Supporting Information

SI-1 Calibration solution preparation

PS and PMMA stock solutions (100 mg/L) were prepared by diluting 1 mL of PS (1%, w/v) and 0.2 mL of PMMA (5%, w/v) into 100 mL volumetric flasks. Subsequently, 1 mg/L solutions of PS and PMMA were derived by diluting 1 mL of the respective 100 mg/L stock solutions to 100 mL.

Given the range of initial NP concentrations in existing laboratory-scale research related to NPs, which encompasses the development of detection methods, NP removal technologies, and toxicological analyses (0.01–50 mg/L) (Bhattacharya et al., 2010; Sendra et al., 2019; Trifuoggi et al., 2019), and considering the abundance of NP concentrations observed in typical aquatic samples (Besseling et al., 2019; Li et al., 2024), NP calibration solutions in this investigation were established at concentrations of 0.005–5 mg/L. Solutions within the concentration range of 0.005–0.1 mg/L were prepared in 50 mL volumetric flasks using PS and PMMA solution of 1 mg/L, while those within the range of 0.5-5 mg/L were prepared using stock solutions of 100 mg/L.

SI-2 UV spectroscopy scan of NPs

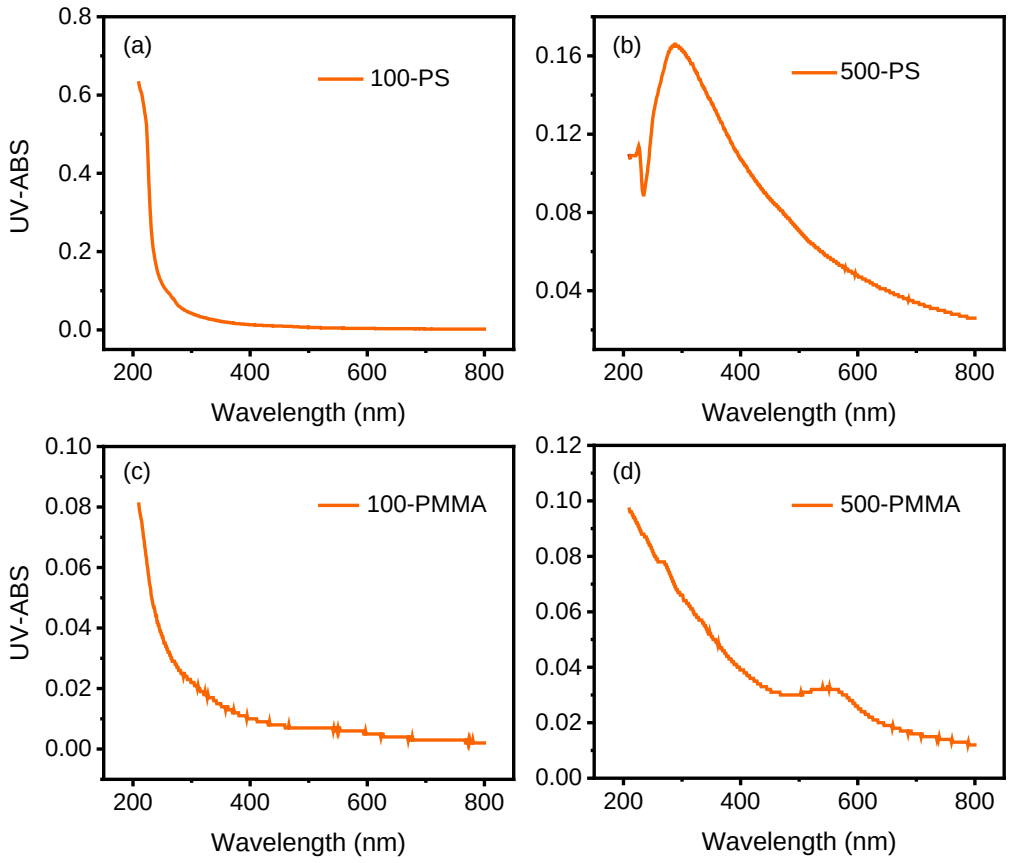

Fig. S1 UV spectroscopy scan of 100-PS (a), 500-PS (b), 100-PMMA (c), and 500-PMMA (d).

