Supporting Information

Fluorescence Turn-On Detection of Glucose via the Ag Nanoparticle Mediated Release of a Perylene Probe

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EXPERIMENTAL SECTION

Reagents and Instrumentation

Silver nitrate and 30% hydrogen peroxide were purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). Sodium citrate and citric acid were obtained from Beijing Chemical Reagent (Beijing, China). Sodium borohydride was purchased from Sigma-Aldrich (Shanghai, China). Glucose oxidase, glucose, fructose, maltose, lactose and sucrose were all obtained from Shanghai Sangon Biological Engineering Technology & Services Co., Ltd. (Shanghai, China). The perylene probe used in the current investigation was synthesized according to the literature procedures.[11] All the reagents were of analytic grade and used as received. Water purified with a Milli-Q A10 filtration system (Millipore, Billerica, MA, USA) was used for the preparation of the stock and buffer solutions.

UV-Vis absorption spectra were obtained with a Cary 50 Bio Spectrophotometer (Varian Inc., CA, USA). Fluorescence spectra were recorded using a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc., USA). The emission spectra were recorded with slits for excitation and emission both of 5 nm with an excitation wavelength at 495 nm. UV-Vis absorption and emission measurements were both taken using quartz cuvettes with 10 mm path length. Zeta potential measurements were performed with a Zetasizer NanoZS (Malvern Instruments, USA). Transmission electron microscopy (TEM) images were taken using a JEM-2100F high resolution transmission electron microscope (Philips, The Netherlands) operated at 200 kV. The

glucose meter was purchased from Changsha Sinocare Co., Ltd (Changsha, China).

Synthesis of the Ag NPs

Ag NPs were prepared according to the reported literature methods with slight modifications.[12] Briefly, 10 mL 10% (w/v) sodium citrate solution was added to a three-neck flask containing 37.5 mL of ultrapure water and the reaction mixture was heated to 70 ºC and stabilized for 15 min. 0.85 mL 1% (w/v) silver nitrate solution was added to the mixture, followed by the quick addition of 1 mL freshly prepared 0.1% (w/v) $NaBH_4$ solution. The resultant solution was kept at 70 ºC for 1 h under vigorous stirring and then cooled to room temperature. The Ag NPs solution was stored at 4 ºC before use.

Fluorescence quenching of the perylene probe by the Ag NPs

20 μL Ag NPs stock solution was added to a mixture of 20 μL citrate buffer and 356 μL water. Various amounts of the perylene probe (4 μL) were added to the diluted Ag NPs solution and mixed several times with the pipette tip. The fluorescence spectra were then recorded at an ambient temperature. Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, perylene probe 40, 80, 120, 160, 200, 240, 280 and 320 nM, respectively.

Effect of GOx on quenching of the perylene probe by the Ag NPs

20 μL Ag NPs stock solution was added to a mixture of 20 μL citrate buffer and 354

μL water. Different amounts of GOx (2 μL) were added to the diluted Ag NPs solution. 4 μL perylene probe was added and mixed with the pipette tip several times. The fluorescence spectra were then recorded. Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, perylene probe 160 nM, GOx 0, 0.25, 0.5, 0.75, 1.00, 1.25, and 1.50 U/mL, respectively.

Effect of GOx on the detection of glucose

20 μL Ag NPs stock solution was added to a mixture of 20 μL citrate buffer and 349 μL water. Different amounts of GOx were added to the diluted Ag NPs solution. 5 μL glucose was then added and the sample solutions were kept at 37 ºC in a water bath for 90 min. 4 μL perylene probe was subsequently added and mixed with the pipette tip several times. And the fluorescence spectra were taken. Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, perylene probe 160 nM, glucose 500 μM, GOx 0, 0.25, 0.5, 0.75, 1.00, 1.25, and 1.50 U/mL, respectively.

Effect of reaction time

20 μL Ag NPs stock solution was added to a mixture of 20 μL citrate buffer and 349 μL water. GOx (2 μL) and glucose (5 μL) were added and the sample solutions were kept at 37 ºC in a water bath for a certain period of time (0, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90 and 100 min, respectively). Afterwards, the perylene probe (4 μL) was added and mixed with the pipette tip several times. The fluorescence spectra were then recorded. Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM,

perylene probe 160 nM, glucose 500 μM, GOx 0.5 U/mL, respectively.

