Electronic Supplementary Information

Noncovalent DNA Decorations of Graphene Oxide and Reduced Graphene Oxide toward Water-Soluble Metal-Carbon Hybrid Nanostructures via Self-Assembly

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Synthesis of graphene oxide[S1,S2]**:** 25 mL of concentrated H_2SO_4 was heated to 90 °C in a 250 mL beaker, followed by additions of 5 g $K_2S_2O_8$ and 5 g P_2O_5 under stirring. The above solution was cooled down to 80 °C, to which 6 g graphite powder (325 mesh, Alfa Aesar) was added and the mixture was maintained at 80 °C for 4.5 hr and then cooled down to room temperature. Deionized (DI) water was added to the above solution to reach a final volume of 1 L, and the diluted solution was left overnight, filtered with a 0.2 micron Nylon Millipore filter and washed with copious amount of water to get rid of acid residues. The solid product, after being air-dried, was transferred to H_2SO_4 (230 mL) under continuous stirring in an ice bath, to which 30 g $KMnO_4$ was carefully added with the solution temperature kept below 10 °C. The mixture was stirred at 35 °C for a period of 2 hours and 460 mL of DI water was supplemented (an ice bath was needed to maintain the solution temperature below 50 °C). After a further stirring of the mixture for 2 hours, the reaction was stopped by adding a large amount of water (1.4 L) and 30% H_2O_2 (25 mL). The as-obtained bright yellow product was subjected to a filtration and washed with 1:10 HCl solution (2.5 L). The resulting GO product was suspended in DI water to form a viscous brown dispersion (2%), which was dialyzed for 2 weeks to remove any residual metal ions and then dried under ambient conditions over weeks to obtain graphene oxide solids.

Gel electrophoretic analysis of DNA damages induced by hydrazine: The extent of DNA damage induced by hydrazine was evaluated by denaturing polyacrylamide gel electrophoresis (PAGE) [S3-S5]. Typically, 2 μg of DNA ($d(GT)_{29}$ or $d(GA)_{29}$), 5 mM EDTA, 0.05 M NaCl (or 0.1 M NaCl) and 0.1 M hydrazine in a total volume of 20 μL were mixed together, and the pH of the mixture was increased to around 10 with 1 M NaOH. The solution was incubated at 55 °C for 6 hours in accordance with the GO reduction process (as for the DNA damage test at room temperature, the solution was incubated at room temperature for 4 or 24 hr). After removal of hydrazine by ethanol precipitation, the DNA was treated with 1 M piperidine at 90 °C for 30 min to induce strand scissions. The sample was allowed to undergo a further ethanol precipitation to remove piperidine followed by passing through a Sephadex G-25 spin column (Amersham Biosciences, Sweden) before being subjected to an electrophoresis on a 20% denaturing polyacrylamide gel (8 M urea).

AFM imaging: Typically, a sample for AFM imaging was prepared by first treating a freshly cleaved mica surface with 1 M $MgCl_2$ for one minute, followed by addition of 2 μL of a sample solution onto the mica surface. The mica substrate was tilted to allow the droplet to spread on the surface. After an adsorption for one minute, the mica surface was washed twice with doubly distilled water (ddH_2O), and dried with compressed air. The sample was then scanned in tapping mode with a Nanofirst-3000 (Shanghai Haizisi Optical-Electronics Co., Ltd., China) atomic force microscope (AFM) using a MikroMasch NSC11 AFM tip. All AFM images were viewed and processed with the help of a freely available software: WSxM 4.0 (www.nanotec.es)[S6].

X-ray Photoelectron Spectroscopy (XPS) measurements: A sample for XPS analysis was prepared by spotting 10 μL GO (or RGO) solution on a piece of aluminum foil (cut into a 1×1 cm^2 square), and the sample drop was allowed to dry in air. This process was repeated three times to ensure enough sample loading. XPS measurements were carried out on an ESCALAB 250 high performance electron spectrometer using Al Kα (1486.6 eV) radiation. The acquired XPS data were fitted with mixed Gaussian-Lorentzian functions on a Shirley background using a freeware: XPSPEAK 4.1.

References:

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S6. I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, A. M. Baro, *Rev. Sci. Instrum.* **2007,** *78*, 013705.

Figure S1. pH induced precipitation of as-prepared RGO products by hydrazine reduction. Left: as-reduced RGO products in the absence and presence of $d(GT)_{29}$ at pH 10; Right: as-reduced RGO products in the absence and presence of $d(GT)_{29}$ with the solution pH switched to 6.0 by additions of HCl.

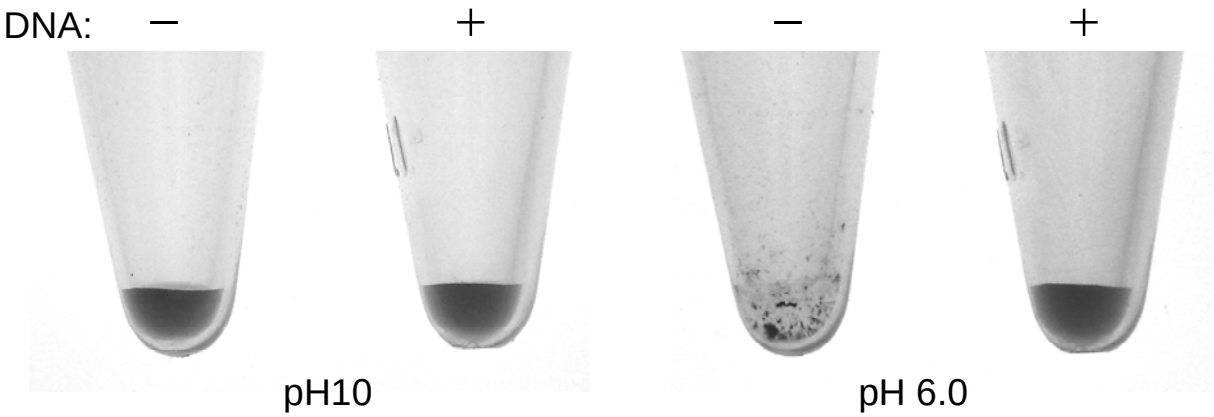
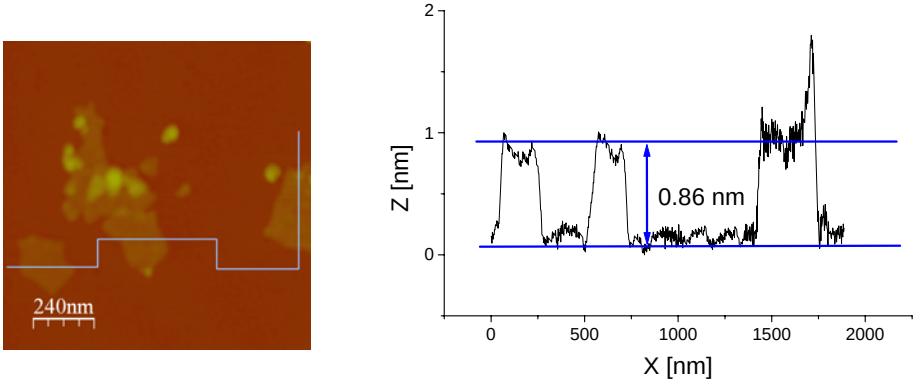
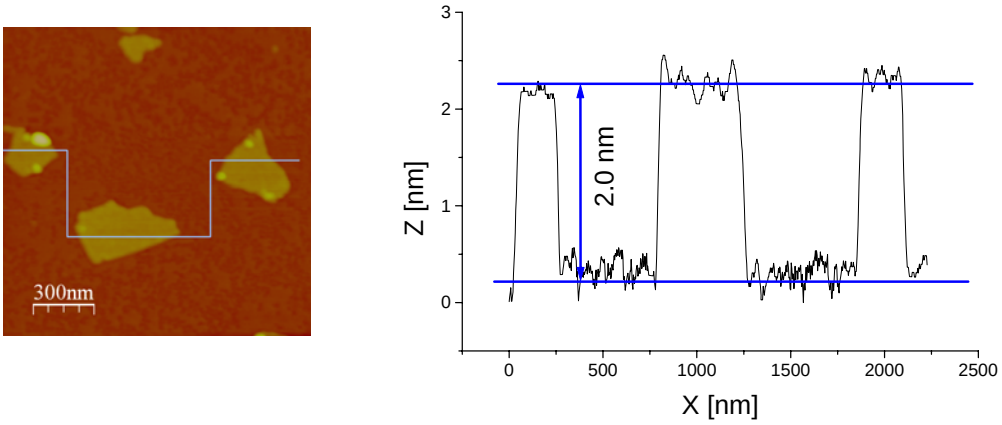


