Supplementary Section

Ultrafast High-Capacity Capture-and-Release of Uranium by a Light- Switchable Nano-Textured Surface

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Materials and Chemicals

Acetone [9005-68, J.T.Baker], Isopropanol [9079-05, J.T.Baker], Deionized water [18 MΩ·cm], Phosphate buffer [PB, 10 mM, pH 8.5], Phosphate buffer [SB, 155 μM, ~pH 8.0], Glutaraldehyde solution [50 wt.% in H_2O, G7651, Sigma-Aldrich], (3-aminopropyl)-dimethyl-ethoxysilane [APDMES, SIA0603.0-5g, Gelest], silicon wafer [Polished, P-type, <100>, 1-10Ωcm, 380±15μm thickness, Wafer Pro], 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) [03450, Sigma-Aldrich] N-hydroxysulfosuccinimide sodium salt (sulfo-NHS) [56485, Sigma-Aldrich], Toluene [244511, Sigma-Aldrich], phosphate-buffered saline (PBS) tablets [P4417, Sigma-Aldrich], 3-hydroxypropionic acid [792659, Sigma-Aldrich], Uranyl specific 5'carboxy ssDNA aptamer (5'-COOH-CTGCA GAATT CTAAT ACGAC TCACT ATAGG AAGAG ATGGC GACAT CTCTG CAGTC GGGTA GTTAA ACCGA CCTTC AGACA TAGGC AGGCG TATAT CTTGT GACGG TAAGC TTGGC AC-3') [IDT syntezza]. Arsenic specific 5'carboxy ssDNA aptamer (5'-COOH- GGTA ATAC GACT CACT ATAG GGAG ATAC CAGC TTAT TCAA TTTT ACAG AACA ACCA ACGT CGCT CCGG GTAC TTCT TCAT CGAG ATAG TAAG TGCA ATCT-3') [IDT syntezza]. Spot urine samples were collected from healthy volunteers, and used within 10 hours from collection after verifying that urine samples were within normal levels using a 12-parameter urine test strip [DUS 12AC, One Step]. Samples were filtered using a syringe-filter with a cellulose acetate membrane [0.45 μm, 16555, Sartorius] and then spiked with stock solutions of uranyl.

Fabrication of SiNP array using metal-assisted etching[1]

The steps utilized in the fabrication of SiNP array are as follows:

1. Wash silicon substrate with acetone and isopropanol, dry with N_2.

2. Preparation of 1% polystyrene beads suspension solution: 100 μl of 10% polystyrene beads suspension (0.5μm, Sigma) centrifuged at 4500 rpm for 16 minutes. Separate the polystyrene beads from water and add 1 ml of 3% w/w TWEEN 80 in methanol. Disperse suspension with shaking.

3. Deposition of the polystyrene beads: 18μl (for 4 cm^2 wafer) of suspension solution to the center of wafer, and start spin coating. Adjust the spin rate and time according to wafer dimension (4 cm^2:1 minute at 475 rpm; 16 cm^2: 2 minutes at 180 rpm).

4. Polystyrene beads plasma etching, O_2 = 50sccm, 40mtorr, 30W, 6 minutes.

5. E-beam Ag-film deposition, 45 nm, 1 Å/sec.

6. Silicon wafer wet etching: 4.6 M HF, 0.44 M H_2O_2, 9 minutes for 3 μm.

7. Ag-wet etching: 20 μl HNO_3 (69 %), 30 seconds, Wash with DIW.

8. Plasma 10 minutes, 100W, 0.200 Torr O_2.

Fabrication of BSiNP array using chemical vapor deposition

1. Wash array with acetone and isopropanol, dry with N_2.

2. Plasma 10 minutes, 100W, 0.200 Torr O_2.

3. Electroless gold deposition: soaked for 30 minutes in 20% DIW, 80% ethanol, 0.05M HF, 110uM NaAuCl4, 1% tween 80.

4. CVD SiNW synthesis: p-type for 2 minutes ,20 sccm argon, 5 sccm SiH_4, 25 torr at 460°C.

5. Gold wet etching: 100 μl gold etchant [GE-8148, Transene], 2 minutes, Wash with DIW.

Preparation of 8-acetoxy-pyrene-1,3,6-trisulfonyl chloride out of 1-hydroxypyrene-1,3,6-trisulfonate (HPTS)[2]

