Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Large-scale synthesis of organometallic polymer flowers with ultrathin petals for hydrogen peroxide sensing

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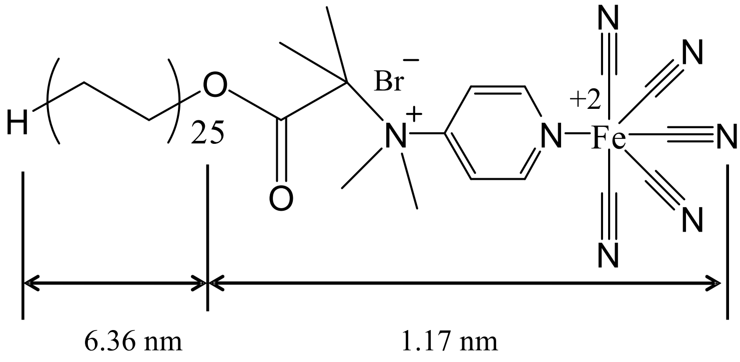
Materials

Polyethylene terminated with [Fe(II)$(CN)_5$(4-(dimethylamino)-pyridine)] (PE-Fe) were synthesized previously in our lab.[1] Polyethylene (PEO, M_n=400 g/mol, 1000 g/mol, 2000 g/mol, 4000 g/mol, 8000 g/mol, 10000 g/mol, 20000 g/mol, respectively), poly(propylene oxide) (PPO, M_n=1000 g/mol). poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymer (M_n=14600 g/mol, $E_{126}P_{61}E_{126}$, the subscripts denote the number of repeating units), *para*-xylene, $Fe(NO_3)_3$ and methanol were all purchased from Aldrich and used as received without further purification.



Scheme S1 Chemical structure of PE-Fe. The length of fully extended PE chain was estimated to be 0.2544 nm × 25 = 6.36 nm by using ChemBioOffice 2010. Therefore, the length of fully extended PE-Fe was 6.36 nm + 1.17 nm = 7.53 nm.

Effect of PPO fractions on the morphology of PE-PB particles

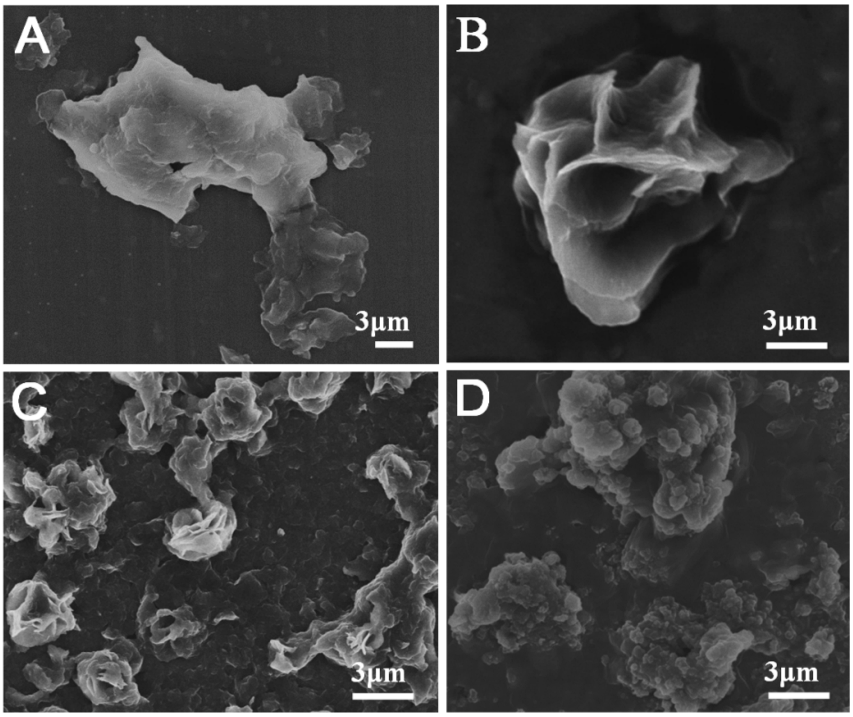


Fig. S1 Scanning electron microscopy (SEM) images of PE-PB particles at various weight ratios of poly(propylene oxide) (PPO) to PE-Fe (A) 0:1, (B) 0.2:1, (C) 0.5:1, (D) 2:1.

