Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis of Enzyme Mimics of Iron Telluride Nanorods for the Detection of Glucose

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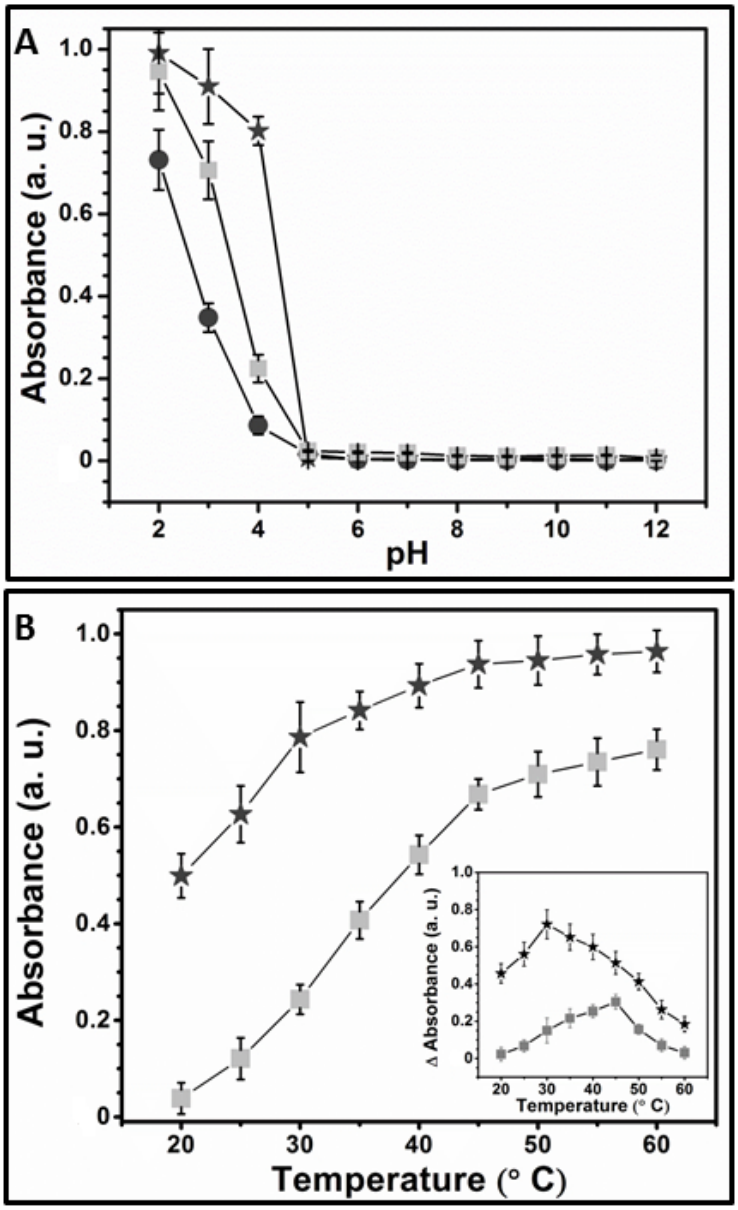

Fig. S1 Effects of pH and temperature on the catalytic activity of the Fe_3O_4 NPs and FeTe NRs for H_2O_2-mediated ABTS reaction. (A) pH and (B) temperature dependent response curves: ⋆ for FeTe NRs, ■ for Fe_3O_4 NPs, and ● for the control. Inset to (B) ΔA against temperature, where $\Delta A = A_{418\,nm}$ (FeTe NRs or Fe_3O_4 NPs) – $A_{418\,nm}$ (Blank). Other conditions are the same as in Fig. 2.