1. Dissolve 20 gr trisodium-1-hydroxypyrene-1,3,6-trisulfonate was in 30 ml NaOH (2 M).

2. Cool to about 0 °C.

3. Add 5 gr acetic anhydride (4.8 ml) dropwise.

4. Stir for 2 hours.

5. Add 20 ml ethanol.

6. Filtrate precipitate and wash three times with 10 ml ethanol.

7. Dry precipitate under reduced pressure for 24 hours.

8. Place 5 gr of precipitate with 150 ml toluene in a round-bottomed flask, equipped with an automatic water separator (Dean-Stark trap) and a condenser.

9. Reflux for 2 hours.

10. Cool to about 60 °C.

11. Add 6ml oxalyl chloride and 2 drops of dimethylformamide

12. Reflux for 8 hours.

13. Filtrate to remove the precipitate.

14. Remove the solvent under reduced pressure.

15. Dry solid residue under vacuum for 24 hours.

Aptamer and HPTS immobilization on SiNP array.

The Antibodies and HPTS modification were done in the following steps:

1. Wash array with acetone, isopropanol, and DIW. Dry gently with N_2.

2. Plasma 10 minutes, 100W, 0.200 Torr O_2.

3. APDMES modification: 100% APDMES, room temperature, 2 hours. In glove box (argon environment).

4. Wash with isopropanol.

5. Dehydration: 115 °C, 30 minutes.

6. HPTS modification: Soak in 8-acetoxy-pyrene-1,3,6-trisulfonyl chloride and pyridine in 10ml toluene, 12 hours.

7. Removal of acetic group: Soak in sodium acetate, 30 minutes, then in isopropanol 50% w/w, 15 minutes finally soak in isopropanol 15 minutes. Dry in 110^0C, 30 minutes.

8. DNA immobilization: Soak in 600 μL of 7.5 μM DNA aptamer, 183 μM sulfo-NHS, and 70 μM EDC in phosphate buffer (10 mM. pH 7.1), 12 hours.

9. Wash phosphate buffer (10 mM, pH 7.1).

10. Blocking: Soak in 600 μL of 90 mM 3-hydroxypropionic acid, 180 mM sulfo-NHS, and 0.9 M EDC in phosphate buffer (10 mM. pH 7.1), 3 hours.
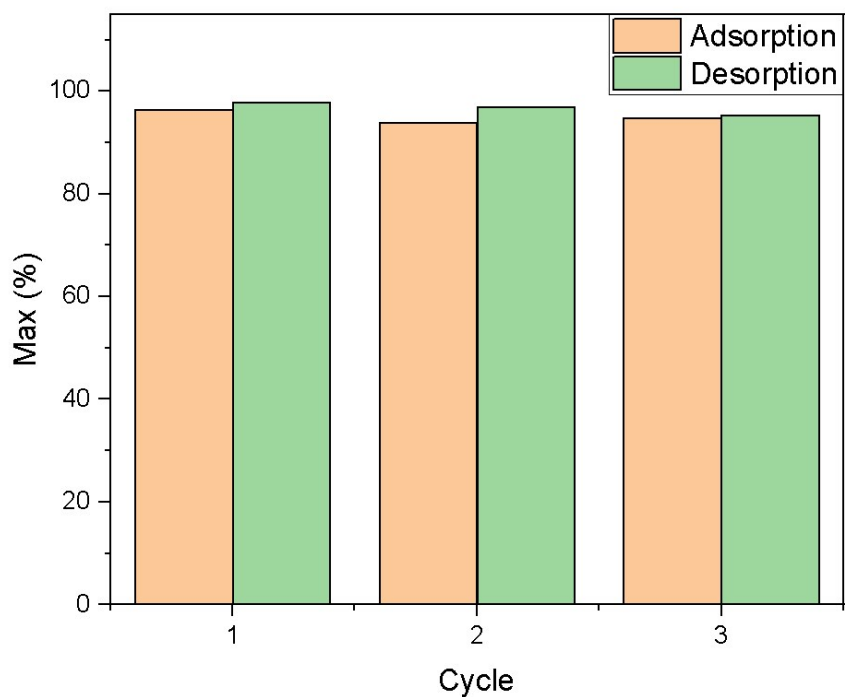
11. Wash phosphate buffer (10 mM, pH 7.1).