SI-3 Multi-index orthogonal test design

A multi-index orthogonal test design was employed for this study. Since the orthogonal experiment involves four factors with three levels each, the minimum orthogonal array $L_9(3^4)$ was selected, as illustrated in Table S1.

Table S1 Orthogonal array $L_9(3^4)$ of the experimental designs.

Test No.	pH	Salinity (%)	SS (mg/L)	HA (TOC, mg/L)
1	9	0.5	10	0.5
2	9	1	1	2
3	7	0.1	10	2
4	7	1	5	0.5
5	7	0.5	1	5
6	5	1	10	5
7	5	0.1	1	0.5
8	9	0.1	5	5
9	5	0.5	5	2

SI-4 The information of different optical indicators for NP quantification

The information on various optical indicators, such as fluorescence intensity (FI), ultraviolet absorbance (UV-ABS), and turbidity, for NP quantification is presented in Table S2. The results highlight FI as the preferred indicator for NP quantification, attributed to its wider signal value range and higher correlation coefficient.

Table S2 Response information of different quantitative indicators to NPs.

NPs	Quantitative indicator	Signal value	Regression equation	R^2
100-PS	FI	0.3527–200.7	$y = 40.4x - 0.0579$	0.9991
	UV-ABS	0.006–0.628	$y = 0.124x + 0.018$	0.9947
	Turbidity	0.2333–7.723	$y = 1.540x + 0.2732$	0.9801
500-PS	FI	0.1657–144.8	$y = 29.1x + 0.741$	0.9969
	UV-ABS	0.010–0.068	$y = 1.540x + 0.2732$	0.6863
	Turbidity	0.2333–23.63	$y = 4.613x + 0.3901$	0.9941
100-PMMA	FI	0.2457–102.1	$y = 19.8x + 0.045$	0.9992
	UV-ABS	0.010–0.086	$y = 0.015x + 0.011$	0.9866
	Turbidity	0.4380–4.7566	$y = 0.854x + 0.4913$	0.9771
500-PMMA	FI	0.3613–101.4	$y = 20.2x + 0.1411$	0.9999
	UV-ABS	0.006–0.114	$y = 0.021x + 0.009$	0.9772
	Turbidity	0.4500–9.240	$y = 1.773x + 0.2863$	0.9973

