Electronic Supplementary Information

Nucleotide-Assisted Decoration of Boron Nitride Nanotubes with Semiconductor Quantum Dots Endows Valuable Visible-Light Emission in Aqueous Solution

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Experimental Section

Materials. All nucleotides were purchased from Wako. Cadmium chloride ($CdCl_2$) and sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$) were purchased from Adrich-Sigma. All reagents were used as received. Multiwalled BNNTs were synthesized by a carbon-free chemical vapor deposition method.[1] A typical photograph and a SEM image of BNNTs are shown in Fig. S1. BNNTs have diameters from several nanometers to 70 nm and lengths up to 10 μm. Most tubes have approximately 50 shells. The surfaces are chemically clean.

Preparation of nucleotide-modified BNNTs. In a typical experiment, 1.5 mg of BNNTs were added into an aqueous solution containing 100 μM (0.04 mg mL^{-1} for GMP) nucleotides in a total volume 3 mL, and then the mixture was sonicated by a Branson Advanced Sonifier Model 250AA (output power: 20 W) for 3 h with a water cooling system, followed by centrifugation at 2000 rpm for 25 min to remove any insoluble materials. The resultant dispersion was then stored at room temperature for further characterizations. The original BNNTs sample was similarly prepared using the same procedure without nucleotides.

Preparation of GMP-capped CdS QDs. 0.75 mg of GMP was mixed with 5 mL of freshly prepared 0.5 mM $CdCl_2$, the solution was mixed for 15 min under N_2 protection to ensure homogeneous mixing, and then 50 μL of freshly prepared 50 mM $Na_2S{\cdot}9H_2O$ was quickly injected into the mixed solution, followed by mixing for further 10 min at room temperature to ensure the

growth of CdS QDs. After these processes, solution color changed from white to orange yellow, suggesting the fabrication of the QDs.

Decoration of BNNT sidewalls with GMP-capped CdS QDs. 1.5 mg of BNNTs were added into 3 mL of the QDs solution, and the mixed solution was sonicated (output power: 20 W) for 3 h using a water cooling system, followed by incubation at room temperature for 24 h. Insoluble materials were precipitated and removed by centrifugation at 2000 rpm for 25 min, and then the supernatants were centrifuged at 15000 rpm for 25 min to collect solid products. Subsequently, the products were redispersed in 1 mL of 0.15 mg mL^{-1} GMP solution, followed by centrifugation at 15000 rpm for 25 min. This redispersion-centrifugation cycle was repeated three times to wash away any unbound QDs. Finally, the solid products were redispersed in 1 mL of 0.15 mg mL^{-1} GMP solution and stocked for further studies. Control experiments were also performed similarly using GMP-capped CdS QDs to exclude the effect of the sonication (see Figs. S8, S9, and S10).

Characterizations. TEM images were obtained with a JEM 2100F (Jeol) instrument with an accelerated voltage of 200 keV using carbon-coated copper grids (300 mesh, Agar Scientific).

AFM images were obtained with a SPM-9600 (Shimadzu) in a tapping mode using standard silicon cantilevers. AFM samples were prepared by spin-coating 10 µL of the resultant dispersion at 600 rpm on a freshly cleaved mica substrate. For AFM statistic analyses, 10 mM of GMP solution was used for dispersing BNNTs. The heights and lengths were measured three times to estimate an average value for each BNNT.

FT-IR spectra were recorded using a Perkin-Elmer Spectrometer, 10 times for each sample, and were Fourier-transformed at a resolution of 4 cm^{-1}. Spectra were corrected with a baseline supported by Perkin-Elmer software. Stock samples were drop-cast onto a gold film substrate, and dried under ambient conditions for measurements. The pristine BNNTs and GMP powder were used to measure FT-IR spectra for the original BNNTs and pure GMP, respectively. GMP-modified BNNTs hybrid solution was dialyzed for 24 h against milli-Q. CdS/GMP@BNNT hybrids were precipitated from solution by using centrifugation at 15000 rpm for 25 min, followed by the aforementioned similar redispersion-centrifugation cycles in milli-Q to remove free GMP, and were collected as solid products.

