

Nanogel for Selective Recognition of Nanoparticles in Water Samples

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Chemicals and Reagents

CdS_xSe_{1-x}/ZnS core/shell QDs of different emission wavelengths, all of which were functionalized with carboxylic acid surface ligands, were obtained from Cytodiagnostics. Cadmium Telluride (CdTe) core-type QDs of different emission wavelengths, all of which were functionalized with carboxylic acid surface ligands, were obtained from Sigma Aldrich. Gold NPs with carboxylic acid surface ligands were obtained from Sigma Aldrich. CdSe/ZnS core/shell QDs, functionalized with amine ligands, were obtained from Sigma Aldrich. CdSeS/ZnS core/shell QDs, functionalized with alkyl ligands, were also obtained from Sigma Aldrich. Azobisisobutyronitrile (AIBN), citric acid, ethylenediamine, ethylene glycol dimethacrylate (EGDMA), hydrofluoric acid and methacrylic acid (MAA) were all obtained from Sigma Aldrich as well. Ammonium hydroxide was obtained from JT Baker. Dilute nitric acid and tetraethyl orthosilicate were obtained from Merck. Ultrapure and deionized water were obtained from a Milli-Q water purification system (Millipore Billerica, MA, USA). pH meter used was from Mettler Toledo. Other solvents used were methanol, ethanol, hexanol, isopropanol, dimethylformamide and dimethyl sulfoxide.

Synthesis of Silica Nanoparticles

Silica NPs used in the polymerization mixture were synthesized using the Stober-Fink-Bohn method.^{1,2} 8 mL of methanol, 20 mL of tetraethyl orthosilicate and 30 mL of deionized water were added into a solution of 20 mL of dilute ammonium hydroxide (20 %). The resulting solution was then placed in a water bath under ultrasonic vibration for 30 minutes to allow an invisible hydrolytic reaction to occur. The solution turned cloudy after 10 minutes and the silica NPs were produced in the form of a white precipitate. The crude silica NPs formed amounted to 16.8970 g. This white precipitate, that is, the crude silica NPs, was then obtained by suction filtration and later washed with ethanol by repeated centrifugation at 25 °C and 8000 rcf, with each round of centrifugation being 5 minutes. After washing with centrifugation, the white precipitate was placed in the ultrasonic disperser for another 30 minutes before it was dried overnight at 60 °C to obtain the purified silica NPs as the final product. 5.0289 g of purified silica NPs was obtained.

Synthesis of Carbon Dots

Carbon dots were also synthesized for the use as one of the analytes for the evaluation of the NANO GEL (NPIH). 1.0586 g of citric acid and 335 μ L of ethylenediamine were dissolved in 10 mL of deionized water. The solution was stirred for 15 minutes to form a colourless reaction mixture before it was transferred to a Teflon-lined autoclave and heated at 200 °C for 5 hours. A hydrothermal synthesis method was adopted here. After heating, the reaction mixture was cooled overnight to room temperature. The cooled mixture was then subjected to dialysis for 3 days before the carbon dots were obtained. 15 mL

of a brown-black solution, containing the carbon dots, was obtained (0.0526 g/mL). Literature yield for the above synthesis was stated to be 58 %.

Afterwards, another batch of carbon dots was also synthesized, using the similar experimental procedure as above, with only 1.1064 g of citric acid being dissolved in 10 mL of deionized water. The aim is to synthesize carbon dots with only acidic surface characteristics (carboxylic acid surface ligands as functional groups), for the use as one of the analytes for the evaluation of the NANOGEL as well. All the other experimental conditions adopted remained the same. 10 mL of a pale yellowish solution, containing the carbon dots, was obtained (0.0642 g/mL).

Characterization of Carbon Dots

As the carbon dots used in the evaluation of the nanogel were synthesized, further characterization was performed to ensure that that the product was successfully synthesized. Fourier Transform Infrared (FT-IR) spectroscopy was conducted using the Shimadzu IRPrestige-21. Fluorescence and UV-vis spectroscopy of the carbon dots were also conducted using the Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer and the Agilent Technologies Cary 60 UV-Vis respectively.

