Supplementary Information to

Complexation and intercalation modes: a novel interaction of DNA and graphene quantum dots

Liping Lu*, Linqing Guo, Xiayan Wang*, Tianfang Kang, Shuiyuan Cheng
College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China. Email: lipinglu@bjut.edu.cn,xiayanwang@bjut.edu.cn

Materials and Reagents

NaCl, NaH_2PO_4, Na_2HPO_4 and KCl from Beijing Chemical Works, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) was purchased from Sigma Chemical Co. Ltd. N-Hydroxysuccinimide (NHS) was purchased from Sinopharm Chemical Reagent Co., Ltd. Graphene quantum dots(GQDs) and Graphene oxide(GO)were purchased from Nanjing XFNANO Materials Tech Co., Ltd. Other reagents were purchased from Beijing Dingguo Changsheng biotechnology Co. Ltd. Ultrapure water used in these works from a Millipore Waters Milli-Q water purification system. All reagents were of analytical grade. All oligonucleotide sequences was synthesized by SBS Genetech Co., Ltd(Shnaghai,China).

Table S1. All oligonucleotide sequences

ssDNA-1	5′ -GAC TGA-3′
ssDNA-2	5′ -NH_2-C_6-CCT CGG ACG -3′
ssDNA-3	5′ -CT CGG ACG -3′
ssDNA-4	5′ -CGT CCG AGG TCA GTC -3′
ssDNA-5	5′ -GAC TGA CCT CGG ACG -3′
ssDNA-wm	5′ -GGA TCC TCA GCT CAG CAC GCA CTT GCA GCT CAT GCA GCC GGG GCC GCT GGC GCC CCC GAG -3′
ssDNA-total	5′ -CTC GGG GGC GCC AGC GGC CCC GGC TGC ATG AGC TGC AAG TGC GTG CTG AGC TGA GGA TCC -3′
ssDNA-abase-1	5′ -GGA TCC TCA GCT CAG CAC GCA CTT G -3′
ssDNA-NH_2-1	5′ -NH_2-C_6-AGC TCA TGC AGC CGG GGC CGC TGG CGC CCC CGA G -3′
ssDNA-abase-2	5′ -AGC TCA TGC AGC CGG GGC CGC TGG CGC CCC CGA G -3′
ssDNA-NH_2-2	5′ -GGA TCC TCA GCT CAG CAC GCA CTT GC -3′

Characterization

Fluorescence spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. The excitation wavelength was set at 380 nm, and the emission spectra were recorded in the wavelength range of 400–680 nm. The excitation and emission slits widths were both set 10 nm. The UV-visible spectra were recorded on a SHIMADZU UV-2450 spectrophotometer. Circular dichroism spectra was recorded on a Applied Photophysics

Pistar π-180 CD spectrometer and the wavelength ranged from 350 to 200 nm. AFM was recorded on a BRUKER Dimension 3100 atomic force microscope images. TEM was recorded on a JEM-2100 Transmission Electron Microscope Native-PAGE was performed with a mini-gel apparatus (DYY-7C, Beijing Liuyi Scientific Equipment Ltd, China) using a 20% acrylamide gel, imaged on a Bio-Rad Gel Doc XR+ Imaging System.

Synthesis of dsDNA

A mixture solution **AM-DNA**(NH_2-labled DNA) was obtained by hybridized of ssDNA-1 , ssDNA-2 ,and ssDNA-4; **AB-DNA**(a single base deletion DNA) was obtained by hybridized of ssDNA-1, ssDNA-3 and ssDNA-4, **WM-DNA**(well match DNA) was obtained by hybridized of ssDNA-4 and ssDNA-5, AM-60bp-DNA(NH_2-labled 60 bp DNA) was obtained by hybridized of ssDNA-total , ssDNA-NH_2-1 ,and ssDNA-NH_2-2; AB-60bp-DNA(a single base deletion 60bp DNA was obtained by hybridized of ssDNA-total , ssDNA-abase-1 ,and ssDNA-abase-2, WM-60bp-DNA(well match 60bp DNA) was obtained by hybridized of ssDNA-total and ssDNA-wm in Phosphate buffer(5mM PBS, 0.1M NaCl, pH=7.5) was first prepard (Table S2.). DNA synthesis reactions were carried out in a Bio-RAD T100 Thermal Cycler. The thermocycler parameters were as follows: (1) hold for 50s at 90°C, followed by 1 min at 90°C, (2) annealing for 700 cycles, each cycle consisting of denaturation 0.01°C for 8 sec[1]. The mixture solution was subsequently cooled down slowly at 0.01°C /8s to room temperature to ensure that NH2-DNA, abase-DNA and WM-DNA were hybridized to form DNA completely[2].

