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An Autonomic and "Off-On-Off"-Switchable Polymer Microreactor

Rong Luo, Maiyong Zhu, Xinhua Yuan, and Songjun Li*

School of Materials Science & Engineering, Jiangsu University, Zhenjiang 212013, China

Abstract: An originally designed autonomic and "off-on-off"-switchable polymer microreactor is reported. This polymer microreactor was made of nickel nanoparticles and a unique shape-memory polymer consisting of poly(acrylamide) and pendent dodecyl side chains that exhibited switchable domains. This reactor showed weak reactivity at relatively low temperatures due to the low mobility of molecular chains in the switchable domains, which inhibited the access of substrate to the encapsulated nickel nanoparticles (*i.e.*, catalytic 'off' status). This reactor showed also weak reactivity at relatively high temperatures, in response to the dramatically increased hydrophobicity (*viz.*, catalytic 'off' status). This reactor only demonstrated significant catalysis at modest temperatures, arising from the relative balance between the mobility of molecular chains and the hydrophobicity in the switchable domains (*i.e.*, catalytic 'on' status). In this way, this polymer microreactor demonstrated the autonomic "off-on-off" catalytic ability. This novel design opens up the opportunity to develop smart polymer microreactors for controlled catalytic processes.

Keywords: Polymers; shape memory; switching behavior; metal nanoparticles.

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* Corresponding to Prof. S. Li, *Distinguished Professor* to Jiangsu University and *President* of the Chinese Advanced Materials Society
URL: http://material.ujs.edu.cn/szjs-dsfc-view.asp?id=25
Email: Lsjchem@ujs.edu.cn

1. Introduction

There are tremendous implications in metal nanoparticles due to their importance in a broad range of applications and particularly in catalytic applications. The recent advances in this field and synthetic polymers offer new opportunities to develop functional catalysts by incorporating both of them into individual entitles.[1,2] Prominent among these are the so-called polymer microreactors, which gain traction due to the tantalizing prospect of controlling catalytic processes in chemical synthesis and in inaccessible environments. From the earliest endeavors, exemplified by poly(*N*-isopropylacrylamide) (PNIPAm)-encapsulated Ag nanoparticles,[3,4] polymer microreactors have been shown to demonstrate tunable catalysis in water. This results from the temperature-dependent hydrophilic/hydrophobic transition of PNIPAm, which causes either impeded or unobstructed access into the encapsulated Ag nanoparticles. In this way, catalysis by the polymer microreactors demonstrates a tunable process in conjunction with the increasing temperature. Despite the innovative properties, these polymer microreactors has not found valuable potentials, mainly because most of the controlled catalytic processes would desire the microreactors that can work at a specified temperature in order to cater to an optimized reaction condition.[5] Unfortunately, it is not realistic to directly acquire such polymer microreactors basing on currently available technology and methods. As such, new technology and methods are urged.

For centuries, mankind has been learning and achieving knowledge from nature. A body of knowledge is already available. One of these is the shape-memory polymers (SMPs),[6] which appear to share a promising prospect with the stuck polymer microreactors. Although the SMPs and their mechanisms are diverse, the common ground lies in the conceptual combination of static netpoints and switchable domains, such as crosslinked poly(acrylic acid-*co*-stearyl acrylate),[7] where the crosslinked netpoints stabilize the permanent shape and the switchable domains fix the temporary shape. The change in the mobility of aliphatic side chains in the switchable domains is the major driving force that transforms a temporary shape to the permanent shape (depending on the temperature whether it is below or above the transition temperature). Below the transition temperature, the "frozen" molecular chains in the switchable domains make the polymer behave like a hard polymer. Above the transition temperature, the increased mobility of the aliphatic side chains would contribute to the flexibility of this polymer. The temporary shape may be maintained by applying a deforming force during the cooling process. Heating this polymer again above the transition temperature would result in the recovery of the permanent shape. In this way, the molecular mobility of aliphatic side chains in the switchable domains acts as a molecular switch for the occurrence of the shape-memory effect. Although these works are not related to catalytic applications, the methods developed by SMPs scientists provide a new insight into the stuck polymer microreactors, which makes feasible the switchable domains.