SI-5 Calibration curves of NPs in nine simulated water samples

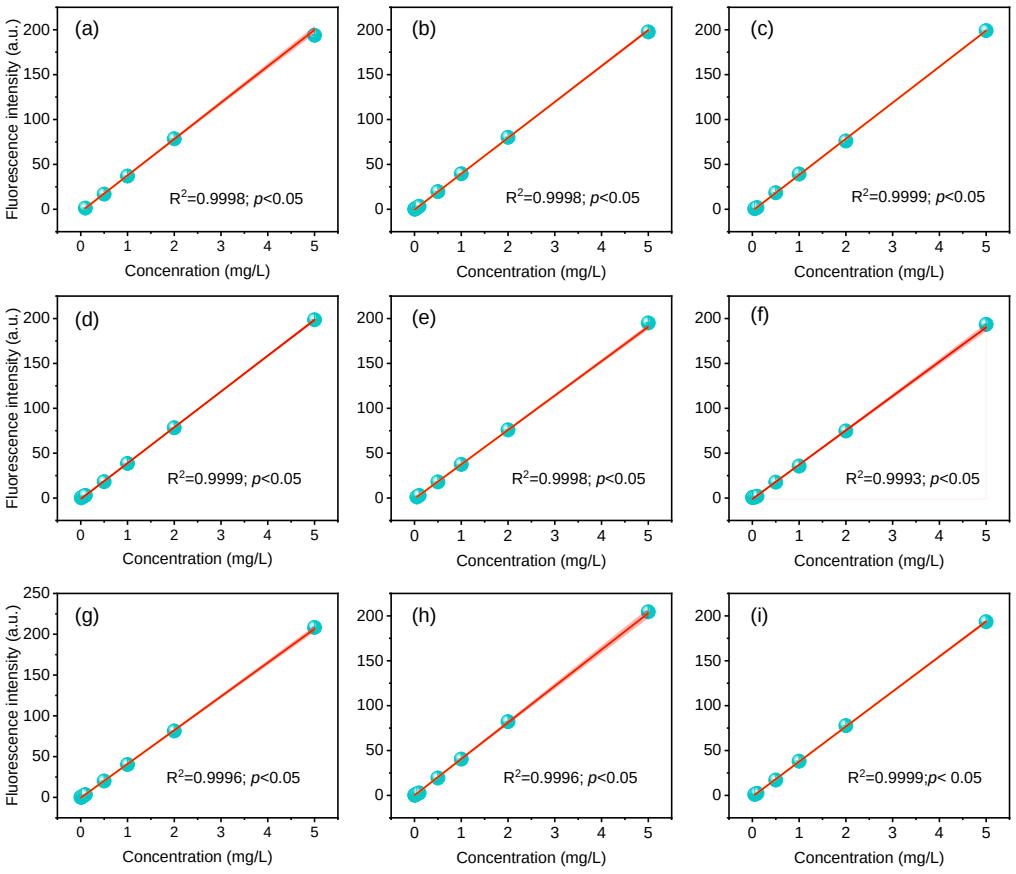

Fig. S2 Calibration curves for 100-PS in simulated water samples (a)–(i), corresponding to orthogonal test 1–9 (Table S1).

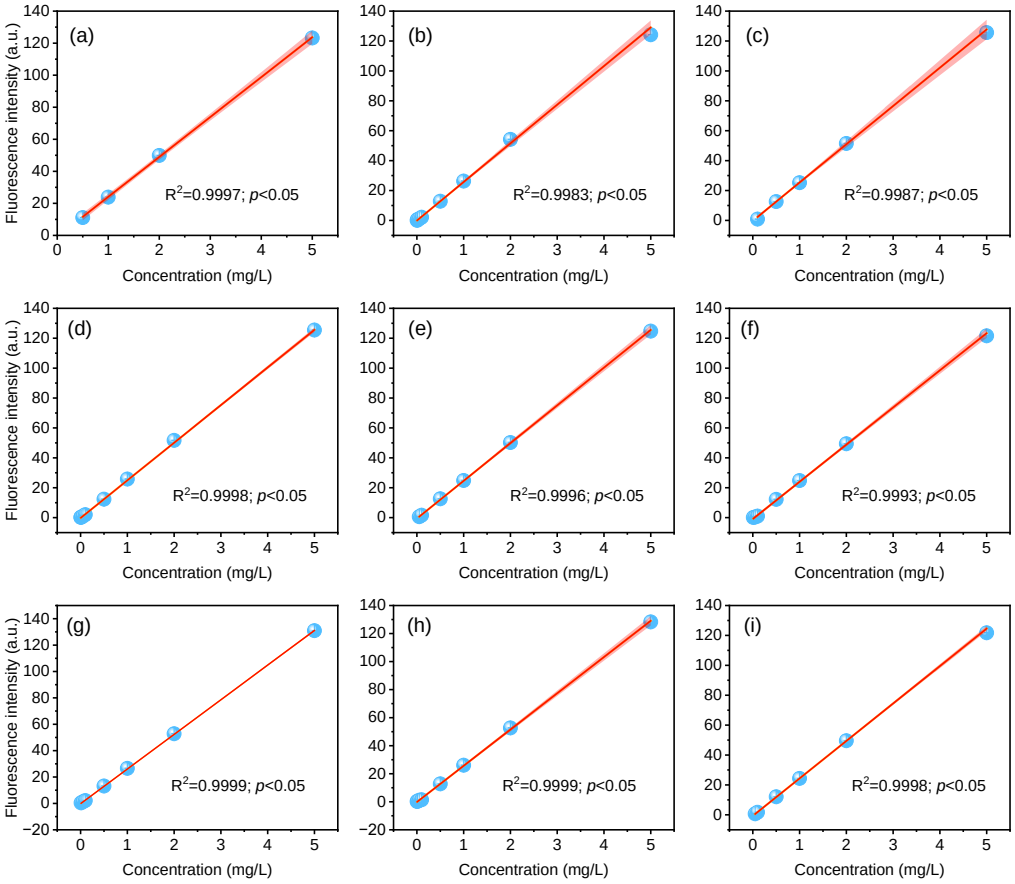

Fig. S3 Calibration curves for 500-PS in simulated water samples (a)–(i), corresponding to orthogonal test 1–9 (Table S1).