Table S2. All DNA sequences

AB-DNA	5′-CGT CCG AGG TCA GTC-3′ 3′-GCA GGC TC AGT CAG-5′
AM-DNA	5′-CGT CCG AGG TCA GTC-3′ 3′-GCA GGC TCC AGT CAG-5′ Modification status:C-C6-NH_2
Wm-DNA	5′-CGT CCG AGG TCA GTC-3′ 3′-GCA GGC TCC AGT CAG-5′
abase-60bp-DNA	5′- GGA TCC TCA GCT CAG CAC GCA CTT G_A GCT CAT GCA GCC GGG GCC GCT GGC GCC CCC GAG -3′ 3′- CCT AGG AGT CGA GTC GTG CGT GAA CGT CGA GTA CGT CGG CCC CGG CGA CCG CGG GGG CTC -5′
NH2-60bp-DNA	5′- GGA TCC TCA GCT CAG CAC GCA CTT GCA GCT CAT GCA GCC GGG GCC GCT GGC GCC CCC GAG -3′ Modification status:A-C6-NH_2 3′- CCT AGG AGT CGA GTC GTG CGT GAA CGT CGA GTA CGT CGG CCC CGG CGA CCG CGG GGG CTC -5′
Wm-60bp-DNA	5′-GGA TCC TCA GCT CAG CAC GCA CTT GCA GCT CAT GCA GCC GGG GCC GCT GGC GCC CCC GAG-5′ 3′-CCT AGG AGT CGA GTC GTG CGT GAA CGT CGA GTA CGT CGG CCC CGG CGA CCG CGG GGG CTC-3′