Glucose assay procedures

20 μL Ag NPs stock solution was added to a mixture of 20 μL citrate buffer and 349 μL water. GOx (2 μL) and different concentrations of glucose (5 μL) were added and the sample mixtures were kept at 37 ºC in a water bath for 90 min. 4 μL perylene probe was added and mixed several times with the pipette tip. The fluorescence spectra were then recorded. Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, perylene probe 160 nM, GOx 0.5 U/mL, glucose 0, 2.5, 5, 10, 25, 50, 75, 100, 200, 300, 400, 500 and 600 μM, respectively.

Selectivity of the assay

A number of related carbohydrates, including fructose, maltose, lactose and sucrose were tested (500 μM each). Assay procedures were the same as those described in the glucose assay section except different carbohydrates were used.

Glucose sensing in human serum samples

The human serum samples were obtained from a local hospital. Prior to analysis, the samples were centrifuged using an Amicon Ultra filter with a 3000 molecular weight cutoff at 7000 rpm for 15 min. The samples were spiked with different concentrations of glucose (0, 5, 10, 25, 50, 75 and 100 μM, respectively) and the glucose concentrations of the sample mixtures were determined as described above.

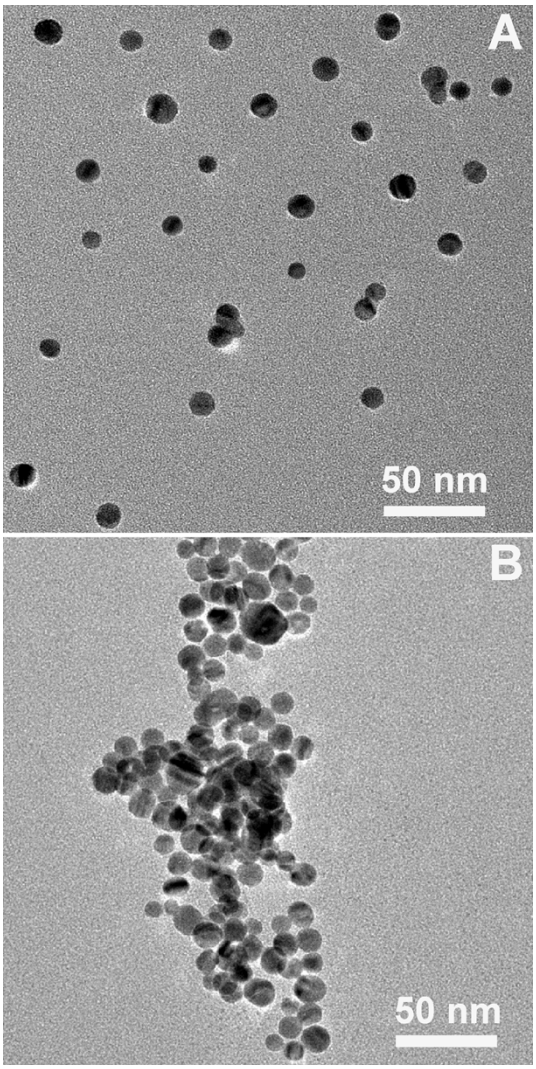

Fig. S1 TEM images of the Ag NPs in the absence (A) and presence (B) of the perylene probe. Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, perylene probe 160 nM, respectively.

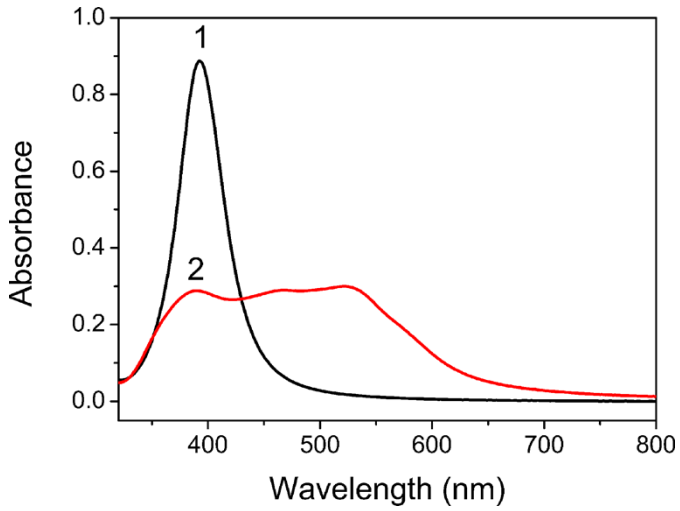

Fig. S2 Surface plasmon absorption spectra of the Ag NPs (1), and the NPs mixed with the perylene probe (2). Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, perylene probe 160 nM, respectively.