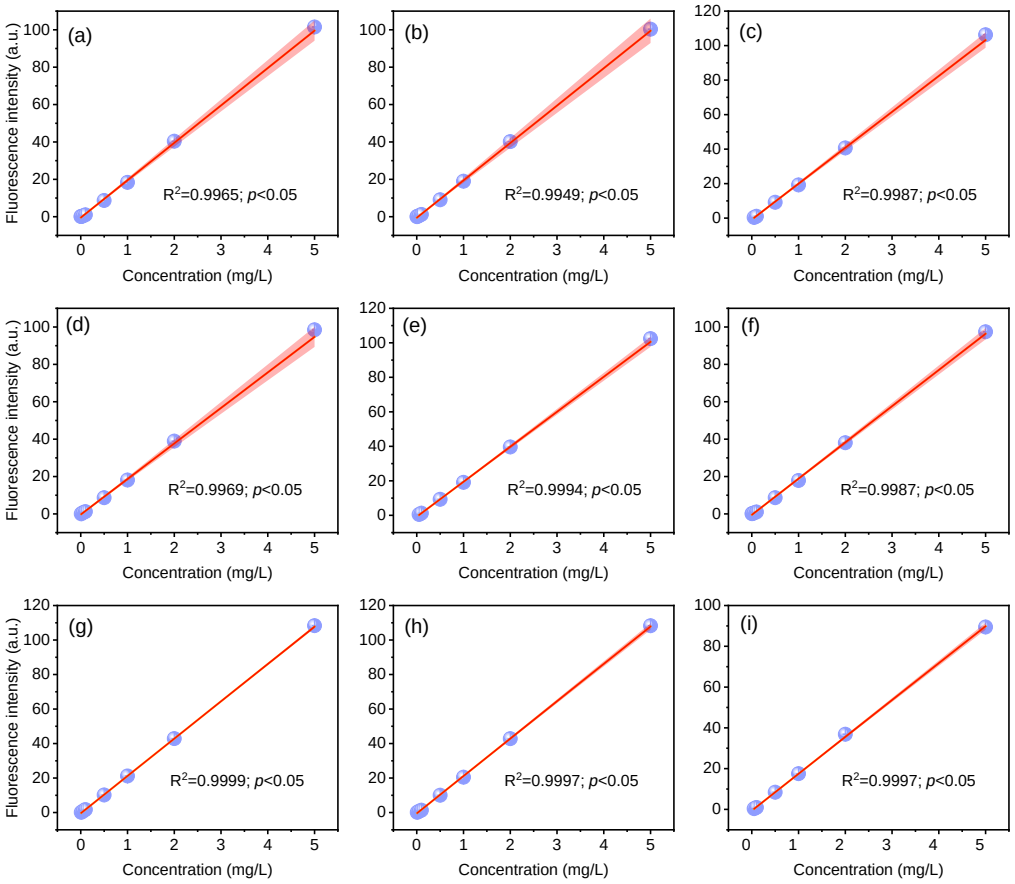

Fig. S4 Calibration curves for 100-PMMA in simulated water samples (a)–(i), corresponding to orthogonal test 1–9 (Table S1).

