Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

DNA adsorption by magnetic iron oxide nanoparticles and its application for arsenate detection

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Experimental Section

Chemicals. All of the DNA samples were purchased from Integrated DNA Technologies (IDT, Coralville, IA) and were purified by standard desalting. The FAM-labeled 24-mer DNA sequence is FAM-ACGCATCTGTGAAGAGAACCTGGG. For the DNA homopolymers, FAM was labeled on the 5′-end. Fe_3O_4 NPs, NaI, NaBr, Na_2SO_4, Na_2SO_3 and $NaClO_4$ were purchased from Sigma-Aldrich. Sodium phosphate, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), sodium acetate, sodium nitrate, and all the ribonucleosides were purchased from Mandel Scientific (Guelph, Ontario, Canada). Milli-Q water was used for preparing all the solutions and buffers.

Characterization of Fe_3O_4 NPs. To measure the ζ-potential of Fe_3O_4 NPs, 100 μg/mL Fe_3O_4 NPs was dispersed in 10 mM buffer (HEPES, pH 7.6). The ζ-potential was then recorded using Zetasizer Nano 90 (Malvern). The TEM image was acquired on a Philips CM10 transmission electron microscope. The absorption spectrum of Fe_3O_4 NPs (dispersed in 5 mM HEPES, pH 7.6) was measured by a UV-vis spectroscopy instrument (Agilent 8453A).

DNA adsorption by Fe_3O_4. To study the effect of DNA length, 50 nM FAM-labeled DNA (A_5, A_{15}, or A_{30}) was dissolved in buffer A (10 mM HEPES, pH 7.6, 300 mM NaCl). The fluorescence was recorded by a microplate reader (Infinite F200 Pro, Tecan). After adding Fe_3O_4 NPs (final concentration = 25 μg/mL) and 30 min incubation, the fluorescence was recorded and compared to the initial intensity to calculate the adsorbed DNA. This buffer condition and Fe_3O_4 NPs concentration were for all the experiment unless otherwise indicated. To test the effect of DNA sequence, 10 nM FAM-A_{15}, T_{15}, C_{15}, or G_{15} was used. The adsorption kinetics were recorded for 30 min after a quick addition of Fe_3O_4 NPs. For the displacement experiment, 2 mM phosphate or thymidine was added to the FAM-T_{15}/Fe_3O_4 NPs conjugate in buffer A followed by fluorescence recording for 40 min. To obtain the adsorption isotherm, FAM-C_{15} was used.

Arsenate detection (method 1). The sensor was prepared by adsorbing FAM-C_{15} (30 nM) onto Fe_3O_4 NPs (25 μg/mL) in buffer A in a total volume of 10 mL. The adsorption was allowed to take place for 1 h. This mixture was then divided into 100 μL aliquots in a 96-well plate. Then a small volume (1-5 μL) of arsenate with designed concentrations was added into 100 μL of the conjugate to induce desorption. The kinetics were obtained by monitoring the fluorescence for 3 h in triplicate. For the selectivity test, a final concentration of 10 μM anions (arsenate, arsenite, phosphate, bromide, iodide, nitrate, perchlorate, acetate, carbonate, sulfate, or sulfite) were added, and the fluorescence was recorded after 1 h. The detection of arsenate (10 μM) in the presence of high anion concentration (1 mM) was also tested. To mask the phosphate signal, phosphate or arsenate (1 mM) was treated with $BaCl_2$ (5 mM) in the presence of NaOH (20 mM). After 10 min incubation, the samples were centrifuged (15,000 rpm) for 5 min. Then 1 µL of the supernatant was added into FAM-C_{15}/Fe_3O_4 NPs dispersion. The fluorescence was recorded after 1 h.

Arsenate detection (method 2). Alternatively, Fe_3O_4 NPs (25 µg/mL) were incubated with various concentrations of arsenate in buffer A with a volume of 10 mL for 1 h. After that, the samples were agitated to fully disperse the Fe_3O_4 NPs, and 100 µL was taken out to mix with FAM-C_{15} probe DNA (30 nM). The fluorescence was measured after 1 h incubation.