Figure S2. AFM Height profiles of RGO nanosheets in the absence (upper part) or presence (lower part) of d(GT)$_{29}$. (*The Z-axis of the AFM scanner was calibrated with a 18±1nm vertical calibration grating, TGZ01, obtained from MikroMasch, Inc.*)

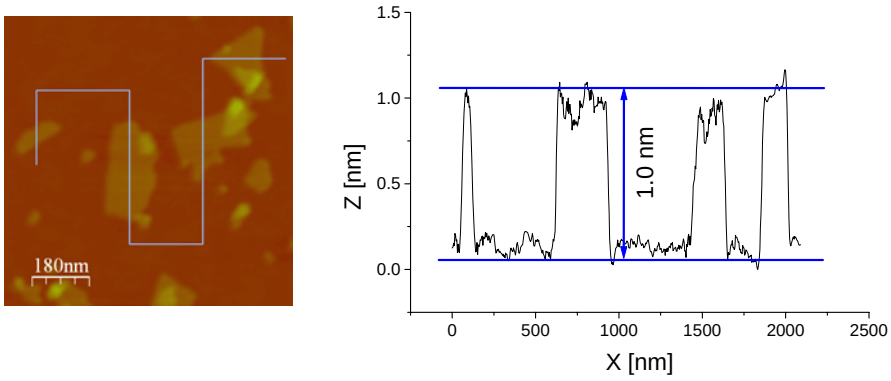


Reduced graphene oxide (RGO)

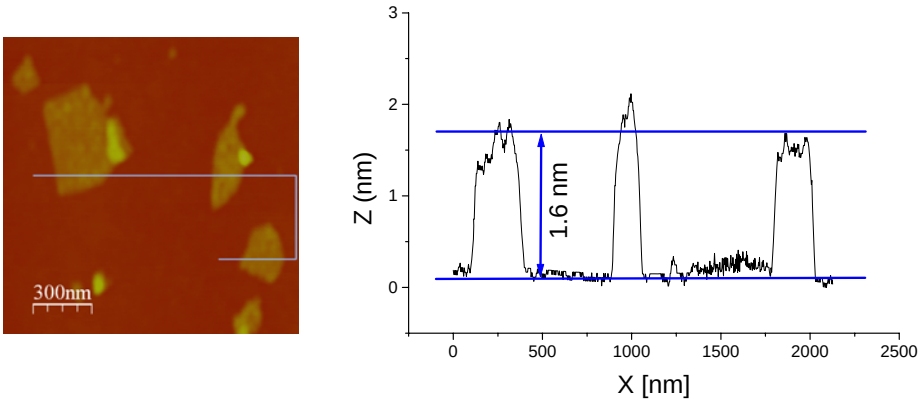


d(GT)$_{29}$ decorated RGO

Figure S3. AFM Height profiles of GO nanosheets in the absence (upper part) or presence (lower part) of d(GT)$_{29}$. (*The Z-axis of the AFM scanner was calibrated with a 18±1nm vertical calibration grating, TGZ01, obtained from MikroMasch, Inc.*)



Graphene oxide



d(GT)$_{29}$ decorated graphene oxide

Figure S4. Extra AFM images showing gold nanoparticle decorated RGO nanosheets.

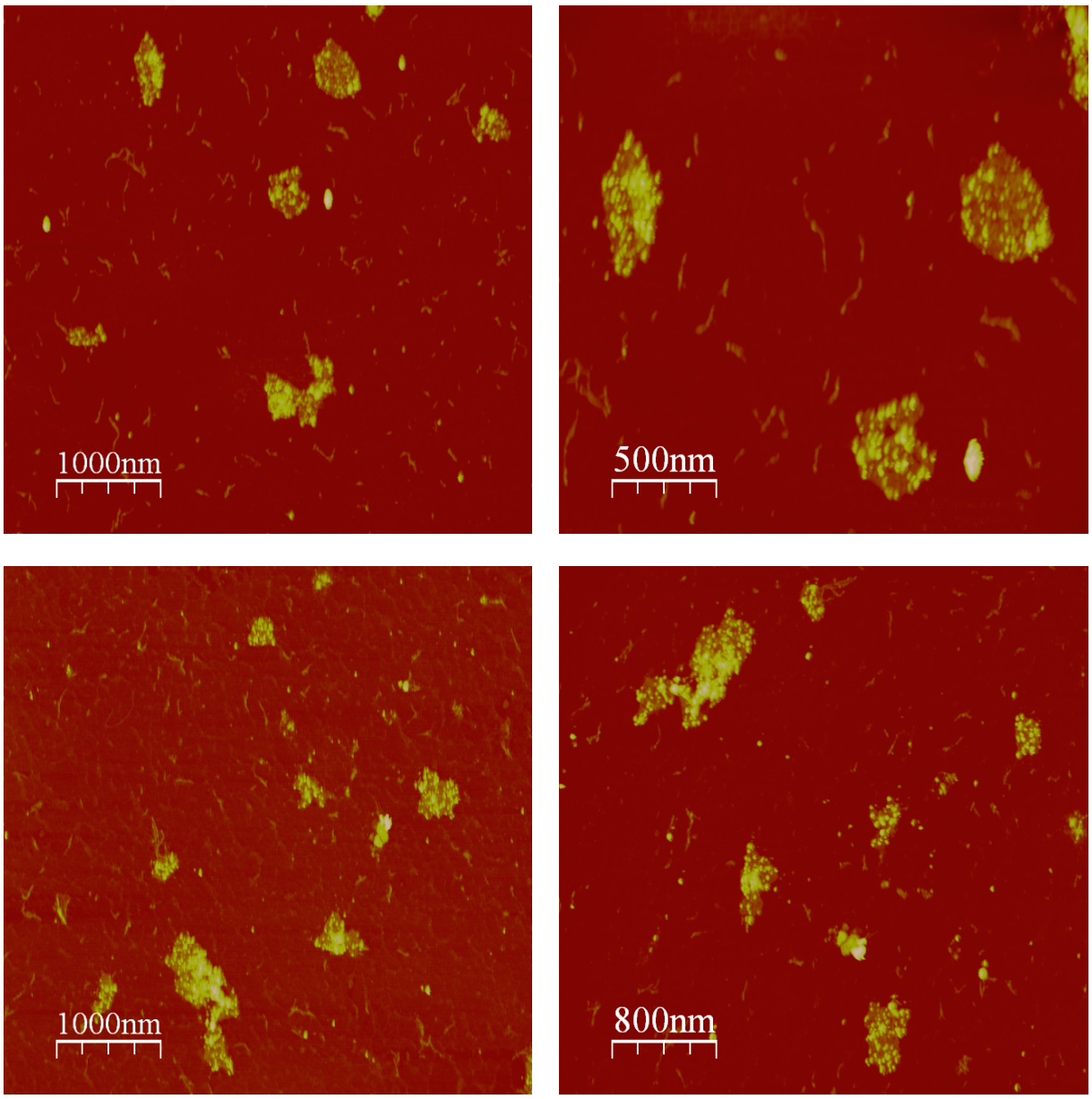


Figure S4. Extra AFM images showing gold nanoparticle decorated RGO nanosheets (continued).