Inspired by this principle, herein we reported an autonomic and "off-on-off"-switchable polymer microreactor (*i.e.*, NiPR-S). This polymer microreactor was constructed from nickel nanoparticles and a unique shape-memory polymer consisting of crosslinked poly(acrylamide) (PAAm) and pendent dodecyl side chains that exhibited switchable domains. The mobility of molecular chains in the switchable domains acted as a molecular switch for providing access to the encapsulated metal nanoparticles. As outlined in **Scheme 1**, two opposing factors can be involved in the switchable domains. The increased mobility of molecular chains with increasing temperature intended to provide access to the encapsulated metal nanoparticles (*cf.* Route *A*). This access was, however, terminated with a further increase in the temperature, arising from the dramatically increased hydrophobicity (*cf.* Route *C*). As a result, a compromise was reached under a modest temperature condition (*cf.* Route *B*), in response to the relative balance between the mobility of molecular chains and the hydrophobicity in the switchable domains. In this way, this polymer microreactor demonstrated the autonomic "off-on-off" catalytic ability. The objective of this study is to demonstrate that polymer microreactors that can work at a specified temperature can be realized by using this novel protocol, which opens up the opportunity to develop smart polymer reactors for controlled catalytic processes.

Scheme 1. Proposed mechanism for the NiPR-S microreactor

2. Experimental section

2.1. Preparation of polymer microreactors

Unless otherwise noted, the chemicals used were of analytic grade and used as received from Sigma-Aldrich. The preparation of the polymer microreactor, as outlined in **Scheme 1**, was based on the classic design of polymer microreactors[8] and SMPs.[9] In detail, *N*-dodecylacrylamide (0.24 g; 1 mmol), acrylamide (1.0 g; 14 mmol), *N*,*N*'-methylenebisacrylamide (0.12 g; 0.75 mmol), and AIBN (0.10 g), along with nickel nitrate hexahydrate (1.10 g; 3.7 mmol), were dissolved in dimethyl sulfoxide (6.5 mL). After being dispersed and deoxygenated with sonication and nitrogen, the mixture system was heated up to 65 ^{o}C and allowed to react for 2h. The encapsulated ionic nickel was then reduced by an excess of sodium borohydride (tenfold, with regard to ionic nickel). The resulted polymer microreactor (*i.e.*, NiPR-S) was profusely washed with ethanol and water, cut into pieces and then dried under flowing nitrogen.

For a comparative study, two controls, *i.e.*, "NiPR-N" and "PR-S", were also prepared under comparable conditions. NiPR-N was the non-responsive nickel microreactor prepared as NiPR-S but replacing *N*-dodecylacrylamide with acrylamide (herein the 'N' suffix in NiPR-N denotes a non-responsive polymer in contrast to the switchable polymer, denoted by 'S'). PR-S was the polymeric carrier of NiPR-S and prepared without using nickel. For the sake of convenient discussion, all of the prepared polymer reactors and carrier were mentioned henceforth as the conceptual microreactors (but not specified by microreactors or carrier).

2.2. Characterization

The TEM images of the as-prepared microreactors are obtained using a transmission electron microscope (TEM) (JEM-2100, Japan). The infrared spectra were recorded using a FTIR apparatus (Nicolet MX-1E, USA). The change in shape with temperature was recorded using a digital camera, where the slice of polymer microreactors were taken out from hot water and immediately photographed (25 °C, unless otherwise noted).

2.3. Thermal transition behavior

The thermal transition behavior in the switchable domains was studied as a function of temperature by using dynamic light scattering (DLS) (Bettersize-2000, China). In order to allow for equilibrium to be reached, all samples were kept at the specified temperatures for at least 10 min before acquiring the hydrodynamic radius (R_h). By a comparison between the switchable microreactors (*i.e.*, NiPR-S and PR-S) and the non-responsive NiNR-N, the contribution of the thermal transition can be reflected by the change of R_c:[10]

$$R_c = \left[\left(\frac{R_h - R_d}{R_d} \right)_S - \left(\frac{R_h - R_d}{R_d} \right)_N \right] \times 100\%$$

Herein, R_d is the particle size of dried particles. '*S*' represents the switchable microreactors and '*N*' indicates the non-responsive microreactor.