Optical Measurements

A series of experiments were performed by a commercial fluorescence scanner (TECAN Infinite M200).
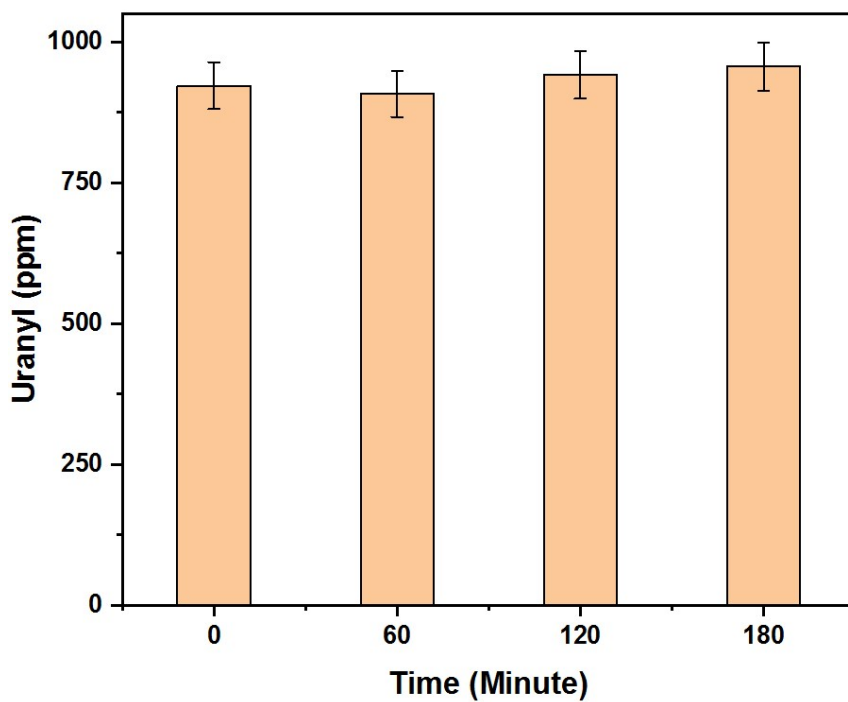
Concentrated salts solution

NaCl 6.1 g/L, $MgCl_2$ 1.3 g/L, Na_2SO_4 1.0 g/L, $CaCl_2$ 290 mg/L, KCl 173 mg/L, $NaHCO_3$ 50 mg/L, and H_3BO_3 7 mg/L.

Reusability of BSiNPs platform

Figure S1: Effectiveness of uranyl capture and release for several cycles on the same array.

Uranyl precipitation test

Figure S2: Uranyl concentration over time in phosphate buffer 10mM pH 8.5.

X-ray photoelectron spectroscopy

X-ray Photoelectron Spectroscopy (XPS) measurements were performed in UHV (2.5x10 $^{-10}$ Torr base pressure) using 5600 Multi-Technique System (PHI, USA). The samples were irradiated with an Al K_α monochromated source (1486.6 eV) and the outcome electrons were analyzed by a 'Spherical Capacitor Analyzer' using the slit aperture of 0.8 mm. Some samples were charged during measurements and this charging was compensated by using a charge neutralizer and additional mathematical peak shifting, with SiO_2 at 103.0 eV taken as an energy reference for all the peaks.

Performed Measurements:

Survey: spectrum in a wide energy range (0 - 1400 eV). It gives an estimation of the elements present on the sample surface and is taken at a low resolution.