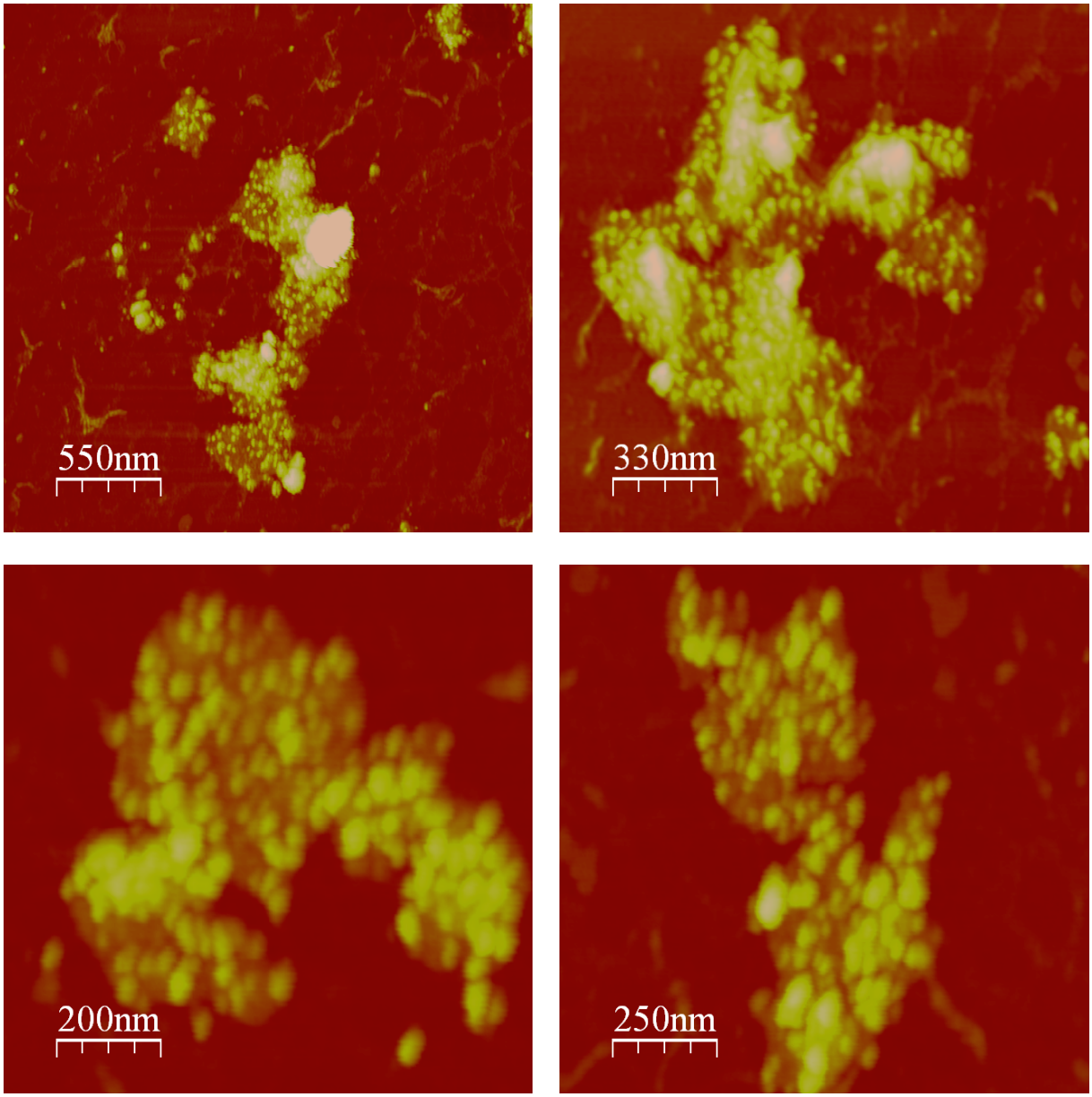


Figure S5. Extra AFM images of the products obtained from a control experiment using thiol-free DNA decorated RGO nanosheets to assemble gold nanoparticles.

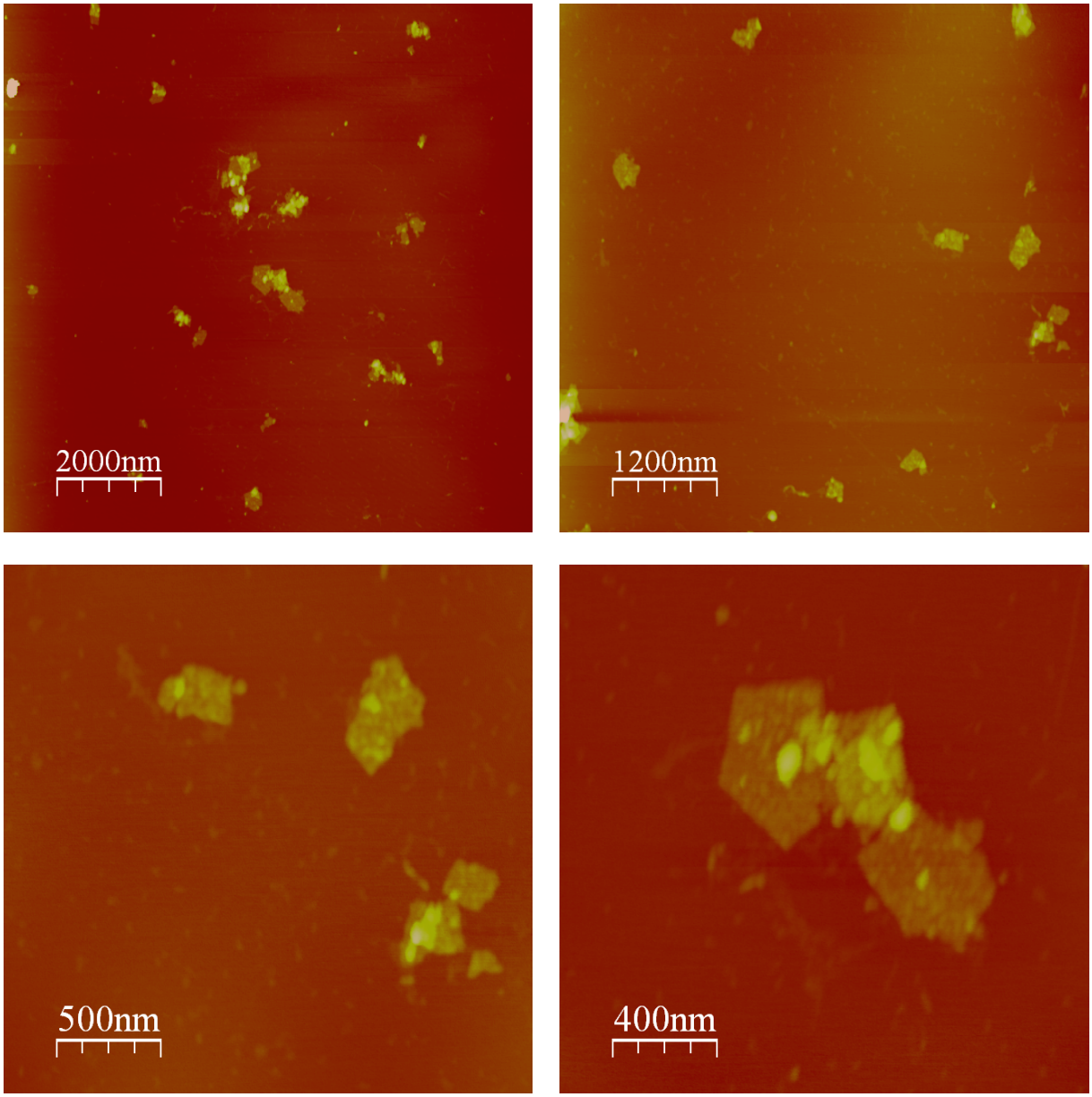


Figure S6. Extra AFM images showing gold nanoparticle decorated graphene oxide nanosheets.

