Short Communication

Thermo-responsive polymer micelle-based nanoreactors for intelligent polyoxometalate catalysis

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ABSTRACT

A series of polymer micelle-based nanoreactor containing polyoxometalates and poly(N-isopropylacrylamide)-block-poly(L-lysine) (PNIPAM-b-PLys-POM) have been successfully constructed. By adjusting the molar ratio of NIPAM/Lys, the temperature-depend catalytic activity of PNIPAM-b-PLys-POM towards catalytic wet hydrogen peroxide oxidation can be controlled. This work highlights the potential of using thermo-responsive micelles as a platform for developing smart catalyst system.

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1. Introduction

Stimuli-responsive recyclable catalysts, namely "smart" catalysts, have gained increasing attention in recent years [1]. Polymeric micelles are useful functional assemblies due to their well-defined phase-separated core–shell structure. The uses of micelle formed by amphiphilic copolymers in the stabilization of metal nanoparticles have been extensively studied and some metal-functionalized micelles have been utilized in a range of catalysis reactions such as hydrogenations, oxidations, reductions, and Heck reactions [2,3]. Although these catalytic systems are effective for many reactions, the colloidal nature of the catalyst sites and the difficulty in recycling of catalysts have largely limited their further development and applications. To improve the performance of the micelle-based catalysis system, combing metal nanoparticles with stimuli-responsive polymeric micelles may generate novel functions in reaction processes [4].

Polyoxometalates (POMs), the oxo-clusters of early transition metals in their highest oxidation states, are extensively used as homogeneous and heterogeneous catalysts [5]. Traditionally, to overcome the disadvantages of the homogeneous POM-catalytic systems including weak thermal stability, low surface area and separation problems from reaction, many measures have been taken by supporting or encapsulating them on suitable materials [6]. However, few studies had drawn the attention to the controllable and recyclable catalysis field [7].

Catalysts combined with thermo-responsive polymers have attracted much interest to date. Typical thermo-responsive polymers, such as poly (N-isopropylacrylamide) (PNIPAM), poly (N, N-diethylacrylamide) (PDEAM) and their derivatives, undergo sharp and reversible phase transitions at their lower critical solution temperature (LCST), resulting in special solubility behavior in aqueous solutions. Using thermo-responsive polymers to load metal particles or to combine them with organic molecules to prepare "smart" catalysts may switch on and off the catalytic activities by adjusting the temperature below or above the LCST. A thermo-responsive nanoreactor for catalyst shows a homogenerous nature at a temperature below the LCST, whereas phase separation occurs at a temperature above the LCST, which can be easily recycled from the solution for the next cycle [8]. Hiromi Hamamoto et al. [9] reported a networked PNIPAAm-PW$_{12}$O$_{40}$ catalyst, which showed an increase in catalyst affinity for organic substrates in water at higher temperatures and a loss of affinity at lower temperatures, allowing easy separation of the organic products upon completion of the reaction. This kind of catalyst could be applied in organic/aqueous two-phase system. With the developments of green chemistry and biological engineering, the aqueous-phase catalysis system has drawn much attention during the last decades, and the exploitation of smart catalyst which can be implemented in an aqueous solution became a useful strategy to achieve the goal of green chemistry [10].

In this report, a series of polymer micelle-based nanoreactor containing molybdovanadophosphoric polyoxometalates and poly(N-isopropylacrylamide)-block-poly(L-lysine) (PNIPAM-b-PLys-POM) was prepared via the electrostatic force between POMs and the amino groups of poly(L-lysine). And then, the catalytic wet hydrogen peroxide oxidation (CWPO) of phenol was chosen as a catalysis model. The catalytic activity of PNIPAM-b-PLys-POM could be controlled by not only the temperature but also the molar ratio of NIPAM/Lys. This work highlights the potential of using these temperature-responsive micelles as a platform for intelligent controllable heterogeneous catalysts.

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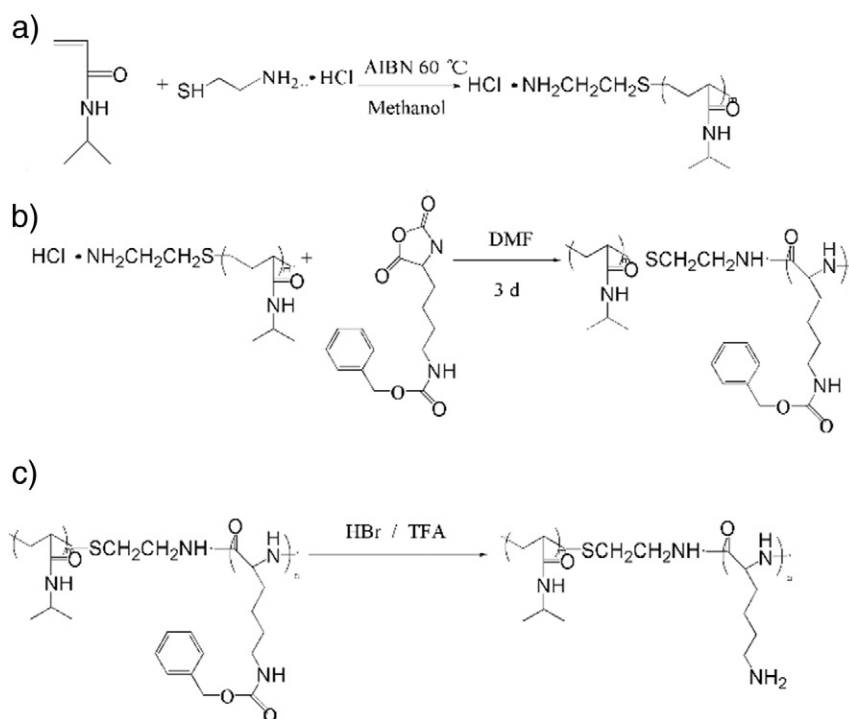
Scheme 1. Synthesis routes of PNIPAM-NH2 (a), PNIPAM-b-PZL (b) and PNIPAM-b-PLys (c).