2.4. Catalysis test

The catalytic properties of the prepared microreactors were evaluated in a batch format, using the classic model reaction of reducing methylene blue (MB) with $NaBH_4$.[11] MB was added into $NaBH_4$ aqueous solution with an initial concentration of 0.05 mmol mL^{-1} (totally 4 mL; $NaBH_4$, 20 folds with regard to MB). The solid content of microreactors in the reaction system was 2.5 mg mL^{-1}. The reduction of MB was monitored spectrophotometrically. The catalytic activity of these microreactors was obtained from the average of three runs.

2.5. Electrochemical test

The electrochemical test was further employed to achieve information on the switching behavior in the prepared polymer microreactors.[12] Using an electrochemical workstation (CHI760E, China), a Pt wire encircled by a thin film of the polymer reactors (*ca.* 0.05 mm) was adopted as the working electrode in a three-electrode configuration (Au-plate counter electrode and Ag/AgCl ref. electrode). The redox process of $HPO_4^{2-}/H_2PO_4^-$ (*i.e.*, PBS; pH 7.0) was used as a probe to record the current change upon changing temperature.

3. Results and discussion

3.1. Analysis of composition and structure

The polymer microreactor NiPR-S, as aforementioned, was made of nickel nanoparticles and a unique shape-memory polymer consisting of poly(acrylamide) and pendent aliphatic side chains. FTIR was first used to characterize the composition of this polymer microreactor, as shown in **Figure 1**. Three major bands (2900-3700, 1600-1750, and 1000-1500 cm^{-1}) appeared in the spectrum of this polymer reactor. These bands were complex due to the complicated composition, which may be associated with the stretching of O-H/N-H, C=O, and C-N/C-C.[13] For a comparative study, we also included the two controls described above in **Figure 1**. PR-S exhibited almost the same spectrum as NiPR-S whereas that of NiPR-N failed to. The same spectra between PR-S and NiPR-S can be ascribed to the comparable composition between PR-S and the polymer carrier of NiPR-S. The difference between NiPR-S and NiPR-N at 1000-1500 cm^{-1} may be ascribed to the presence of aliphatic side chains within NiPR-S. **Figure 2** and **Figure 3** present the TEM images and a digital photograph of NiPR-S, respectively. Nickel nanoparticles with a size of *ca.* 50 nm were encapsulated in the polymeric building blocks. Thus, this novel polymer reactor was prepared in the desired form.

Figure 1. FTIR spectra of the prepared polymer microreactors

Figure 2. TEM images of metal nanoparticles contained in the prepared polymer microreactors (a: NiPR-S; b: NiPR-N; c: PR-S)

Figure 3. Digital photograph in the outward appearance of a slice of NiPR-S

3.2. Thermal transition behavior and shape-memory effect

Using DLS, the thermal transition behavior in the switchable domains was studied as a function of temperature. As shown in **Figure 4**, NiPR-S and PR-S revealed a significant dependence upon temperature in contrast to NiPR-N. The maximal value of R_c in NiPR-S appeared at *ca.* 43 $^\mathrm{o}$C. Below this temperature, NiPR-S revealed a low R_c associating with the low mobility of molecular chains in the switchable domains, which inhibited swelling of the polymer. Above this temperature, NiPR-S also revealed a low R_c, in response to the increased exposure of the hydrophobic side chains. A maximal value of R_c was reached at the transition temperature (*i.e.*, 43 $^\mathrm{o}$C). This result suggests that the switchable properties have been incorporated into the prepared polymer microreactors.

To further address the switchable properties in NiPR-S, **Figure 5** displays the shape-memory effect. A rod-like slice (*cf. a*) was bent by a loading above the transition temperature (*i.e.*, 50 $^\mathrm{o}$C), followed by cooling to room temperature (*i.e.*, ~25 $^\mathrm{o}$C), which fixed the bent shape (*cf. b*). Heating this polymer again above the transition temperature resulted in the recovery of the rod-like shape (*cf. c*, *d*). The recovering behavior was repeatable and the system can be made to switch between the initial- and the temporary shapes. In conjunction with the study in **Figure 4**, this result further suggests the switchable properties have been incorporated into the prepared polymer microreactors.