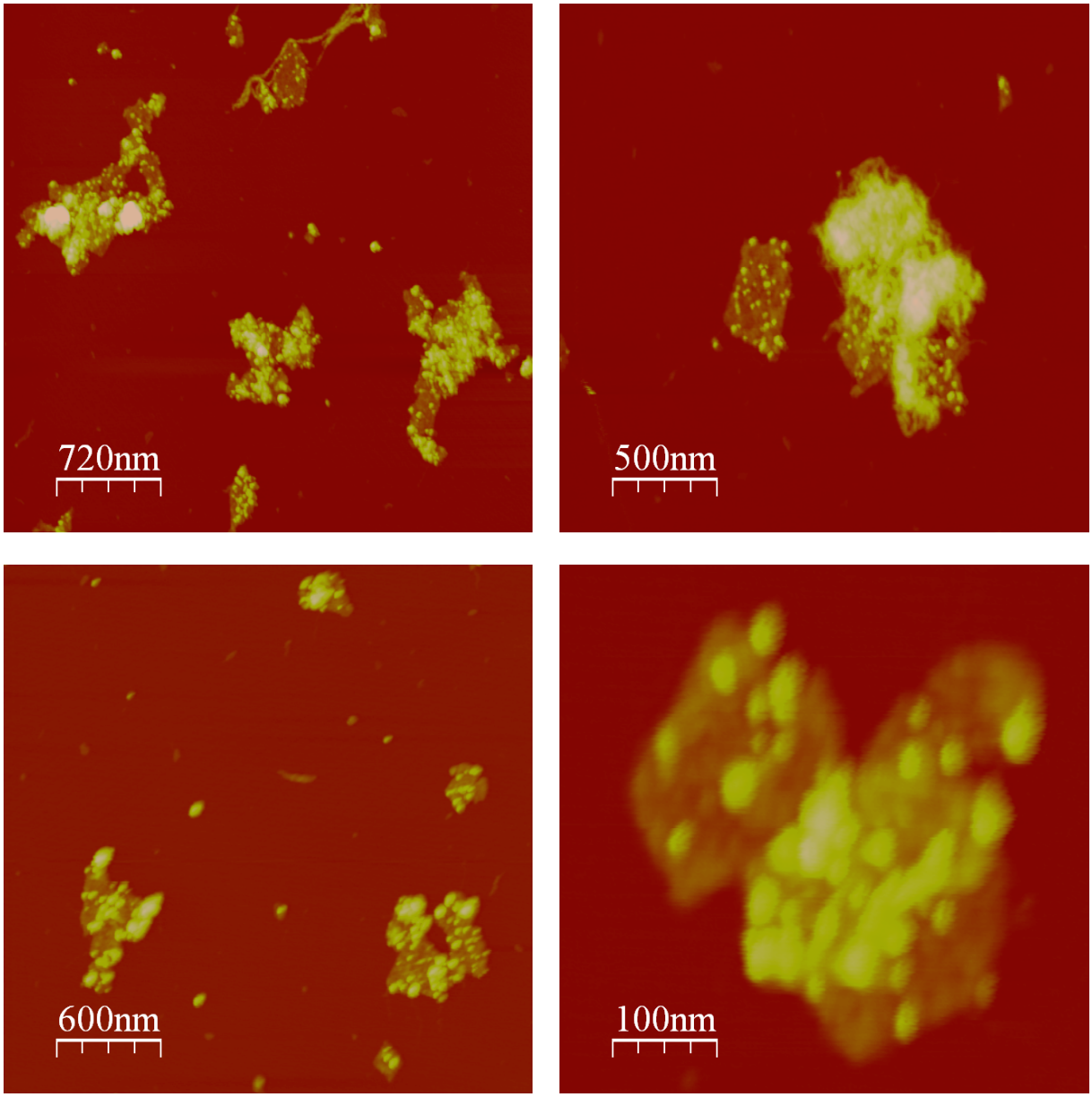


Figure S7. Extra AFM images of the products obtained from a control experiment using thiol-free DNA decorated graphene oxide nanosheets to assemble gold nanoparticles.

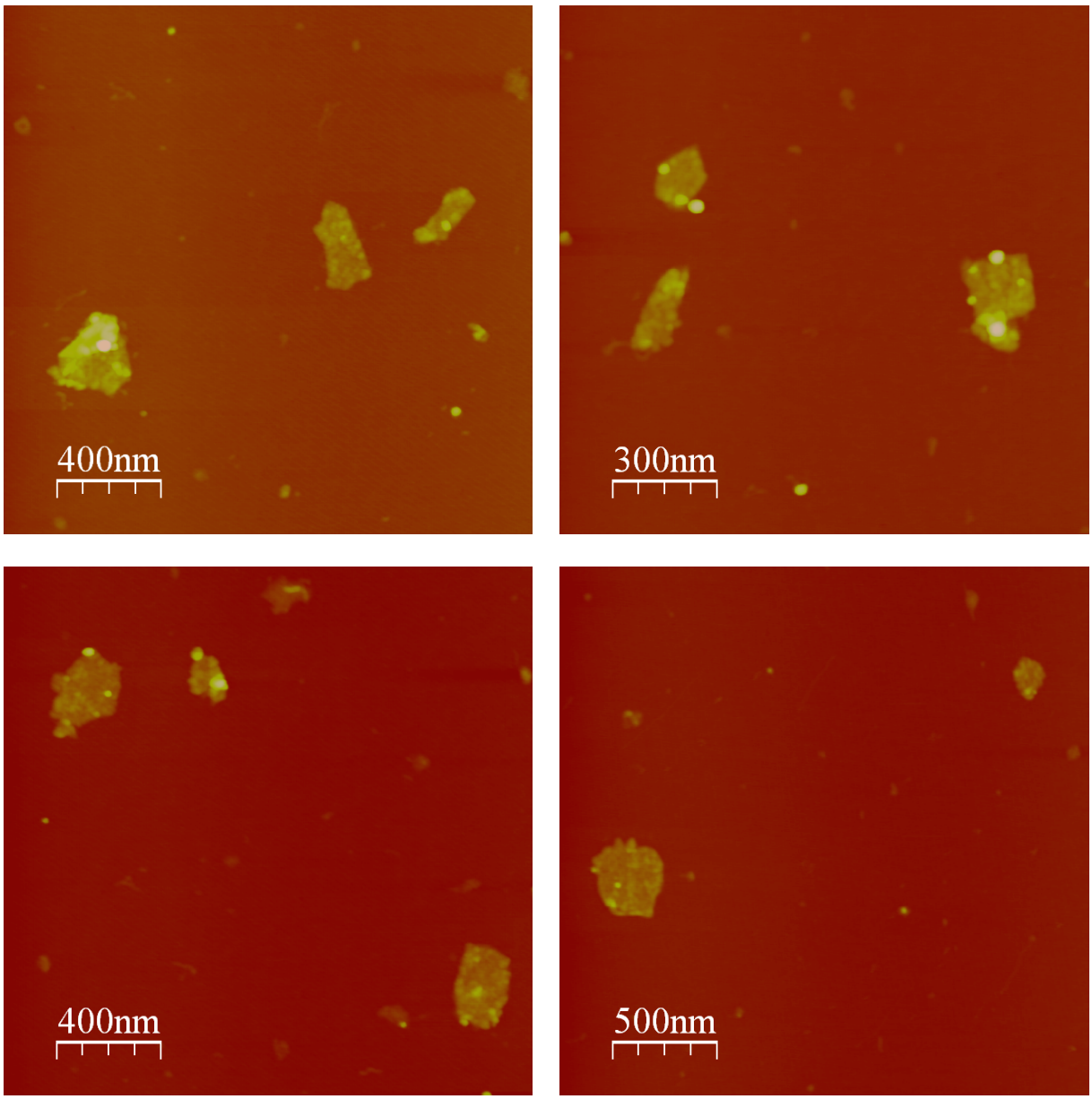


Figure S8. Assemblies obtained after incubations of $d(GA)_{29}SH$ (upper panels) and $d(GA)_{29}$ (lowers panels) decorated RGO nanosheets with gold nanoparticles.