UV-vis spectra were recorded by a JASCO V-670 spectrophotometer at ambient conditions.

Fluorescence spectra were measured with a JASCO FP-6500 spectrofluorometer by excitation at 372 nm with a scan rate of 100 nm s^{-1}.

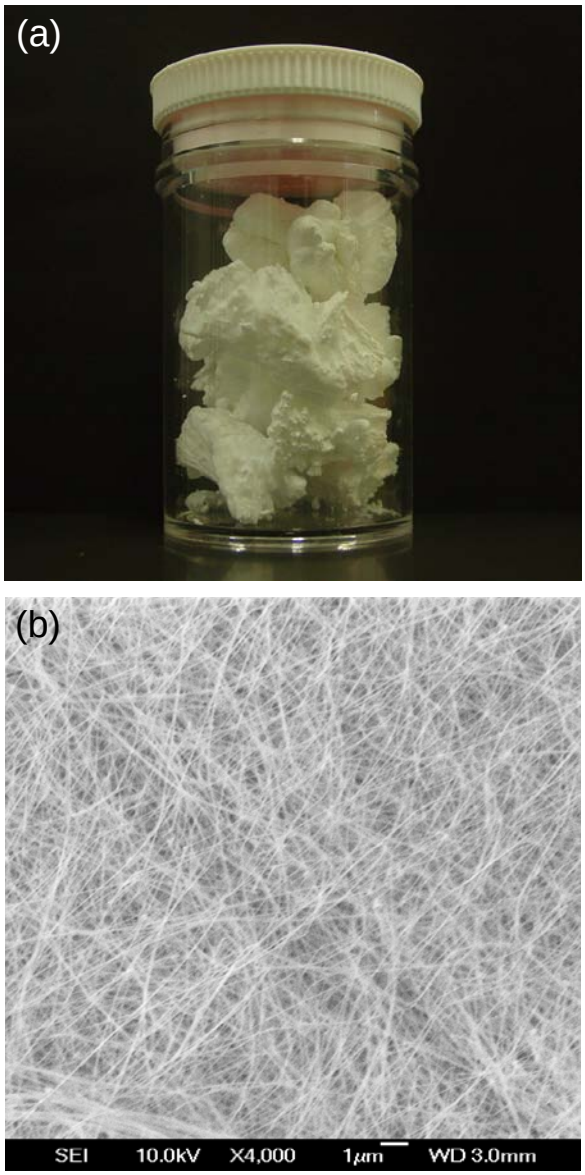

Fig. S1 (a) Typical photograph and (b) SEM image of pristine BNNTs.

