Electronic Supplementary Material (ESI) for Dalton Transactions.

Magnetically internal heating induced high perfermance Prussian blue nanoparticles preparation and excellent catalytic activity

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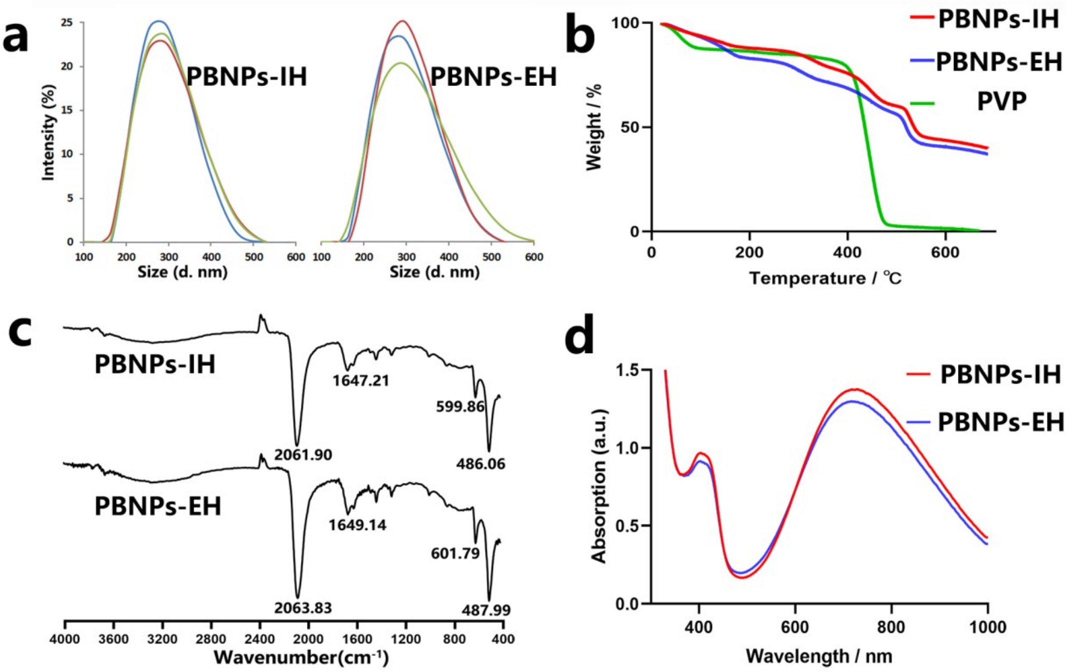

Fig. S1 (a) Hydrodynamic size distribution profiles of PBNPs-IH and PBNPs-EH; (b) Thermogravimetric curve of PBNPs and PVP; (c) FTIR spectrum of PBNPs; (d) UV-VIS absorption spectrum of PBNPs.

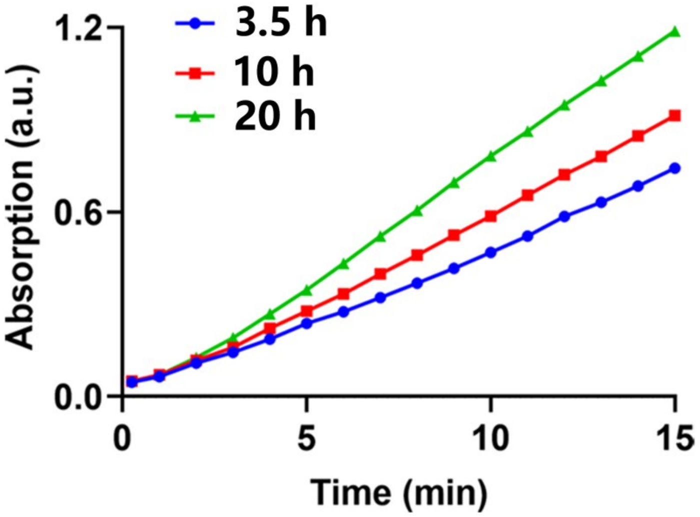

Fig. S2 POD-like activity of PBNPs undergoing different ripening times.