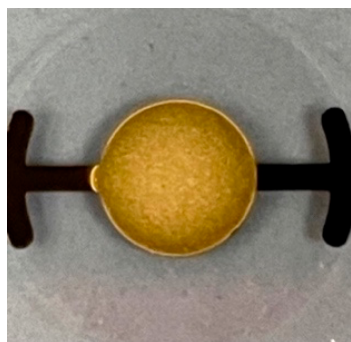


Figure S1. NANOGEL-coated QCM chip after air drying.

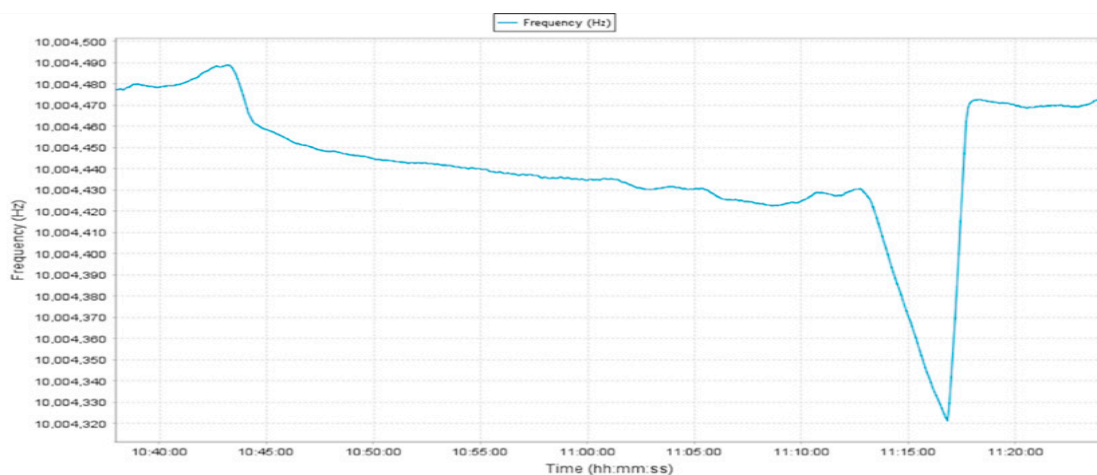


Figure S2. Frequency changes during regeneration.

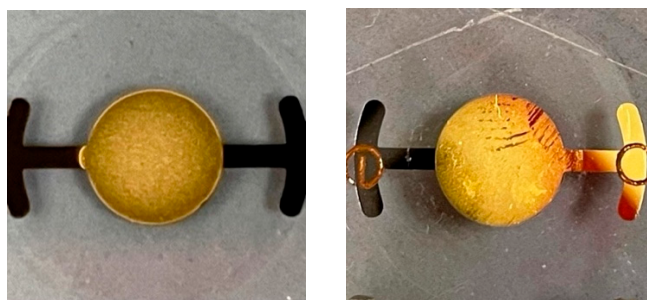


Figure S3. NANOgel on the surface of the QCM chip before (left) and after (right) exposure to solutions with extreme acidic and basic pH.