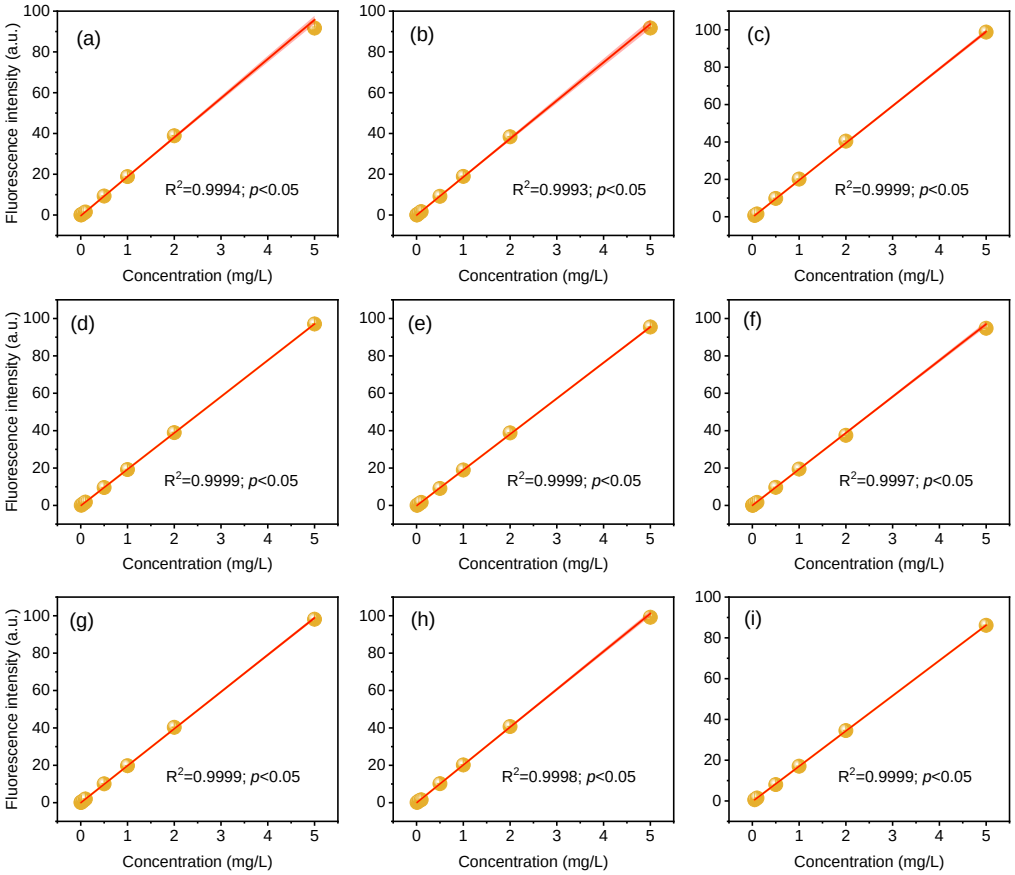

Fig. S5 Calibration curves for 50-PMMA in simulated water samples (a)–(i), corresponding to orthogonal test 1–9 (Table S1).

SI-6 Initial concentration of NPs in aquatic environment as reported in previous studies

Table S3 Initial concentration of NPs in laboratory-scale studies on NPs.

Scope	Initial concentration	NP type	Ref.
NP removal	1 g/L	PS PMMA	(Sarcletti et al., 2021)
NP removal	20 mg/L	PS	(Ramirez Arenas et al., 2021)
NP removal	10 NTU	PS PMMA	(Tian et al., 2023)
NP removal	0.01–30 mg/L	PS	(Bayarkhuu and Byun, 2022)
NP removal	330 mg/L	PMMA PVA	(Batool and Valiyaveettil, 2020)
NP removal	2 g/L	PS PMMA	(Li et al., 2022)
NP removal	250 mg/L	PS	(Tiwari et al., 2020)
NP exposure	0.125 mg/L	PS	(Lin et al., 2022)
NP toxicology	0–50 mg/L	PS	(Xiao et al., 2022)
NP toxicology	0.1–5 mg/L	PS PMMA	(Trifuoggi et al., 2019)
NP toxicology	0.1–50 mg/L	PS	(Sendra et al., 2019)

SI-7 LOQ of NPs in various simulated water samples

Table S4 LOQ values of NPs in various simulated water samples.

