Nanoscale Growth and Patterning of Inorganic Oxides Using DNA Nanostructure Templates

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1. Materials and Instruments

Silicon wafer (Si[110], with native oxide) was purchased from University Wafers. Gold wafer was purchased from Platypus technologies (template stripped gold strip, AU 1000 SWTSG). Tetraethylorthosilicate (TEOS, >99+%), titanium isopropoxide (>98+%), conc. ammonium hydroxide (30 wt%), *n*-propanol and *iso*-propanol (99+%) were purchased from Sigma Aldrich. Synthetic and M13mp18 DNA for preparing the origami[1] were purchased from IDT and New England Biolabs, respectively. The silicon substrate was cleaned with hot piranha solution (7:3 concentrated H_2SO_4: 35% H_2O_2). *Warning: Piranha solution presents an explosion danger and should be handled with extreme care; it is a strong oxidant and reacts violently with organic materials. All work should be performed in a fume hood. Wear proper protective equipment.*

Tapping mode atomic force microscopy was carried out on a Veeco Dimension 3100 in air.

X-ray photoelectron (XPS) spectra were collected on a custom built multi-technique surface analysis instrument operating at a base pressure of less than $1x10^{-10}$ torr. Spectra were collected using the Al-Kα X-ray line and a Leybold-Heraeus EA-10 hemispherical energy analyzer typically operating with a bandpass of 50 eV. Data analysis was carried out using in house written software for both background subtraction and peak fitting.

Ellipsometry measurement was obtained using a spectroscopic phase modulated ellipsometer (Horiba Jobin Yvon UVISEL).

EDX analysis was carried out using a Philips XL-30 field emission scanning electron microscope equipped with an EDAX CDU LEAP detector.

Plasma etching was carried out using a Trion Technology Phantom III LT reactive ion etching system.

2. Methods

(a). Triangular DNA origami preparation

The DNA origami triangles were prepared using a previously published procedure[1,2]. In a typical procedure, the desired set of 253 shorts strands (16 nM, a 10 fold excess of staple strands) were

mixed with M13mp18 (1.6 nM) in a 100 μL total volume of 1X Tris-Acetate-EDTA (TAE) buffer (400 mM Tris acetate, 10 mM EDTA, 20 mM Na^+) with 12.5 mM magnesium acetate (pH=8.3). The sample was then annealed from 95 ℃ to 20 ℃ at the rate of 1 ℃/min. After the completion of annealing, excess staples were removed from the origami solution by washing at least 3 times with 300 μL of TAE/Mg^{2+} buffer in 100 kDa MW centrifuge filters (Microcon YM-100, Millipore, Billerica, MA) on a single speed bench top microcentrifuge (VWR Galaxy Ministar) for 30 – 90 seconds. It is ensured that the filter is not centrifuged to dryness and there is always 50 – 100 μL of the sample left in the filter. After filtration the origami solutions were stored at 4 ℃.

(b). Rectangle/DNA-alphabet shape single strand tile (SST) DNA nanostructure preparation

The SST DNA nanostructures were prepared following a published procedure[3]. Multiple single-stranded DNA strands were mixed in a roughly equal molar final concentration of 100 nM (rectangle) or 200 nM (DNA-alphabets)) per strand in a 50 uL final volume in 0.5× TE buffer (5mM Tris, pH 7.9, 1mM EDTA) and 15 mM $MgCl_2$. The sample solution was then annealed in a PCR thermal cycler from 90 ℃ to 25 ℃ over a period of 17 h. The annealed samples were subjected to 2% agarose gel (pre-stained with SYBR Safe) electrophoresis with 0.5× TBE/10 mM $MgCl_2$ as running buffer on an ice-water bath. Then the target gel bands were excised from gel and extracted using a Freeze 'N Squeeze column (Bio-Rad). Target structures were recovered from the gel by a centrifugation at a speed of 438g for 3 min. Sample concentrations were measured by the ultraviolet absorption at 260 nm. Purified DNA nanostructure solutions were stored at 4 ℃.

(c). Plasma etching of negative tone pattern of CVD grown SiO_2 on Si [110] substrate.

The plasma etching was carried out using a Trion Technology Phantom III LT reactive ion etching system. The negative tone CVD grown SiO_2 substrate was placed inside the etching chamber and etched using SF_6 and O_2 plasma. The pressure inside the chamber was 20 mtorr and the flow rate of SF_6 and O_2 was maintained at 20 sccm (standard cubic centimeter) and 8 sccm respectively. The etching duration varied from 5 sec to 15 sec depending upon the thickness of

the CVD grown SiO_2 layer. After plasma etching, the substrate was immersed in dilute HF (1%) for 20 min to remove the SiO_2 resulting in trench patterns (triangular) on the Si substrate.

3. Assembly of DNA nanostructures on substrates

(a) Assembly of DNA nanostructures on Si substrate

The DNA nanostructure solution (2 μL) was pipetted onto a clean silicon wafer and left undisturbed for 30 min in a closed container with its lid covered by a moistened Kimwipe to minimize evaporation. The substrate was then dried by blowing N_2 gas such that the drop of buffer solution on the substrate is drove in one direction. The substrate was then immersed in 1:9 water : ethanol solution for 3 sec (twice) to remove the salt impurities and then dried using blow N_2 gas.

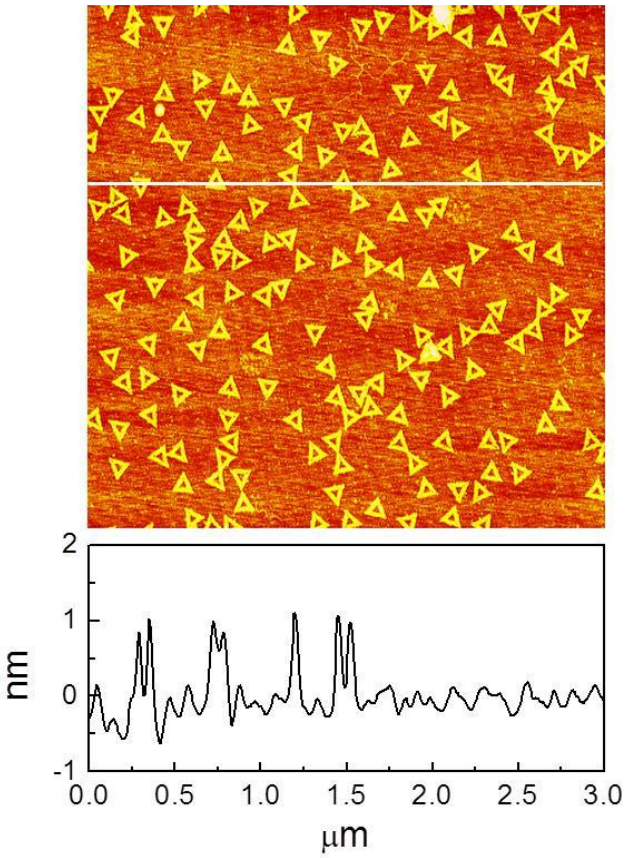

Figure S1. AFM image of DNA origami triangle assembled on the Si substrate.

(b). Assembly of DNA nanostructures on mica substrate

The DNA nanostructure solution (2 μL) was pipetted onto a freshly cleaved mica substrate and dried by blowing N_2 gas such that the drop of buffer solution on the substrate was drove in one direction. The substrate was then immersed in 1:9 water : ethanol solution for 3 sec to remove the salt impurities and then dried using blow N_2 gas.

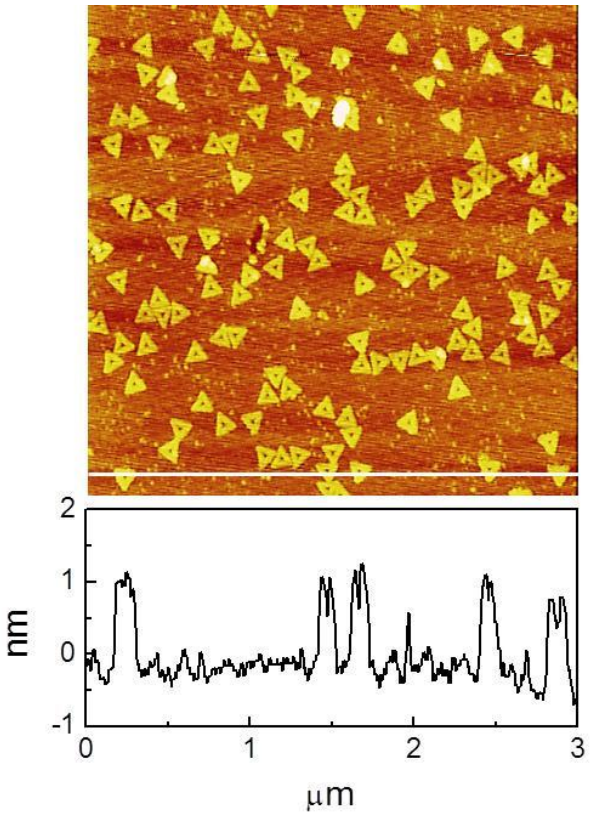

Figure S2. AFM image of DNA origami triangle assembled on the mica substrate.