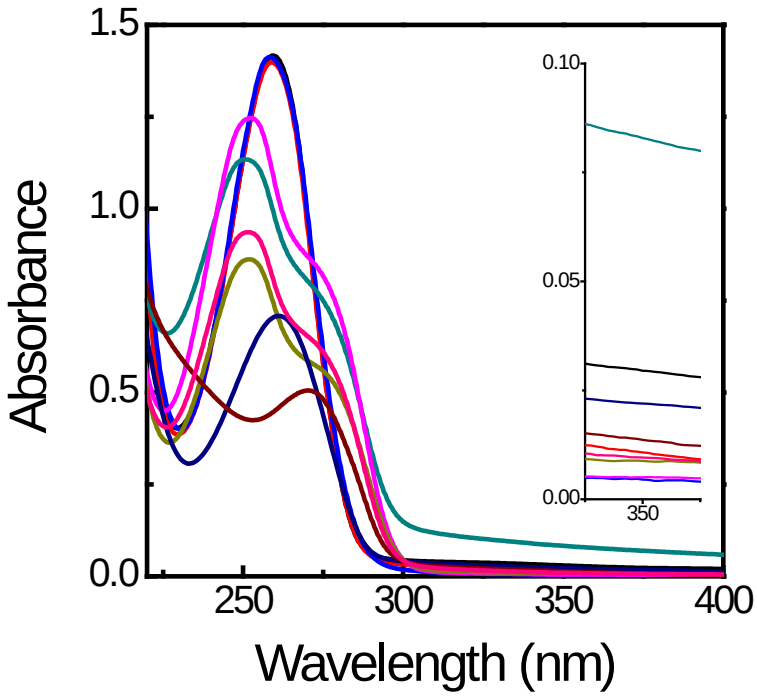

Fig. S2 UV-vis absorption spectra of nucleotides-modified BNNTs. AMP-modified BNNTs (black), ADP-modified BNNTs (red), ATP-modified BNNTs (blue), GMP-modified BNNTs (dark cyan), GDP-modified BNNTs (magenta), GTP-modified BNNTs (dark yellow), UMP-modified BNNTs (navy), CMP-modified BNNTs (wine), and Gua-modified BNNTs (pink). The inset shows an enlarged part from 345 nm to 355 nm.

