Electronic Supplementary Information

Experimental section

Materials

Ct-DNA and 3, 3′, 5, 5′-Tetramethylbenzidine (TMB) Substrate System was purchased from Sigma-Aldrich. Cerium nitrate hexahydrate (99.9%, $Ce(NO_3)_3 \cdot 6H_2O$), acetate sodium buffer, Polyvinylpyrrolidone (PVP, K30), and Hydrogen peroxide solution (30%, H_2O_2) were obtained from Aladdin. All the reactants were analytical grade and were used without further purification or modification. Deionized water and absolute alcohol were used throughout.

The synthesis of CeO_2 nanocrystals (P1)

60.8 mg cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) were dissolved in 14 ml ethanol-water solution, and 62.0 mg PVP were added slowly, the mixture was stirred for 10 minutes to dissolve completely, and then stirred for 20 min. The clear solution was transferred into a PTFE reactor of 25 mL, heated for 24 h at 180 ℃. When the autoclave was cooled at room temperature, the light purple products were collected and washed with deionized water and absolute alcohol two times sequentially. Finally, the products were dried at 60 ℃ for 4 h.

The synthesis of DNA doped CeO_2 nanocrystals (P2–P7)

60.8 mg cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) were dissolved in 14 ml ethanol-water solution, and 62.0 mg PVP were added slowly, the mixture was stirred for 10 minutes to dissolve completely, and then 2 mL DNA solution of different concentrations and types (36 $\mu g \cdot mL^{-1}$, 90 $\mu g \cdot mL^{-1}$, 180 $\mu g \cdot mL^{-1}$, 270 $\mu g \cdot mL^{-1}$, 360 $\mu g \cdot mL^{-1}$ ct-DNA and 360 $\mu g \cdot mL^{-1}$sperm DNA) was added to the above solution. The mixture was stirred for 20 min. There is some floc precipitate in the solution, all were transferred to the PTFE reactor, heated for 24 h at 180 ℃. When the autoclave was cooled at room temperature, the light purple products were obtained.

Instrumentation and characterization

UV-Vis absorption and catalytic experiment were conducted on a U-3310 UV-Vis

Spectrophotometer (Pgeneral, Hitachi). The phase purity of the sample was examined by using a Bruker D8 ADVAHCL* X-ray diffractometer with Cu-Kα radiation (λ= 0.15418 nm) at 40 mV and 40 mA (2θ from 2 ° to 80 °). The step value is 0.1 °. For XRD analysis, approximately 15 mg of the sample was prepared. Laser Raman Spectra (LRS) were recorded on a Renishaw Invia Raman Microscope with Ar^+ radiation (532 nm). The laser light was focused onto the samples by using a microscope equipped with a 6100-objective lens. The micro-structure and morphology of the products were characterized using a transmission electron microscope (TEM, JFEI Electron optics-GZF2.0), a field-emission scanning electron microscope (FE-SEM, Hitachi) equipped with an energy-dispersive. X-ray spectrometer (EDS) and a high-resolution transmission electron microscope (HRTEM, JEM-2100, 200 kV). The elements of the samples were determined by element analyzer (EI) with a VarioEL III analyzer (Germany, Eloman).

Standard assay for the peroxidase catalytic activity study

The catalytic reactions were performed at 25 ℃ adding 45 μL (2.7 mg·ml^{-1}) P1-P6 samples in a reaction volume containing with 300 μL (800 mM) TMB as a substrate and 150 μL H_2O_2 (80 mM). To compare the substrate selectivity, H_2O_2 were also used as part of the experiment. The substrates can be oxidized by H_2O_2 in the presence of a catalyst to produce a coloured product. For the TMB substrate, the corresponding absorbance at λ=639 nm was measured continuously within 500 seconds using P1-P6. By varying the concentration of the DNA doped CeO_2 nanoparticles catalyst (36 μg•mL^{-1}, 90 μg•mL^{-1}, 180 μg•mL^{-1}, 270 μg•mL^{-1}, 360 μg•mL^{-1} ct-DNA), absorbance of the TMB substrate was measured.

Note: P1-P6 samples was dissolved in 1000 μL sodium acetate buffer (100 mM, pH=4)

XRD results

The Scherrer equation, in X-ray diffraction and crystallography, is a formula that relates the size of sub-micrometre particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern. It is named after Paul Scherrer. It is used in the determination of size of particles of crystals in the form of powder.

The Scherrer equation can be written as:

$$D = \frac{K\lambda}{\beta COS\theta}$$

where:

D is the mean size of the ordered (crystalline) domains;

K is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite;

λ is the X-ray wavelength;

β is the line broadening at half the maximum intensity , after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as Δ(2θ);

θ is the bragg angle.

The crystalline size of P1-P6 are all around 12 nm calculated on (111) peak using Scherrer's formula. (P1-P6 : 13.35 nm,12.91 nm,13.19 nm nm,13.18 nm,12.77 nm and 11.41nm)