(c). Assembly of DNA nanostructures on gold substrate

Due to the hydrophobic nature of gold, DNA nanostructure does not assemble on the freshly stripped gold substrate. To assemble the DNA nanostructure, gold was treated with UV/ozone (PSD Pro Series Digital UV Ozone System) for 15 min. DNA nanostructure solution (5 µL) was pipetted on to the UV/ozone treated gold substrate and left undisturbed for 30 min in a closed container. The substrate was then dried by blowing N_2 gas such that the drop of buffer solution on the substrate is drove in one direction. The substrate was then immersed twice in 1:9 water : ethanol solution for 3 sec to remove the salt impurities and then dried using blow N_2 gas.

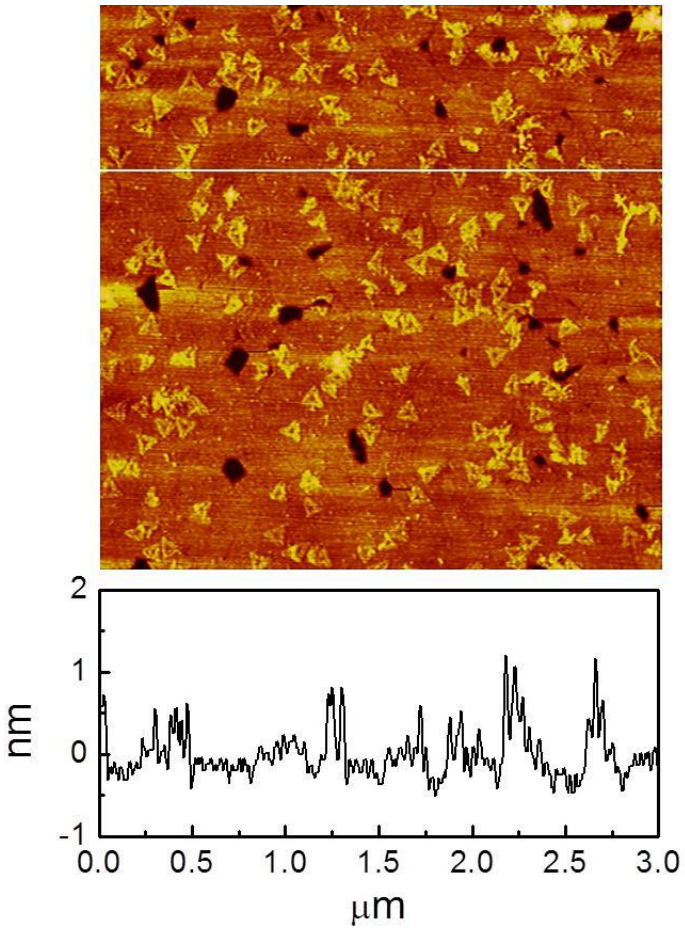

Figure S3. AFM image of DNA origami triangle assembled on the gold substrate.

(d) Assembly of DNA alphabets on Si substrate

A drop of buffer (5 μL, Tris-Acetate-EDTA (TAE) buffer (400 mM Tris acetate, 10 mM EDTA, 20 mM Na^+) with 12.5 mM magnesium acetate) was placed on a clean Si wafer and left undisturbed for 5 min. DNA alphabet solution (2 μL) was added to it and the sample was left undisturbed for 30 min inside a petri dish covered with wet Kimwipe for 30 min. The sample was then blow dried using nitrogen followed by a rinse in 90:10 ethanol: H_2O solution and finally blow drying using nitrogen.

Note: It is to be noted that the yield of the DNA alphabets assembled on the Si wafer using above mentioned procedure is very low and lots of DNA alphabets appear to be broken on the Si wafer. The AFM images for the positive tone SiO_2 growth on DNA alphabets show the versatility of the CVD growth technique in terms of shape.

4. Negative tone CVD synthesis/patterning of SiO_2 on substrates

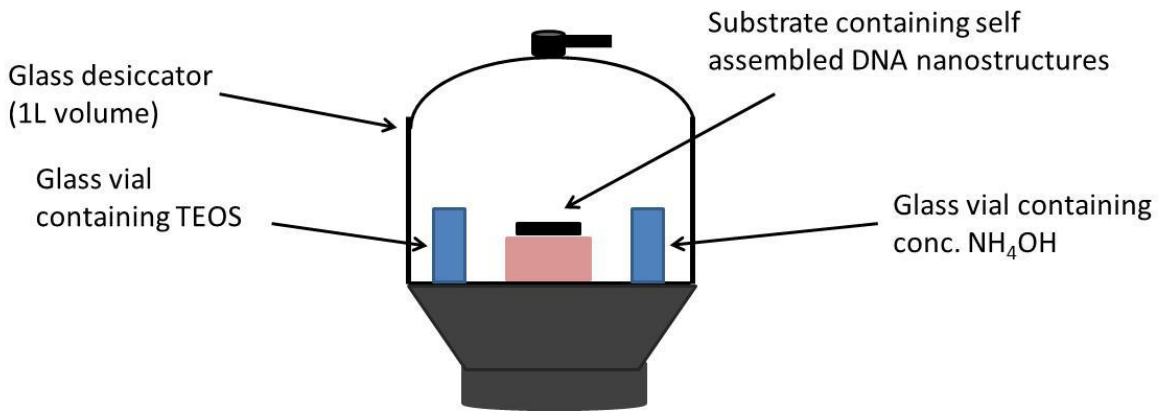

Figure S4. Cartoon showing the reaction set-up for the negative tone CVD synthesis/patterning of SiO_2

In a typical procedure, a substrate sample containing self-assembled DNA nanostructures was placed inside a glass desiccator equipped with two un-capped vials containing conc. NH_4OH and TEOS, respectively. The desiccator was covered with its lid and the sample was left undisturbed inside the desiccator for a specific time. The sample was then taken out and the surface of the sample was imaged using tapping mode AFM.

Note: Size of desiccator plays an important role in growth kinetics on CVD grown SiO_2. The experiments reported here were carried out using a desiccator of a volume of 1500 cm^3. A larger container produced positive tone growth under the same condition. The mechanism behind the size effect is currently under investigation.

(i) For a reaction time of 12 h

(a) Si substrate yielded negative tone pattern (b) mica substrate yielded negative tone pattern but with a very small contrast (c) gold substrate yielded positive tone pattern

(a) Si substrate

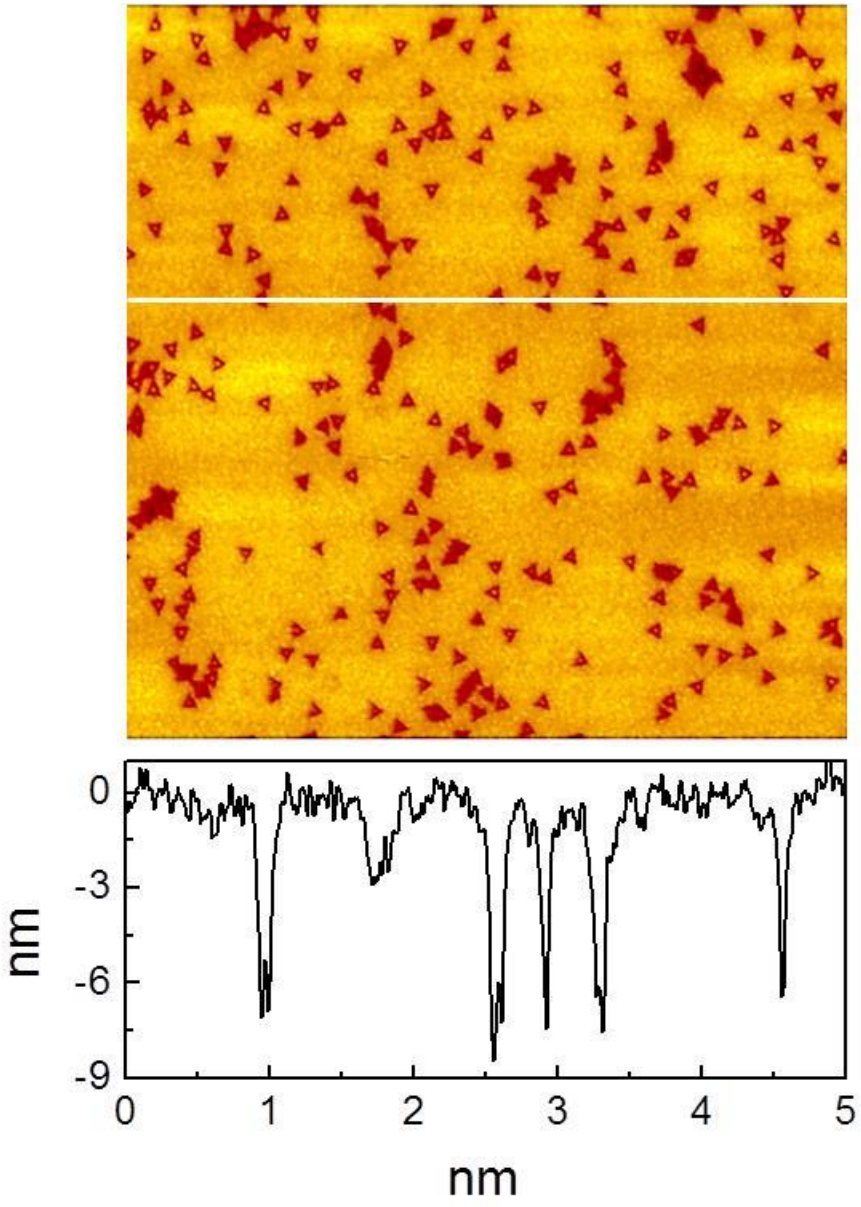

Figure S5. AFM image of CVD grown SiO_2 on the Si substrate for a growth time period of 12 h under negative tone SiO_2 growth conditions (TEOS, NH_4OH) using DNA origami triangles as templates. Note: the large holes are due to aggregation of DNA nanostructures.