Isothermal crystallization kinetics of PE-Fe in xylene

The relative degree of crystallinity can be evaluated according to the equation:

$$X(t) = Q_t / Q_\infty = \int_0^t (dH/dt)dt \Big/ \int_0^\infty (dH/dt)dt \qquad \text{(S1)}$$

where Q_t and Q_∞ are the heat generated at time t and infinite time, respectively, and dH/dt is the heat flow rate. The plots of relative degree of crystallinity against crystallization time at 46 °C for PE-Fe and PE-Fe/PPO are shown in Fig. S2. It is obvious that crystallization of PE-Fe/PPO is slower than those of pristine PE-Fe. Crystallization halftime ($t_{1/2}$) for PE-Fe/PPO was 0.45 min, double of that for PE-Fe (0.21 min), showing slower crystallization rate in contrast to PE-Fe. This indicated that crystallization of PE-Fe was hindered in the presence of PPO.

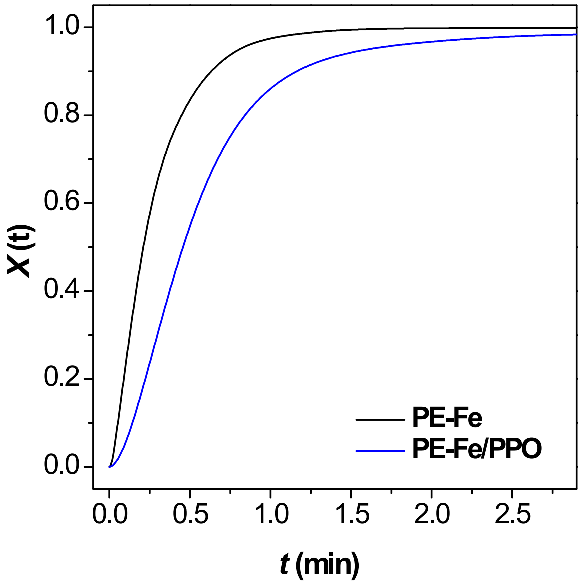


Fig. S2 Plots of relative degree of crystallinity against crystallization time at 46 °C for PE-Fe and PE-Fe/PPO.

The isothermal crystallization kinetics can be analyzed in terms of Avrami theory:[2, 3]

$$1 - X(\mathrm{t}) = \exp(-K t^{\mathrm{n}}) \tag{S2}$$

$$\ln[-\ln(1-X(t))] = \ln K + n \ln t \tag{S3}$$

where K is the crystallization rate constant, and n is Avrami exponent whose value is dependent on the mechanism of nucleation and the form of crystal growth. The crystallization rate constant K and Avrami exponent n can be obtained from the intercept and slope from the lineal region of the plots of $\ln[-\ln(1-X(\mathrm{t}))]$ against $\ln t$, respectively, as shown in Fig. S3. The values of n and K are summarized in Table S1. The values of n for PE-Fe and PE-Fe/PPO were 1.30 and 1.58, respectively, illustrating quasi-two-dimensional crystallization with heterogeneous nucleation. Moreover, the crystallization rate constant, K, of PE-Fe/PPO was much lower than that of PE-Fe, indicating a slower crystallization rate. These are consistent with the results of crystallization halftime.

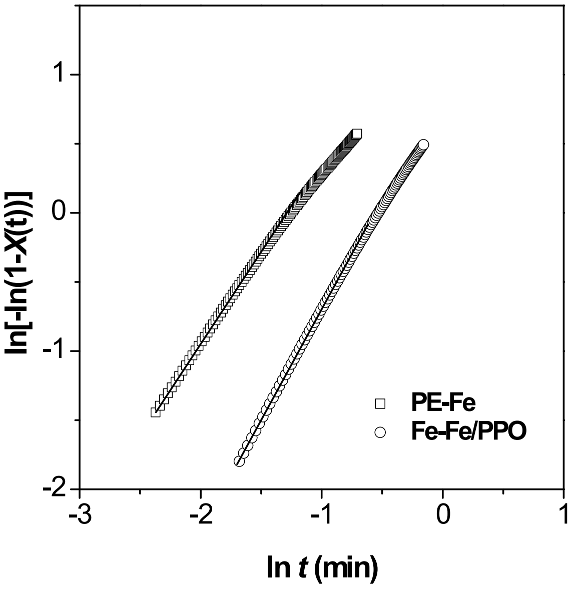


Fig. S3 Plots of ln[-ln(1-*X*(*t*))] versus ln*t* for PE-Fe and PE-Fe/PPO at 46 °C.

