Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

The phosphatase-like activity of zirconium oxide nanoparticle and its application in near-infrared intracellular imaging

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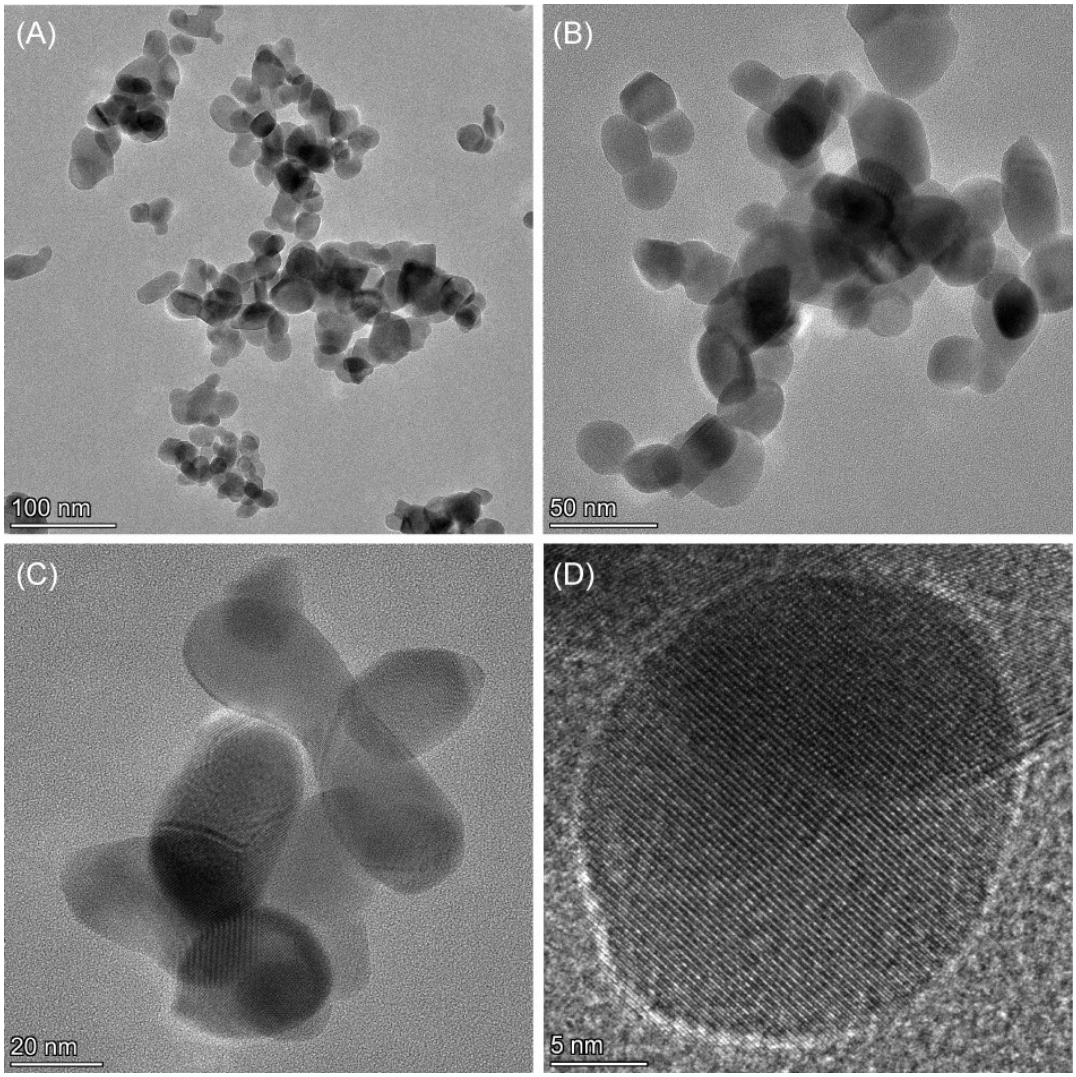

Fig. S1 The TEM images of ZrO_2 NPs under different magnification. Scale bars: (A) 100 nm; (B) 50 nm; (C) 20 nm; (D) 5 nm.