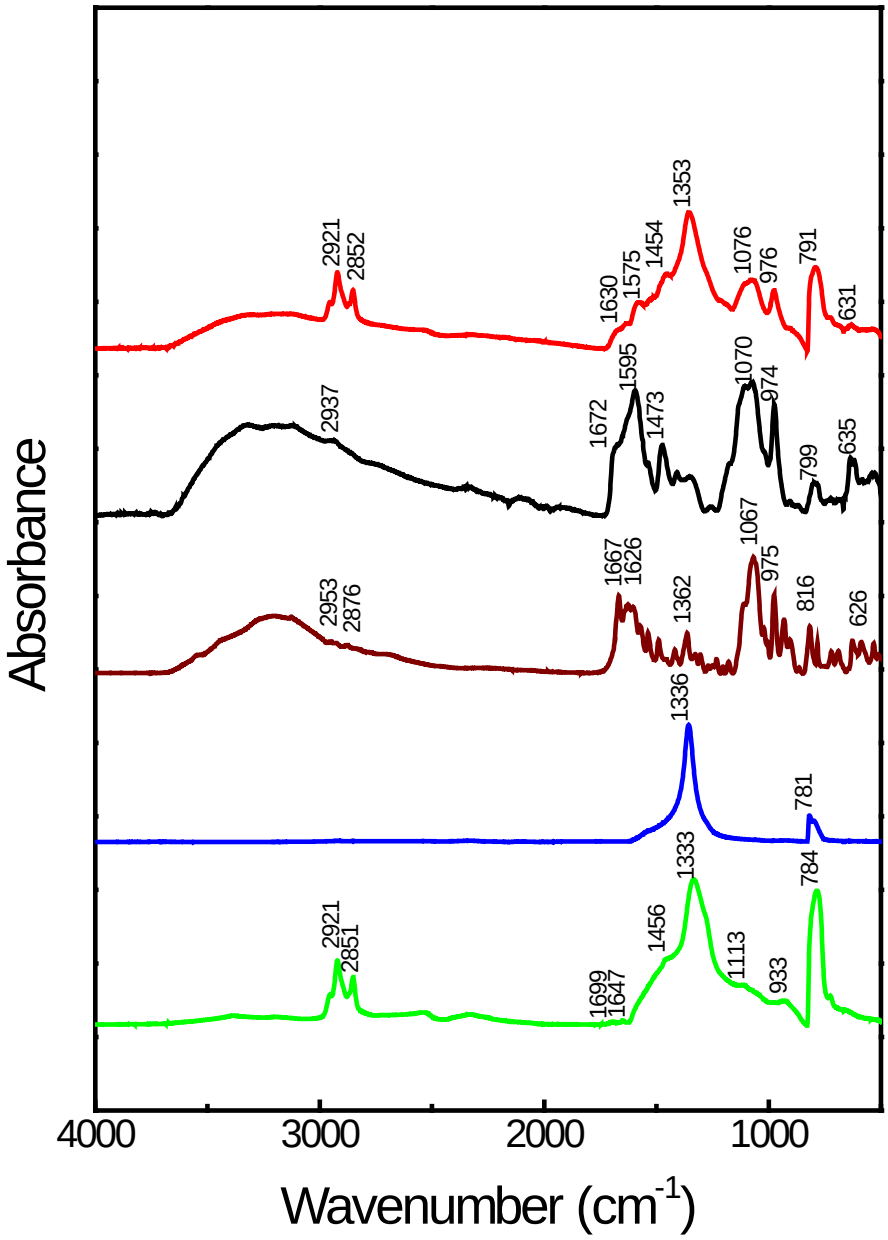

Fig. S3 FT-IR spectra of CdS/GMP@BNNT hybrids (red), GMP-capped CdS QDs (black), pure GMP (wine), the original BNNTs (blue), and GMP-modified BNNTs (green).

Table S1. FT-IR data of CdS/GMP@BNNT hybrids, GMP-capped CdS QDs, pure GMP, original BNNTs, and GMP-modified BNNTs.

Group/Moiety	**Na_2GMP (cm^{-1})**	**GMP-modified BNNTs (cm^{-1})**	**GMP-capped CdS (cm^{-1})**	**Original BNNTs (cm^{-1})**	**CdS/GMP@BNNTs (cm^{-1})**
>C=O	1667	1699	1672	No	1630
N7-C8 +C8-H	1362	1456	1473	No	1456
$-NH_2$	1626	1647	1595	No	1575
PO_3^{2-}	1067	1113	1070	No	1076
P-O-5´-sugar	816	disappeared	799	No	disappeared
LO	No	1333	No	1336	1353
TO	No	784	No	781	791
υ (C-H)	2876	2921 2851	2937	No	2921 2852

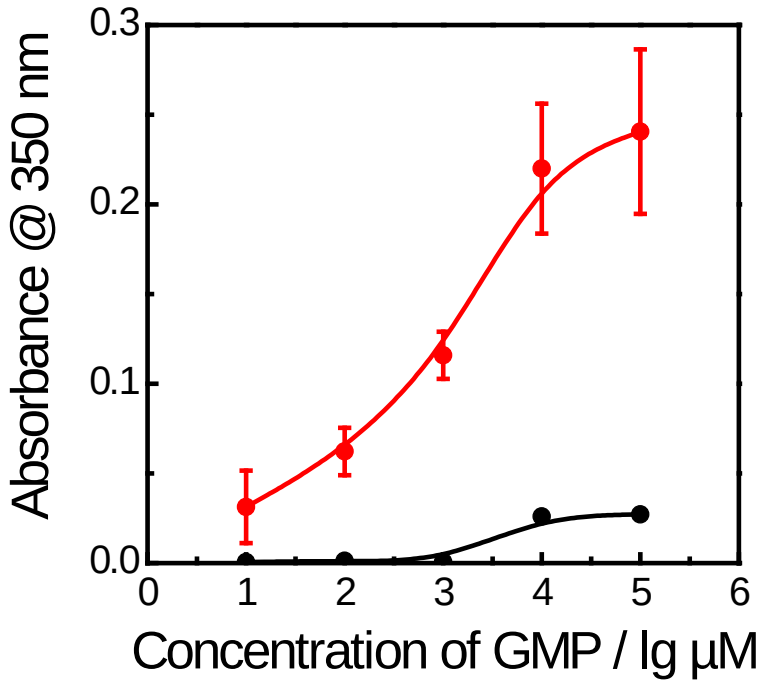

Fig. S4 Dependence of the dispersed amounts of BNNTs (red) on the concentration of GMP, and absorption of GMP solution (black).