(b) Mica substrate

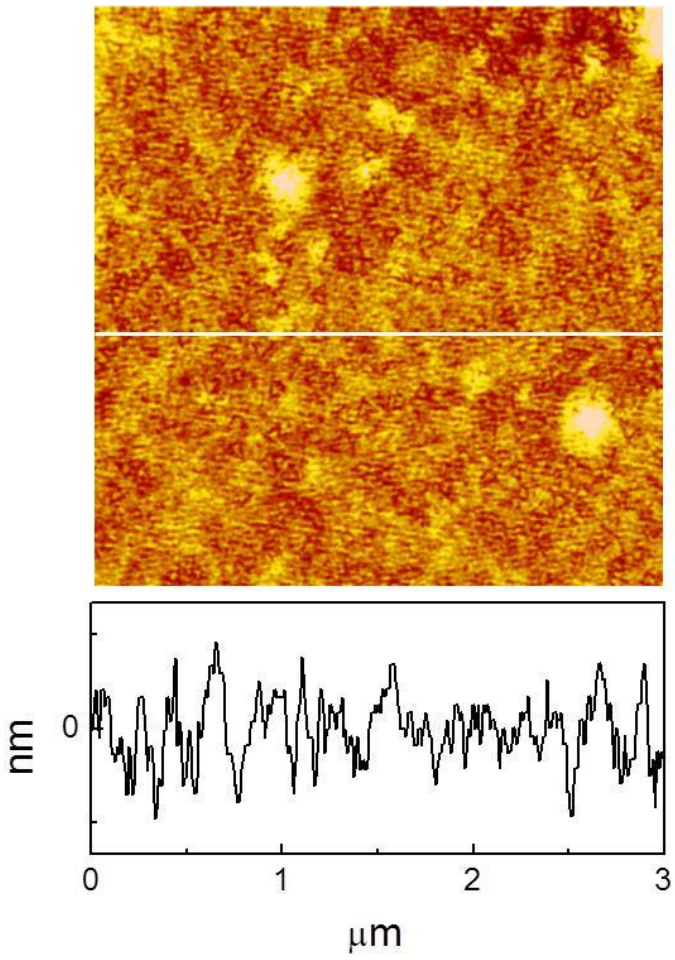

Figure S6. AFM image of CVD grown SiO_2 on the mica substrate for a growth time period of 12 h under negative tone SiO_2 growth conditions (TEOS, NH_4OH) using DNA origami triangles as templates.

(c) Gold substrate

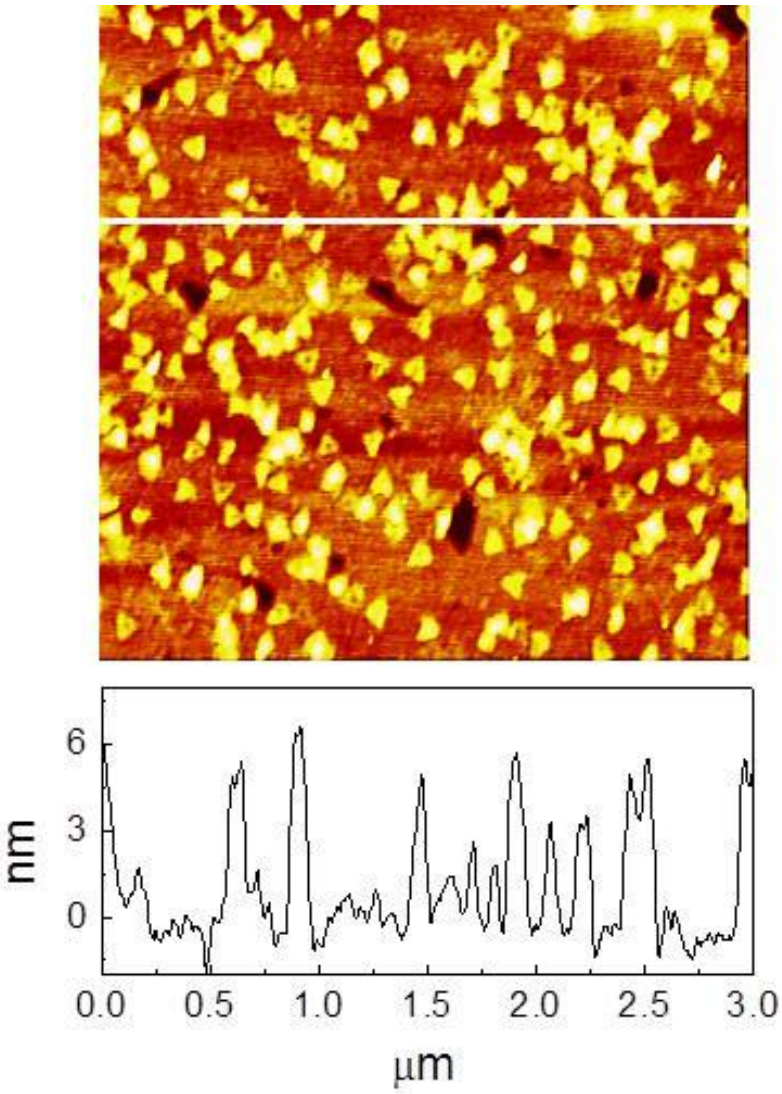

Figure S7. AFM image of CVD grown SiO_2 on the gold substrate for a growth time of 12 h under negative tone SiO_2 growth conditions (TEOS, NH_4OH) using DNA origami triangles as templates.

(ii) For a reaction time of 24 h, (a) SiO_2 and (b) mica substrate showed very fair negative tone patterns (very small contrast), while gold substrate still showed positive tone patterns.

(a) Si substrate

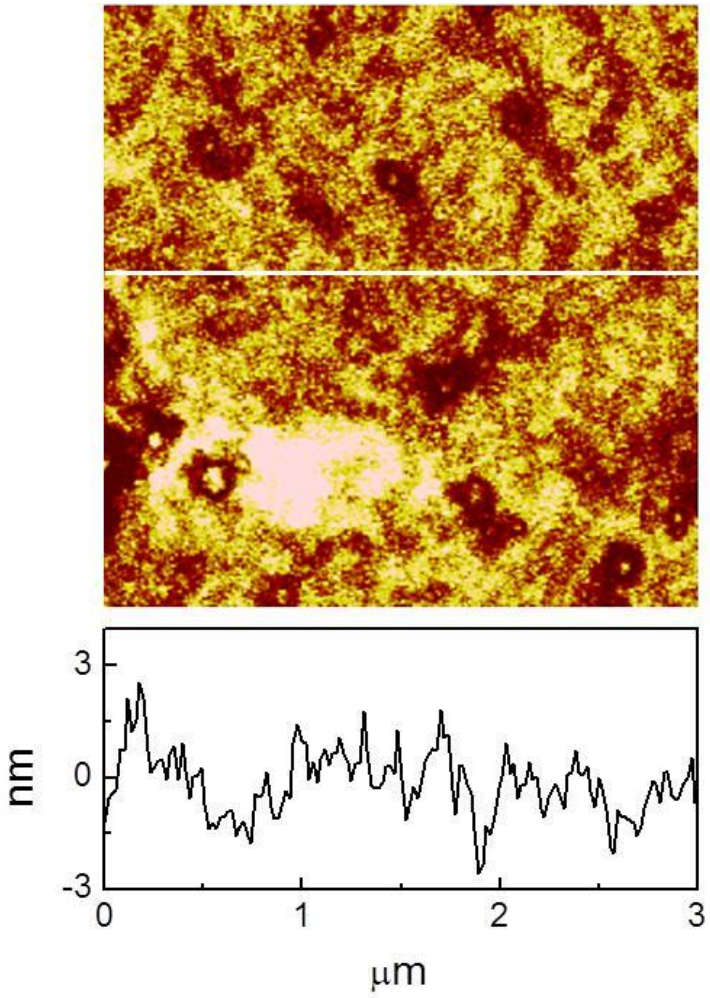

Figure S8. AFM image of CVD grown SiO_2 on the Si substrate for a growth time period of 24 h under negative tone SiO_2 growth conditions (TEOS, NH_4OH) using DNA origami triangles as templates.