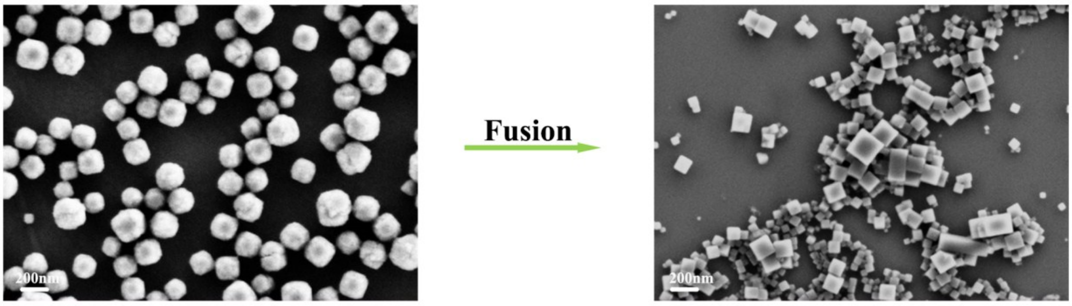

Fig. S3 The transformation process from mesocrystals to single crystal of PBNPs by a self-driving fusion over time.

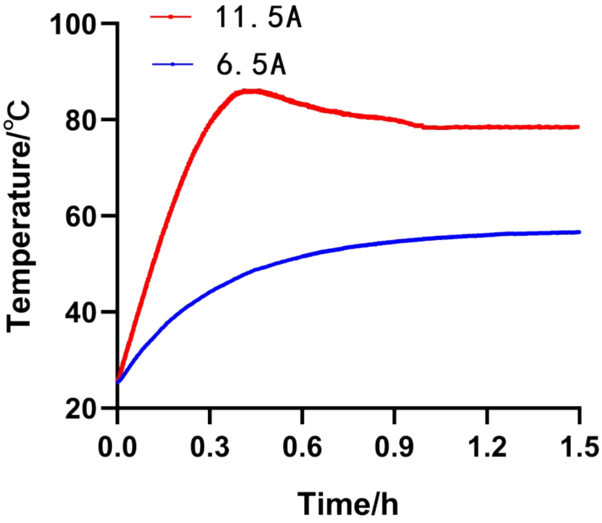

Fig. S4 The temperature curve of reaction system with time under 6.5A and 11.5A output current intensity.

Experimental Section

Materials and reagents

Polyvinylpyrrolidone (PVP, K30) and potassium ferricyanide ($K_3[Fe(CN)_6]$) were obtained from Aladdin Chemical Reagent Company (China). Hydrochloric acid (HCl), hydrogen peroxide (H_2O_2) and dimethyl sulfoxide (DMSO) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). 3,3',5,5'-Tetramethylbenzidine (TMB) was from Sigma-Aldrich (USA). Solutions were prepared with deionized water (>18.2 MΩ.cm, Ulupure, China).

Synthesis of PBNPs

PBNPs were prepared by an alternating magnetic field (AMF)-assisted synthetic approach (schematically illustrated in Scheme. 1). Firstly, 750.0 mg PVP and 27.5 mg $K_3[Fe(CN)_6]$ were dissolved simultaneously in 10 ml deionized water under vigorous stirring. In this process, partial Fe ion could be coordinated to the amide unit in PVP. Afterwards, pH of the resulting homogeneous solution was adjusted to 2.0 with hydrochloric acid to facilitate the release of Fe^{3+} from $[Fe(CN)_6]^{3-}$ during the preparation process. The obtained reaction precursor solution was placed in the center of a coil of an electromagnetic induction heating apparatus (Shuangping SPG-06-Ⅳ, China). The oscillating frequency of electromagnetic induction heating device and the coil diameter were 1355 KHz and 3 cm respectively. The output current was adjusted to 6.5 A or 11.5 A. The reaction was carried out for 10 h. The product was washed three times with a mixed solvent composed of ethanol and water (2:1) to remove the redundant PVP, $[Fe(CN)_6]^{3-}$, K^+, CN^-, H^+ and Cl^-. After freeze-drying for 24 h, PVP-modified Prussian blue nanoparticle, hereafter called PBNPs-IH (PBNPs prepared by magnetically internal heating synthesis strategy), were obtained. Furthermore, another PBNPs-EH (PBNPs synthesized by conventional external heating method) was also prepared by the same method as described above except that it was heated in a water bath of 80°C.