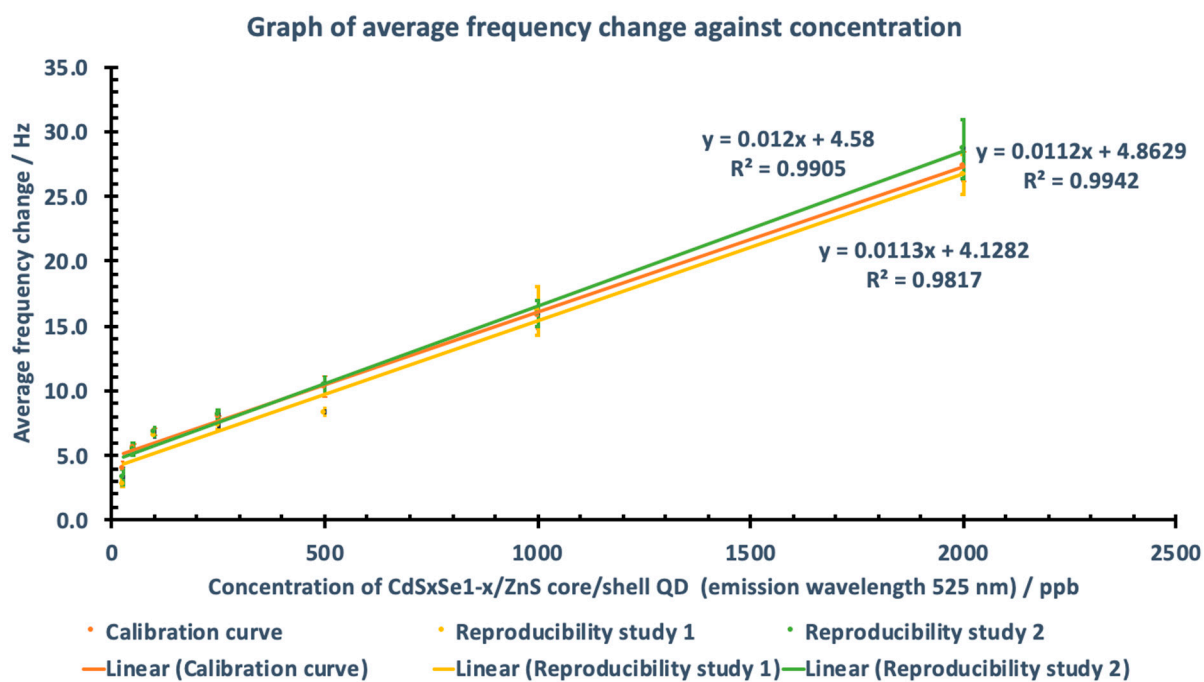
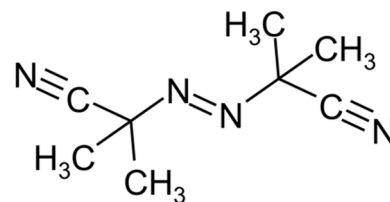


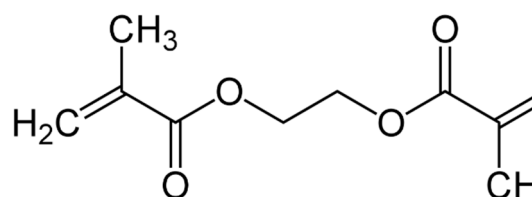
Figure S4. Graph of average frequency change against concentration for the duplicates in comparison to the earlier calibration plot (Figure 7).

Table S1. Structure of monomers.

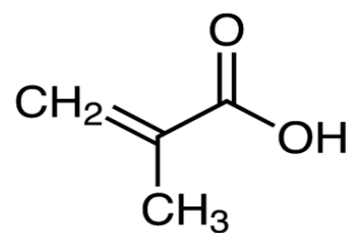
AIBN



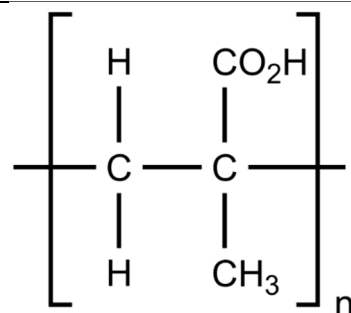
EGDMA



MAA



PMAA



Preparation of Polymerization Mixture

Table S2. Effect of the ratio of different reagents in the pre-polymerization mixture on the amount of NANOGEL obtained.

Volume of MAA added / μL	Volume of EGDMA added / μL	Volume of AIBN added / μL	Volume of eth- anol added / mL	Mass of NANOGEL ob- tained / g
200	10	30	2	0.0008234
200	200	30	2	0.1038
300	300	30	2	0.3276
400	400	30	2	0.3912

Characterization of Hydrogel

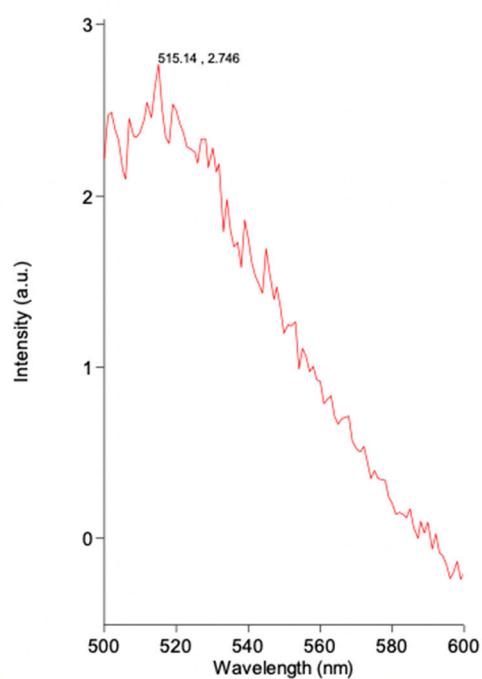
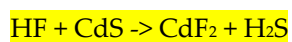


Figure S5. Fluorescence spectroscopy of NANOgel filtrate. (Excitation at 340 nanometres).