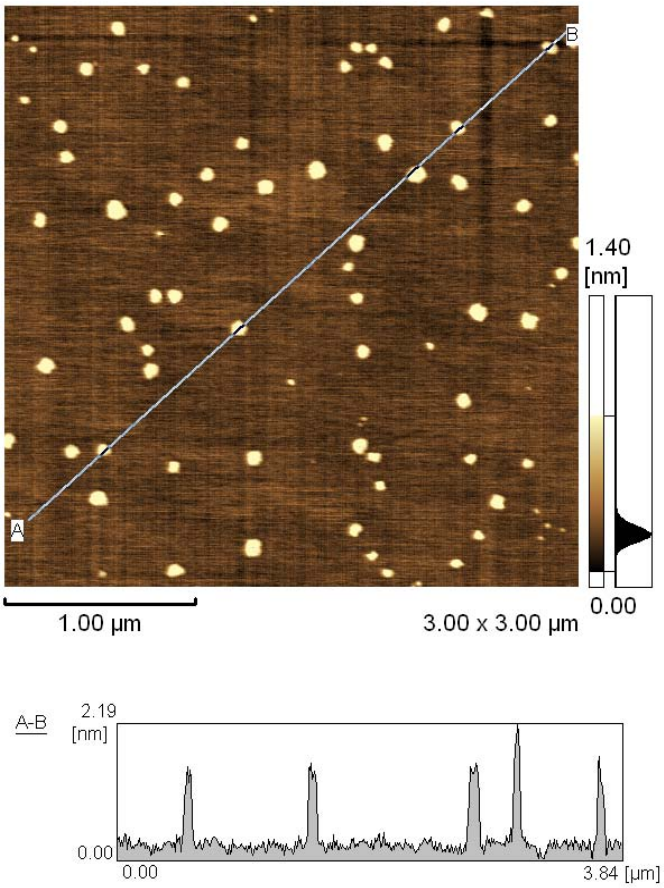

Fig. S5 AFM image and height profile of as-prepared GMP-capped CdS QDs. Most QDs have sizes around 2 nm. A small number of QDs have sizes around 8 nm.

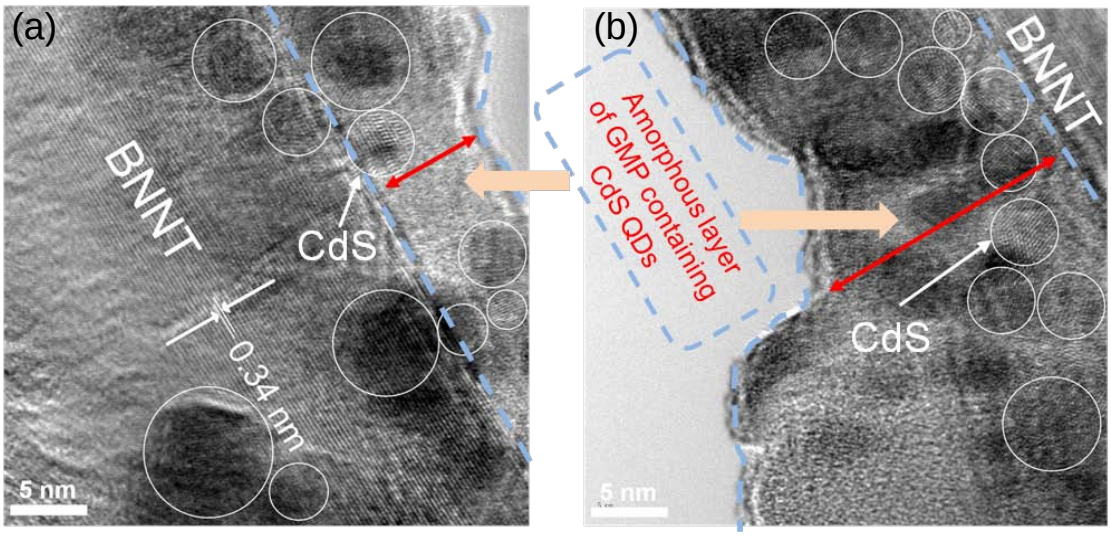

Fig. S6 (a,b) High-resolution TEM images of CdS/GMP@BNNT hybrids. Crystalline CdS QDs were observed on the sidewalls of multiwalled BNNTs (encircled areas).