Figure 4. DLS curves of the prepared polymer microreactors

Figure 5. The shape-memory effect of NiPR-S

(*a*: Initial shape; *b*: fixed temporary shape (polymer was re-shaped at 50 °C followed by quenching to 25 °C); *c*: shape recovering (at 50 °C); *d*: recovered permanent shape)

3.3. Switchable catalysis

The catalytic properties of these polymer microreactors are presented in **Figure 6**. PR-S did not exhibit significant catalysis due to the lack of catalytic nickel nanoparticles. In contrast, NiPR-S and NiPR-N showed significant catalytic ability, where the conversion increased rapidly with time. To verify the switchable catalysis, three representative temperatures, *i.e.*, 30, 43 and 50 ^{o}C (lower, equal to or higher than the transition temperature of NiPR-S, respectively), were selected for a comparative study. In the control microreactor NiPR-N, the catalytic activity increased with increasing temperature. In contrast, the catalytic activity of NiPR-S underwent an initial increase and then a decrease, reaching a maximal value at 43 ^{o}C. Specifically, NiPR-S at both 30 ^{o}C and 50 ^{o}C showed a lower catalytic activity than NiPR-N and nonetheless a higher activity than NiPR-N at the transition temperature (*i.e.*, 43 ^{o}C). NiPR-S therefore demonstrated the switchable catalysis in an 'off-on-off' paradigm, as desired.

Figure 6. Catalytic activity of the prepared polymer microreactors

3.4. Access-regulating behavior

The electrochemical test was further employed to achieve information on the switching behavior in the prepared polymer microreactors.[12] By a comparison between the switchable microreactors (*i.e.*, NiPR-S and PR-S) and the non-responsive NiPR-N, the effect of the switchable properties on the access to the polymer inner was thus exposed. As shown in **Figure 7**, NiPR-N revealed an increase of current with increasing temperature (*cf. b*). In contrast, the current in NiPR-S and PR-S underwent an initial increase and then a decrease, reaching a maximal value at the transition temperature, *i.e.*, 43 ^{o}C (*cf. a*, *b*). Specifically, NiPR-S at both 30 ^{o}C and 50 ^{o}C revealed a smaller current value than NiPR-N and nonetheless a higher current value than NiPR-N at 43 ^{o}C. This result suggests that switching of the aliphatic domains regulated access to the polymer interior in NiPR-S and PR-S. In conjunction with the catalytic study (**Figure 6**), this result further suggests that the switchable properties in these polymer microreactors allows for fine tuning of the access of substrate to the encapsulated metal nanoparticles, which thereby makes switching of the catalytic activity feasible.

Figure 7. CV profiles with tunable access to the polymer interior of the prepared microreactors (a: NiPR-S; b: NiPR-N; c: PR-S)

4. Conclusions

An originally designed autonomic and "off-on-off"-switchable polymer microreactor is reported in this study. This polymer microreactor was constructed from nickel nanoparticles and an unique shape-memory polymer consisting of poly(acrylamide) and pendent dodecyl side chains that behaved as thermally switchable domains. The mobility of molecular chains in the switchable domains acted as a molecular switch for tuning of the access of substrate to the encapsulated metal nanoparticles. Below the transition temperature (~34 ^{o}C), this polymer microreactor revealed weak reactivity due to the low mobility of molecular chains in the switchable domains, which inhibited access to the encapsulated nickel nanoparticles. Above the transition temperature, this polymer microreactor revealed also weak reactivity, due to the dramatically increased hydrophobicity in the switchable domains. This polymer microreactor only provided significant catalysis under a modest temperature condition, resulting from the compromise reached at the transition temperature. In this way, this polymer microreactor demonstrated the autonomic "off-on-off" catalytic ability. It is therefore confirmed that polymer microreactors that can work at a specified temperature can be prepared using this novel protocol, which opens up the opportunity to develop smart polymer microreactors for controlled catalytic processes. Future development in this field will significantly increase the applications, and will lead to the appearance of novel catalytic materials and functional catalysts.