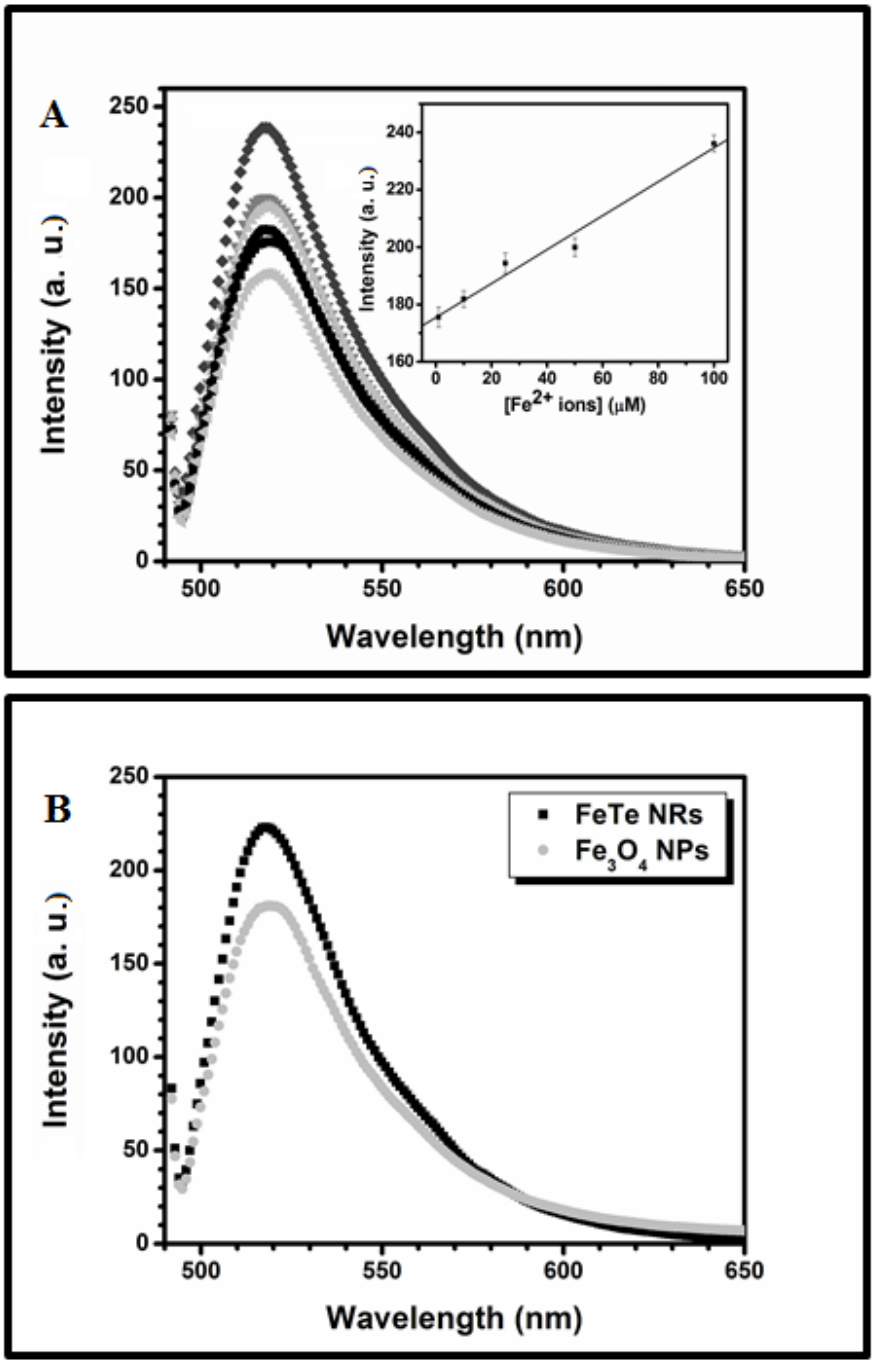

Fig. S2 Fluorescence spectra of FITC (0.1 mM) in the presence of (A) various concentrations of Fe^{2+} ions and (B) FeTe NRs and Fe_3O_4 NPs at 30 ºC. (A) FITC concentrations range from 0.5 to 100 µM. Inset is the linear range from 1 to 100 µM. Concentrations: Iodine solution (0.3 µM), Phosphate buffer: (10 mM, pH 6.4).