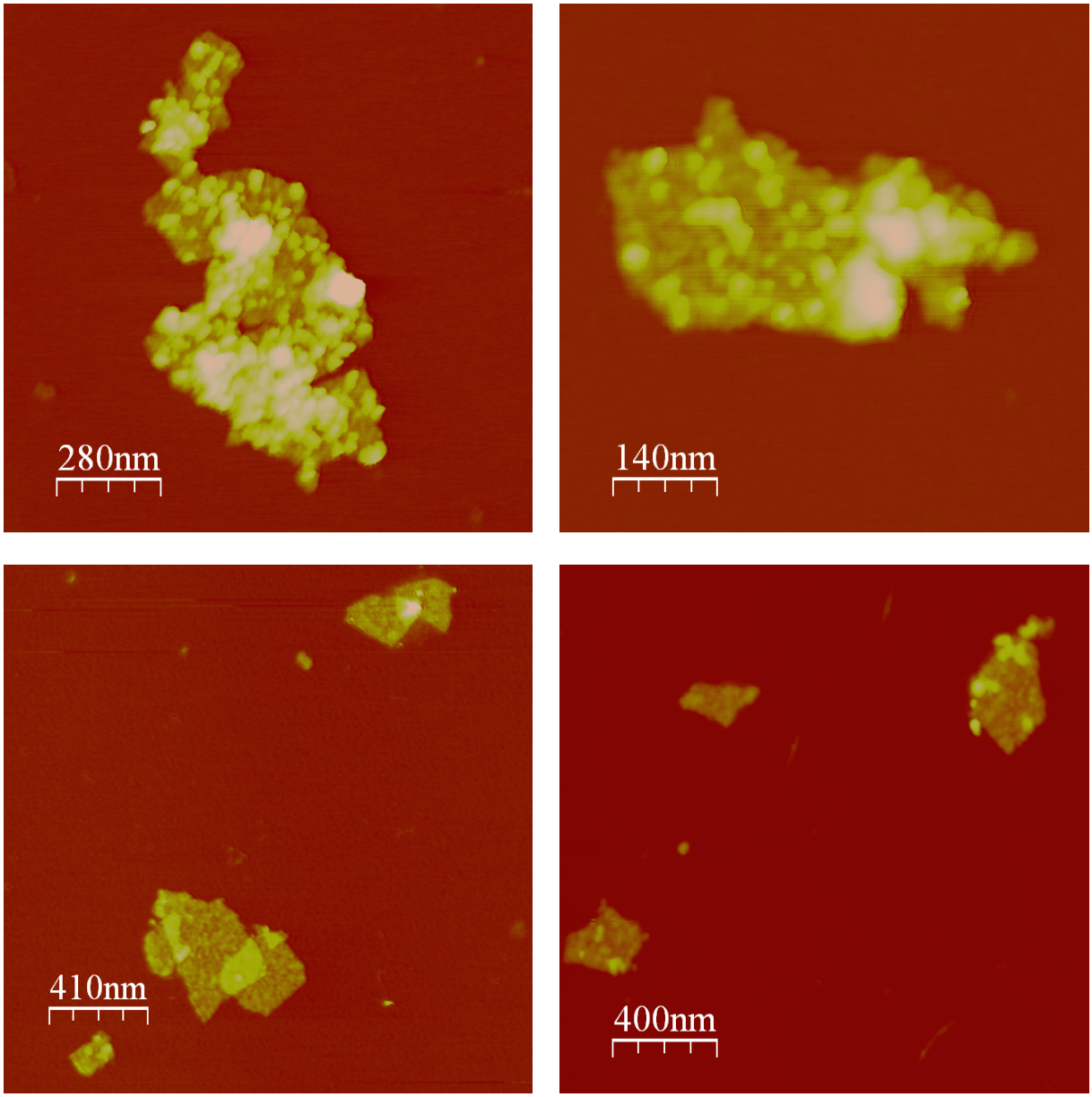
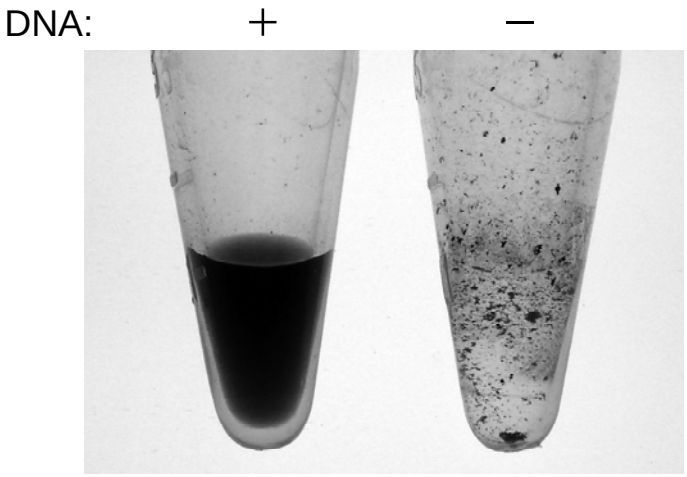
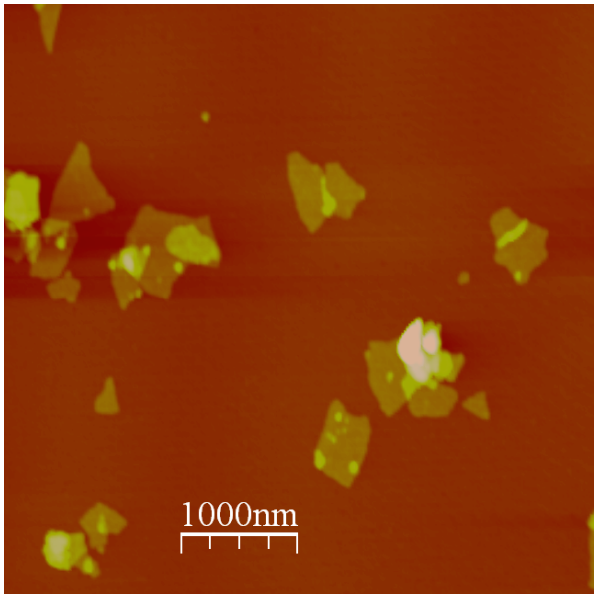


Figure S9. Sonication of reduced graphene oxide in the presence of DNA resulted in a stable and homogeneous aqueous suspension (left tube, and AFM images shown below), while omitting DNA during the process of sonication failed to give a dispersed solution of reduced graphene oxide (right tube).





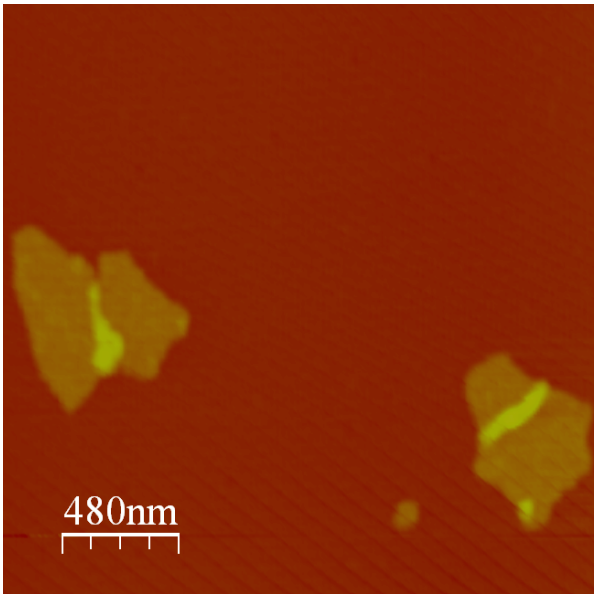


Figure S10. NaCl test of the stability of DNA-RGO samples obtained by addition of $d(GT)_{29}$ after a hydrazine reduction was finished at pH 10. Left picture: as-reduced RGO products in the absence (left tube) and presence (right tube) of $d(GT)_{29}$; Right picture: 3 hours after additions of NaCl to the microtubes as shown on the left picture.