TEM characterization.

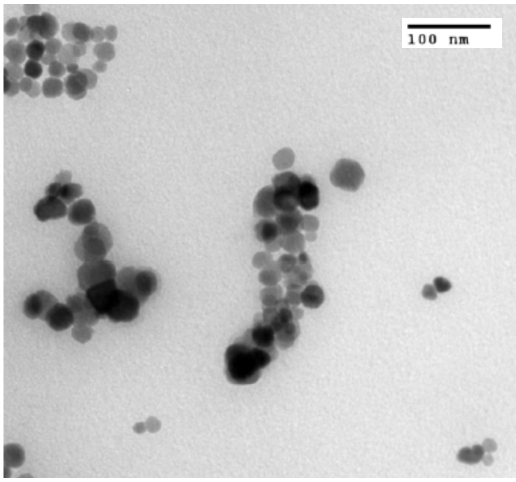

Figure S1. TEM micrograph of Fe_3O_4 NPs used in this work.

NaCl-dependent DNA adsorption. Almost no DNA was adsorbed in the absence of salt (black trace, Figure S2). Significant fluorescence drop indicating DNA adsorption was observed with just 30 mM NaCl. Further increase of NaCl concentration promoted adsorption slightly. We chose to use 300 mM NaCl for most of our experiments.

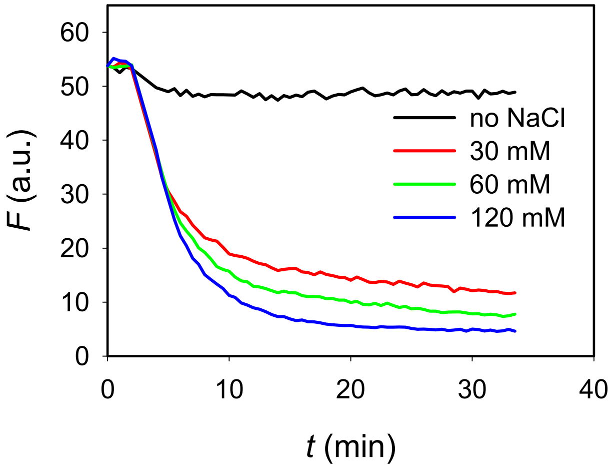

Figure S2. Adsorption kinetics of FAM-labeled 24-mer DNA by Fe_3O_4 NPs in the presence of different NaCl concentrations.

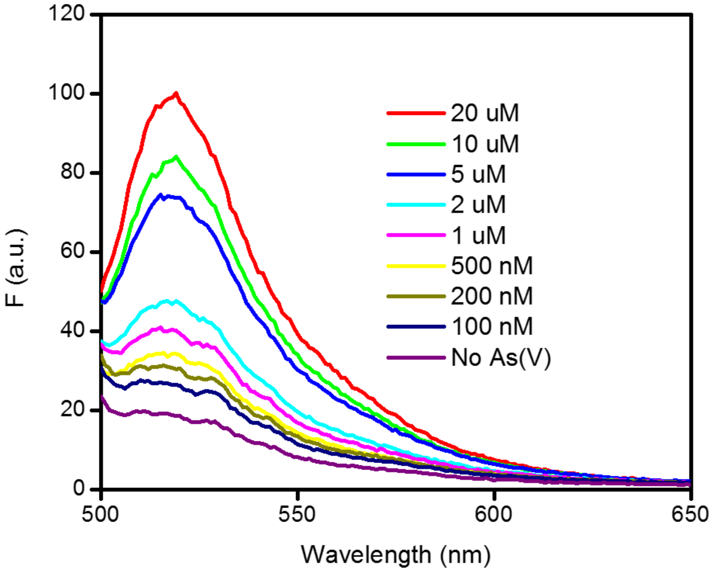

Figure S3. Fluorescence spectra of the sensors for detecting arsenate by adsorbing arsenate first before the addition of DNA.