(b) Mica substrate

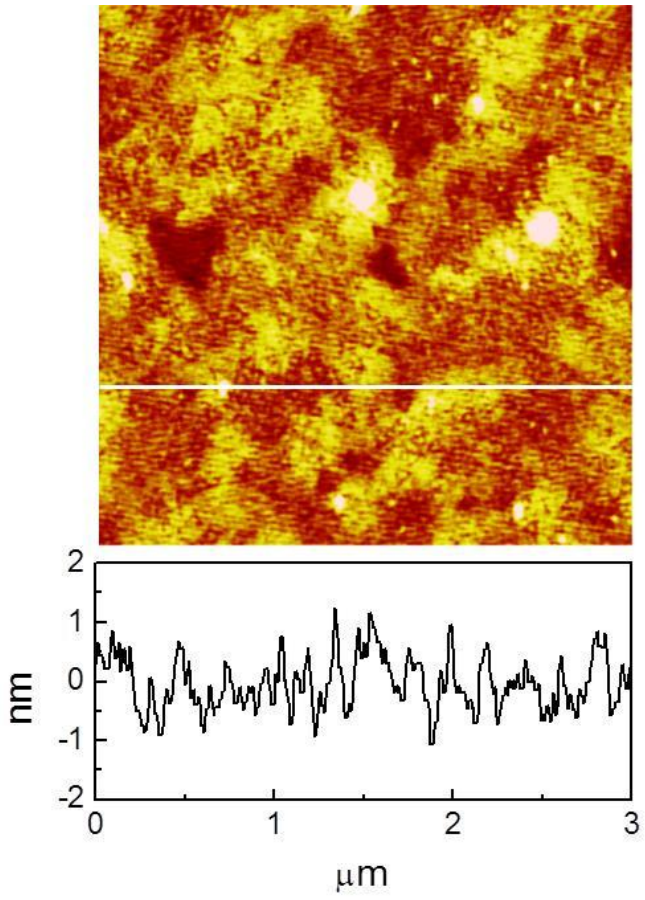

Figure S9. AFM image of CVD grown SiO_2 on the mica substrate for a growth time period of 24 h under negative tone SiO_2 growth conditions (TEOS, NH_4OH) using DNA origami triangles as templates.

(c) Gold substrate

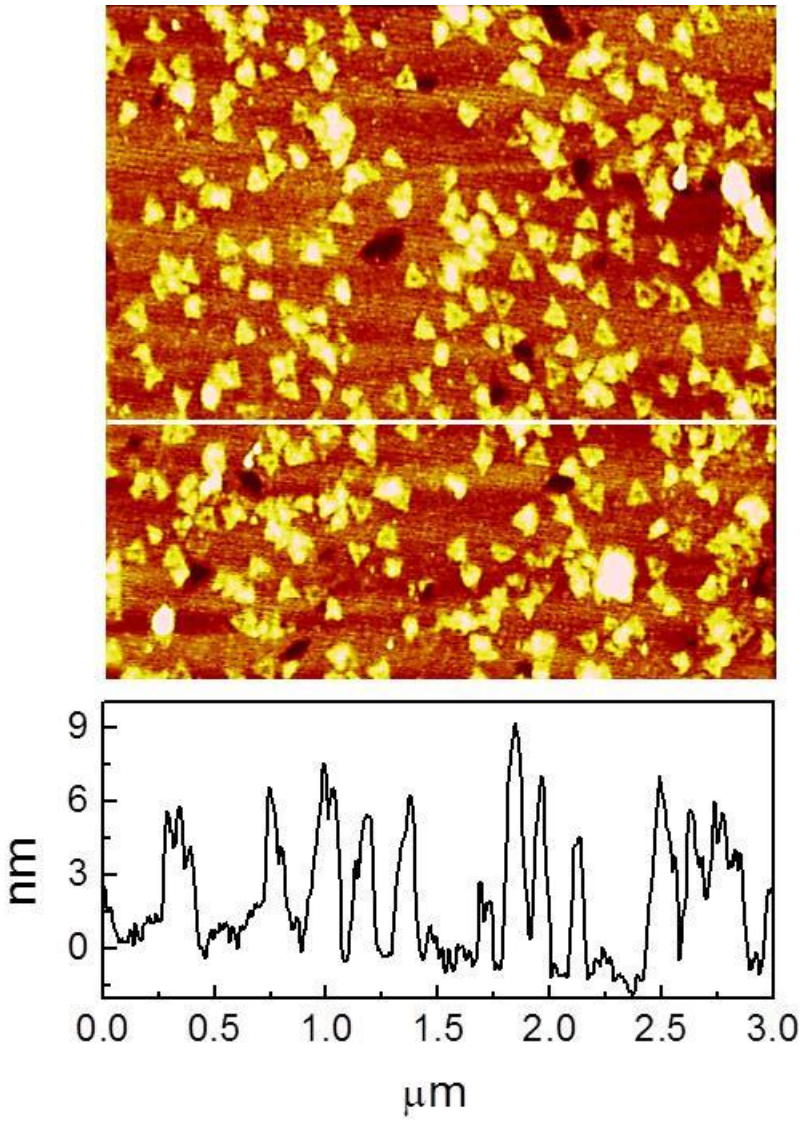

Figure S10. AFM image of CVD grown SiO_2 on the gold substrate for a growth time period of 24 h under negative tone SiO_2 growth conditions (TEOS, NH_4OH) using DNA origami triangles as templates.

5. Positive tone CVD synthesis/patterning of SiO_2

In a typical procedure, a substrate containing self-assembled DNA nanostructures was placed inside a glass desiccator equipped with four un-capped vials containing conc. NH_4OH, TEOS, *n*-propanol (or *iso*-propanol) and water respectively. The desiccator was covered with its lid and the sample was left undisturbed inside the desiccator for a specific time. The sample was then taken out and the surface of the sample was imaged using tapping mode AFM.

(i) For a reaction time of 6 h

(a) Si substrate

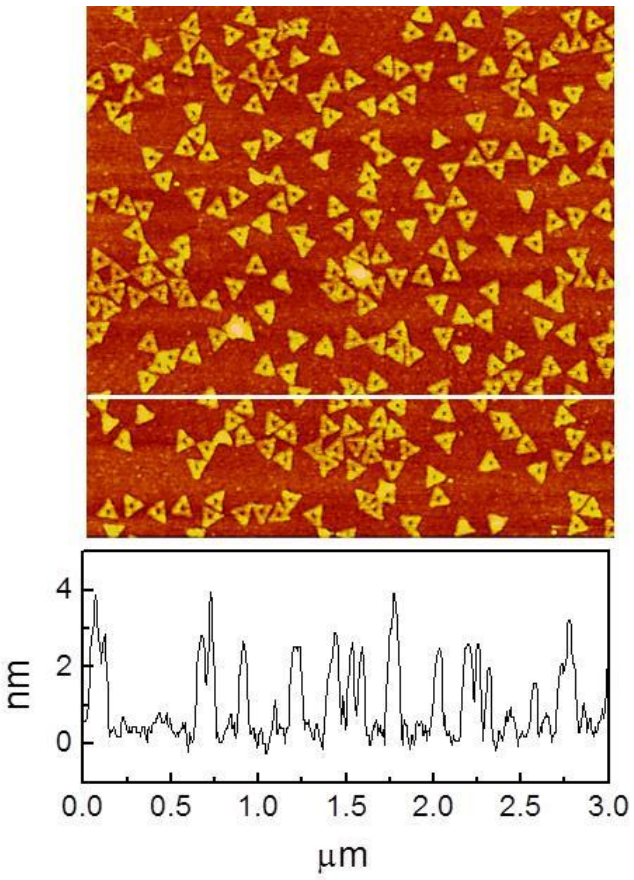

Figure S11. AFM image of CVD grown SiO_2 on the Si substrate for a growth time period of 6 h under positive tone SiO_2 growth conditions (TEOS, NH_4OH, *iso*-propanol, water) using DNA origami triangles as templates.

(b) Mica substrate

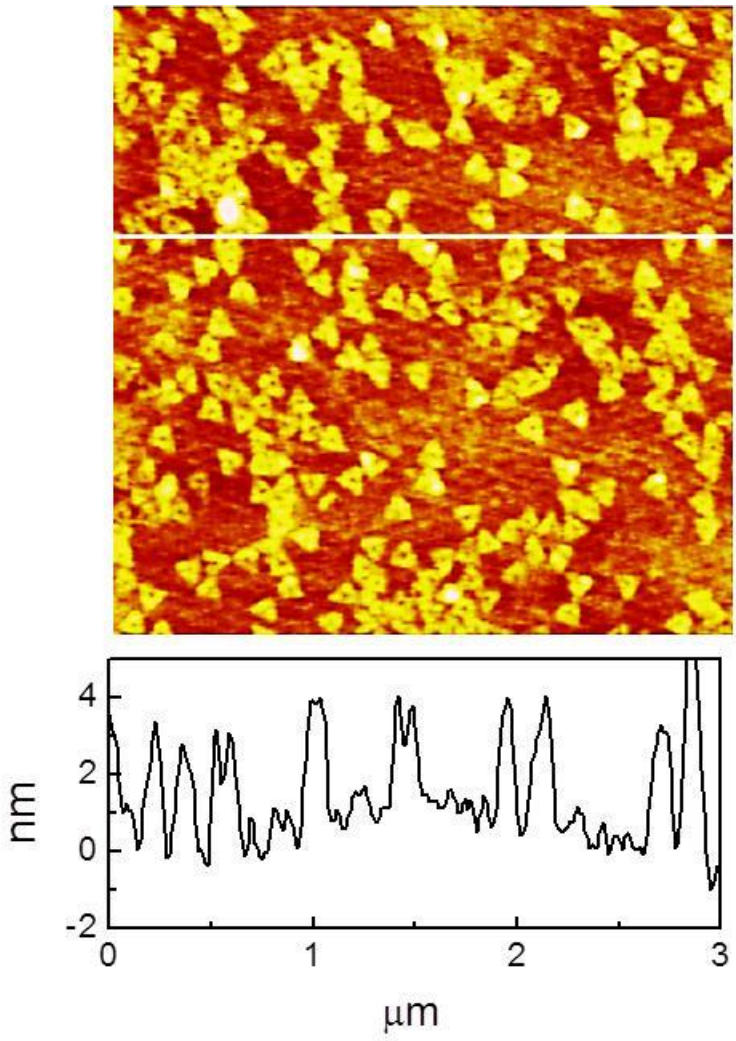

Figure S12. AFM image of CVD grown SiO_2 on the mica substrate for a growth time period of 6 h under positive tone SiO_2 growth conditions (TEOS, NH_4OH, *iso*-propanol, water) using DNA origami triangles as templates.