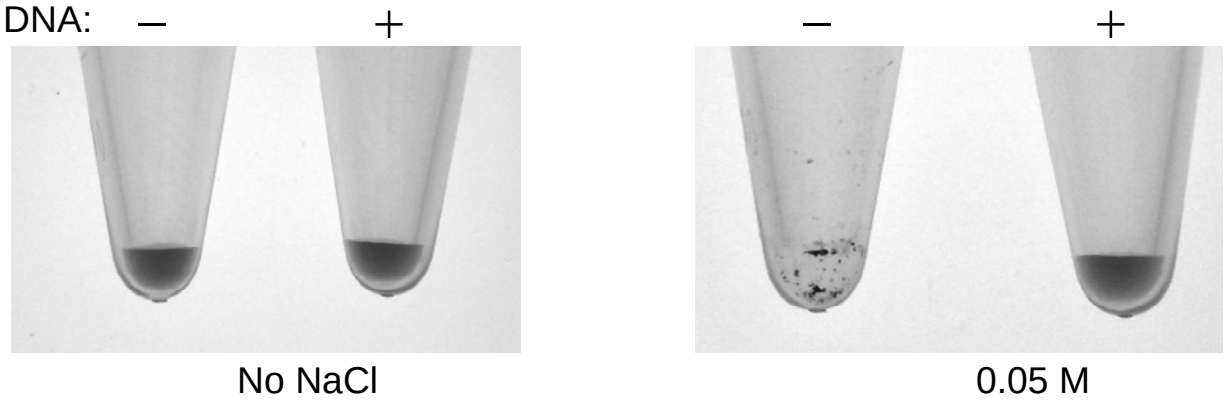


Figure S11. pH stability test of the DNA-RGO samples produced by addition of $d(GT)_{29}$ after a hydrazine reduction was finished. Left picture: as-reduced RGO products in the absence (left tube) and presence (right tube) of $d(GT)_{29}$ at pH 10; Right: as-reduced RGO products in the absence (left tube) and presence (right tube) of $d(GT)_{29}$ with the solution pH switched to 6.0 by additions of HCl.

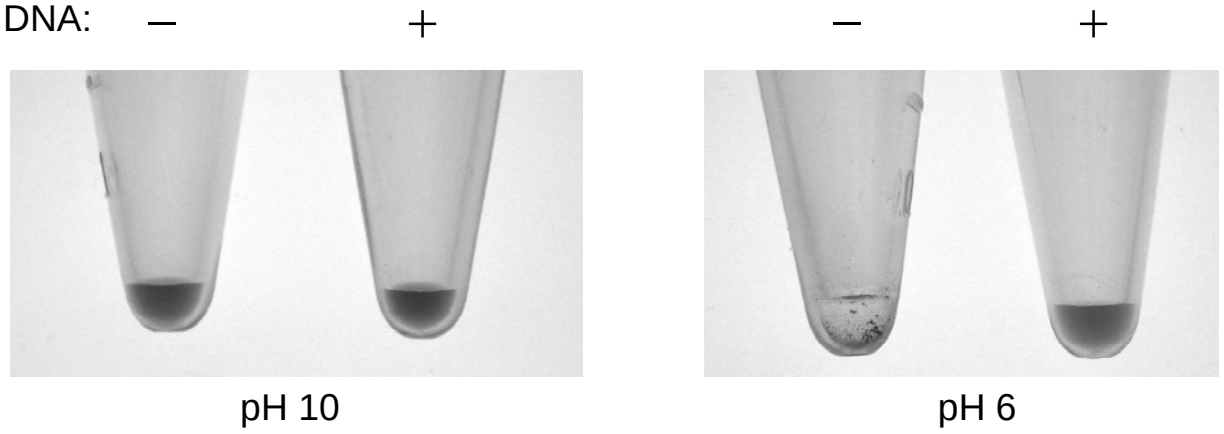


Figure S12. Electrophoretic analysis showed a success for the assembly of AuNP-RGO conjugates with the RGO templates obtained by post-addition of $d(GT)_{29}SH$ after the hydrazine reduction reaction was completed to avoid DNA damages. Lanes 1-4: (1) $d(GT)_{29}$-RGO; (2) $d(GT)_{29}$-RGO+AuNPs; (3) $d(GT)_{29}SH$-RGO+AuNPs; (4) $d(GT)_{29}SH$-RGO.

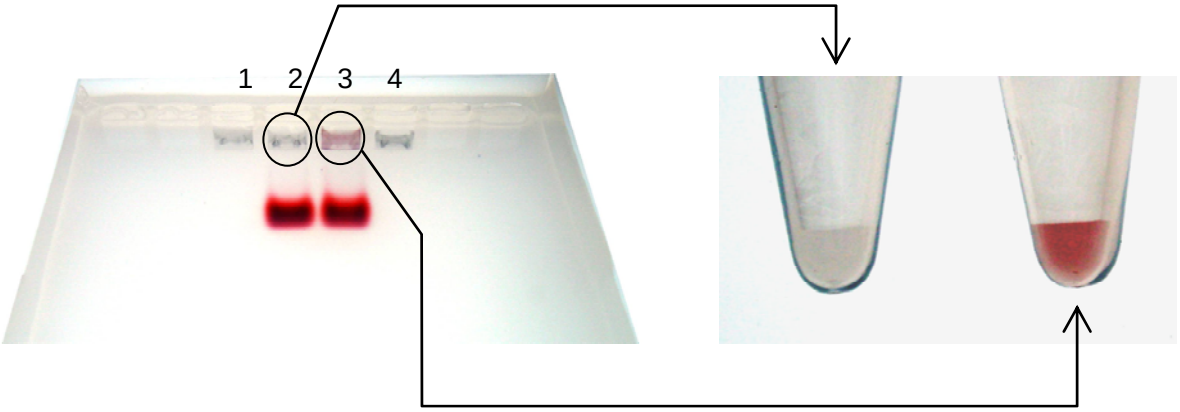


Figure S13. AFM images for the sample recovered from lane 3 in the agarose gel shown in Figure S12.