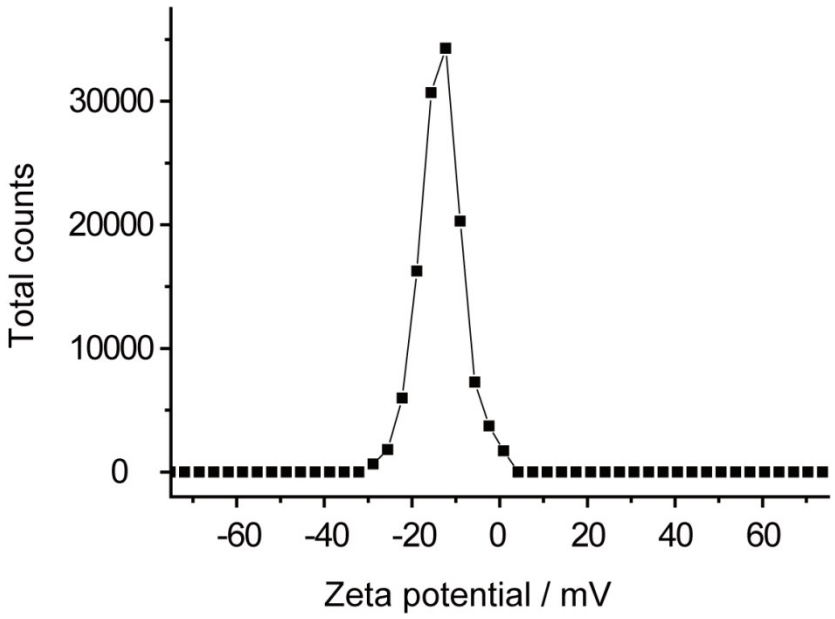

Fig. S2 The apparent zeta potential distribution of the ZrO_2 NPs.

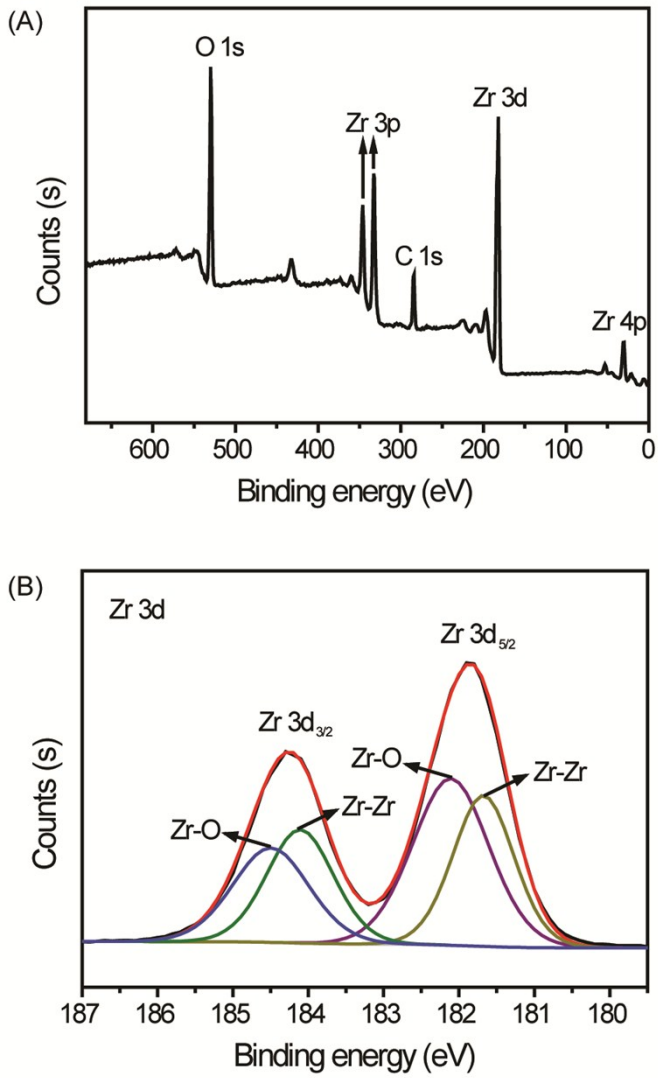

Fig. S3 (A) XPS survey spectrum of ZrO_2 NPs. (B) Zr 3d XPS spectra of the ZrO_2 NPs.