EXPERIMENTAL SECTION

Chemicals. Sodium dodecyl sulfate (SDS, 99%), hexadecyltrimethylammonium bromide (CTAB, 99%), iron (III) chloride hexahydrate (99%); acetic acid (99.8%), L(+)-ascorbic acid (99%), dopamine (99%) and iodine (99.5%) were purchased from Acros (Geel, Belgium). Tellurium dioxide powder (99.9%), hydrazine monohydrate (80%), and hydrogen peroxide (35%) were purchased from SHOWA (Tokyo, Japan). Iron oxide (Fe_3O_4) nanoparticles (98%), fluorescein isothiocyanate (FITC, 90%), GOx, ABTS (99.8%), β-D-glucose (99%), maltose (99%), D-fructose (99%), α-lactose (99%), epinephrine (95%) and iron (II) chloride tetrahydrate (99%) were purchased from Sigma Aldrich (St. Louis, Missouri, USA). Sodium acetate trihydrate (99%) was purchased from Merck (Madison, Wisconsin, Milwaukee, USA). Monosodium phosphate monohydrate (99%) and disodium phosphate heptahydrate (99%) were purchased from J. T. Baker (Phillipsburg, New Jersey, USA) and Janssen Chimica (Geel, Belgium), respectively. Horse radish peroxidase (HRP) was purchased from TCI (Tokyo, Japan). Ultrapure water was obtained using a Milli-Q ultrapure (18.2 MΩ-cm) system.

Preparation of Te NWs. Hydrazine (10 mL) was added slowly to a beaker containing tellurium dioxide (0.016 g) at room temperature under constant magnetic stirring. The solution changed color from colorless to blue after 120 min, indicating the formation of Te NWs (average length: 785 nm; average diameter: 16 nm). To terminate the reaction and stabilize the Te NWs, the mixture was diluted 10-fold with CTAB (10 mM).

Synthesis of FeTe NRs. Prior to use in the preparation of FeTe NRs, the as-prepared Te NWs was subjected to a centrifugation/wash cycle to remove most of the matrix (e.g., hydrazine). In a typical process for the synthesis of FeTe NRs, the Te NW pellet was re-dispersed in 10 mM CTAB. After 10 min, $FeCl_{3(aq)}$ (final concentration: 10 mM) was added to the mixture, which was then left at 60 °C for 1 h. The solution changed color from blue to yellow, indicating the formation of FeTe NRs. Then the FeTe NRs were subjected to three centrifugation/wash cycles to remove most of the matrices. Centrifugation was conducted at 15000 rpm for 10 min and ultrapure water (100 mL × 3) was used to wash the pellets. The pellets (FeTe NRs) were dried in air at ambient temperature (25 °C) prior to characterization and catalytic tests.

Characterization. A double-beam UV–Vis spectrophotometer (Cintra 10e, GBC) was used to measure the absorption spectra of the Te NWs and FeTe NRs. JEOL JSM-1230 and FEI Tecnai-G2-F20 transmission electron microscopes (TEM) were used to measure the sizes and shapes of the as-prepared Te NWs and FeTe NRs. The re-dispersed Te NWs and FeTe NRs were separately placed on formvar/carbon film Cu grids (200 mesh; Agar Scientific) and dried at ambient temperature. An energy

dispersive X-ray (EDAX) system (Inca Energy 200, Oxford) was used to determine the composition of the as-prepared NMs. Raman spectra were recorded using a Raman spectrometer (Dong Woo 500i, Korea) equipped with a 50× objective and a charge-coupled detector. The excitation wavelength was 532 nm and the spectral aperture was 50 μm. The signal collection time for each sample was 30 s. Fluorescence spectra were recorded using Cary Eclipse Spectrophotometer equipped with a Xenon lamp.