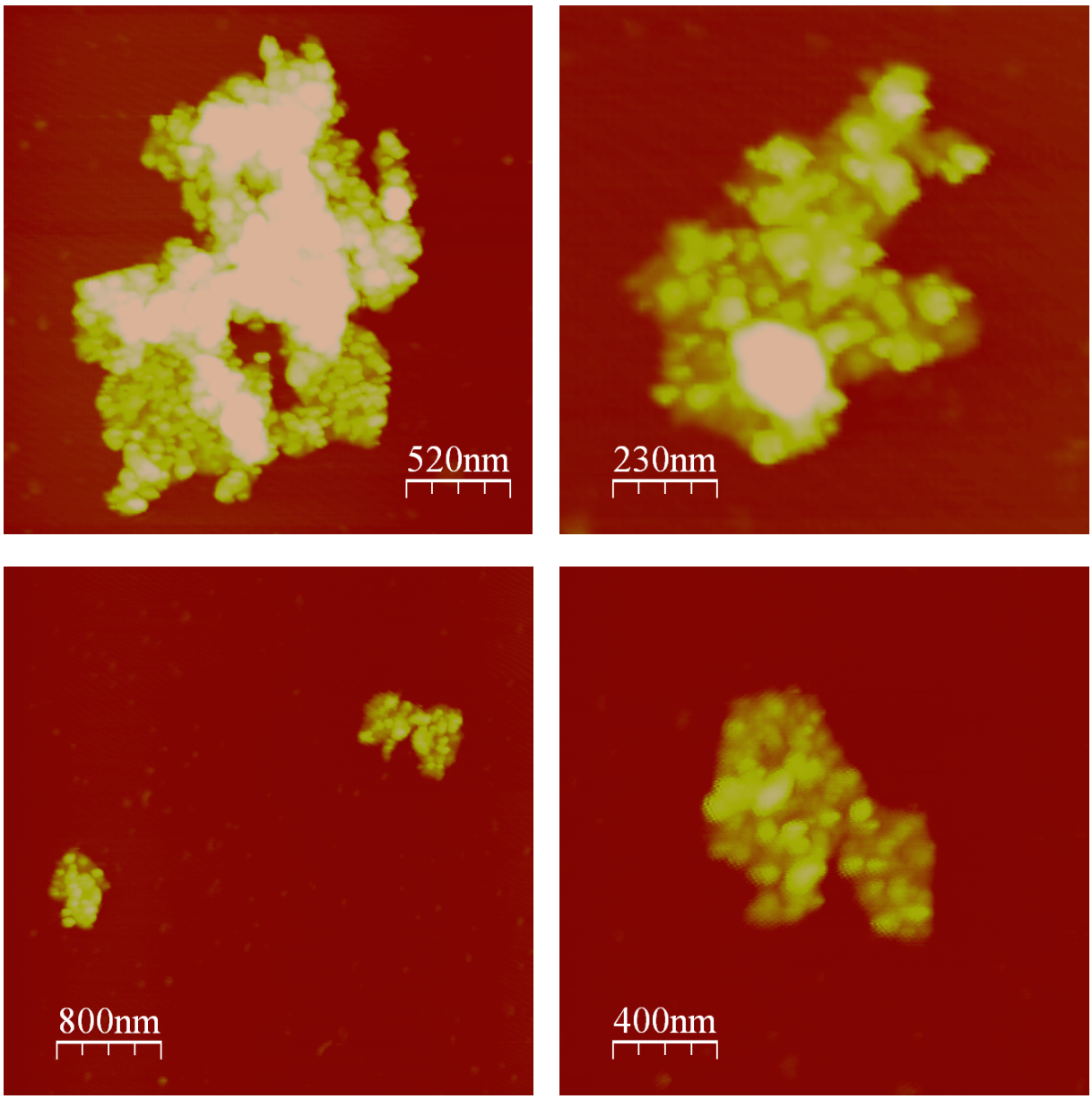


Figure S14. AFM images for the sample recovered from lane 2 in the agarose gel shown in Figure S12.

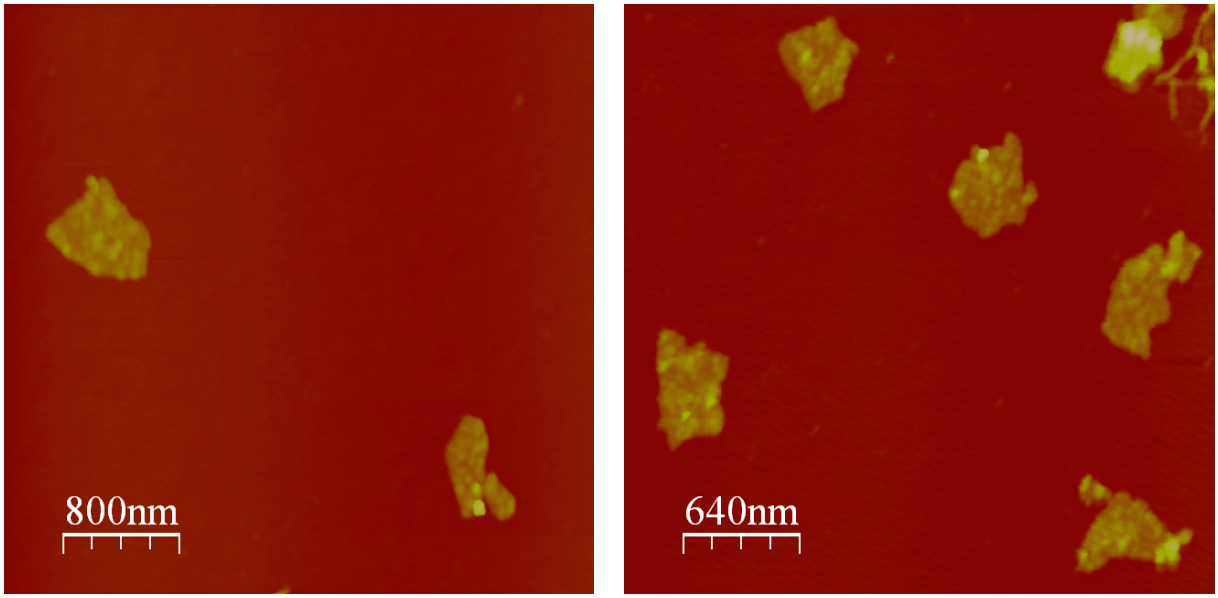


Figure S15. UV absorbance spectra of a sample containing simply mixed GO and $d(GT)_{29}$ at a weight ratio around 10:1. Absorbance peak of DNA at around 260 nm was hard to resolve due to the strong absorbance of GO.

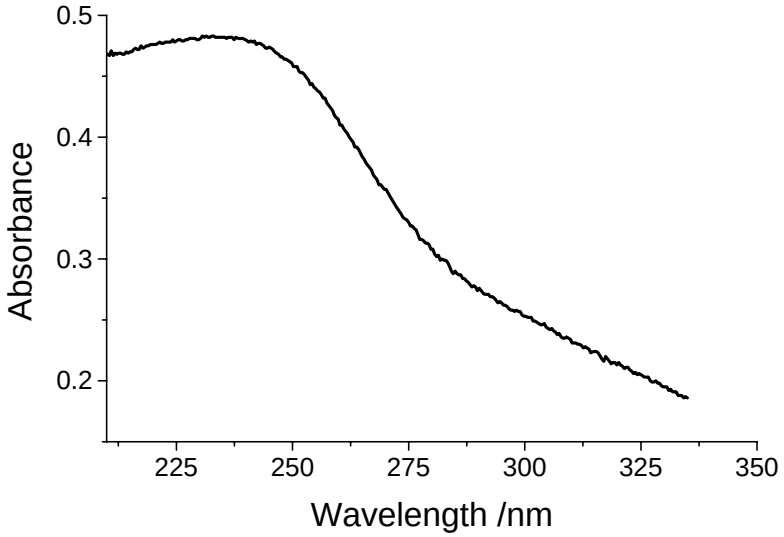
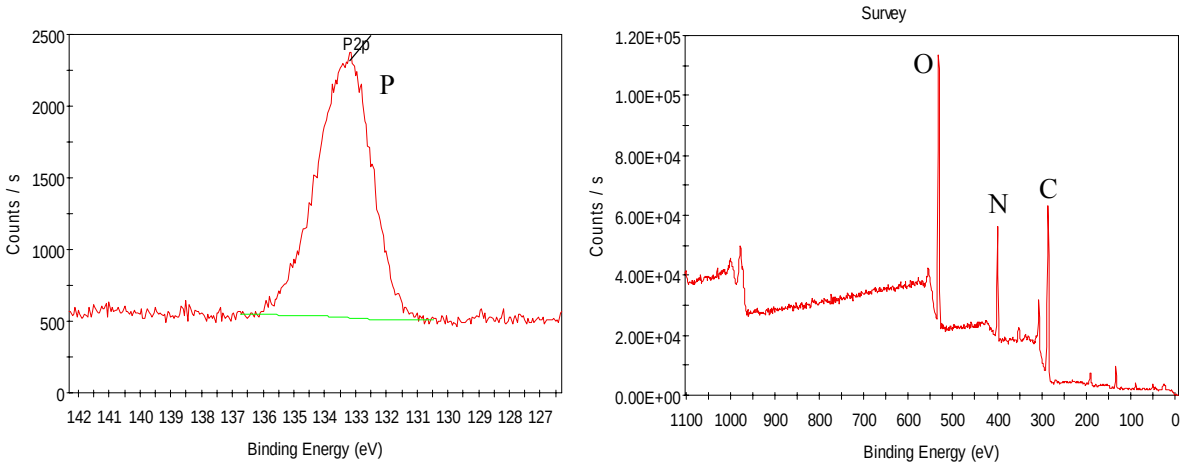
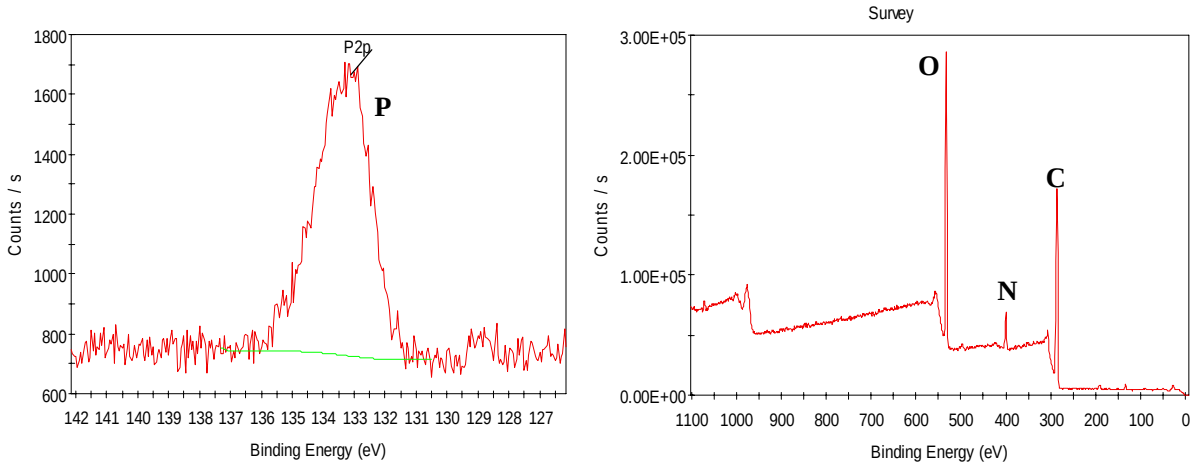


Figure S16. XPS results of a pure DNA sample showing the elemental profiles of P, O, N and C. Right: a survey san; Left: a high resolution scan of P_{2p} peak (corresponding to the phosphate backbone of DNA).