Utility Multiplex: spectra taken for different peaks in a low energy range window at an Intermediate (Utility) Resolution. It is taken for all the elements present for the atomic concentration (AC%) calculation. An AC table is given as an output of these measurements.
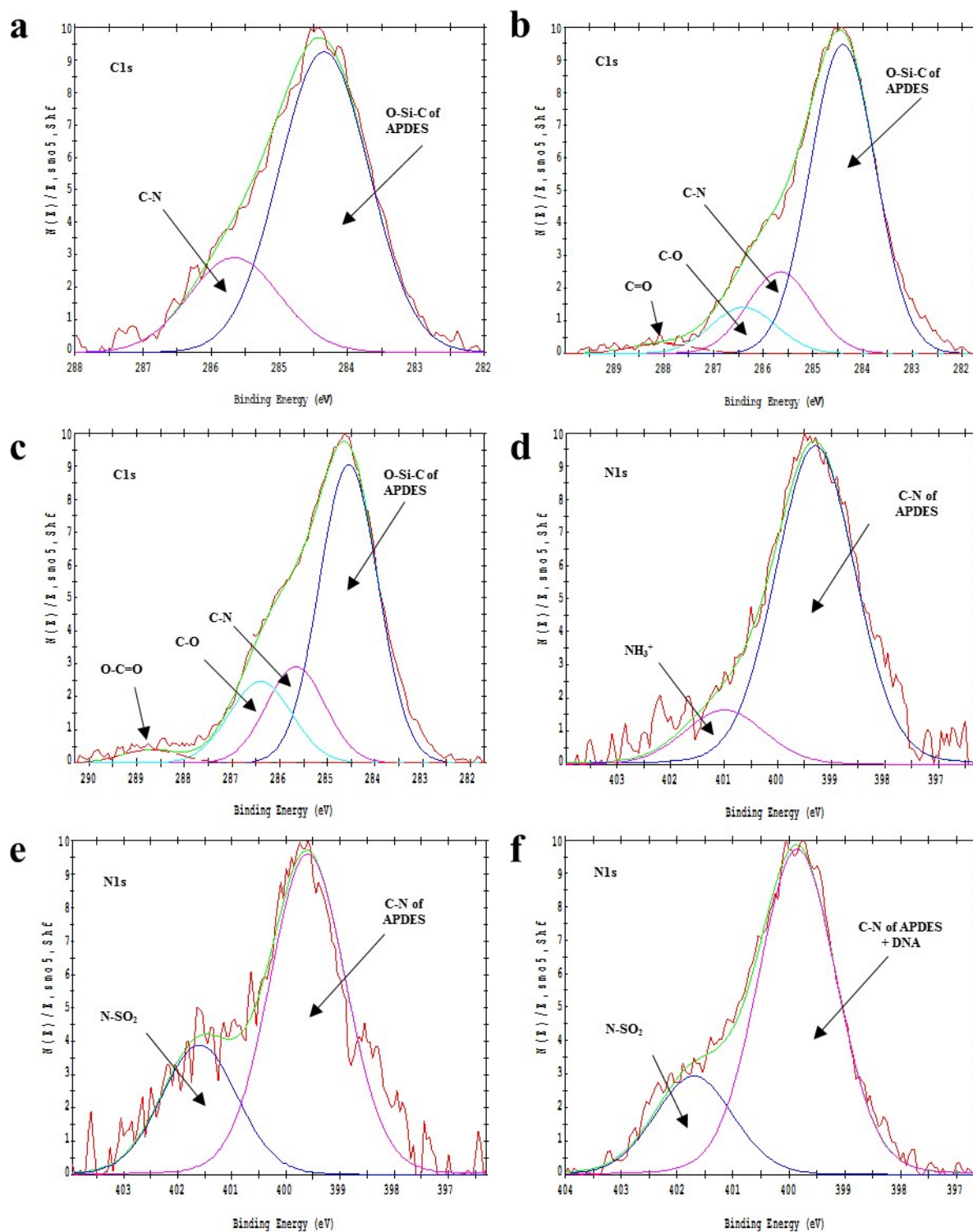
High-Resolution Multiplex: spectra taken for different peaks in a low energy range window at a High Resolution (PE = 11.75 eV, 0.05 eV/step). These measurements allow precise energy position and peak shape determination, necessary for bond bonding analysis.