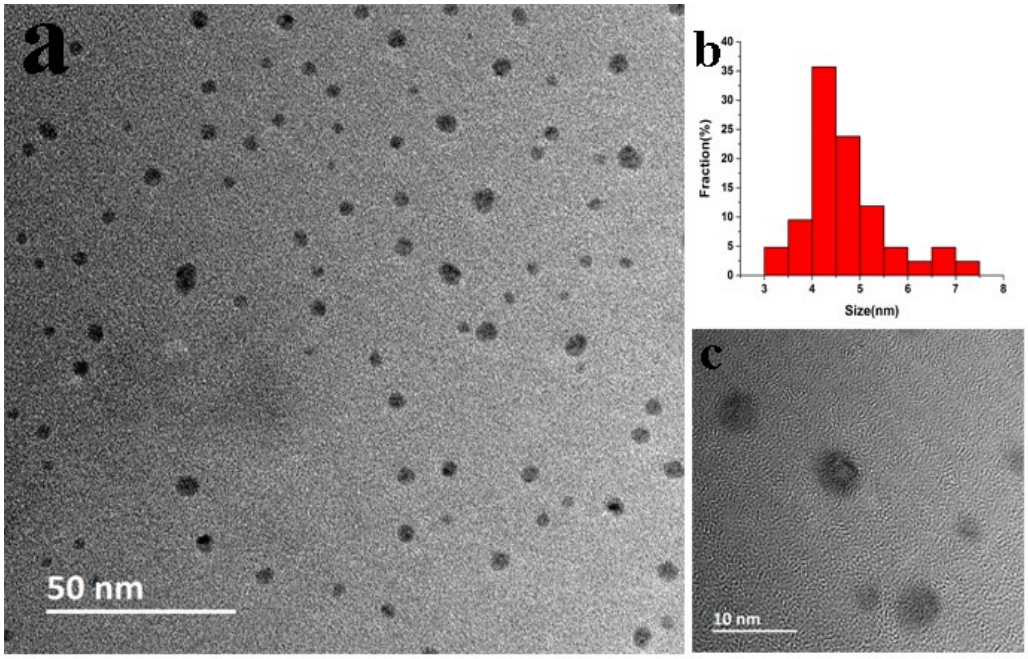
Synthesis of GQDs- DNA complexes

Firstly, 0.1M EDC and 0.1M NHS was added into GQDs aqueous dispersions to activate carboxylic acid group, AM-DNA was added into EDC-NHS activated GQDs to form GQDs-AM-DNA complex, AB-DNA and WM-DNA were incubated in GQDs solutions for 15 min in the shaker to form GQDs-AB-DNA and GQDs-WM-DNA.

Polyacrylamide gel electrophoresis detection of DNA and GQDs- DNA complexes

Approximately 10 mL of gel solution is needed to cast each gel. The final concentration of each gel is 20% (w/v) acrylamide (29:1), 1× TBE buffer, 0.7% (w/v) ammonium persulfate, and 0.065% (w/v) TEMED. Immediately after the incorporation of the ammonium persulfate and TEMED, the gel solution is mixed and poured directly between the glass plates. A 10-tooth comb is placed between the plates and two additional spring clamps are

used to hold the comb tightly against the back plate. The plate sandwich with gel solution is then kept at room temperature for about 40 min to allow gel polymerization. DNA samples are loaded with a standard pipette, loading volume can be up to 5 µL. Electrophoresis is performed at approximately 110 V for 3 h[3].



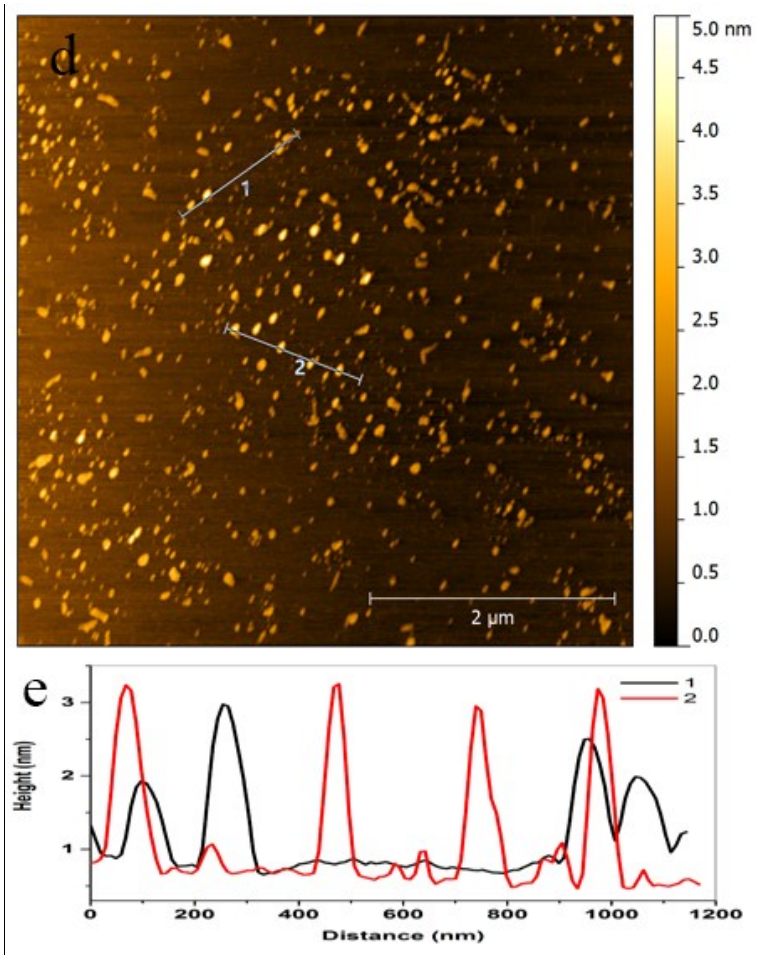


Fig.S1, High-resolution transmission electron microscopy image of GQDs (a,c) and size distribution (b); (d) is AFM image of GQDs prepared by drop-casting the ultrapure water dispersion on a Gold-plated silicon substrate;(e) is height profile along the lines in (d).