2. Methods

2.1. Material and reagent

ε-(Benzyloxycarbonyl)-L-lysine and trifluoroacetic acid were purchased from GL Biochem (Shanghai) Ltd., China. Lys (Z)-NCA was prepared according to the method described by the Fuchs-Farthing using triphosgene [16]. 33% HBr solution in acetic acid (HBr/AcOH) was purchased from Acros. N,N-Dimethylformamide (DMF) was obtained from the Shanghai Chemical Reagent Co. and used after distillation under reduced pressure. $H_5PV_2Mo_{10}O_{40}$ was synthesized according to the previous reference [17]. Other chemicals were obtained from commercial suppliers, they were of AR grade and used without further purification.

Fig. 1. ^1H NMR spectrum of PNIPAM-b-PZL (a) and PNIPAM-b-PLys (PNL-2) (b).

2.2. Preparation of catalysts

2.2.1. Synthesis of PNIPAM-b-PZL

Amine-terminated PNIPAM (PNIPAM-NH$_2$) was synthesized and characterized according to Ref. [16]. The PNIPAM-b-PZL copolymers were synthesized by the ROP of Lys (Z)-NCA using PNIPAM-NH$_2$ as a macro-initiator. Typically, 1.0 g of PNIPAM-NH$_2$ and 2.0 g of Lys(Z)-NCA were dissolved in anhydrous DMF in a dried flask, respectively. The DMF solution of PNIPAM-NH$_2$ was then added into the DMF solution of Lys(Z)-NCA under stirring. The solution was stirred for 72 h at 40 °C under argon atmosphere. Then DMF was evaporated under reduced pressure and the resulting product was dissolved in 40 mL of chloroform, and then precipitated into an excess of diethyl ether. The yield was 2.4 g (89.2%). The composition of PNIPAM-b-PZLL was determined by ^1H NMR in trifluoroacetic acid.

2.2.2. Preparation of PNIPAM-b-PLys

PNIPAM-b-PLys was prepared by the deprotection of PNIPAM-b-PZys using HBr. Typically, PNIPAM-b-PZL of 1.0 g was dissolved in 8.0 mL of trifluoroacetic acid. Then, 4 equiv of 33% HBr/AcOH with respect to the benzyl carbamate (Z) group was added, and the solution was stirred for 1 h at room temperature. To precipitate the polymer, the solution was slowly poured into an excess of diethyl ether under vigorous stirring. Then the product was washed with diethyl ether 5 times, and the polymer was isolated and dried at room temperature. Subsequently, the product was dissolved in double distilled water and dialyzed with a cellulose membrane (cutoff Mn = 3500) for 3 days. After dialysis, the solution was immediately lyophilized. The ^1H NMR measurement of the obtained PNIPAM-b-PLys was carried out in trifluoroacetic acid to determine the composition.

2.2.3. Loading of POMs

PNIPAM-b-PLys and $H_5PV_2Mo_{10}O_{40}$ (5 mol equiv. as an ammonium unit) were added together into 20 mL aqueous solution. A self-assembly process of PNIPAM-b-PLys with $H_5PV_2Mo_{10}O_{40}$ in water at room temper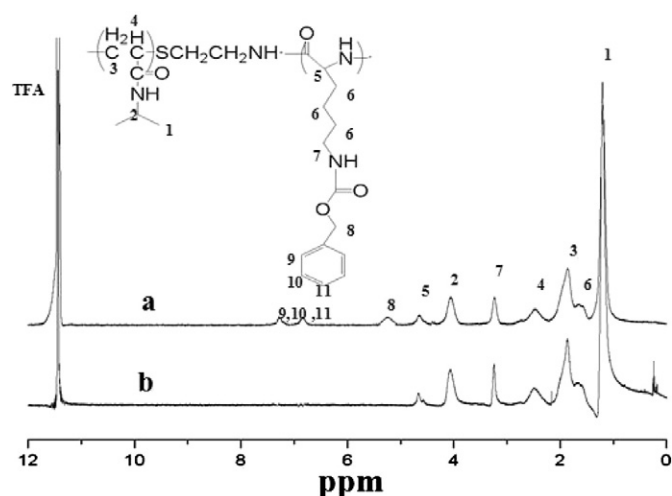ature resulted in the formation of PNIPAM-b-PLys-POM,