Chemical reactions that occur during template removal using hydrofluoric acid



Characterization of Carbon Dots

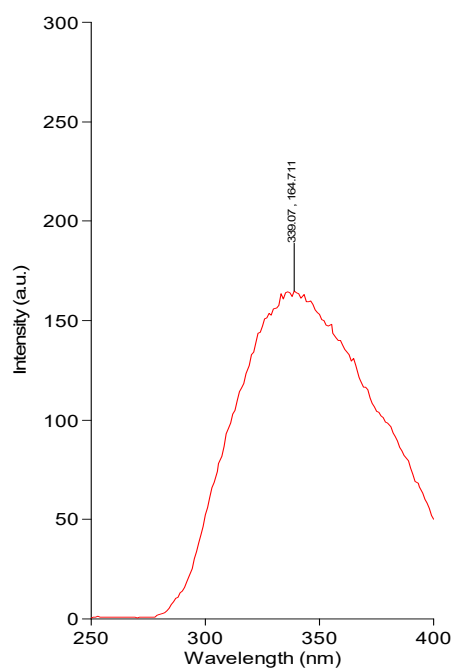


Figure S6. Excitation spectra for fluorescence spectroscopy of carbon dots with acidic and basic surface characteristics.

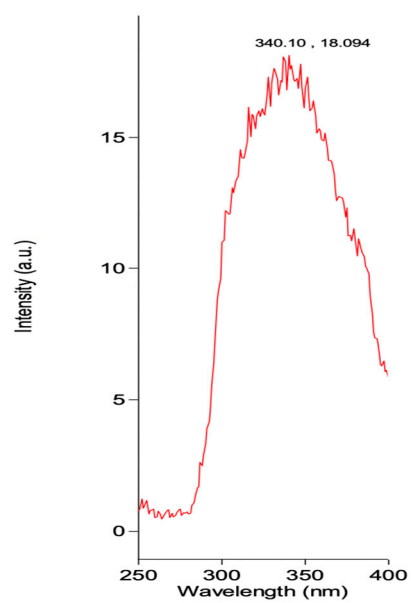


Figure S7. Excitation spectra for fluorescence spectroscopy of carbon dots with acidic surface characteristics.

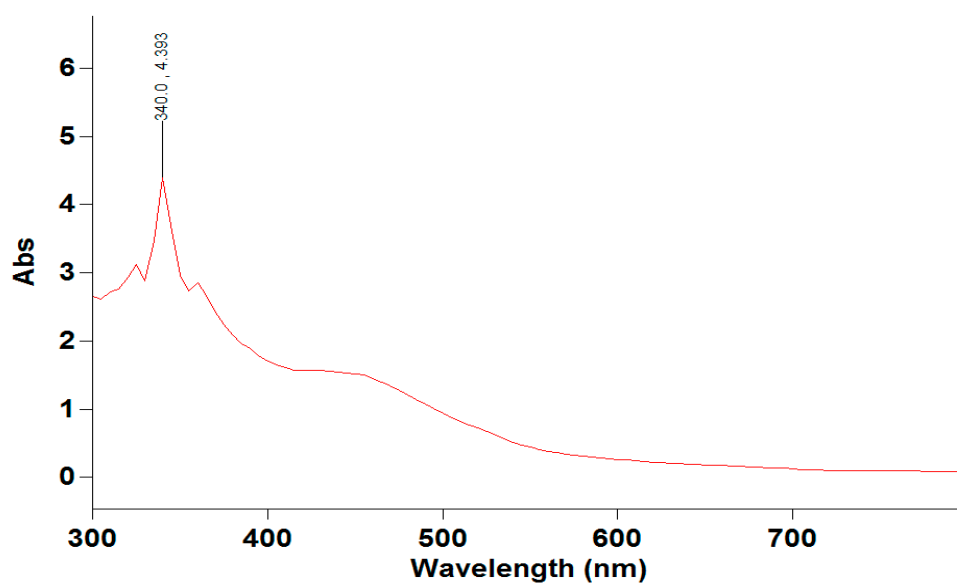


Figure S8. UV-vis spectroscopy of carbon dots with acidic and basic surface characteristics in de-ionized water.