Acknowledgements

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Graphic captions:

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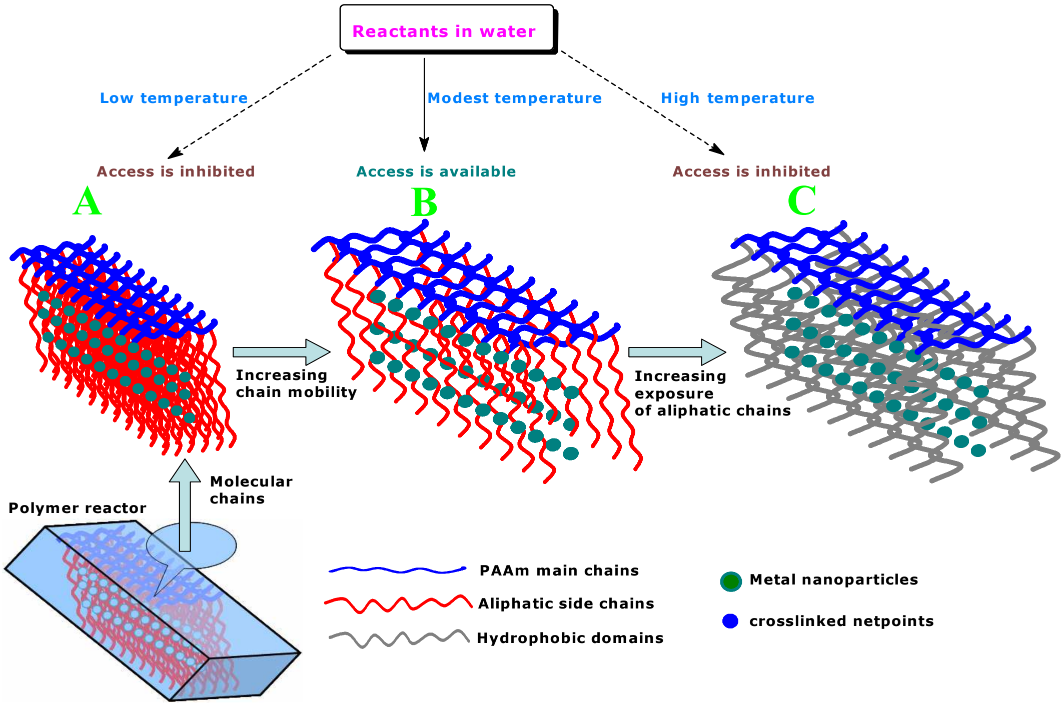

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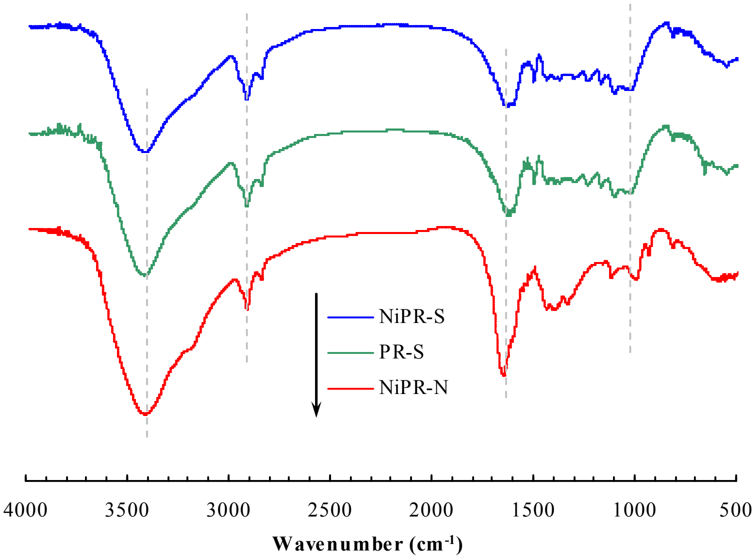