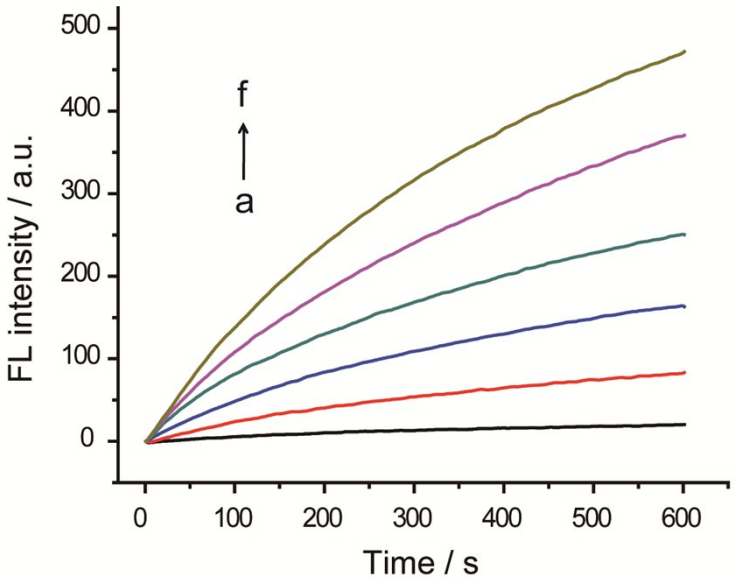

Fig. S4 The fluorescent kinetic curves of 5 μM 4-MUP in the presence of different concentrations of ZrO_2 NPs. From a to f: 0 μg/mL, 15 μg/mL, 30 μg/mL, 50 μg/mL, 80 μg/mL, and 100 μg/mL ZrO_2 NPs. The fluorescence emission at 455 nm were recorded under excitation at 360 nm

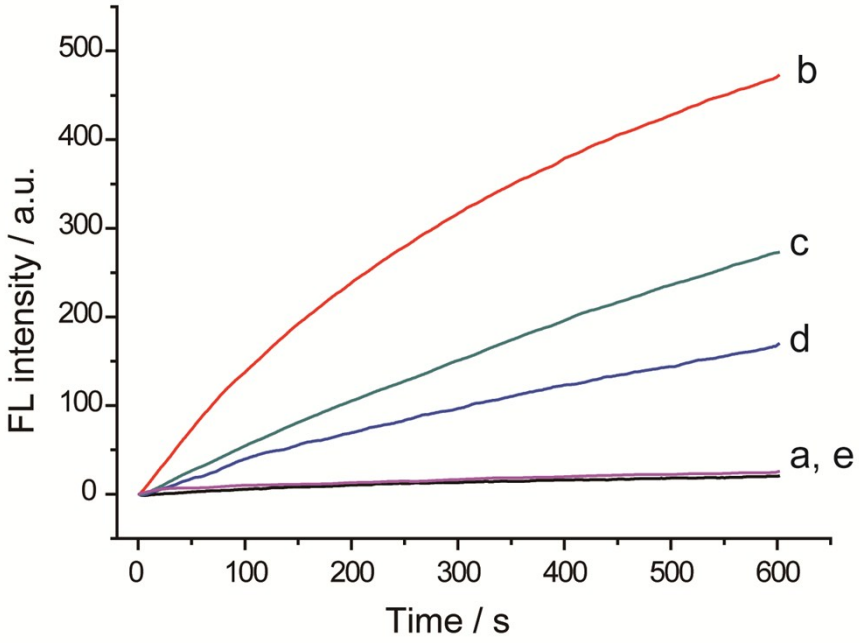

Fig. S5 The kinetic curves of 5 μM 4-MUP in the presence of 20 mM HEPES buffer (a), 100 μg/mL ZrO_2 NPs (b), 100 μg/mL $ZrOCl_2$ (c), 100 μg/mL $Zr(OH)_4$ (d), and the supernatant of 100 μg/mL ZrO_2 NPs after centrifugation (e).