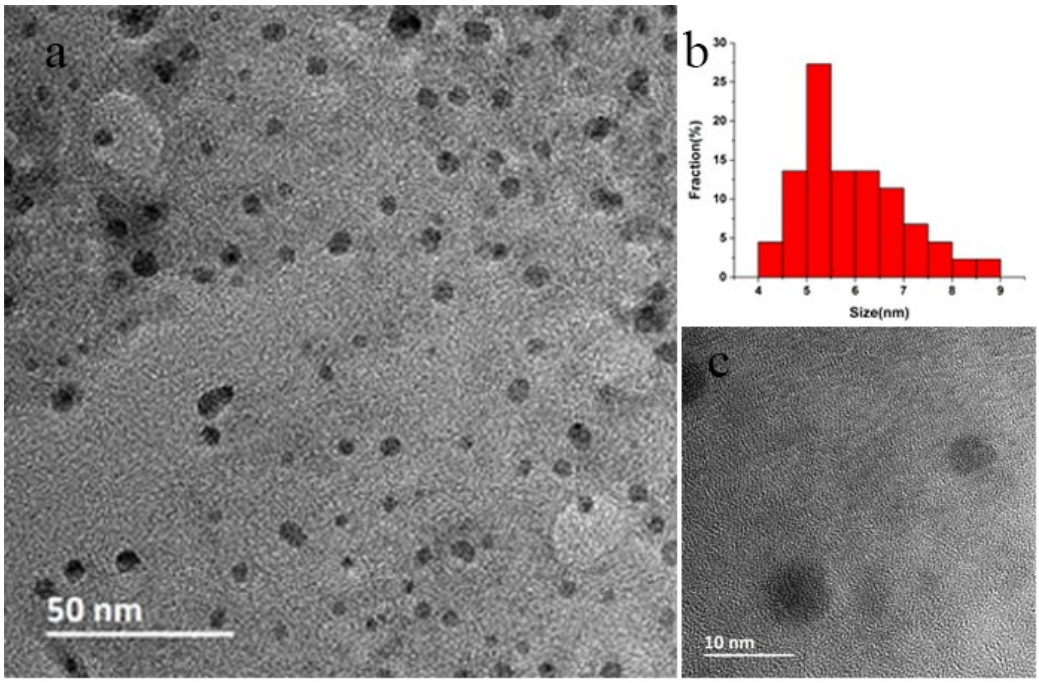


Fig.S2, High-resolution transmission electron microscopy image of GQDs-DNA (a,c) and size distribution (b)

TEM was used to detect the complexes(GQDs-DNA). Figure S2 (a, c) displays typical characterization results of the resulting GQDs-DNA. The size distribution shows that the GQDs-DNA have an average lateral diameter of 5.9 nm with an average diameter of 4 to 9 nm(Figure S2, b). Compared with Figure S1, the size change bigger when GQDs interacted with DNA, which proved GQDs is really interacted with GQDs.