(c) Gold substrate

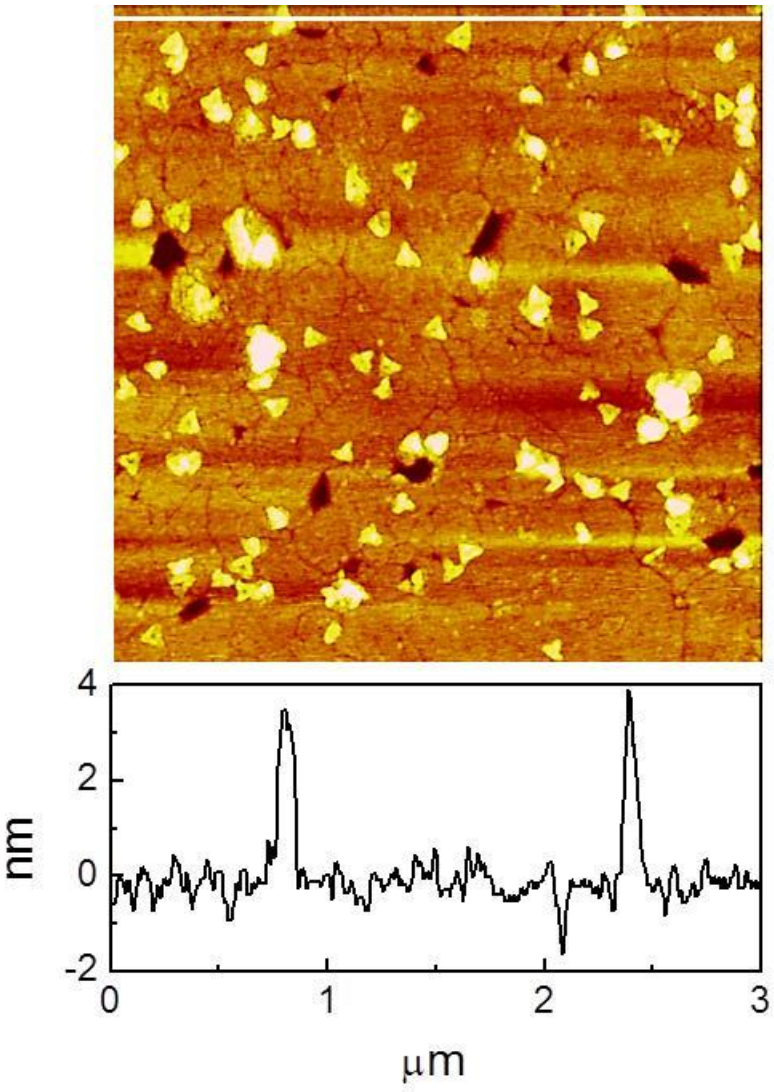

Figure S13. AFM image of CVD grown SiO_2 on the gold substrate for a growth time period of 6 h under positive tone SiO_2 growth conditions (TEOS, NH_4OH, *iso*-propanol, water) using DNA origami triangles as templates.

(ii) For a reaction time of 24 h.

(a) Si substrate

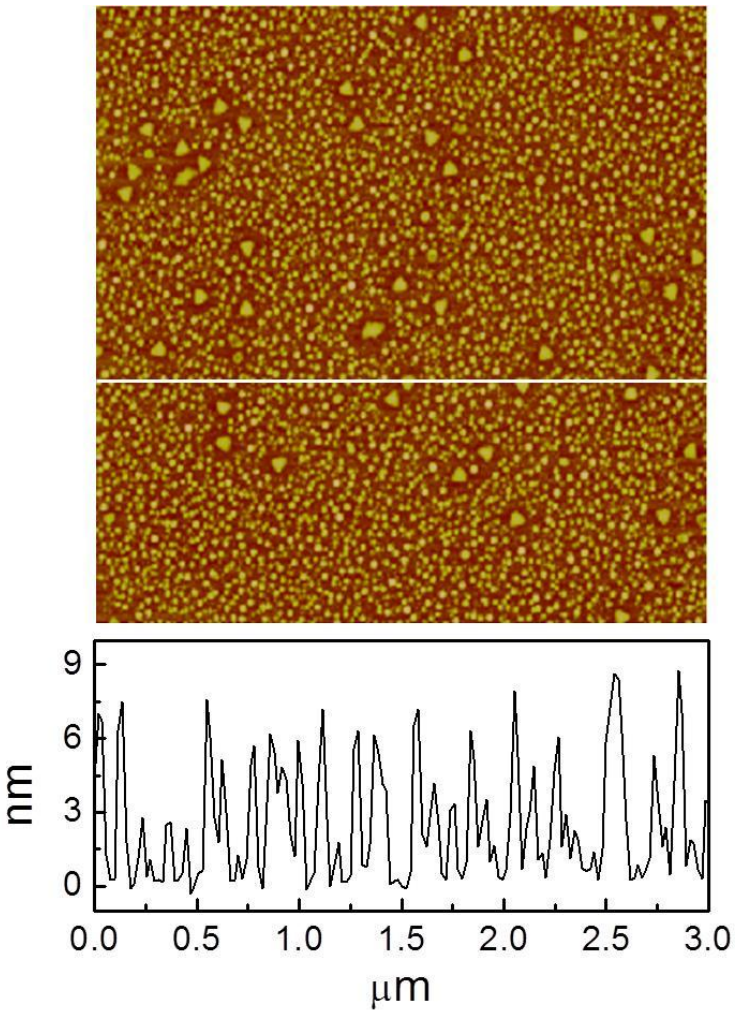

Figure S14. AFM image of CVD grown SiO_2 on the Si substrate for a growth time period of 24 h under positive tone SiO_2 growth conditions (TEOS, NH_4OH, *n*-propanol, water) using DNA origami triangles as templates.

(b) Mica substrate

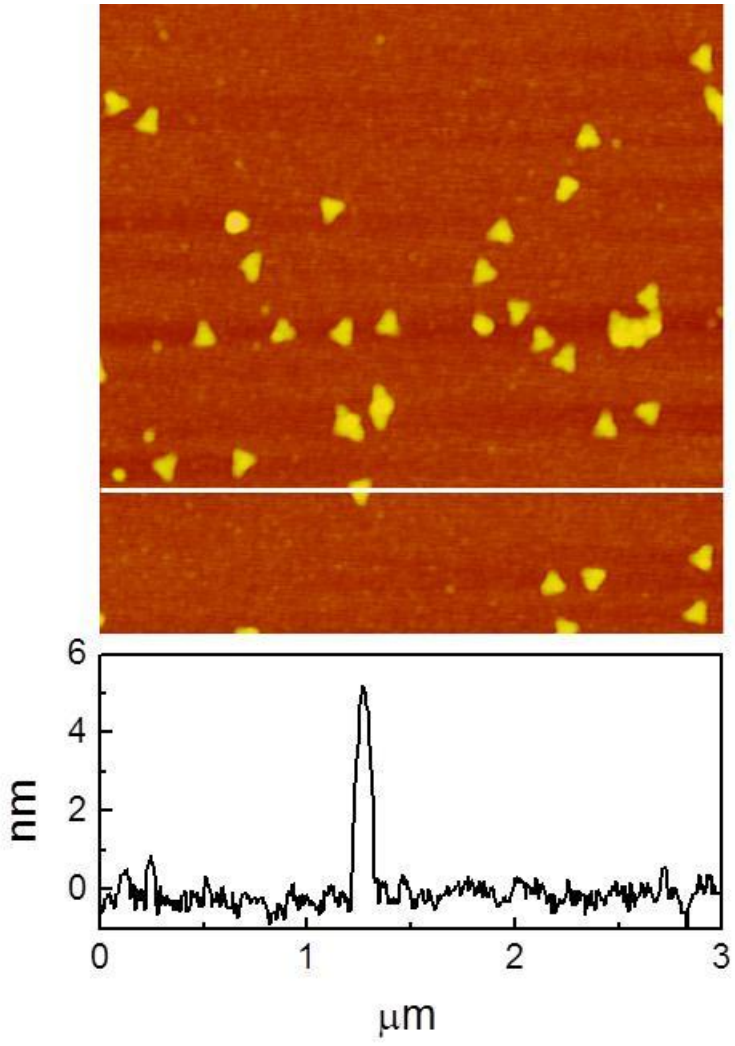

Figure S15. AFM image of CVD grown SiO_2 on the mica substrate for a growth time period of 24 h under positive tone SiO_2 growth conditions (TEOS, NH_4OH, *n*-propanol, water) using DNA origami triangles as templates.