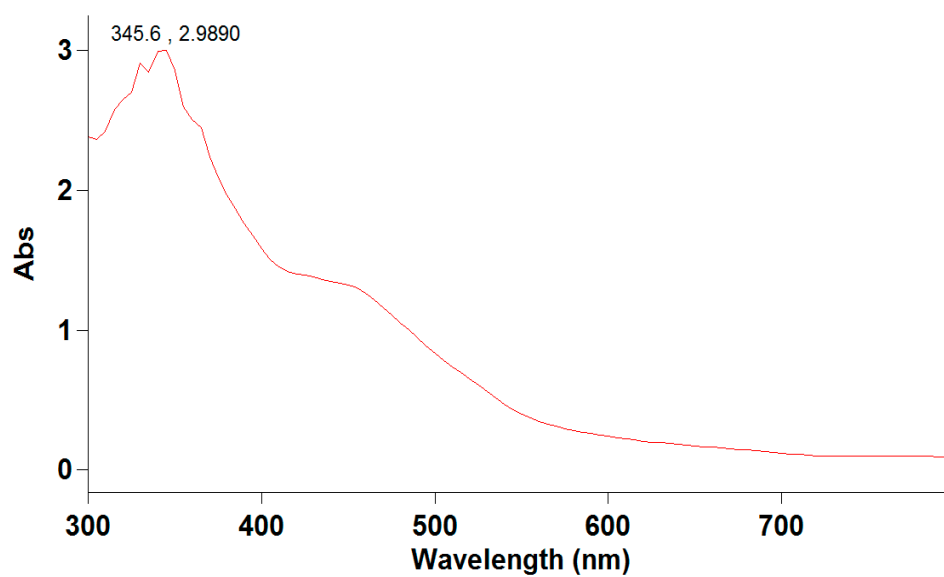


Figure S9. UV-vis spectroscopy of carbon dots with acidic surface characteristics in deionized water.

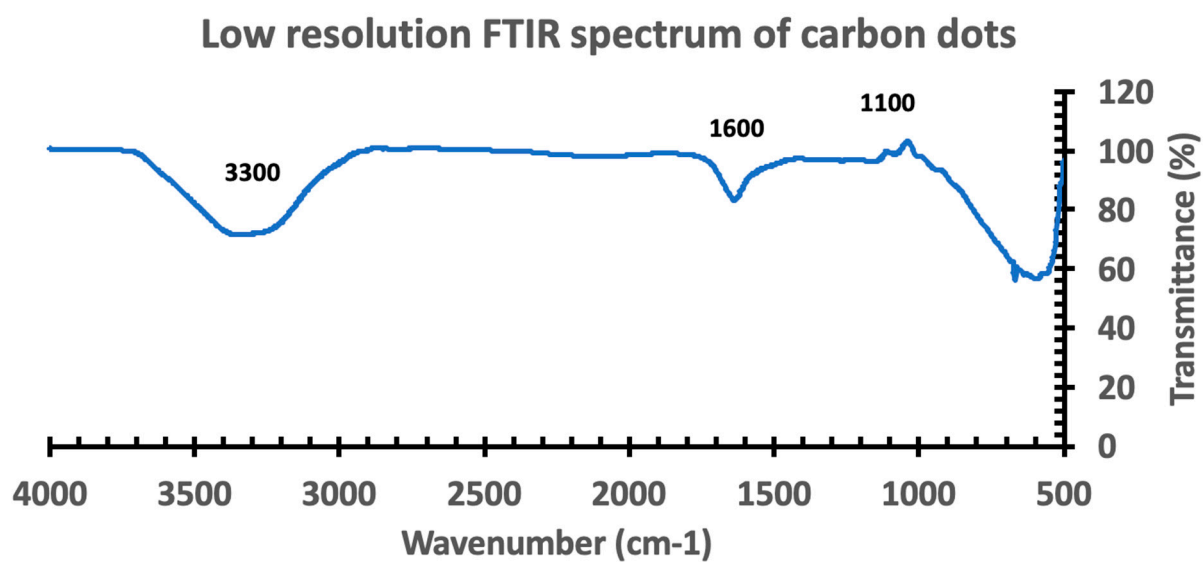


Figure S10. Low resolution FT-IR spectrum of carbon dots with acidic and basic surface characteristics.