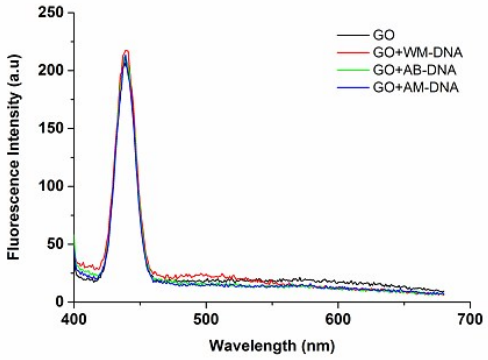


Fig.S3 The fluorescence spectrum of GO aqueous solutions upon addition of different sequence of DNA. ex =380nm

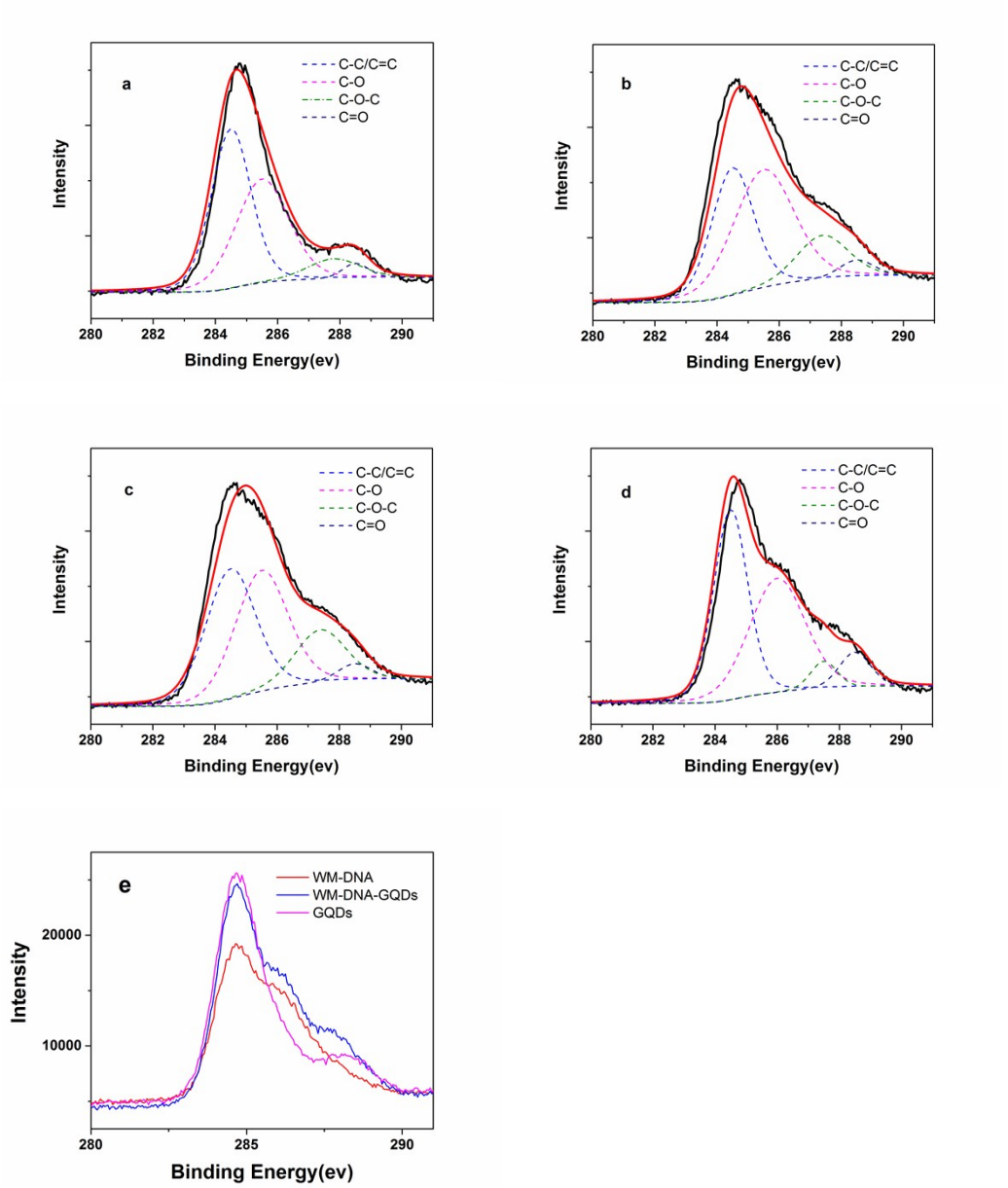


Fig. S4 C1s of XPS survey scans of GQDs(a), AB-DNA-GQDs (b); AM-DNA-GQDs (c); WM-DNA-GQDs (d) and superposition curves(e).