(c) Gold substrate

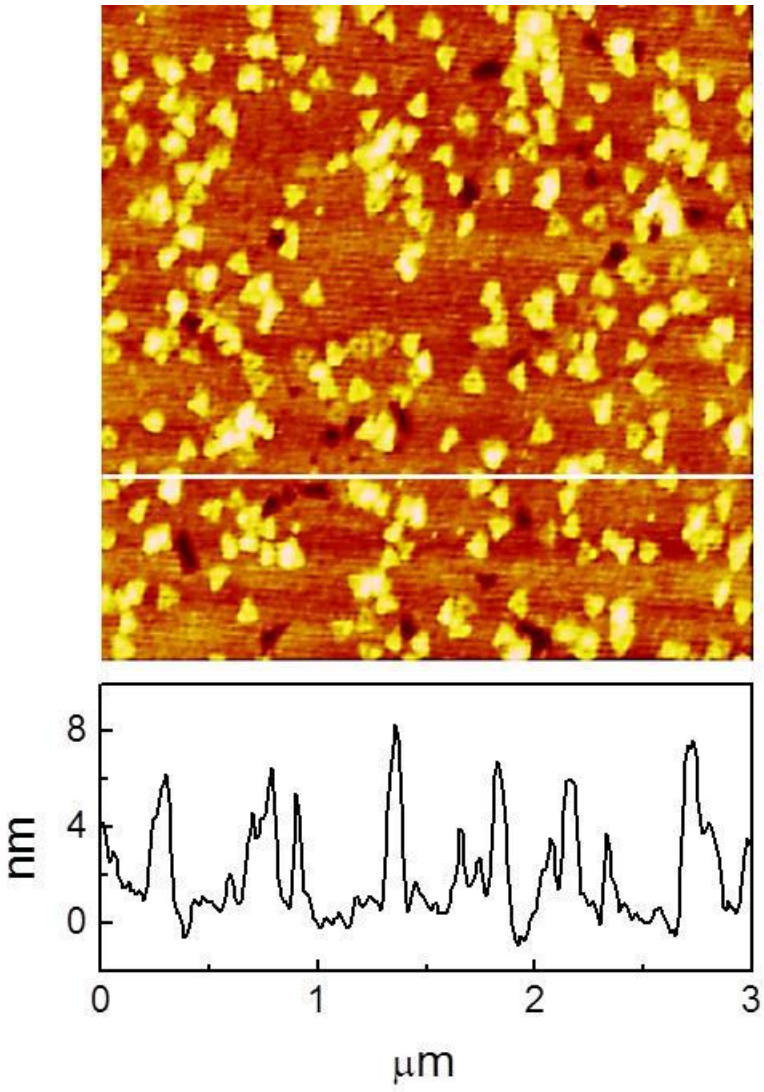

Figure S16. AFM image of CVD grown SiO_2 on the gold substrate for a growth time period of 24 h under positive tone SiO_2 growth conditions (TEOS, NH_4OH, *n*-propanol, water) using DNA origami triangles as templates.

6. CVD synthesis of TiO_2

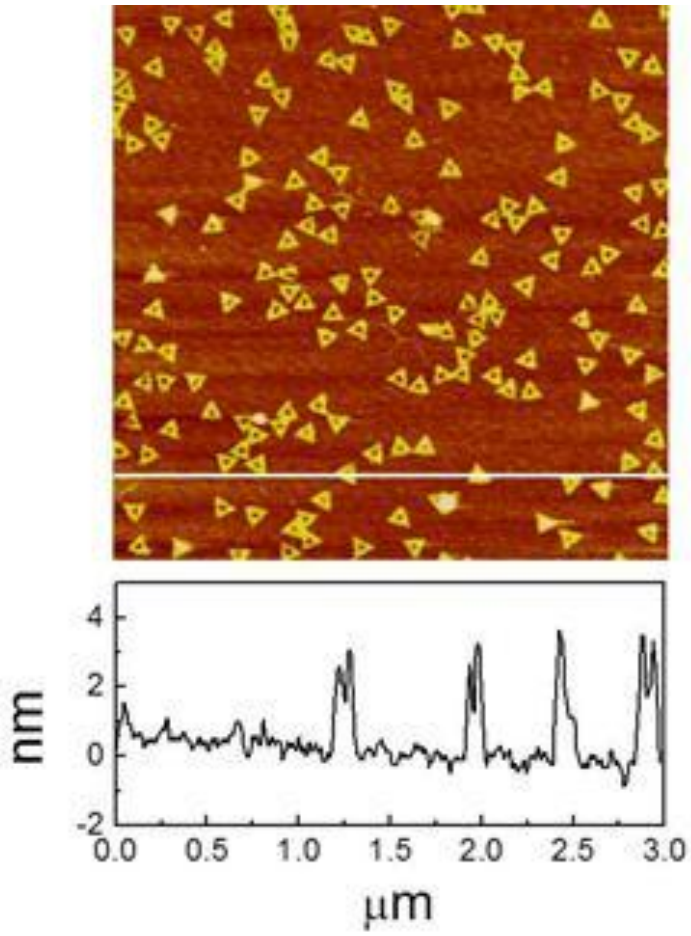

Figure S17. AFM image of CVD grown TiO_2 on the Si substrate for a growth time period of 12 h using titanium isopropoxide and water.

7. Confirmation of metal oxide growth

(a) XPS analysis of the CVD grown SiO_2 on the gold substrate

It was difficult to confirm the growth of SiO_2 on the Si surface using XPS since XPS is a surface sensitive technique and there is always native oxide present on the surface of Si surface. Therefore, it would be difficult to confirm whether the XPS signals obtained for the SiO_2 are from CVD grown SiO_2 or from native oxide on the Si surface. Therefore, we carried out XPS analysis of CVD grown SiO_2 on the gold substrate.

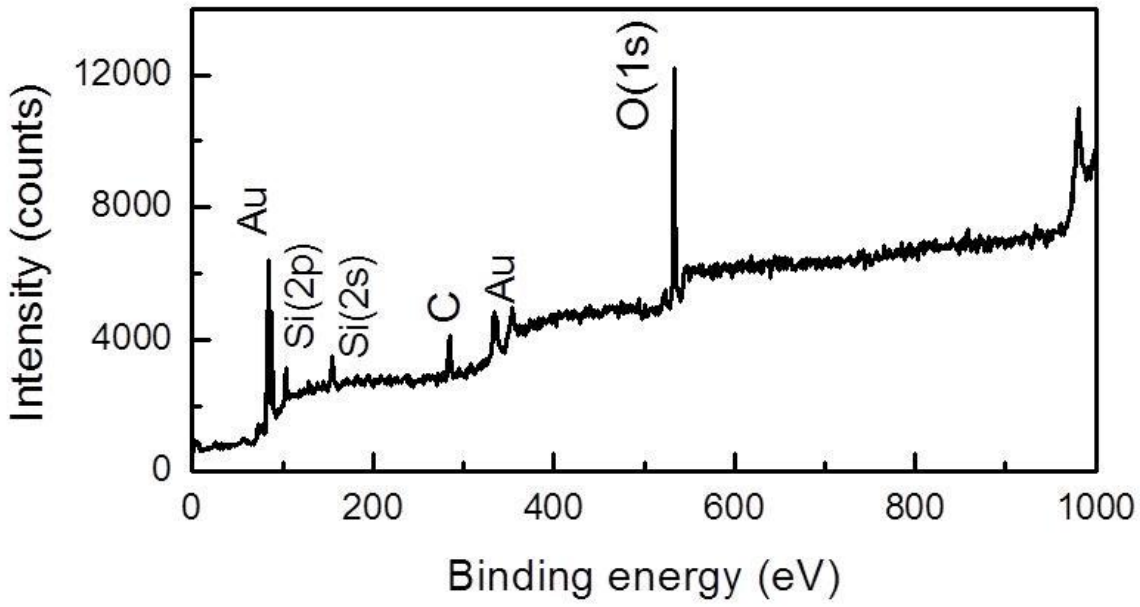

Figure S18. XPS Survey scan of a gold sample containing positive tone CVD grown SiO_2.