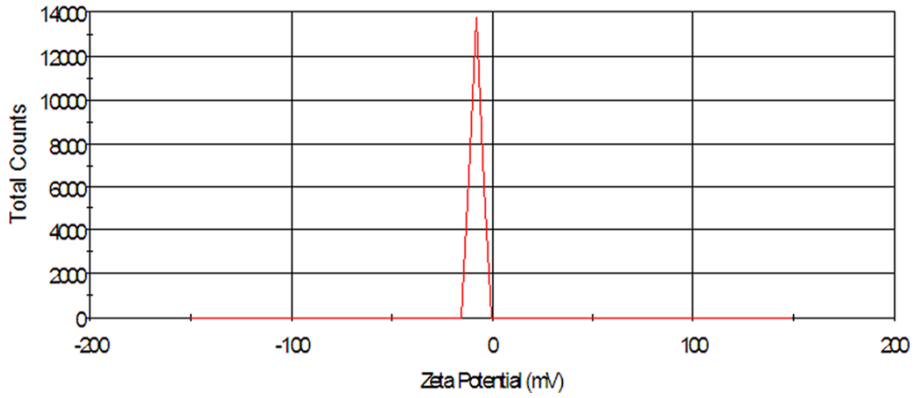

Fig. S3 Zeta potential of the Ag NPs. Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, respectively.

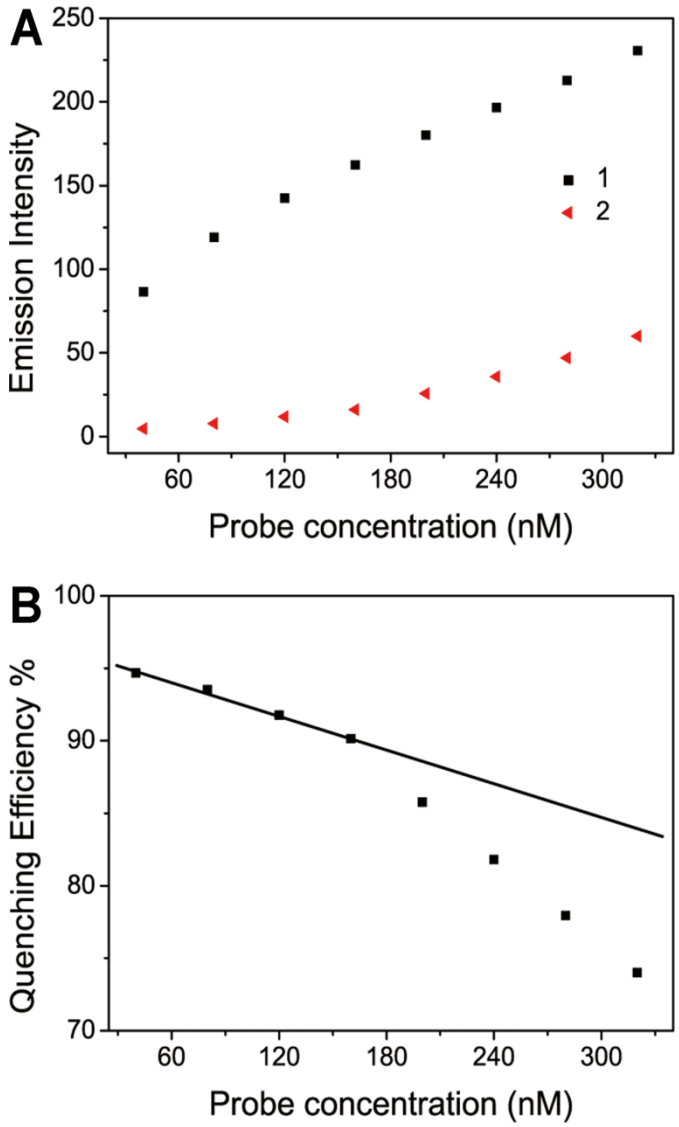

Fig. S4 (A) Plot of the changes in emission intensity of the perylene probe at 545 nm in the absence (1) and presence (2) of the Ag NPs. (B) Changes in quenching efficiency with probe concentration. Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, perylene probe 40, 80, 120, 160, 200, 240, 280 and 320 nM, respectively.