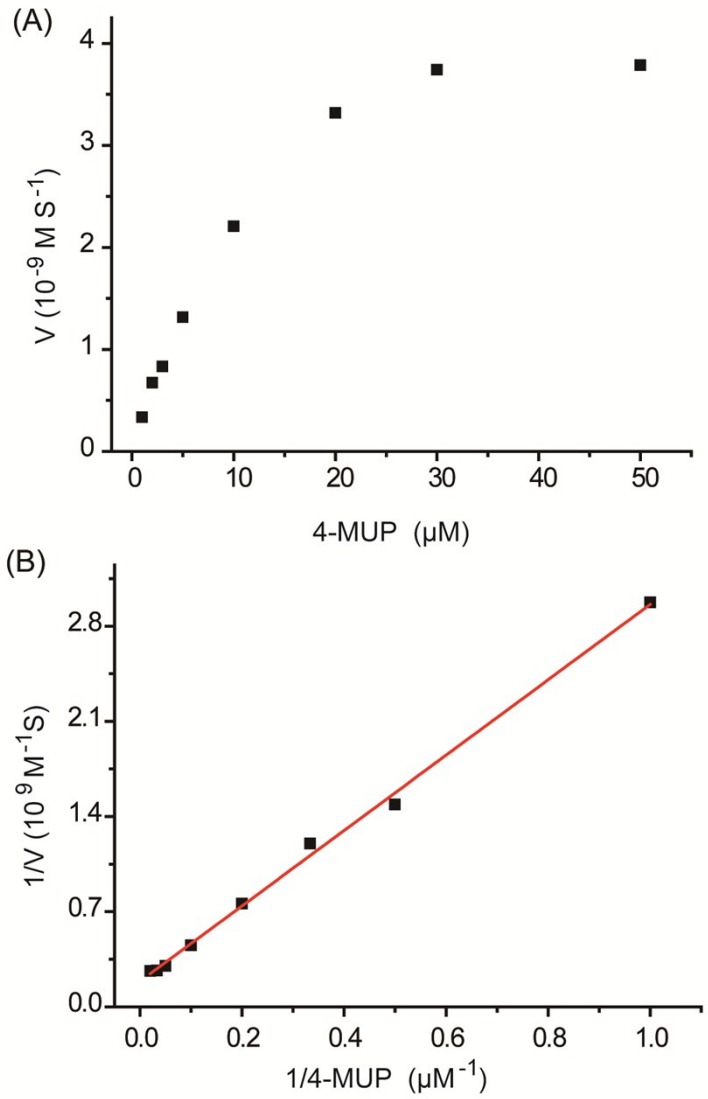

Fig. S6 (A) The Steady-state kinetic assays of ZrO_2 NPs at pH 8.5, the concentration of ZrO_2 NPs was 100 μg/mL.. (B) The Lineweaver-Burk plots of the double reciprocal of the Michaelis-Menten equations, which was obtained from the kinetic data of ZrO_2 NPs.

Table S1 Comparison of the kinetic parameters of ZrO_2 NPs with that of CeO_2 NPs and ALP (pH 8.5). K_m is the Michaelis-Menten constant, V_{max} is the maximal reaction rate, K_{cat} is the catalytic constant, $K_{cat} = V_{max}/[E]$, and $[E]$ is the concentration of catalyst. The kinetic parameters of CeO_2 NPs and ALP were obtained from our lab, which were calculated using the same protocol with ZrO_2 NPs. The concentration of ZrO_2 NPs was 1.94 nM (100 μg/mL), while the concentration of ALP was 0.18 nM (0.01 μg/mL) and the concentration of CeO_2 NPs was 0.34 μM (100 μg/mL).

Catalyst	Substrate	K_m / μM	V_{max} / M s^{-1}	K_{cat} /s^{-1}	K_{cat}/K_m [s^{-1} μM^{-1}]
ZrO_2	4-MUP	14.7	5.31×10^{-9}	2.74	0.19
CeO_2	4-MUP	16.5	2.76×10^{-8}	0.08	0.005
ALP	4-MUP	1.13	1.87×10^{-9}	10.39	9.19