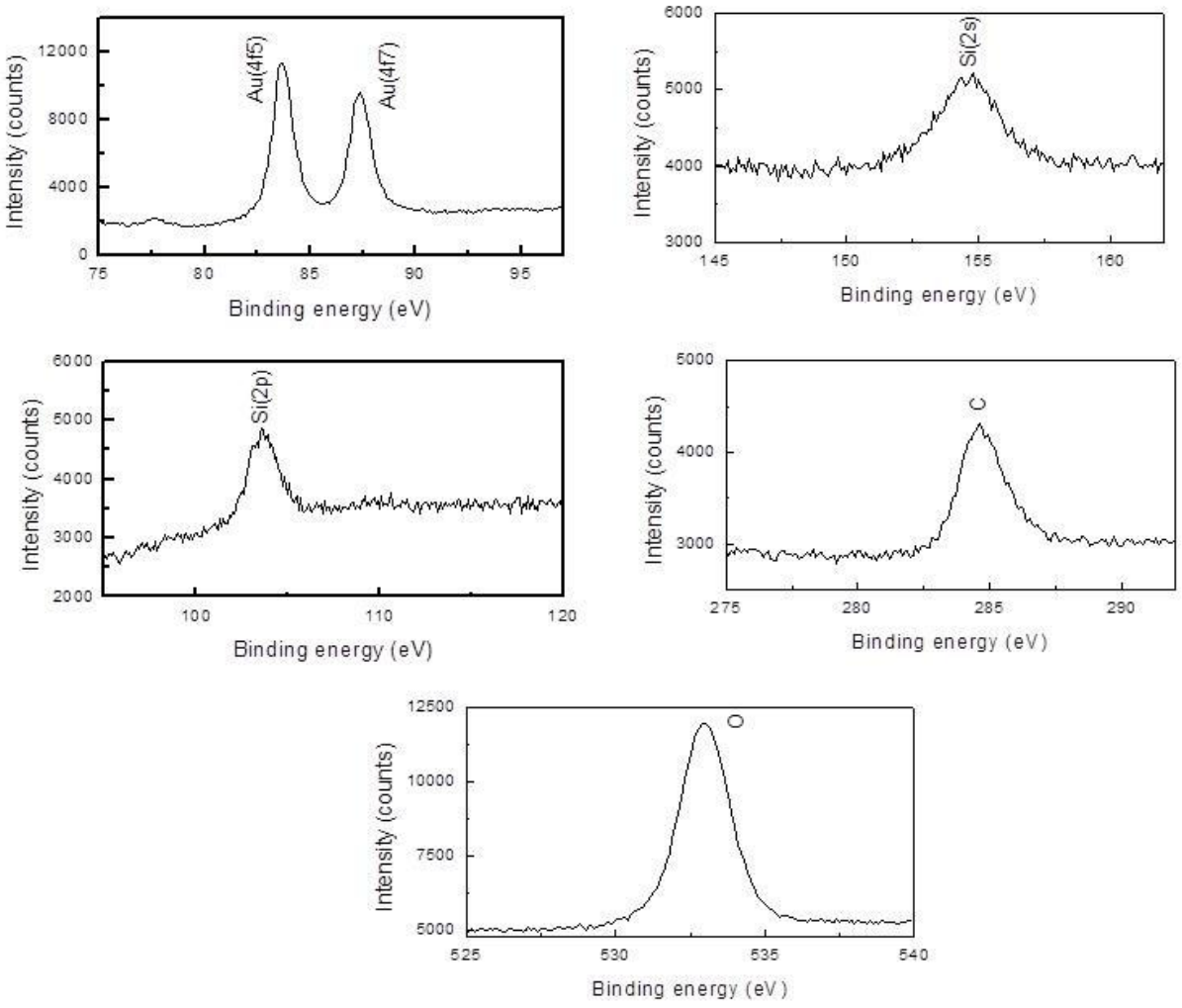

Figure S19. XPS scan for individual elements for a gold substrate containing positive tone CVD grown SiO_2.

(b) EDX analysis of the CVD grown SiO_2 and TiO_2 on Si substrate

Three samples, positive tone CVD grown SiO_2 on Si wafer, positive tone CVD grown TiO_2 on Si wafer and a bare Si wafer (control) were placed on a sample holder with double sided carbon tape and sputter coated with Pd (~ 1 nm). The Pd coating is necessary to avoid sample charging during SEM imaging and EDX analysis. The samples were then placed inside the SEM sample chamber and the elemental analysis of the samples was determined using EDX. The signal intensity depends largely depends on the surface coverage of SiO_2 and TiO_2. EDX signals for SiO_2, TiO_2 could be obtained only at locations where the density of growth was high (entire surface was covered).

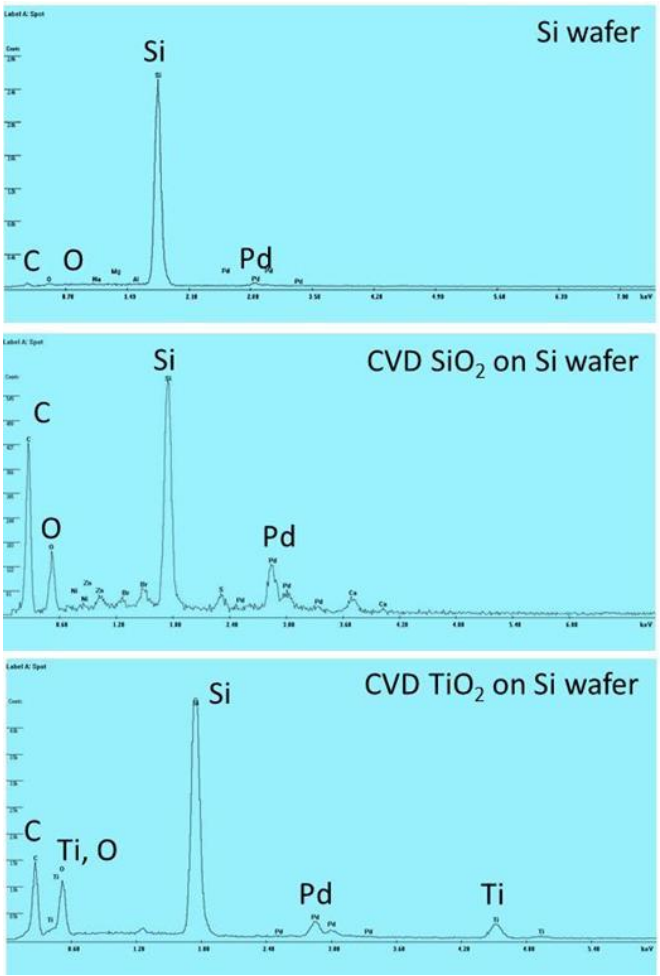

Figure S20. EDX spectra of Si substrate (top), positive tone CVD grown SiO_2 on Si substrate (middle), and positive tone CVD grown TiO_2 on Si substrate.

(c) Positive tone CVD grown SiO_2 heated at 600 ℃ for 15 min

The triangular feature survived the high temperature treatment. If it were DNA or any kind of organic impurity on DNA surface, the feature would have decomposed at such high temperature. A decrease in height of ~ 1.2 nm was observed (3.2 nm before heating to 2.0 nm after heating, as shown in AFM image below) indicating decomposition of DNA underneath the SiO_2. Note: Control experiment using DNA nanostructure shows a triangular pattern after heating to 300 ℃, possibly salt residue; however, these salt residues give an AFM height of ~ 0.5 nm, significantly smaller than observed in the case with SiO_2 coating.

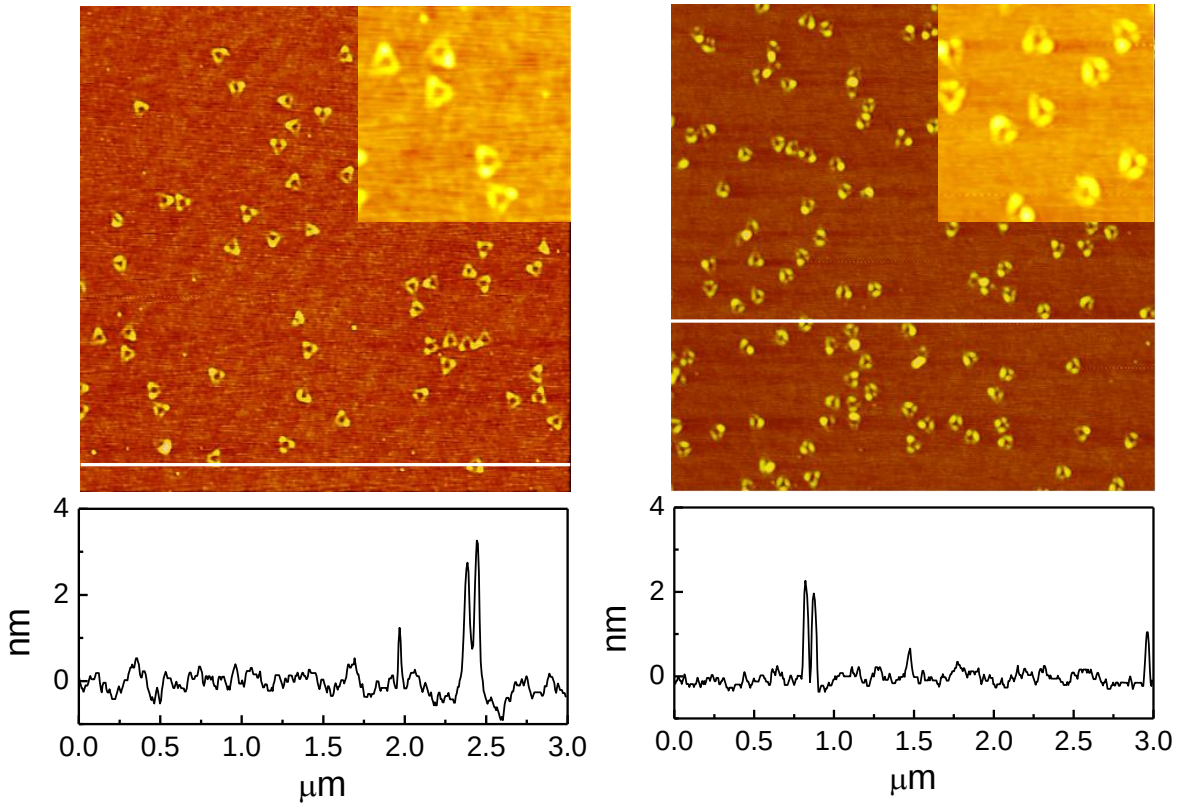

Figure S21. AFM images of CVD grown SiO_2 on the Si substrate before (left) and after (right) heating at 600 ℃ for 15 min. The insets (image size: 700 nm x 700 nm) show magnified views of selected nanostructures.