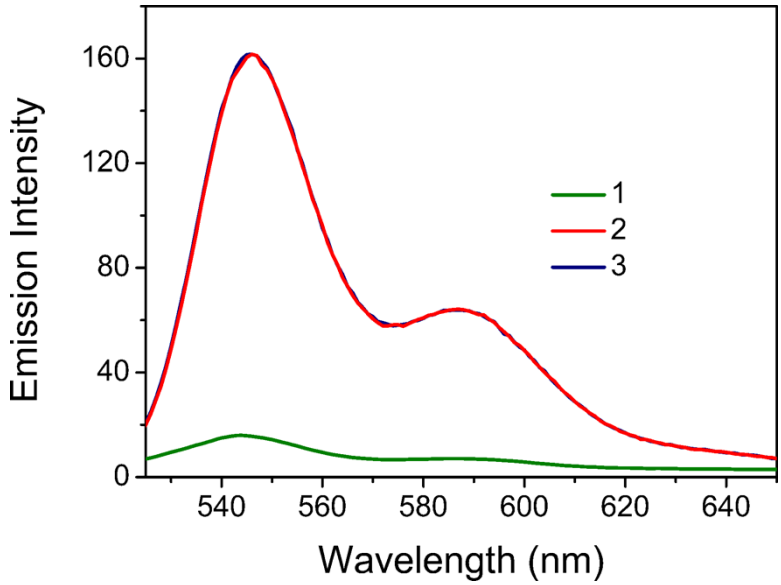

Fig. S5 Fluorescence spectra of the perylene probe mixed with Ag NPs (1), with Ag NPs and H_2O_2 (2), with Ag NPs, H_2O_2 and GOx (3). Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, perylene probe 160 nM, H_2O_2 1.0 μM, GOx 0.5 U/mL, respectively.

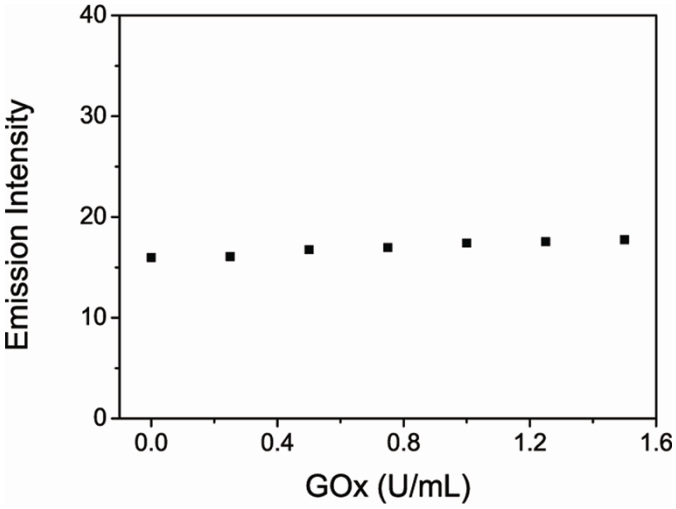

Fig. S6 Changes in emission intensity of the perylene probe at 545 nm with GOx concentration in the absence of glucose. Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, perylene probe 160 nM, GOx 0, 0.25, 0.5, 0.75, 1.00, 1.25, and 1.50 U/mL, respectively.