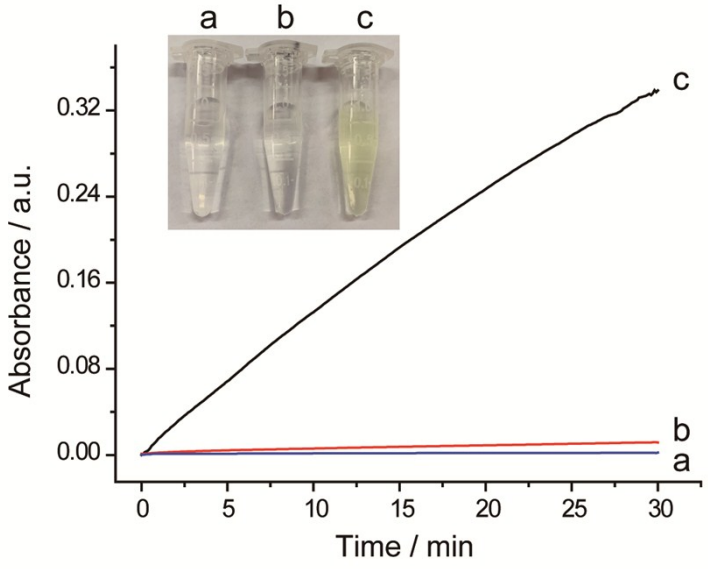

Fig. S7 The time-dependent absorbance changes of 20 mM HEPES buffer (pH 8.5) (curve a), 500 μM *p*-NPP (curve b), and 500 μM *p*-NPP in the presence of 100 μg/mL ZrO_2 NPs (curve c). The absorbance were measured at a wavelength of 405 nm. Inset: the corresponding images captured by a mobile phone.

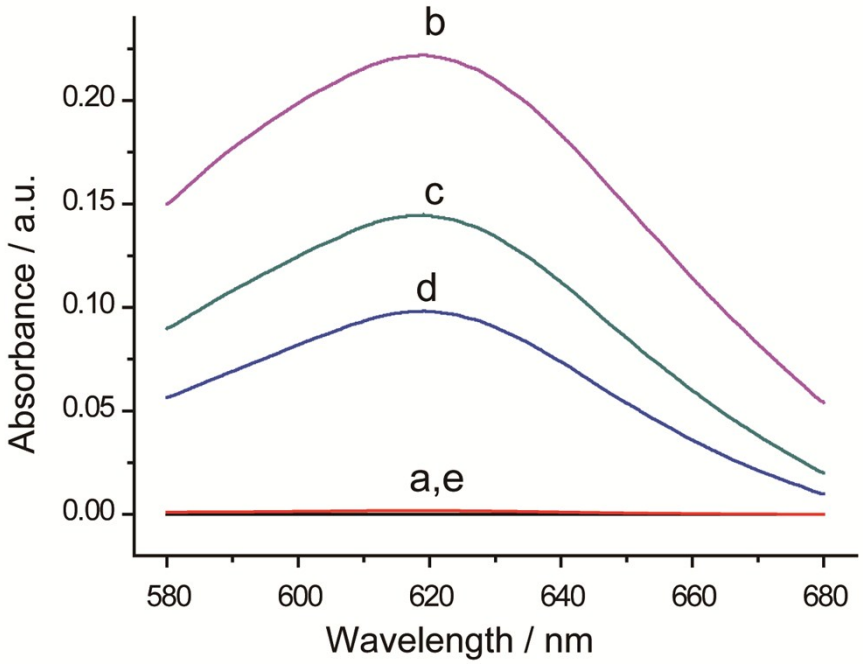

Fig. S8 The absorbance values of the malachite green assay in the presence of 20 mM HEPES buffer (curve a), 25 μM 4-MUP (curve b), 25 μM ATP (curve c), 25 μM *o*-phospho-L-tyrosine (curve d), and 25 μM DNA strand S1 (curve e). The malachite green solution was prepared according to the kit instructions, and the absorbance values at 620 nm represents the formation of free phosphate in the solutions.