(d) Positive tone CVD grown TiO_2 heated at 600 ℃ for 15 min

Similar to SiO_2 study, the triangular feature survived the high temperature heat treatment as well confirming the growth of TiO_2.

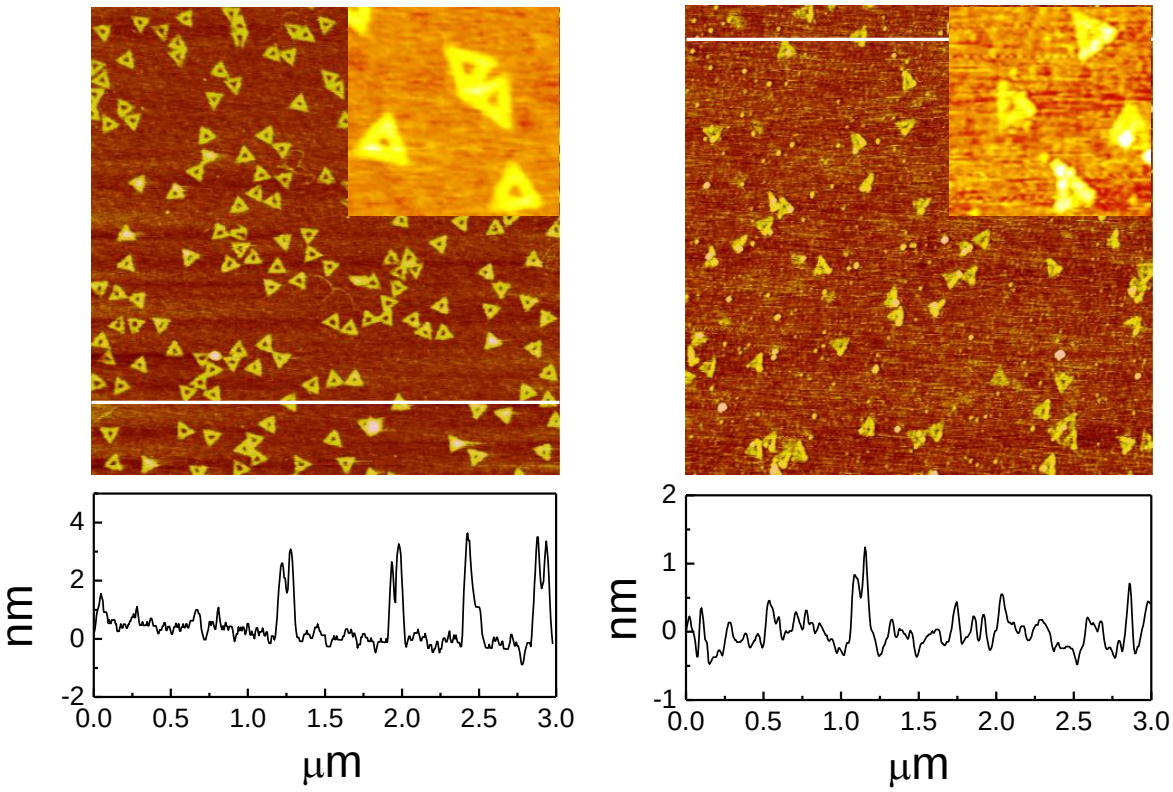

Figure S22. AFM images of CVD grown TiO_2 on the Si substrate before (left) and after (right) heating at 600 ℃ for 15 min. The insets (image size: 480 nm x 480 nm) show magnified views of selected structures.

8. Controls: Role of *n*-propanol in positive tone growth

CVD growth of SiO_2 in presence of TEOS, NH_4OH, and *n*-propanol (no water)

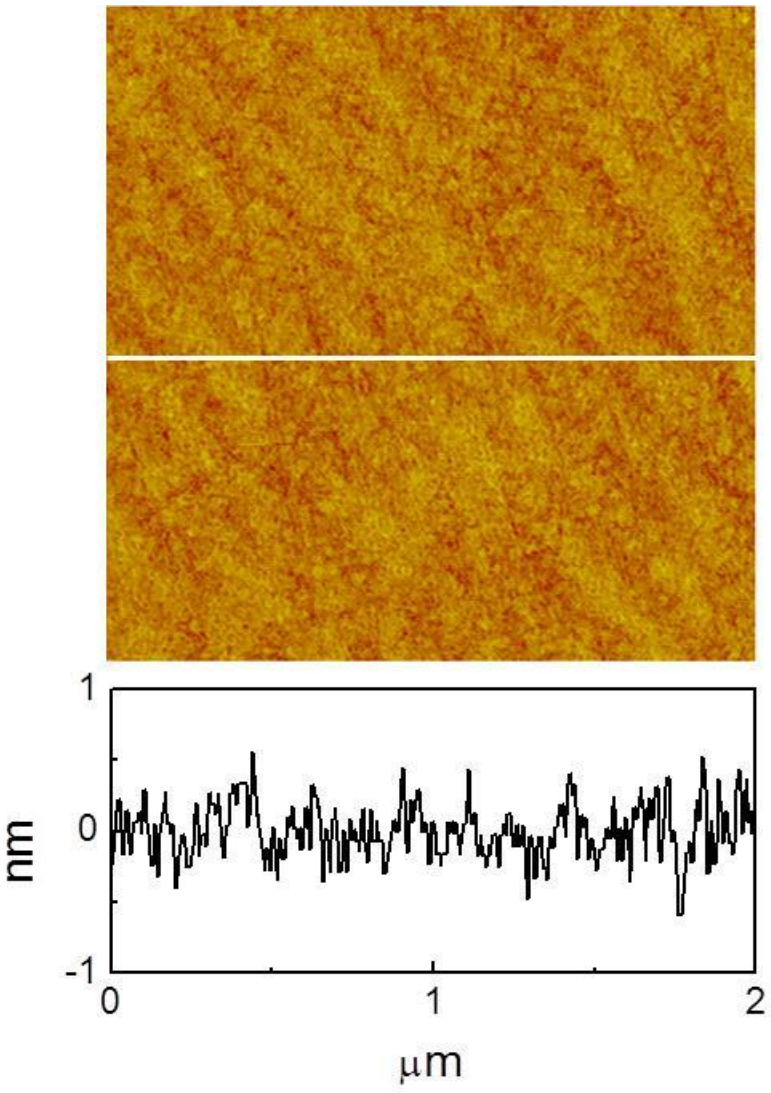

Figure S23. AFM image of CVD grown SiO_2 on the Si substrate for a growth time period of 12 h in presence of TEOS, NH_4OH and *n*-propanol inside the reaction chamber (No open vial of water).

9. Dimension of oxide nanostructures and calculation of deposition selectivity

Number of Measurement	Figure 1b		Figure 1c		Figure 4	
	FWHM (nm)	Depth of trench (nm)	FWHM (nm)	Height of ridge (nm)	FWHM (nm)	Depth of trench (nm)
1	40.47	8.72	39.43	2.48	52.43	25.44
2	47.13	5.55	36.56	2.44	57.41	25.19
3	36.84	6.78	34.44	2.60	56.71	26.66
4	44.48	7.21	39.89	2.47	55.60	25.24
5	42.74	7.14	38.70	2.51	52.84	26.95
6	42.22	6.70	37.75	2.52	57.95	23.22
7	39.86	7.18	38.43	2.53	56.43	24.12
8	43.85	8.97	36.27	2.48	57.55	24.69
9	45.27	7.43	39.67	2.51	55.18	24.72
10	42.77	6.12	34.25	2.50	55.46	23.18
Average range	42 ± 5 nm	7 ± 2 nm	37 ± 3 nm	2.6 ± 0.5 nm	55 ± 3 nm	25 ± 2 nm

Table S1. Dimension of oxide nanostructures

Deposition selectivity for negative tone condition:

The native oxide thickness was 2.6 nm. At 12 hr of reaction, the total oxide thickness was 14.5 nm. Thus the CVD deposited 11.9 nm of oxide. The trenches were 7 ± 2 nm deep, assuming that the height of DNA nanostructure is 2 nm, this implies that the oxide grown on top of DNA nanostructure is on average 2.9 nm. The selectivity was calculated as 11.9 nm / 2.9 nm = 4.1. In this case, the deposition was faster on existing SiO_2.

Deposition selectivity for positive tone condition:

The native oxide thickness was 2.6 nm. At 24 hr of reaction, the overall oxide thickness was 5.7 nm. Thus the CVD deposited 3.1 nm of additional oxide. The height of the DNA nanostructure was 7 nm, assuming that the height of DNA nanostructure is 2 nm, this implies that the oxide grown on top of DNA nanostructure was 7 nm + 3.1 nm – 2 nm = 8.1 nm. The selectivity was calculated as 8.1 nm / 3.1 nm = 2.6. In this case, the deposition was faster on DNA.

Note:

(1) In the calculation we did not use the height of the DNA measured by AFM (1.2 nm) because it is known that AFM underestimate the height of DNA[4]. The theoretical diameter of a double stranded DNA (2 nm) was used instead.

(2) Ellipsometry measures the average thickness of oxide. This value was used as the oxide thickness of the area not covered by DNA nanostructures. This approximation is acceptable because the coverage of DNA nanostructure was very low (< 10%).

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