AC range	Accuracy
Around 50%	±2%
Around 20%	±5%
Around 5%	±10%
Around 1%	±20%

Table S1: AC calculation accuracy by AC range.
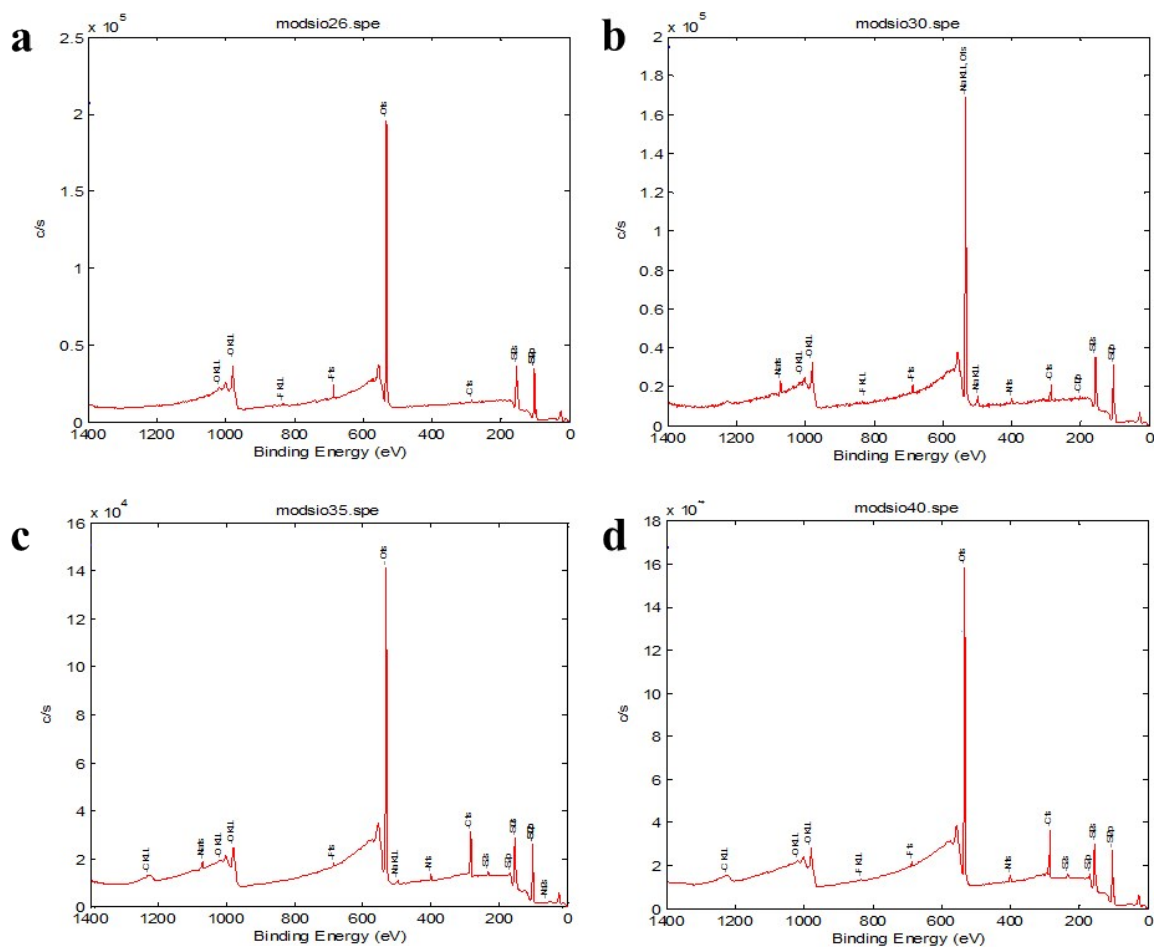
Figure S3: XPS representative survey spectra for the SiNPs before modification **(a)**, after APDMES modification **(b)**, after APDMES and HPTS modification **(c)**, after APDMES and HPTS modification and DNA immobilization **(d)**.

Figure S4: High-Resolution Multiplex spectras of SiNPs after APDMES modification **(a,d)**, after APDMES and HPTS modification **(b,e)**, after APDMES and HPTS modification and DNA immobilization **(c,f)**. N-SO$_2$ peak at 401.1 eV determined in Döring **(1988),** Zeitschrift für anorganische und allgemeine Chemie.[3]

**Calculations of the average pH near silica surfaces[4]**

Photon source and units

1. LED light emitter power 9.4 mW at 390 nm.

2. Absorption cross section per HPTS molecule for $\varepsilon=60000$ $M^{-1}cm^{-1}$ (at $\lambda\approx400$ nm) $= 1.6\times10^{-16}cm^2$.