H_2O_2 Detection through Peroxidase Mimics of FeTe NRs and Fe_3O_4 NPs. To explore the possibility of using FeTe NRs as peroxidase mimics, the catalytic oxidation of the peroxidase substrate ABTS in the presence of H_2O_2 was tested. Briefly, ABTS (60 mM, 24 μL), FeTe NRs and Fe_3O_4 NPs (2.17 mg/mL, 10 μL), and different amounts of H_2O_2 (final concentrations 0.1–200 μM) were added into an acetate buffer solution (0.2 M, pH 4.0, 185 μL). The mixture was incubated at 30 ºC for 10 min, and then the FeTe NRs and Fe_3O_4 NPs were removed through centrifugation at 15000 rpm for 10 min. The supernatant was diluted by a factor of 10 with water prior to absorption measurement. In order to investigate the influence of incubation temperature on the catalytic activity of FeTe NRs and Fe_3O_4 NPs, reactions were conducted at various temperatures (20–60 ºC). We also studied catalytic reactions over a pH range 2.0–12.0 in acetate solutions (0.2 M). The activity of HRP (40 mM, 10 μL) toward ABTS in the presence of H_2O_2 at an optimized condition (30 ºC, pH 7.0) was investigated.

Detection of Released Fe^{2+} Ions from FeTe NRs and Fe_3O_4 NPs. A ferrous stock solution (10 mM) was prepared by dissolving iron (II) chloride in diluted hydrochloric acid solution (20 mM, 50 ml). The stock solution was used to prepare diluted standard Fe^{2+} solutions (0.5–100 μM) by appropriate dilution with 20 mM hydrochloric acid solution. FITC solution (0.1 mM) was prepared by dissolving the necessary weight of FITC in ethanol, which was then diluted with water to 1 μM. An iodine solution (0.3 μM) in ethanol was freshly prepared every time. To each 1.5-ml vial, FITC solution (1 μM, 100 μL), 600 μL of phosphate buffer solution (10 mM, pH 6.4), and standard Fe^{2+} solution (0.5–100 μM) were added to. To each of the mixture, iodine solution (0.3 μM, 90 μL) was added before dilution with ultrapure water (0.690 mL). The fluorescence intensity was then measured against a reagent blank at 515 nm with excitation at the wavelength 485 nm. The concentrations of the released Fe^{2+} ions from the FeTe NRs and Fe_3O_4 NPs were measured in a similar way to that for the standard Fe^{2+} solutions.

Detection of Glucose. Phosphate buffered saline (PBS, 220 μL, 10 mM, pH 7.0) solutions containing glucose (1– 500 μM) and GOx (6 μM) were incubated at 37 °C for 30 min. To the solutions, ABTS (60 mM, 24 μL), FeTe NRs stock solution (10 μL), and acetate buffer (0.2 M, pH 4.0, 800 μL) were added into. After each of the mixtures was incubated at 30 ºC for 10 min, the FeTe NRs were removed through centrifugation at 15000 rpm for 10 min. Each of the supernatant was diluted 10 times with water prior to

absorption measurement. To investigate the specificity of the present assay, 5-mM maltose, fructose, lactose, dopamine, epinephrine and ascorbic acid instead of glucose were used as controls.

Detection of Glucose in Blood Samples. 20 μL plasma was mixed with 10-μL acetonitrile, which was then diluted a hundred fold with ultrapure water prior to centrifugation. Aliquots (20 μL) of the pretreated plasma solution (supernatant) were then spiked with a standard glucose solution (20 μL; 10 to 90 μM). The spiked samples were then subjected to the detection of glucose by applying the present assay. This was followed by comparing the results obtained from conducting a commercial blood glucose electrochemical approach (Abbott Laboratories, Alameda, CA, USA).