Table S1 Isothermal crystallization parameters for PE-Fe and PE-Fe/PPO.

sample	n	K	$t_{1/2}$ (min)
PE-Fe	1.30	5.27	0.21
PE-Fe/PPO	1.58	2.45	0.45

Amperometric performance of PB particles and bare electrodes

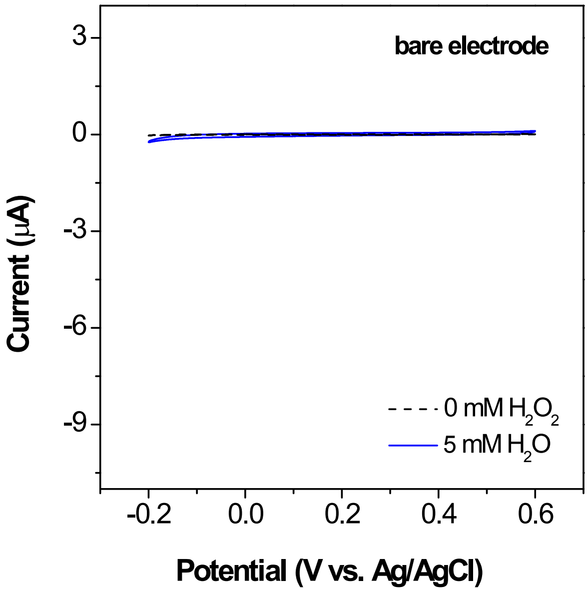


Fig. S4 Cyclic voltammogram of bare glassy carbon electrode in 20 mM phosphate buffer solution in the absence (dashed curves) and the presence of 5 mM H_2O_2 (solid curves). Scan rate: 50 mV s^{-1}, under N_2.

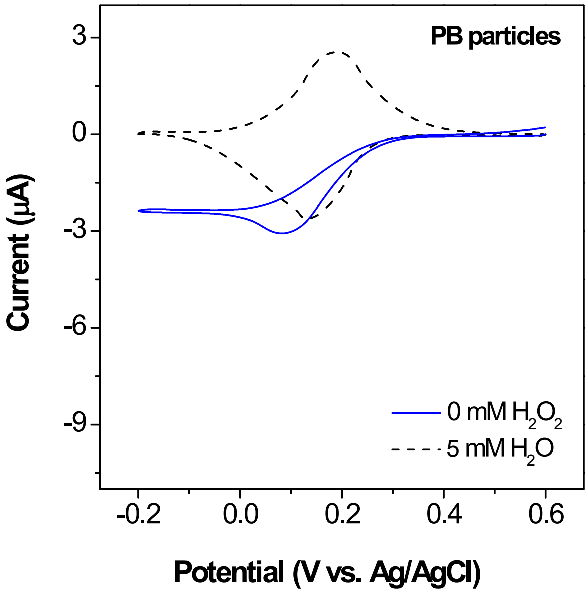


Fig. S5 Cyclic voltammogram of conventional PB particles decorated electrode in 20 mM phosphate buffer solution in the absence (dashed curves) and the presence of 5 mM H_2O_2 (solid curves). Scan rate: 50 mV s^{-1}, under N_2.

1 S. P. Bao, T. T. Liu, G. D. Liang, H. Y. Gao, F. M. Zhu and Q. Wu, *Chem. Eur. J.*, 2012, **18**, 15272−15276.

2 M. Avrami, *J. Chem. Phys.*, 1939, **7**, 1103-1112.

3 A. Jeziorny, *Polymer*, 1978, **19**, 1142-1144.