Fig.S4 displays the high-resolution C 1s peaks from conditioned GQDs before and after DNA interaction. The fitted spectrum of C1s illustrate a C1s peak (C-C/C=C) at 284.5eV, a C-O peak at 285.5eV, a C=O peak at 286.8eV and a COOH peak at 287.4eV[4, 5]. The presence of C=C, C-O, C=O and COOH bands confirmed that the presence groups in GQDS. Moreover， the C 1s atomic% of three complexes approximately equal to the sum of their two monomers, respectively. These results proved interaction between GQDs and DNAs. The difference of GQDS, WM-DNA and WM-DNA-GQDs indicated the interaction between DNA and GQDs do exist.

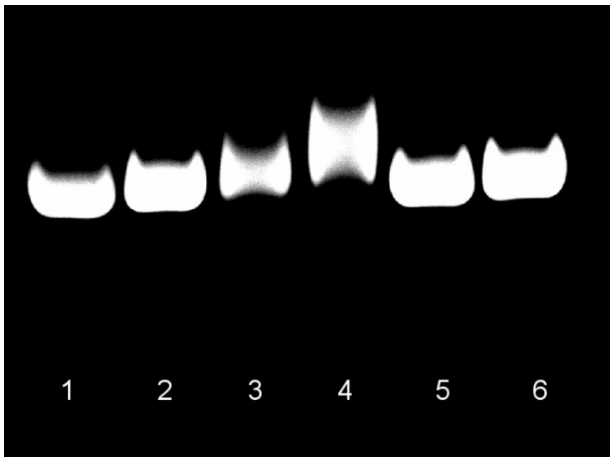


Fig.S5 Electrophoretic mobility of Lane 1- AM-60bp-DNA, Lane 2 – GQDs- AM-60bp-DNA, Lane 3 –AB-60bp-DNA, Lane 4- GQDs-AB-60bp-DNA, Lane 5 –WM-60bp-DNA, Lane 6 –GQDs- WM-60bp-DNA

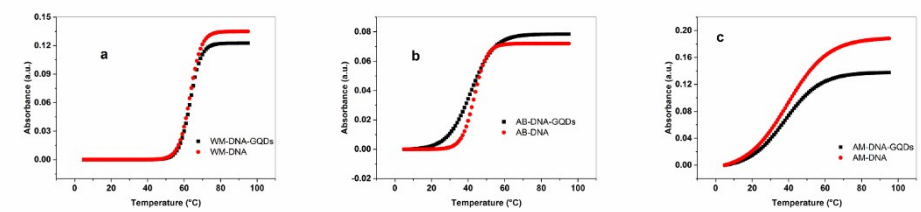


Fig.S6 Melting curves for WM-DNA(a),AB-DNA(b) and AM-DNA(c) from the temperature dependence of CD at 260nm

References:

1. T. P. Makhalanyane, A. Valverde, N. Birkeland, S. C. Cary, I. M. Tuffin and D. A. Cowan, *The ISME journal*, 2013, **7**, 2080-2090.

2. Y. Hu, Y. Wu, T. Chen, X. Chu and R. Yu, *Anal. Methods*, 2013, **5**, 3577-3581.

3. D. Wang, J. Shi, S. R. Carlson, P. B. Cregan, R. W. Ward and B. W. Diers, *CROP SCI*, 2003, **43**, 1828-1832.

4. J. Peng, W. Gao, B. K. Gupta, Z. Liu, R. Romero-Aburto, L. Ge, L. Song, L. B. Alemany, X. Zhan and G. Gao, *NANO LETT*, 2012, **12**, 844-849.

5. Y. Li, Y. Hu, Y. Zhao, G. Shi, L. Deng, Y. Hou and L. Qu, *ADV MATER*, 2011, **23**, 776-780.