched the fluorescence. The addition of a silicate or phosphate anion resulted in a fluorescence recovery.	—	0.76mM PO_4^{3-} 0.02mM SiO_3^{2-}	Low sensitivity	—	[32]
RSS	Both SiO_3^{2-} and PO_4^{3-} reacted with AMS to form SiMo and PMo. Citric acid was added, and the PMo was decomposed. As the concentration of SiO_3^{2-} (PO_4^{3-}) increased, the SiMo (PMo) adhered to the $CD_{N/Au}$ surface, resulting in a linear increase in the RRS at 555 nm.	3.33-19.98μg L^{-1}	0.32μg L^{-1} PO_4^{3-} 0.28μg L^{-1} SiO_3^{2-}	Simple, High sensitivity	PO_4^{3-}:0.55-2.1%. SiO_3^{2-}:0.28-1.48%.	This method

Table S3A Effect of interference on RRS determination of silicates

Coexisting substance	Tolerance (times)	Relative error (%)	Coexisting substance	Tolerance (times)	Relative error (%)
Na^{+}	100	-7.78%	glutamic acid	70	-2.84%
Fe^{2+}	100	-9.28%	glycine	70	-4.14%
Al^{3+}	100	7.37%	Fe^{3+}	70	2.56%
Co^{2+}	100	-9.09%	Hg^{2+}	70	-6.68%
Mn^{2+}	100	-0.06%	Cu^{2+}	70	-4.22%
F^{-}	100	-7.26%	Br^{-}	70	2.38%
Ba^{2+}	100	4.74%	CO_3^{2-}	70	-2.78%
K^{+}	100	1.9%	I^{-}	70	-2.36%
Cr^{6+}	100	4.74%	Ca^{2+}	50	-7.24%
NO_2^{-}	100	1.05%	Cr^{3+}	50	-1.79%
NH_4^{+}	70	-2.55%	HCO_3^{-}	50	-5.66%
Mg^{2+}	70	-3.66%	phenylalanine	50	-7.35%
Zn^{2+}	70	-3.52%	SO_4^{2-}	50	-5.34%

Table S3B Effect of interference on RRS determination of phosphates

Coexisting substance	Tolerance (times)	Relative error (%)	Coexisting substance	Tolerance (times)	Relative error (%)
Na^{+}	100	-6.45%	glutamic acid	70	-3.64%
Fe^{2+}	100	-7.58%	glycine	70	-6.34%
Al^{3+}	100	4.65%	Fe^{3+}	70	1.45%
Co^{2+}	100	-8.46%	Hg^{2+}	70	-4.35%
Mn^{2+}	100	1.24%	Cu^{2+}	70	3.21%
F^{-}	100	-9.53%	Br^{-}	70	-1.32%
Ba^{2+}	100	5.73%	CO_3^{2-}	70	-1.86%
K^{+}	100	2.41%	I^{-}	70	-4.65%
Cr^{6+}	100	-3.42%	Ca^{2+}	50	4.67%
NO_2^{-}	100	3.26%	Cr^{3+}	50	1.15%
NH_4^{+}	70	-6.25%	HCO_3^{-}	50	-6.88%
Mg^{2+}	70	2.54%	phenylalanine	50	-5.24%
Zn^{2+}	70	4.61%	SO_4^{2-}	50	-4.69%

Table S4A Results for the detection of dissolve silicate in samples

Water samples	Single value （μg L^{-1}）	Average value (μg L^{-1})	Added silicate (μg L^{-1})	Recovery（%）	RSD （%）	Found silicates (mg L^{-1})
A	11.96， 11.98， 12.11， 12.15， 12.21	12.08	3.33	106.2	0.9	0.6
B	12.45， 12.36， 12.41， 12.32， 12.39	12.39	3.33	97.8	0.4	0.62
C	9.16， 8.98， 9.20， 9.25， 8.95	9.11	3.33	112.1	1.48	0.46
D	9.64， 9.66， 9.61， 9.70， 9.68	9.66	3.33	104.3	0.36	0.48
E	8.64， 8.62， 8.71， 8.68， 8.69	8.67	3.33	107.8	0.43	0.43
F	10.34， 10.31， 10.33，	10.31	3.33	94.7	0.28	0.52

10.29, 10.27

Table S4B Results for the detection of phosphate in samples

Water samples	Single value (μg L^{-1})	Average value (μg L^{-1})	Added phosphate (μg L^{-1})	Recovery (%)	RSD (%)	Found phosphates (mg L^{-1})
A	1.66, 1.65, 1.61, 1.60, 1.58	1.62	3.33	105.5	2.10	0.08
B	2.89, 2.9, 2.88, 2.91, 2.87	2.89	3.33	114.2	0.55	0.14
C	2.39, 2.41, 2.34, 2.31, 2.41	2.37	3.33	113.7	1.89	0.12
D	4.82, 4.79, 4.84, 4.73, 4.82	4.80	3.33	95.8	0.90	0.24
E	2.12, 2.1, 2.08, 2.12, 2.09	2.10	3.33	103.6	0.85	0.11
F	1.55, 1.56, 1.54, 1.53, 1.56	1.55	3.33	97.4	0.84	0.08