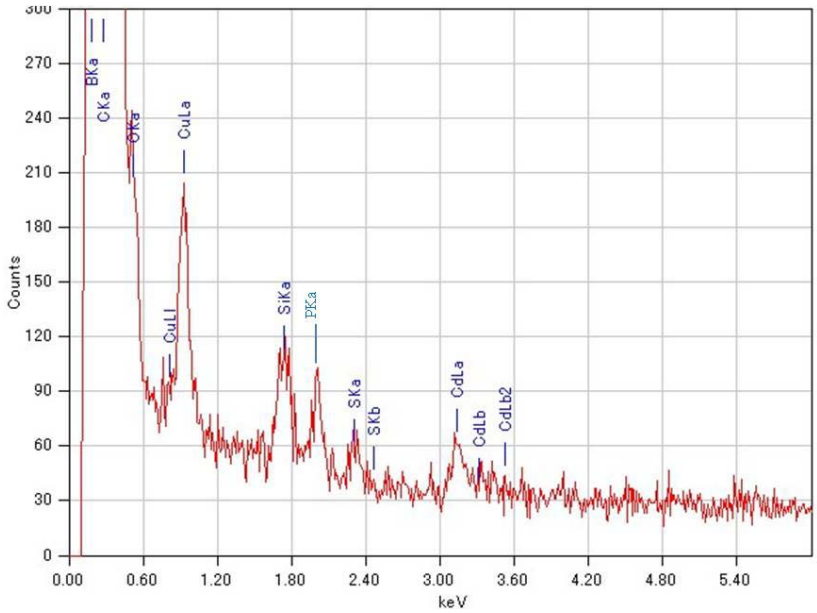

Fig. S7 EDS data of CdS/GMP@BNNT hybrids. The peak of PKa suggests the presence of GMP in the hybrids, and the peaks of SKa, SKb, CdLa, CdLb, and CdLb2 suggest the presence of CdS in the hybrids.

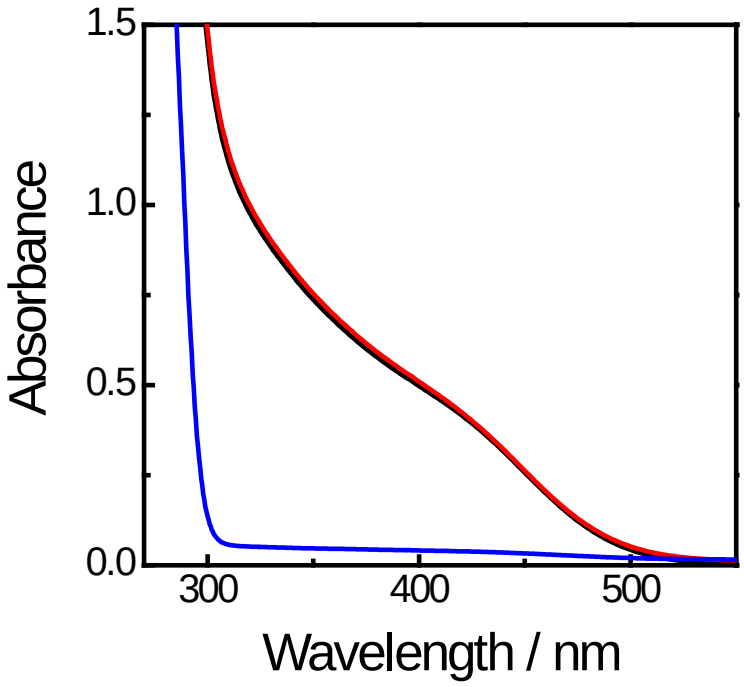

Fig. S8 Comparative UV-vis spectra of as-prepared GMP-capped CdS QDs (black), the QDs solution after sonication for 3 h (red), and the QDs solution after sonication for 3 h, incubation for 24 h, and purification processes, similarly with CdS/GMP@BNNT hybrids (blue).