Additional Figures and Data

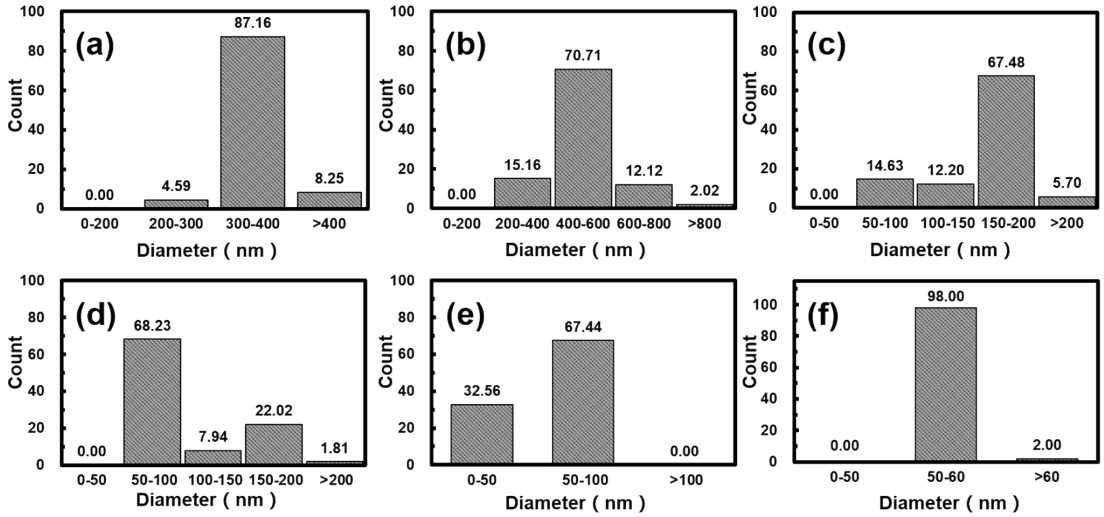

Fig. S1 The corresponding diameter distribution of the as-prepared samples: (a) P1, (b) P2, (c) P3, (d) P4, (e) P5 and (f) P6.

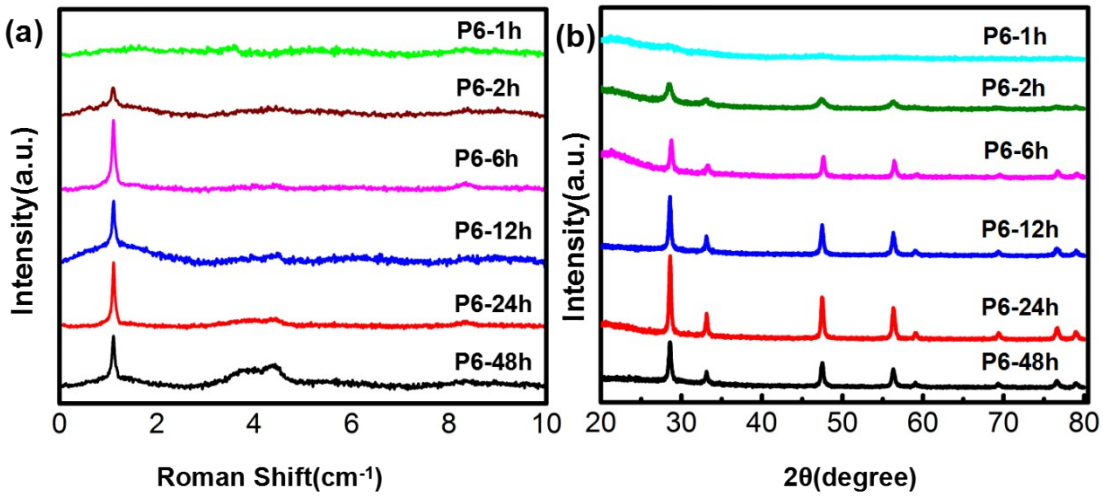

Fig. S2 Raman spectra (b) and XRD (a) of P6 samples at different reaction time.

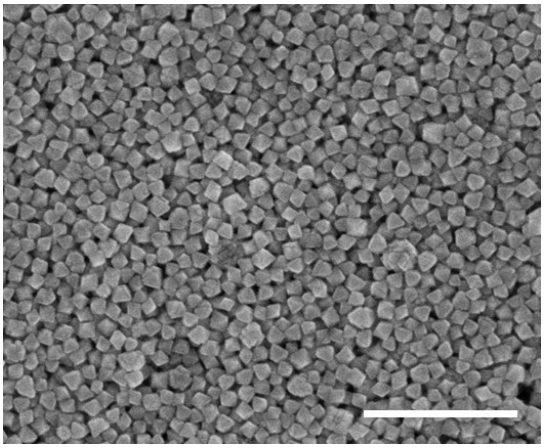

Fig. S3 SEM images of samples synthesized with herring sperm DNA. (scale bar: 500 nm.)

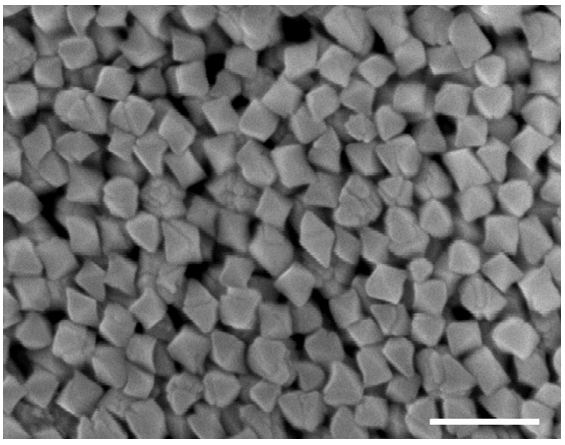

Fig. S4 SEM images of samples synthesized with 720 μg·mL^{-1} ct-DNA. (scale bar: 200 nm.)

Name	Content[%]		
	N	C	H
CeO_2	0.312	1.874	0.218
CeO_2@DNA	0.475	2.594	0.336

Table 1 Element analysis of P1 and P6.

Element	Content[%]		
	N	C	H
theoretical	0.229	0.588	0.071
actual	0.163	0.720	0.118

Table 2 Element analysis of P1 and P6. Theoretical value was calculated assuming that DNA was completely doped into nanocrystals and actual result was obtained from experimental data.