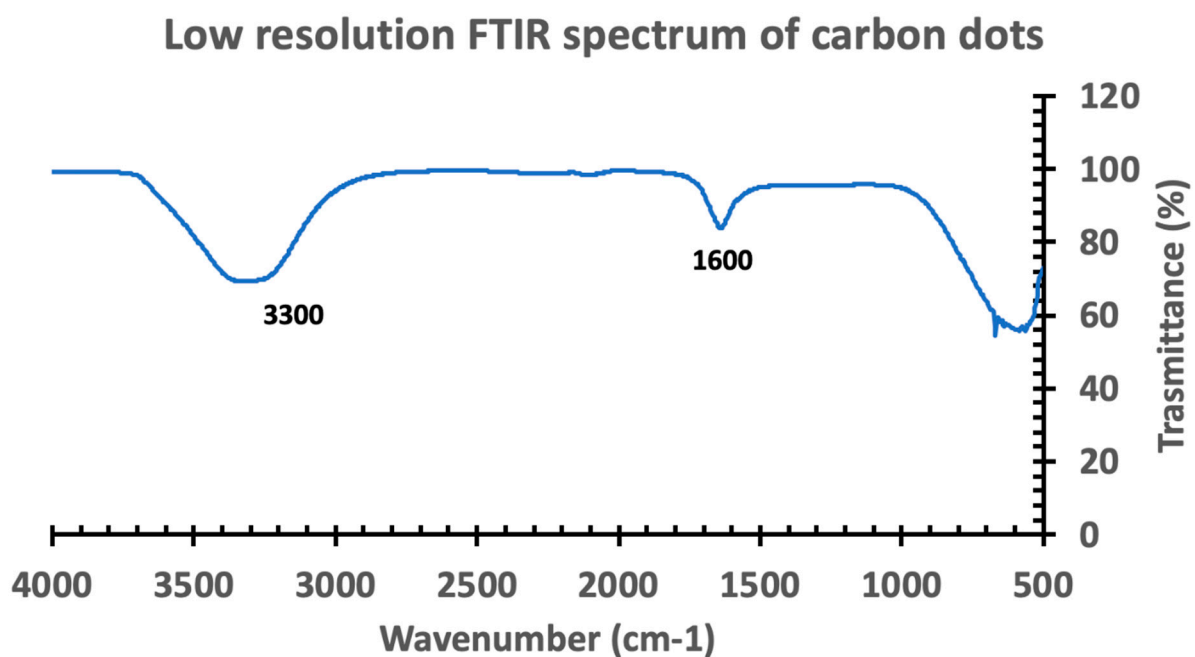


Figure S11. Low resolution FT-IR spectrum of carbon dots with acidic surface characteristics.

Sensitivity, Linearity, Limit of Detection (LOD) and Limit of Quantification (LOQ)

Table S3. Graph of average frequency change against concentration.

Concentration of template QDs / ppb	Average frequency change / Hz	% RSD
25	4.0	12.5
50	5.7	5.1
100	6.8	4.2
250	8.0	0.0
500	10.3	7.4
1000	15.8	6.6
2000	27.3	4.2

Selectivity Study

Comparison to Non-Imprinted Hydrogel (NIH)

Table S4. Selectivity of NANOGEL in comparison to non-imprinted hydrogel (NIH).

Hydrogel	Average frequency change / Hz	% RSD
NIH	-3.3	-210.7
NANOGEL	15.8	6.6

Effect of pH

Table S5. Effect of pH on QCM response.

pH	Average frequency change / Hz	% RSD
1.44	-43.0	-8.4
2.95	-15.3	-42.4
5.32	10.5	21.8
7.34	15.5	34.0
9.21	-10.0	-8.7
11.05	-18.0	-43.4

13.11	-19.0	-26.3
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Effect of Ionic Solutions

Table S6. Effect of cations on QCM response.