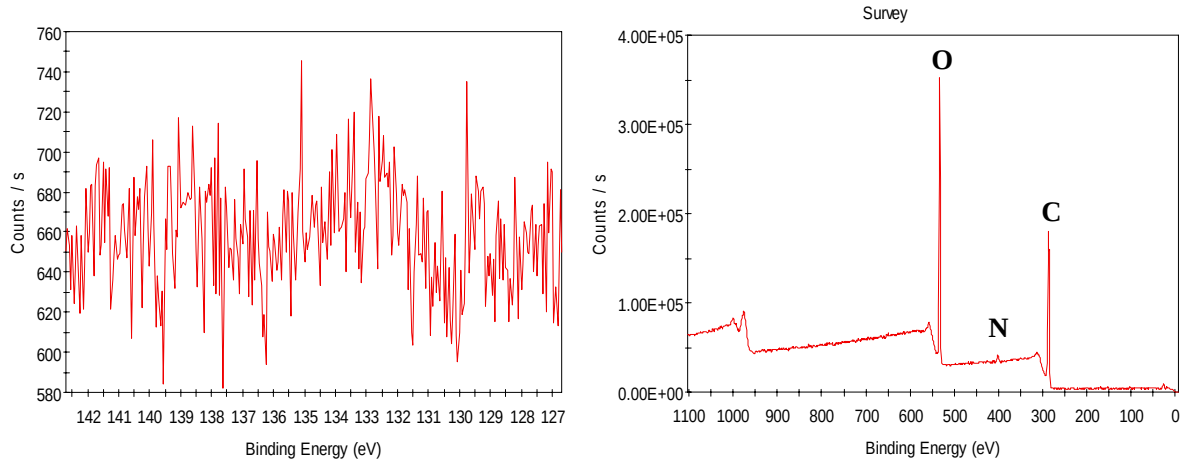


DNA

Figure S17. XPS results of a DNA-GO sample showing the elemental profiles of P, O, N and C. Right: a survey san; Left: a high resolution scan of P_{2p} peak (corresponding to the phosphate backbone of DNA). Note that the GO sample showed very negligible content of phosphorus (P_2O_5 was used during the preparation of graphene oxide, but this step only led to negligible P residue in the final sample). The increase of N content (from DNA bases) in the DNA-GO sample is also very obvious.

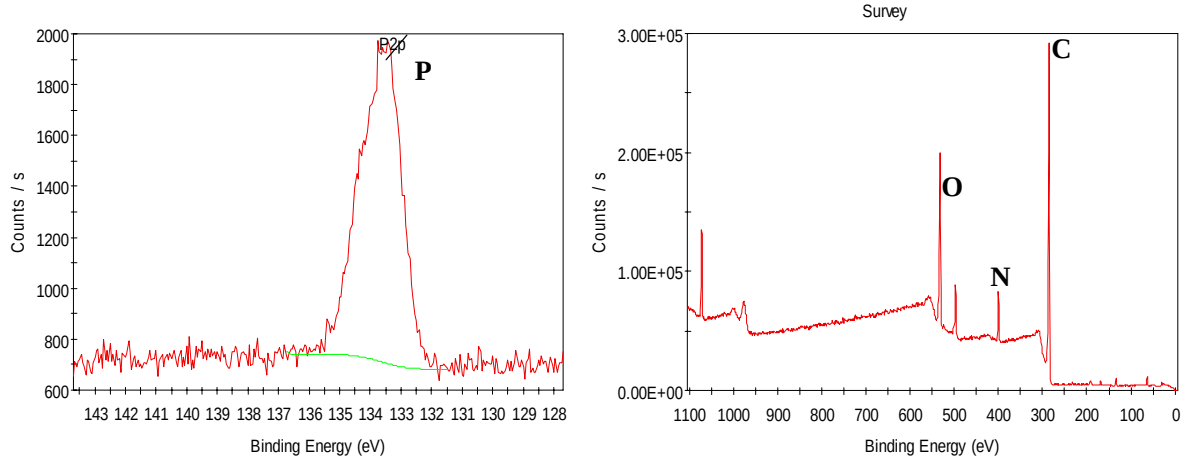


DNA-GO

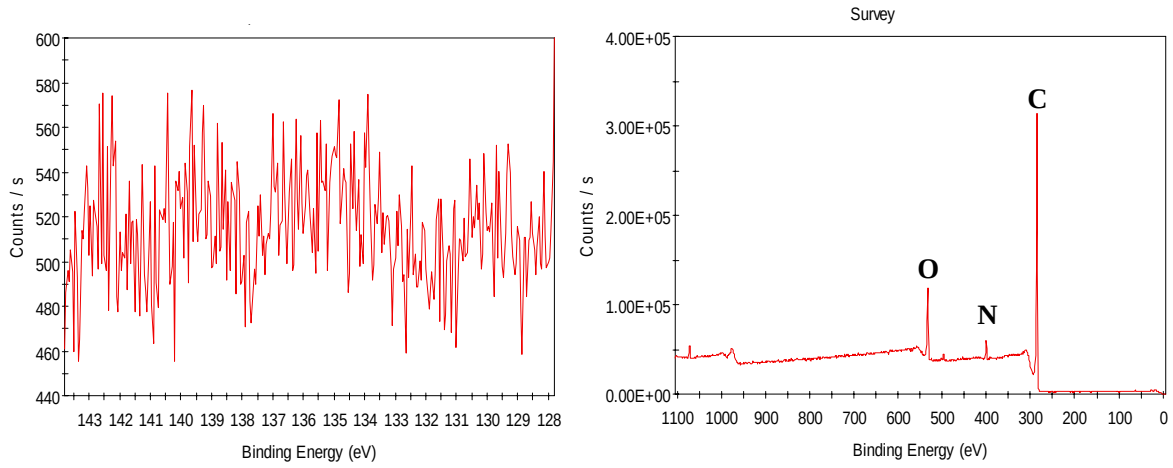


GO

Figure S18. XPS results of a DNA-RGO sample showing the elemental profiles of P, O, N and C. Right: a survey san; Left: a high resolution scan of P_{2p} peak (corresponding to the phosphate backbone of DNA). Note that the RGO sample showed negligible content of phosphorus (the initial chemical treating with P_2O_5 during the preparation of graphene oxide only led to negligible P residue in the sample of RGO). The increase of N content (from DNA bases) in the DNA-RGO sample is also very obvious. *Hydrazine reduction resulted in a slight N doping of RGO.*



DNA-RGO



RGO

Figure S19. AFM Height profile of an RGO nanosheet decorated with gold nanoparticles with the help of $d(GT)_{29}SH$. The measured height of gold nanoparticles was around 4.7 nm. Compared with the 6 nm height of the synthesized gold nanoparticles, this value was slightly smaller, which was quite reasonable since it was hard to draw the profile line so that it passed the centers (where the maximum height of a round-shaped particle can be reached) of all the gold nanoparticles. (*The Z-axis of the AFM scanner was calibrated with a 18±1nm vertical calibration grating, TGZ01, obtained from MikroMasch, Inc.*)