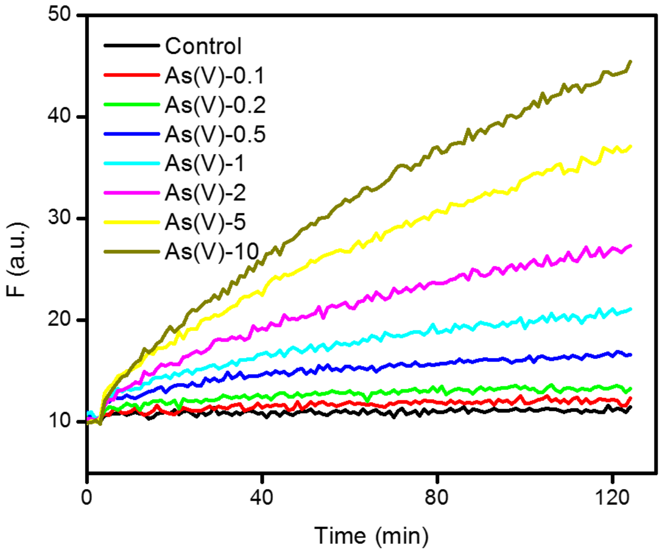

Figure S4. Response of DNA/Fe_2O_3 to various concentrations of arsenate (unit = µM).

Table S1. Literature reported sensors for arsenic detection.

Target Ions	Method	LOD	Reference
As(III) **Reduced As(V)**	Colorimetric assay, UV-vis	2.5 ppb	Domínguez-González, R.; Varela, L.; Bermejo-Barrera, P. *Talanta* 2014.
As(III)	Colorimetric, UV-vis	2.5 ppb	Liang, R.-P.; Wang, Z.-X.; Zhang, L.; Qiu, J.-D. *Chemistry (Weinheim an der Bergstrasse, Germany)* 2013
	Light Scattering	0.5 ppb	
As(III)	Colorimetric, UV-vis	5.3 ppb	Wu, Y.; Zhan, S.; Wang, F.; He, L.; Zhi, W.; Zhou, P. *Chemical Communications* 2012.
As(III)	Colorimetric, UV-vis	20 nM	Xia, N.; Shi, Y.; Zhang, R.; Zhao, F.; Liu, F.; Liu, L. *Analytical Methods* 2012, 4, 3937–3941.
As(III)	Resonance Rayleigh Scattering	0.2 ppb	Wu, Y.; Zhan, S.; Xing, H.; He, L.; Xu, L.; Zhou, P. *Nanoscale* 2012.
As(III)	Colorimetric, UV-vis	0.6 ppb	Wu, Y.; Liu, L.; Zhan, S.; Wang, F.; Zhou, P. *The Analyst* 2012.
As(III)	Fluorescence	0.24 ppb	Ezeh, V.; Harrop, T. *Inorganic Chemistry* 2012.
As(III)	Fluorescence, Confocal microscope and cryo-electron microscopy	femtogram	Liu, R.; Chen, Z.; Wang, Y.; Cui, Y.; Zhu, H.; Huang, P.; Li, W.; Zhao, Y.; Tao, Y.; Gao, X. *ACS Nano* 2011.
As(III)	Fluorescence	20 nM	Wang, X.; Lv, Y.; Hou, X. *Talanta* 2011.

As(III)	SERS	0.76 ppb	Li, J.; Chen, L.; Lou, T.; Wang, Y. *ACS applied materials & interfaces* 2011.
As(III) **Reduced As(V)**	Colorimetric	1 ppb	Kalluri, J. R.; Arbneshi, T.; Khan, S. A.; Neely, A.; Candice, P.; Varisli, B.; Washington, M.; McAfee, S.; Robinson, B.; Banerjee, S.; Singh, A. K.; Senapati, D.; Ray, P. C. *Angewandte Chemie (International ed. in English)* 2009
	DLS	3 ppt	
As(V) **As(III)**	SERS	1 ppb As(V)	Mulvihill, M.; Tao, A.; Benjauthrit, K.; Arnold, J.; Yang, P. *Angewandte Chemie (International ed. in English)* 2008.
As(III)	SPR	Below 10 ppb	Forzani, E.; Foley, K.; Westerhoff, P.; Tao, N. *Sensors and Actuators B: Chemical* 2007