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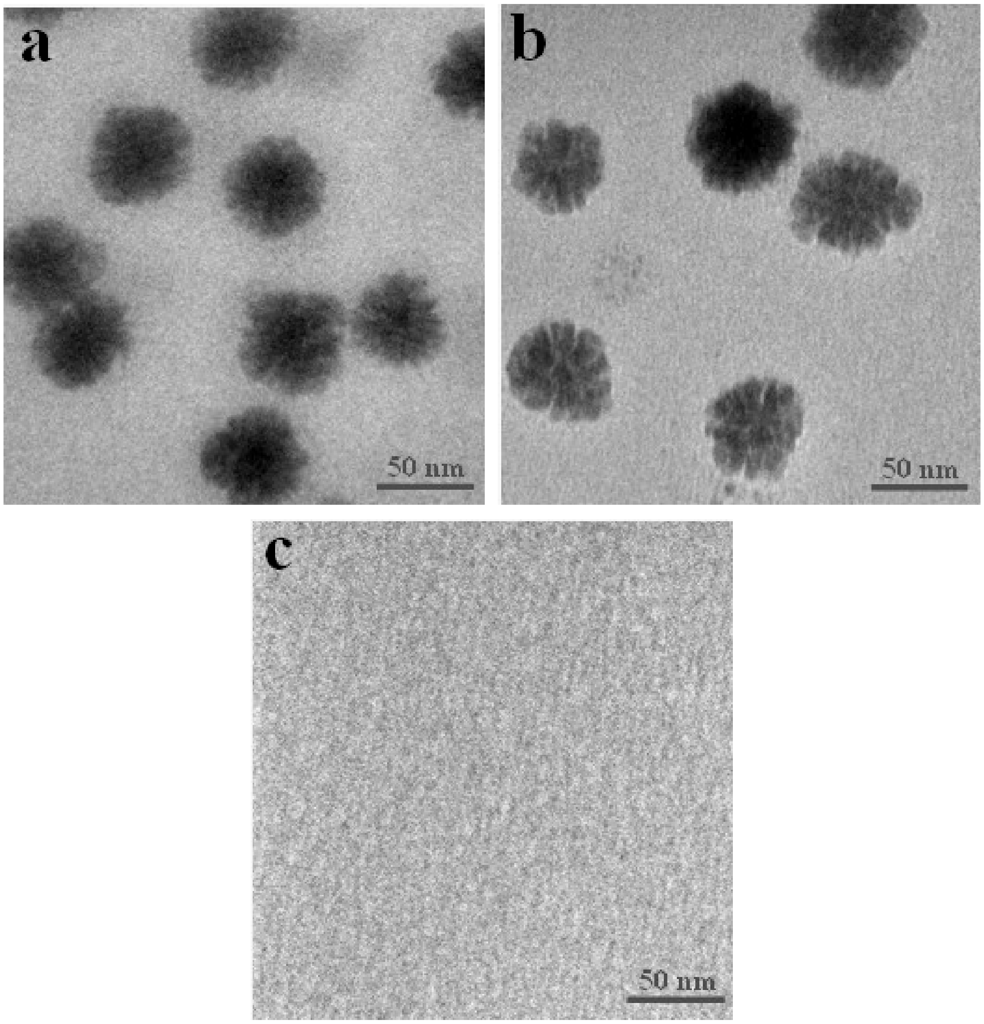

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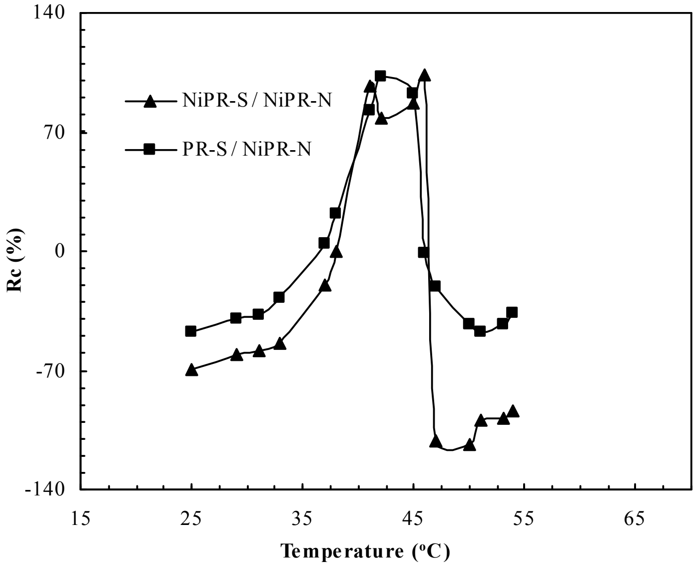