3. Illuminated area by the LED emitter 1.5 mm $=1.76\times10^{-2}cm^2$.

4. Light intensity (power/cm2) on a silica surface: $9.4\times10^{-3}/0.0176= 0.55$ watt/cm^2.

Conversion of light power to photon flux and proton released per second

5. Photon flux $= 0.55 / (3\times1.6\times10^{-19}) = 1.2\times10^{18}$ photons/cm^2·sec.

6. Adsorbed HPTS molecules per cm$^2 = 2\times10^{13}$ molecules/cm^2.

7. Light power absorbed by molecules per second $= 1.6\times10^{-16} \times 2\times10^{13} \times 0.55$ W/cm^2 $= 1.76$ mW/cm^2.

8. Number of released protons per second $= 1.76\times10^{-3} / 4.8\times10^{-19} = 3.66\times10^{15}$ proton/sec.

9. 3.3×10^{18} photons in 1J $=$1Watt/second (3 eV per photon).

10. This large number of released protons recombine with HPTS RO$^-$ to reform ROH.

Proton Recombination Consideration

A photocycle ends at about 0.1 mili-second. The photocycle ends when the photo-proton recombines with the ground state HPTS to reform the protonated photoacid.

$$RO^-_{(g)} + H^+ \xrightarrow{k_D} ROH_{(g)}$$
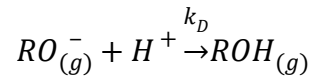
The reaction is bimolecular and thus the recombination rate decreases as

$$\frac{dC_{H^+}}{dt} = k_D\left[C_{H^+}\right]\left[C_{HPTS^*}\right] = k_D\left[C_{H^+}\right]^2$$

The second order kinetics complicates the calculation of the effective pH next to the illuminated surface area. The rate decreases as the time progresses because the proton concentration decreases. This reaction takes place in the ground state. For a double charged RO$^-$, the diffusion controlled rate is $k_D\approx10^{10}$ s^{-1}. $k_D\cong4\pi N'D_{H^+}R_D$

Where $N' = \dfrac{N_A}{1000}\cong 6\times10^{20}$, R_D is the Debye radius, $R_D = \dfrac{ze^2}{4\pi\varepsilon_0\varepsilon_{H_2O}^{bulk}K_BT}$, z the HPTS charge is -2, e the electron charge, ε_0 is the permittivity constant, T the room temperature.

The pseudo first order reaction rate $k'_D = k_D \cdot C_{H^+}$ depends on C_{H^+}. For pH≈5 $k'_D = 10^{10} \times 10^{-5} = 10^5$ s^{-1} and in a homogeneous proton distribution it takes 10^{-5} seconds for the proton to recombine with the RO$^-$ of HPTS and the emitted proton reach a low level of pH 5. The proton production rate by the light source and the pseudo first order recombination rate constant $k_D \cdot C_{H^+}$ determine the average pH. The photo-proton production by the ESPT process per second is 3.66×10^{15} proton/sec. If we assume that the photocycle ends at 10^{-4} second and the proton that recombine are lost, then the production of protons at this time window of 10^{-4} seconds would be $3.6 \times 10^{15} \times 10^{-4} = 3.66 \times 10^{11}$ proton/cm^2.