Characterizations of PBNPs

The micro-morphology of the prepared PBNPs was investigated by transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). High-resolution TEM (HRTEM) and selected area electron diffraction (SAED) tests were also executed to characterize the crystallinity. The crystal structure of PBNPs was further evaluated using a X-ray diffraction analyzer (XRD, Thermo X'TRA, USA) with Cu Kα radiation (λ, 1.5405 Å) at room temperature. The dispersibility of nanoparticles was measured by scanning electron microscope (SEM, Ultra Plus, Zeiss, Germany). The polydispersity index (PDI) and hydrodynamic diameter of PBNPs were recorded using dynamic light scattering (DLS, Zeta Plus, Brookhaven, USA). Weight loss curve of PBNPs during heating was provided by thermogravimetric analyzer (Pyris 1 DSC, PerKinElmer). Fourier transform infrared spectra (FTIR) were obtained in an infrared spectrometer (AVATAR 360, Nicolet, USA). Ultraviolet-visible (UV-VIS) absorption spectra of samples were performed on an UV-VIS-NIR spectrophotometer (UV-3600, Shimadzu, Japan). The concentration of PB was measured by inductively coupled plasma mass spectrometry (ICPS, Optima 5300DV, PE) and UV-VIS-NIR spectrophotometer, respectively. The temperature change of the reaction solution during the preparation was recorded by an optical fiber spectrometer (FISO UMI 4, Canada).

The magnetic properties measurement of PBNPs

The measurement of saturation magnetizations (M_s) was carried out via a vibrating sample magnetometry (VSM, Lakeshore 7407,USA) under a magnetic field of 5000 Oe and temperature of 5.0 K. Since the saturation magnetization was calculated by unit quantity (per gram) of PB, the content of magnetic component is equivalent for PBNPs-IH and PBNPs-EH during the determining process. The residual solvent was not used for the calculation of saturation magnetization of PBNPs. T_1-weighted magnetic resonance images (MRI) of PBNPs with a range of concentrations 1, 0.5, 0.25, 0.125 and 0.0625 mM were taken on a 3.0 T MR scanner (Verio, Siemens, Germany).

The catalytic activity determination of PBNPs

The peroxidase-like activity was evaluated using 3,5,3',5'-tetramethylbenzidine (TMB) as a substrate and hydrogen peroxide as an oxidant in acetate buffer solution (pH 3.6) at room temperature. During reaction process, the optical density (OD) was read by a Microplate Reader (Model 680, BIO-RAD, USA) at a wavelength of 650 nm to imply the catalytic activity. Typically, 50 μL PBNPs solution (6 μg mL^{-1}), 50 μL TMB solution (in DMSO, 10 mg mL^{-1}) and 150 μL H_2O_2 (30%, v/v) were sequentially added to 1000 μL reaction buffer solution (0.2 M HAc-NaAc, pH 3.6) in a 24-well plate. Then the OD value was immediately recorded every minute for 15 min, which were drawn to form a catalytic curve of PBNPs. The reaction rates were calculated as the following equation:

$$V = \frac{\Delta A / \Delta t}{\varepsilon \times l}$$

Where ε is the molar absorption coefficient of the colorimetric substrate, which is typically maximized at 39,000 M^{-1} cm^{-1} at 650 nm for TMB; l is the path length of light traveling in the plate (cm); A is the absorbance; and ΔA/Δt is the initial rate of change in absorbance at 650 nm.

The catalase-like activity assays were conducted by determining the generated oxygen using a specific oxygen analyzer (Multi 3510 IDS, Germany) at room temperature. 1 mL 50 μg mL^{-1} PBNPs solution and 0.5 mL 30% H_2O_2 solution were successively added to 13.5 mL 0.2 M PBS buffer solution (NaH_2PO_4- Na_2HPO_4, pH 7.4) under slightly stirring with 800 rpm. The generated O_2 content (unit: mg L^{-1}) was measured every minute for 3 min. The reaction rates during 60s were calculated as the following equation:

$$V = \frac{\Delta C / \Delta t}{Mr}$$

Where ΔC/Δt is the rate of oxygen generation within 60s; Mr is the Relative molecular mass of O_2, which is 32 g mol^{-1}.

The formation mechanism of PBNPs

The growth process of PBNPs synthesized by conventional external heating method has been reported to be a non-classical crystallization. However, the formation mechanism of PBNPs prepared by magnetically internal heating synthesis strategy still needs to be further explored because of the special growth condition induced by alternating-current magnetic field. In this study, the generation process was investigated by time-dependent TEM images at the early growth stage. In addition, through adjusting the output current intensity during the reaction, and monitoring the temperature of the reaction system and the generation rate of product, some key factors affecting the growth of PBNPs were revealed.

Statistical analysis

The data obtained were expressed as means ± SD (standard deviation). Statistical analysis was performed using Student’s t-test for two groups. The nanocatalytic experiments were conducted in sextuplicate.