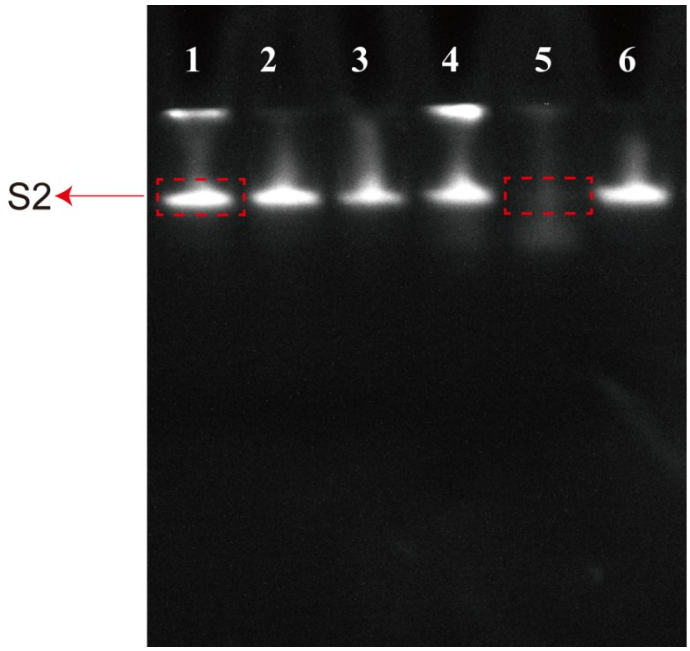

Fig. S9 The gel electrophoresis analysis of the cleavage of DNA by ZrO_2 NPs and CeO_2 NPs. Lane 1: DNA strand S_2 after incubated with 100 μg/mL ZrO_2 NPs at 25 °C; Lane 2: DNA strand S_2 after incubated with 100 μg/mL CeO_2 NPs at 25 °C; Lane 3: DNA strand S_2 after incubated in buffer at 25 °C; Lane 4: DNA strand S_2 after incubated with 100 μg/mL ZrO_2 NPs at 60 °C; Lane 5: DNA strand S_2 after incubated with 100 μg/mL CeO_2 NPs at 60 °C; Lane 6: DNA strand S_2 after incubated in buffer at 60 °C.

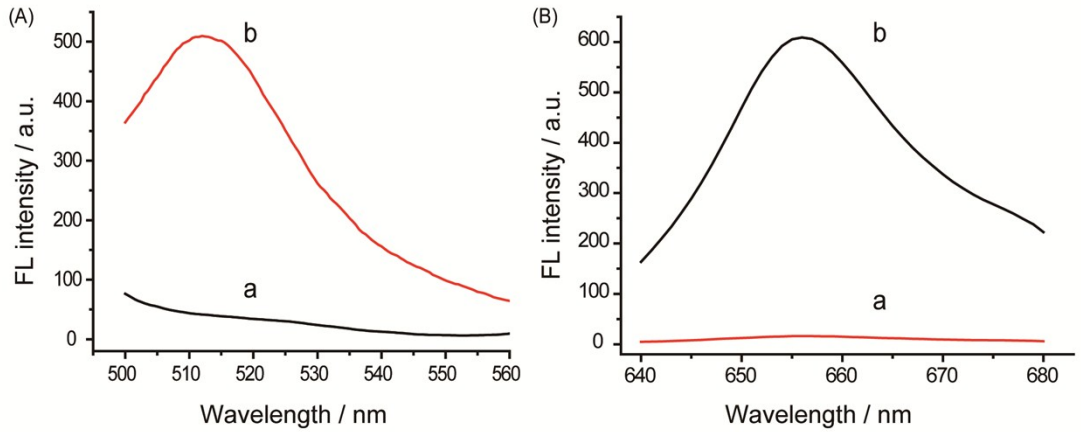

Fig. S10 (A) The fluorescent spectra of 5 μM FDP in the absence (curve a) and presence (curve b) of 100 μg/mL ZrO_2 NPs. The fluorescent spectra were performed by using a excitation wavelength of 490 nm. (B) The fluorescent spectra of 5 μM SunRed phosphate in the absence (curve a) and presence (curve b) of 100 μg/mL ZrO_2 NPs. The fluorescent spectra were carried out by using a excitation wavelength of 620 nm.

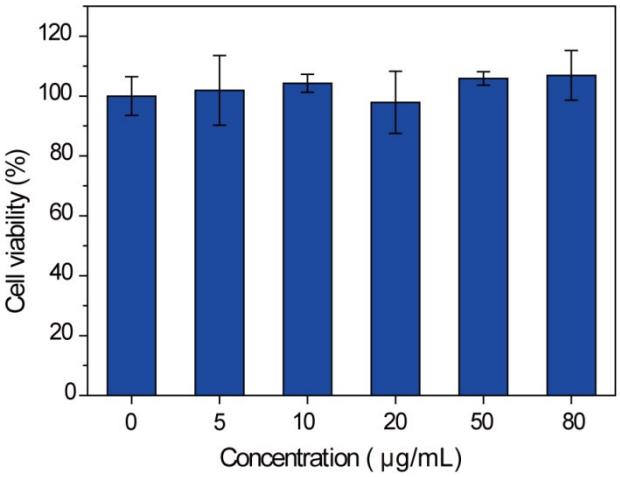

Fig. S11 Cytotoxicity of different concentrations of ZrO_2 NPs after incubation with HeLa cells for 24 h. The error bars represent the standard deviation of three measurements.