Sample	100 nm PS			500 nm PS			100 nm PMMA			500 nm PMMA		
	C_{blank} (mg/L)	SD	LOQ (mg/L)	C_{blank} (mg/L)	SD	LOQ (mg/L)	C_{blank} (mg/L)	SD	LOQ (mg/L)	C_{blank} (mg/L)	SD	LOQ (mg/L)
1	0.1034	0.0018	0.4337	0.0438	0.0109	0.2990	0.0331	0.0080	0.2223	0.0207	0.0023	0.1093
2	0.0142	0.0020	0.0791	0.0056	0.0012	0.0363	0.0308	0.0010	0.1342	0.0090	0.0013	0.0510
3	0.0619	0.0022	0.2722	0.0411	0.0082	0.2582	0.0584	0.0015	0.2509	0.0480	0.0021	0.2160
4	0.0336	0.0007	0.1430	0.0174	0.0021	0.0932	0.0208	0.0014	0.0995	0.0129	0.0021	0.0757
5	0.0234	0.0012	0.1070	0.0487	0.0019	0.2167	0.0652	0.0015	0.2775	0.0102	0.0010	0.0524
6	0.0411	0.0050	0.2209	0.0396	0.0020	0.1812	0.0304	0.0024	0.1484	0.0037	0.0017	0.0322
7	0.0160	0.0024	0.0912	0.0244	0.0040	0.1430	0.0245	0.0017	0.1168	0.0053	0.0032	0.0570
8	0.0019	0.0012	0.0211	0.0150	0.0017	0.0795	0.0288	0.0022	0.1402	0.0086	0.0023	0.0612
9	0.0635	0.0027	0.2843	0.0518	0.0045	0.2576	0.0537	0.0012	0.2287	0.0491	0.0019	0.2182

Notes: Sample 1 to 9 correspond to those sample obtained in orthogonal test 1─9. C_{blank}: Minimum detectable sample concentration. SD: the standard deviation of n measurements. LOQ: Limit of quantification.

SI-8 Influence of different water quality on NP quantification

The relative deviation of the LOQ for each type of NPs in various simulated water samples compared to the LOQ in ultrapure water was calculated using Eq. (S1). It can be used to evaluate the influence of different water qualities on NP quantification.

$$\text{Relative deviation (\%)} = \frac{\left| LOQ_{\text{simulate water}} - LOQ_{\text{ultrapure water}} \right|}{LOQ_{\text{ultrapure water}}} \times 100\% \quad , \quad \text{(S1)}$$

where, $LOQ_{\text{simulate water}}$ represents the LOQ in various simulated water and $LOQ_{\text{ultrapure water}}$ denotes the LOQ in ultrapure water.

SI-9 Fluorescence background values in different simulated water samples

Table S5 Background values of FI in nine simulated water samples under different detection conditions.

Detection condition	1	2	3	4	5	6	7	8	9
Condition 1	12.758	5.263	13.447	6.113	9.447	15.901	3.664	12.349	8.072
Condition 2	4.272	1.882	4.989	2.352	3.064	5.030	1.312	4.251	2.827

Notes: Condition 1: Detecting PS NPs with EX at 488 nm and EM at 518 nm. Condition 2: Detecting PMMA NPs with EX at 540 nm and EM at 580 nm.