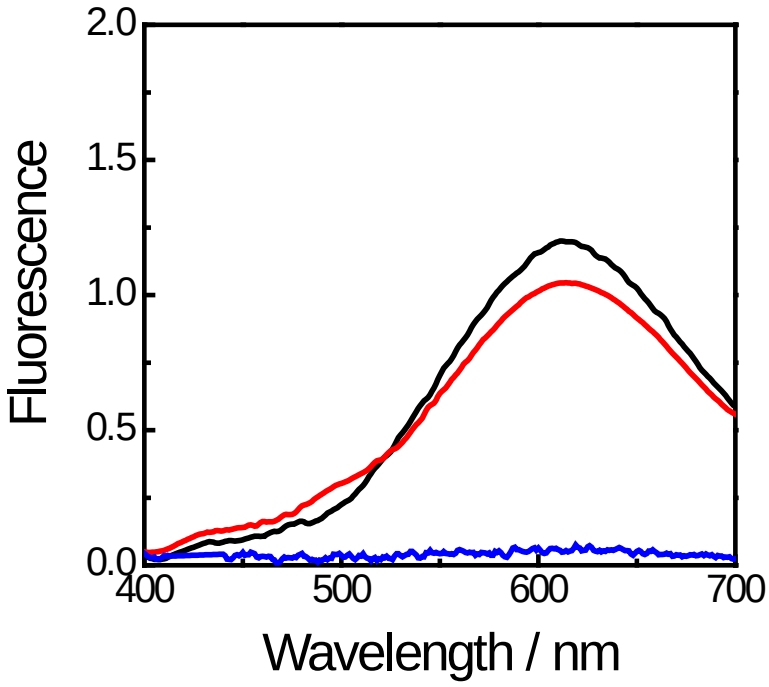

Fig. S9 Comparative fluorescence spectra of as-prepared GMP-capped CdS QDs (black), the QDs solution after sonication for 3 h (red), and the QDs solution after sonication for 3 h, incubation for 24 h, and purification processes, similarly with CdS/GMP@BNNT hybrids (blue).

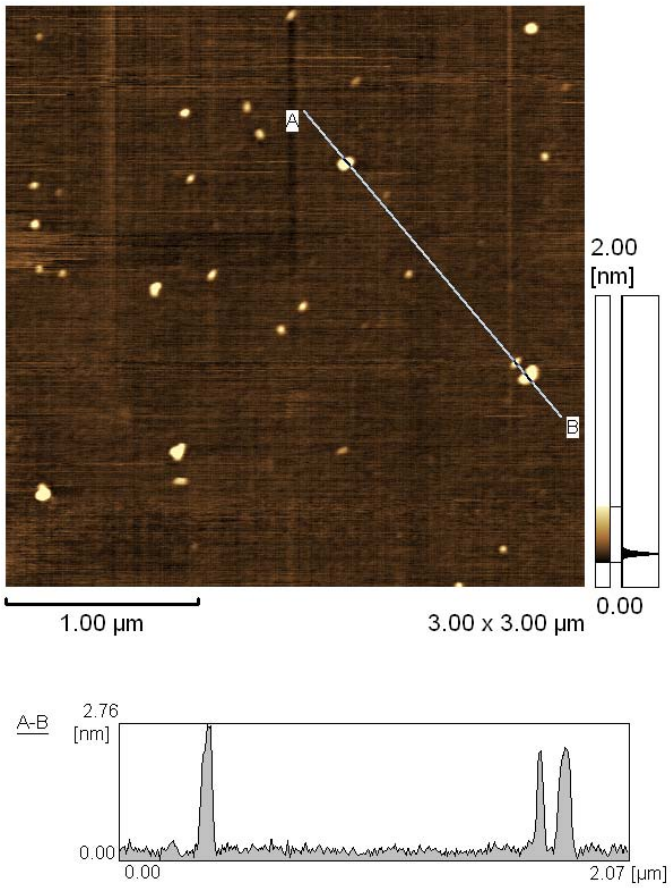

Fig. S10 AFM image and height profile of GMP-capped CdS QDs after sonication for 3 h. Compared with as-prepared QDs (see Fig. S4 for AFM image), the morphological features were almost similar, suggesting that the sonication procedure does not notably affect the QDs.

Reference

1 C. Y. Zhi, Y. Bando, C. Tang, D. Golberg, *Solid State Commun*., 2005, **135**, 67.