Concentration of ionic solution / ppm	Ionic solution	Average frequency change / Hz	% RSD
10	NaCl	17.3	0.5
	MgCl ₂	10.7	0.3
	CaCl ₂	15.7	0.2
	KCl	14.5	0.4
	PbCl ₂	77.0	6.8
	CuCl ₂	62.0	6.3
	CdCl ₂	39.0	2.2
100	NaCl	13.3	0.3
	MgCl ₂	30.7	0.2
	CaCl ₂	34.7	0.5
	KCl	19.7	0.3
	PbCl ₂	126.7	7.3
	CuCl ₂	98.7	8.0
	CdCl ₂	51.3	1.1

Table S7. Effect of anions on QCM response.

Concentration of ionic solution / ppm	Ionic solution	Average frequency change / Hz	% RSD
10	NaCl	17.3	0.5
	Na ₂ SO ₄	21.7	0.7
	Na ₂ CO ₃	-100.0	-18.0
	Na ₃ PO ₄	-37.7	-3.2
100	NaCl	13.3	0.3
	Na ₂ SO ₄	7.8	0.1
	Na ₂ CO ₃	-106.7	-6.2
	Na ₃ PO ₄	-115.0	-5.8

Repeatability Study

Table S8. Average frequency change across a period of 5 days.

Day	Average frequency change / Hz	% RSD
1	15.8	0.2
2	15.8	0.3
3	15.0	0.2
4	15.5	0.3
5	16.0	0.5

Reproducibility Study

Table S9. Graph of average frequency change against concentration for the duplicates.

Duplicate	Concentration of template QDs / ppb	Average frequency change / Hz	% RSD
1	25	2.8	0.0

2	50	5.5	0.0
	100	6.5	0.0
	250	7.3	0.0
	500	8.3	0.0
	1000	16.2	0.3
	2000	26.7	0.4
	25	3.3	0.0
	50	5.5	0.0
	100	6.8	0.0
	250	8.2	0.0
	500	10.5	0.1
	1000	16.0	0.2
	2000	28.7	0.7

Stability Study

Table S10. Average frequency change across a period of 35 days.

Day	Average frequency change / Hz	% RSD
1	14.5	0.3
6	13.8	0.3
9	16.7	0.8
15	13.8	0.3
17	16.0	0.2
21	15.3	0.2
22	13.0	0.1
27	15.3	0.1
29	17.3	0.3
35	15.7	0.3

Use of Hydrogel on Real Water Samples

Table S11. Graph of average frequency change against concentration of QDs spiked into water (for different real water samples).

Real water sample	Concentration of template QDs spiked / ppb	Average frequency change / Hz	% RSD
Tap water	0	140.0	0.0
	25	148.3	4.3
	59	158.3	4.6
	100	165.0	0.0
	250	173.3	4.1
	500	186.7	5.4
	1000	246.7	7.1
Tap water with de-ionized water	0	105.0	0.0
	25	111.7	3.2
	50	120.0	0.0
	100	133.3	3.8
	250	140.0	0.0
	500	153.3	4.4
	1000	206.7	11.9

Optimization of Hydrogel

Table S12. Comparison of the effect of solvent on NANOGEL performance.

Solution	Solvent	Average frequency change / Hz	% RSD
1 ppm template QDs	Ethanol	15.8	0.2
	DMSO	22.7	0.3
	DMF	15.7	0.3
	Isopropanol	12.7	0.1
1 ppm template QDs with 10 ppm PbCl ₂ interference	Ethanol	77.0	6.8
	DMSO	120.0	15.9
	DMF	61.7	2.9
	Isopropanol	45.3	1.7
1 ppm template QDs with 100 ppm PbCl ₂ interference	Ethanol	126.7	7.3
	DMSO	195.0	25.8
	DMF	98.0	1.7
	Isopropanol	60.7	0.4

References:

1. Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. Single-Crystal Colloidal Multilayers of Controlled Thickness. *Chem. Mater.* **1999**, *11*, 2132–2140.
2. Stöber, W.; Fink, A.; Bohn, E. Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range. *J. Colloid Interface Sci.* **1968**, *26*, 62–69.