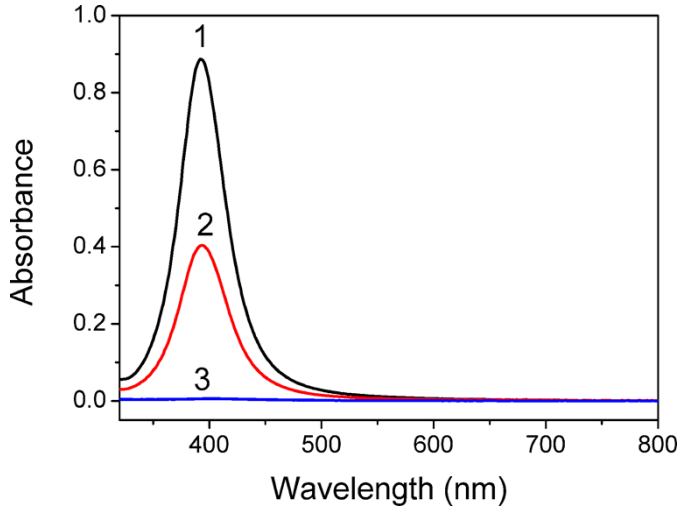

Fig. S7 Surface plasmon absorption spectra of the Ag NPs (1), and the NPs mixed with glucose of different concentrations [100 μM (2), 500 μM (3)]. Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, GOx 0.5 U/mL, respectively.

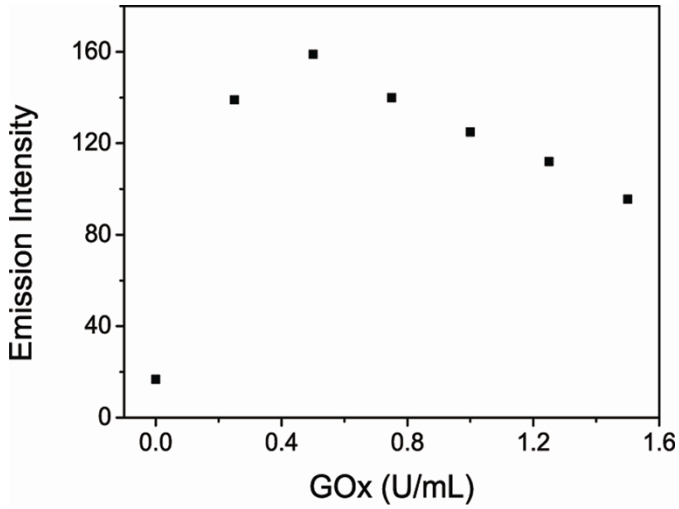

Fig. S8 Changes in emission intensity of the perylene probe at 545 nm with GOx concentration in the presence of glucose. Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, perylene probe 160 nM, glucose 500 μM, GOx 0, 0.25, 0.5, 0.75, 1.00, 1.25, and 1.50 U/mL, respectively.

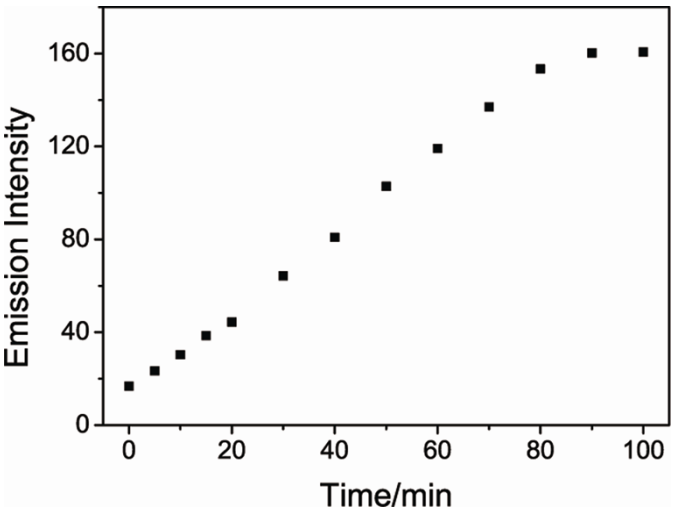

Fig. S9 Changes in emission intensity of the perylene probe at 545 nm with reaction time. Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, perylene probe 160 nM, glucose 500 μM, GOx 0.5 U/mL, respectively.