Assuming two dimensional proton diffusion next to the surface, the proton is limited to diffuse within a thin water layer with a thickness of ~100Å (10 nm),[5] and our active bio-layer has an average thickness of ~3-5nm (40Å average). We derive the value of the layer thickness from our previous study where we found that the proton movements are next to the silica surface and do not escape to the bulk. The plausible reason for the two-dimensional proton diffusion is the APTES base adsorbed on the silica and the large negative charge of adsorbed HPTS. Thus the proton diffusion volume per cm^2 is 10^{-6} cm^3 and the proton average concentration in molecules per cm^3 is $N_{H^+} = 3.66 \times 10^{11}$ / $6 \times 10^{-7} = 6.1 \times 10^{17}$ protons/cm^3. 1M is equivalent to 6×10^{23} molecules per liter and thus 6×10^{20} per cm^3, and the proton concentration $C_{H^+} = 6.1 \times 10^{17}$ / $6 \times 10^{20} = 1 \times 10^{-3}$M Thus for $\tau = 10^{-4}$s, the smallest average pH is ~2.9. This calculation is based on a homogenous 2 dimensional diffusion space and a proton diffusion of D=0.8×10^{-4} cm^2/s as was estimated from our previous study.[2]
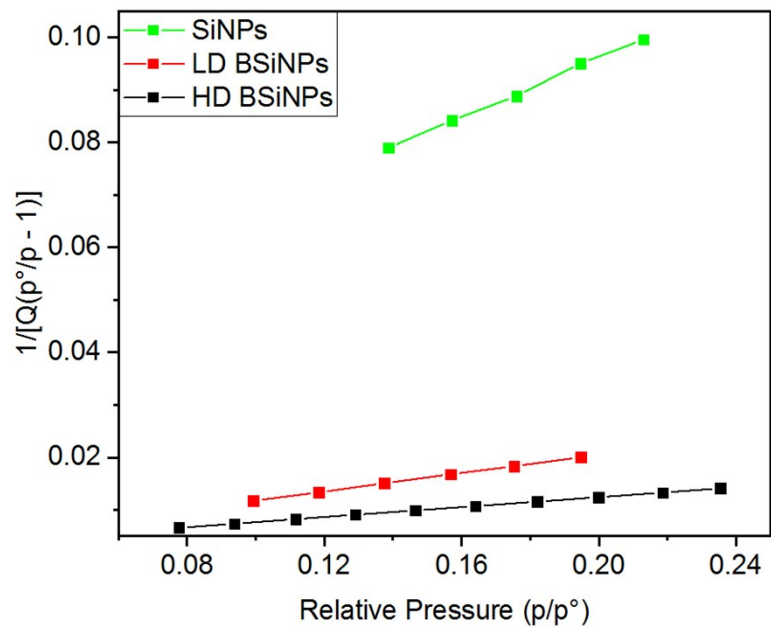
ICP-MS measurements

Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent Technologies 7700 Series) was used for detection of total Uranium concentrations in all the samples. A full quant analysis of Uranium was performed with ICP-MS, with 10 points of calibration (0-1000 ng/mL) with known concentrations of Uranium. During the detection of Uranium in samples, Gd (1 mg/L) was used as an instrumental internal standard to monitor the stability of ionization efficiency in time. The ICP-MS data were processed with instrumental software (MassHunter 4.1 version C.01.01, 2015).

BET mesurments information and results

Measurements were performed by Particle Testing Authority via Dr. Golik Scientific solutions, utilizing TriStar II Plus indtrument. Analysis adsorptive: Kr, Analysis bath temp.: 77.300 K, Thermal correction: no, Equilibration interval: 10 s, Low pressure dose: none , Sample density: 1.000 g/cm³, Automatic degas: no, Correlation coefficient: 0.9999157, Molecular cross-sectional area: 0.2100 nm² Sample was kept under vacuum at 100ºC for 960 minutes, analyzed per ISO 9277, reference material(s) used for instrument performance verification available upon request.
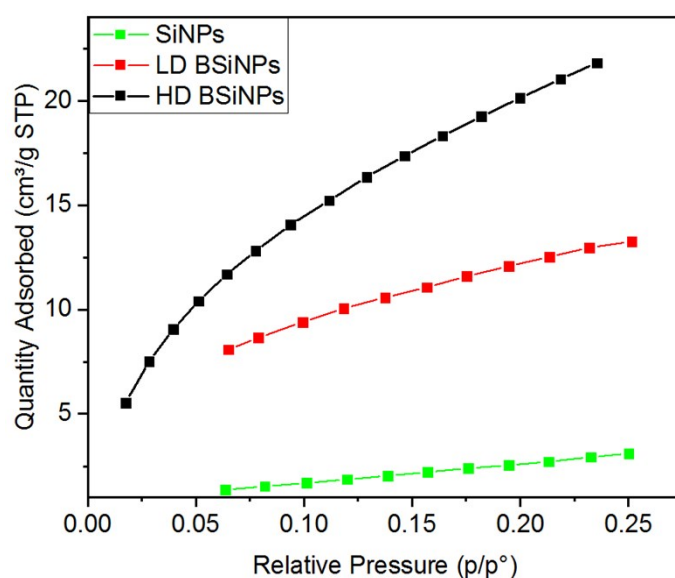
Figure S5: Isotherm linear plots of measurements for SiNP array (green curve), BSiNWs arrays of low density (red curve) and high density (black curve).

Figure S6: BET surface area plots of measurements for SiNP array (red curve), BSiNWs arrays of low density (green curve) and high density (black curve).

References

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