SI-10 Calibration curves of NPs in three real water bodies

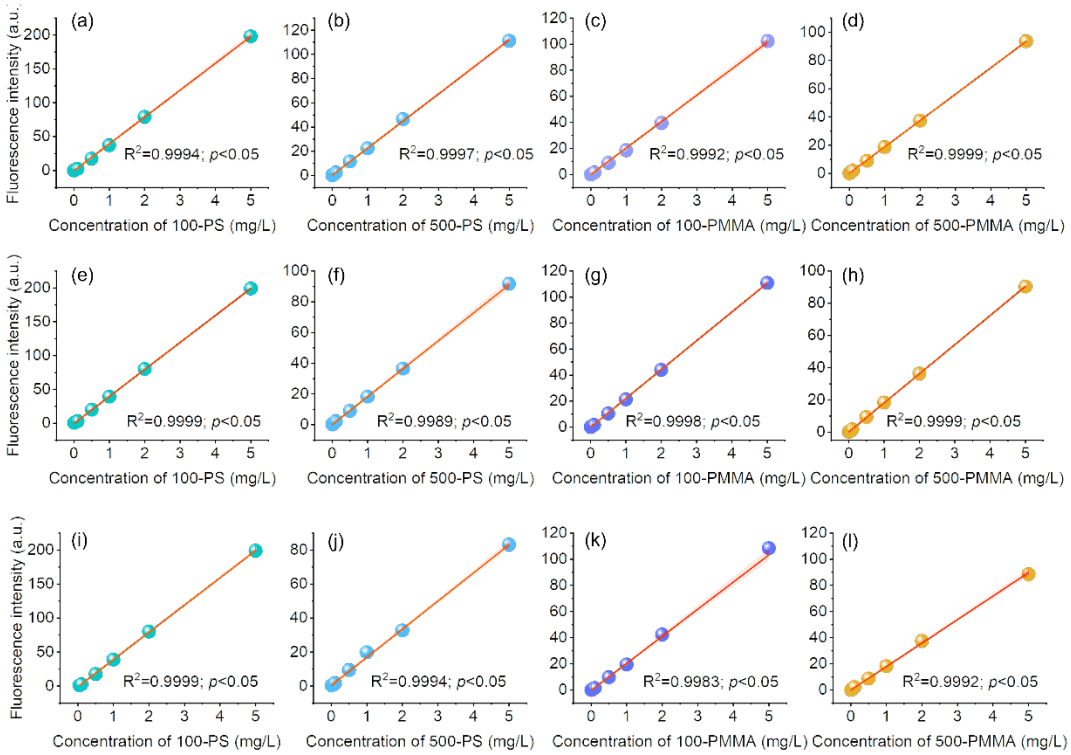

Fig. S6 Calibration curves for four types of NPs (100-PS, 500-PS, 100-PMMA, and 500-PMMA) in drinking water (a)–(d), freshwater (e)–(h), and seawater (i)–(l).

SI-11 LOQ of NPs in real water bodies

Table S6 LOQ values of NPs in real water bodies.

Sample	100 nm PS			500 nm PS			100 nm PMMA			500 nm PMMA		
	C_{blank} (mg/L)	SD	LOQ (mg/L)	C_{blank} (mg/L)	SD	LOQ (mg/L)	C_{blank} (mg/L)	SD	LOQ (mg/L)	C_{blank} (mg/L)	SD	LOQ (mg/L)
Drinking water	0.0159	0.0007	0.0711	0	0.0014	0.0157	0.0065	0.0007	0.0338	0.0067	0.0010	0.0381
Freshwater	0.0166	0.0036	0.1072	0.0056	0.0009	0.0330	0.0106	0.0045	0.0928	0.0055	0.0019	0.0429
Sea water	0.0527	0.0016	0.2286	0.0027	0.0040	0.0557	0.0217	0.00131	0.1027	0.0119	0.0013	0.0625

Notes: C_{blank}: Minimum detectable sample concentration. SD: the standard deviation of n measurements. LOQ: Limit of quantification.

SI-12 Water quality parameters for three real water bodies

The ProQuatro portable water quality detector (YSI, USA) and the total organic carbon analyzer (TOC-LCSH/CPH, Shimadzu, Japan) were employed to measure the water quality parameters in three representative water samples, as detailed in Table S7.

Table S7 Water quality parameters in three representative water bodies.

Water quality parameter	Drinking water	Freshwater	Seawater
pH	6.96	8.46	8.12
Turbidity (NTU)	0.29	0.32	0.19
TOC (mg/L)	0.3011	5.501	4.159
TDS (mg/L)	80.2	361.4	28188

SI-13 Fluorescence background values in three real water bodies

Table S8 Background values of FI in three real water bodies under different detection conditions.

Detection condition	Drinking water	Freshwater	Seawater
Condition 1	1.367	5.739	4.387
Condition 2	0.535	1.831	1.298

Notes: Condition 1: Detecting PS NPs with EX at 488 nm and EM at 518 nm. Condition 2: Detecting PMMA NPs with EX at 540 nm and EM at 580 nm.

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