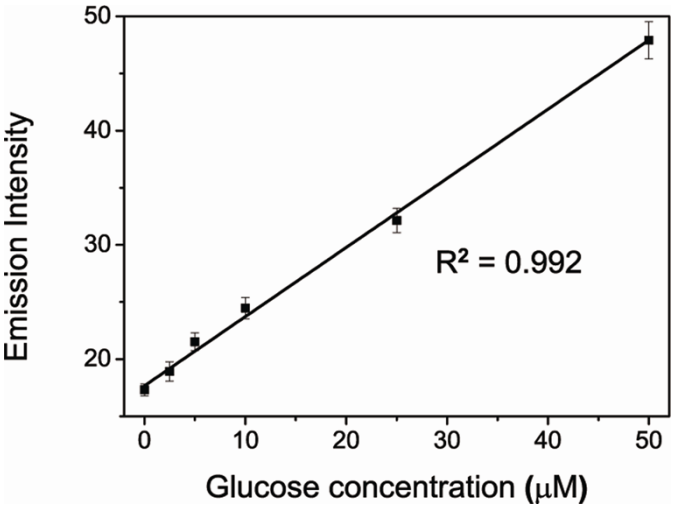

Fig. S10 Plot of the changes in emission intensity of the perylene probe at 545 nm against glucose concentration (0 – 50 μM). Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, perylene probe 160 nM, GOx 0.5 U/mL, glucose 0, 2.5, 5, 10, 25 and 50 μM, respectively.

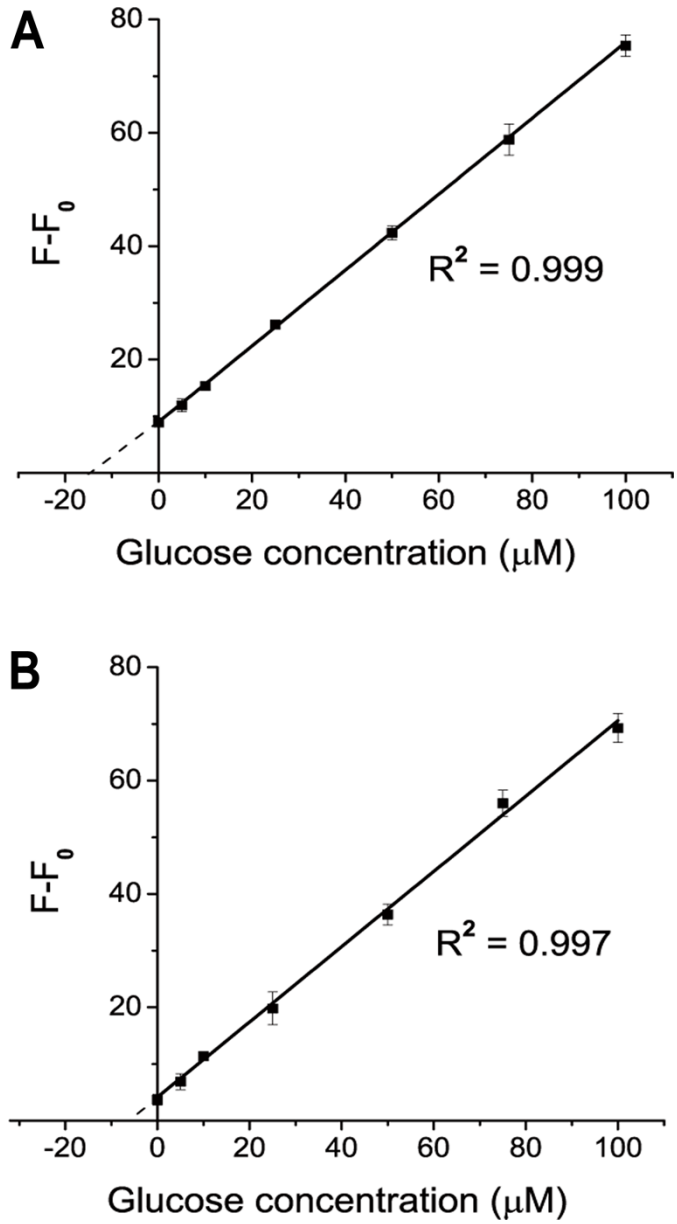

Fig. S11 Quantification of glucose concentration in human serum samples [S1 (A), S2 (B)]. Final concentrations: citrate buffer 5 mM (pH 5.5), Ag (0) 50.5 μM, perylene probe 160 nM, GOx 0.5 U/mL, glucose added 5, 10, 25, 50, 75 and 100 μM, respectively.