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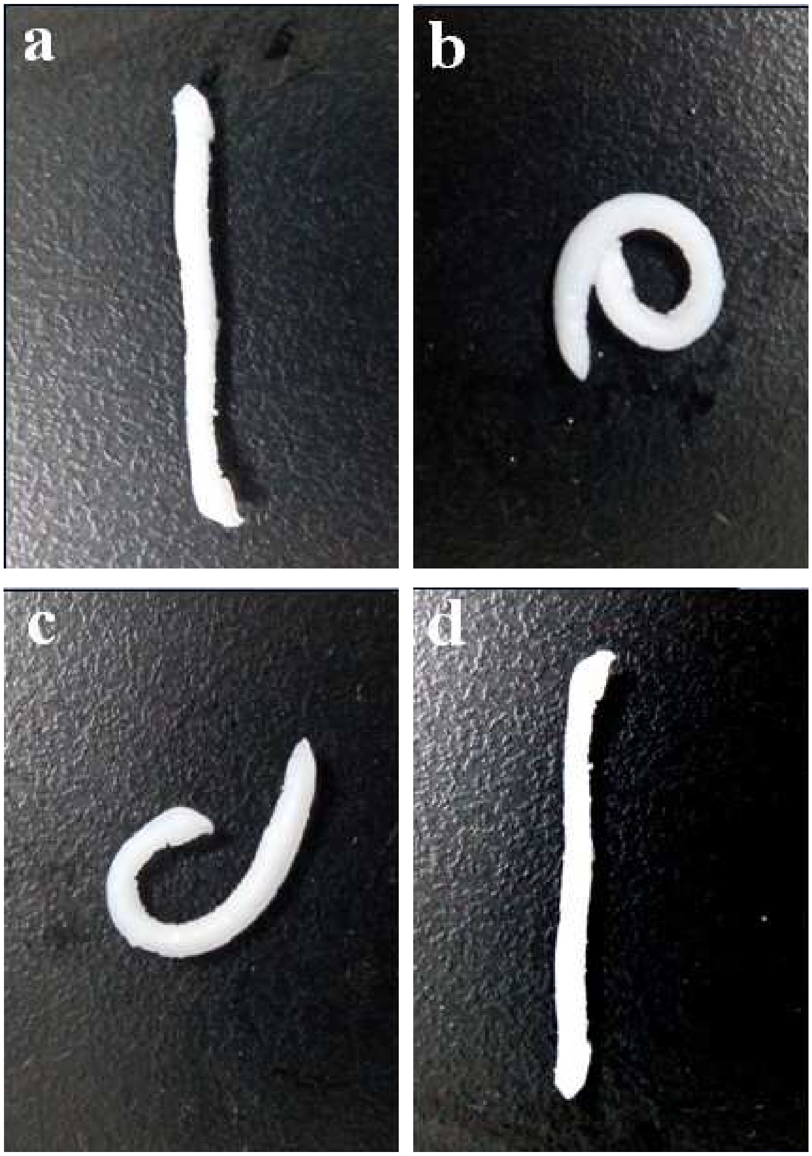

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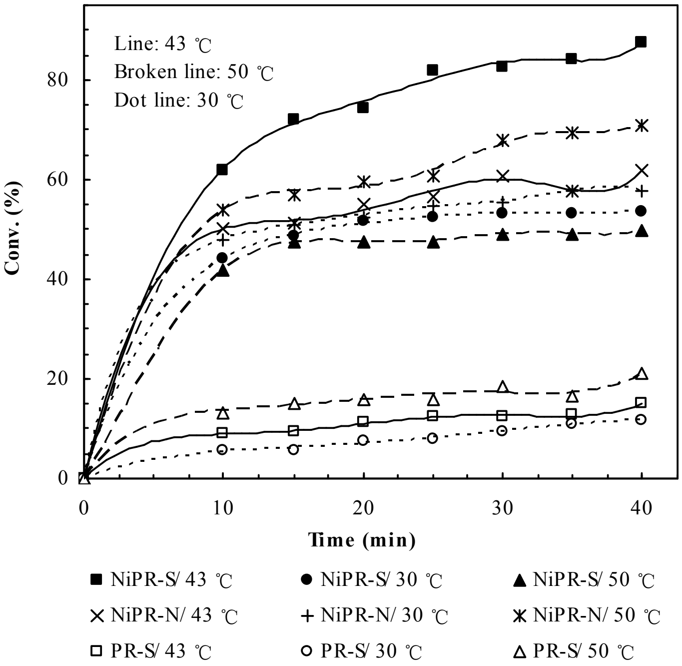

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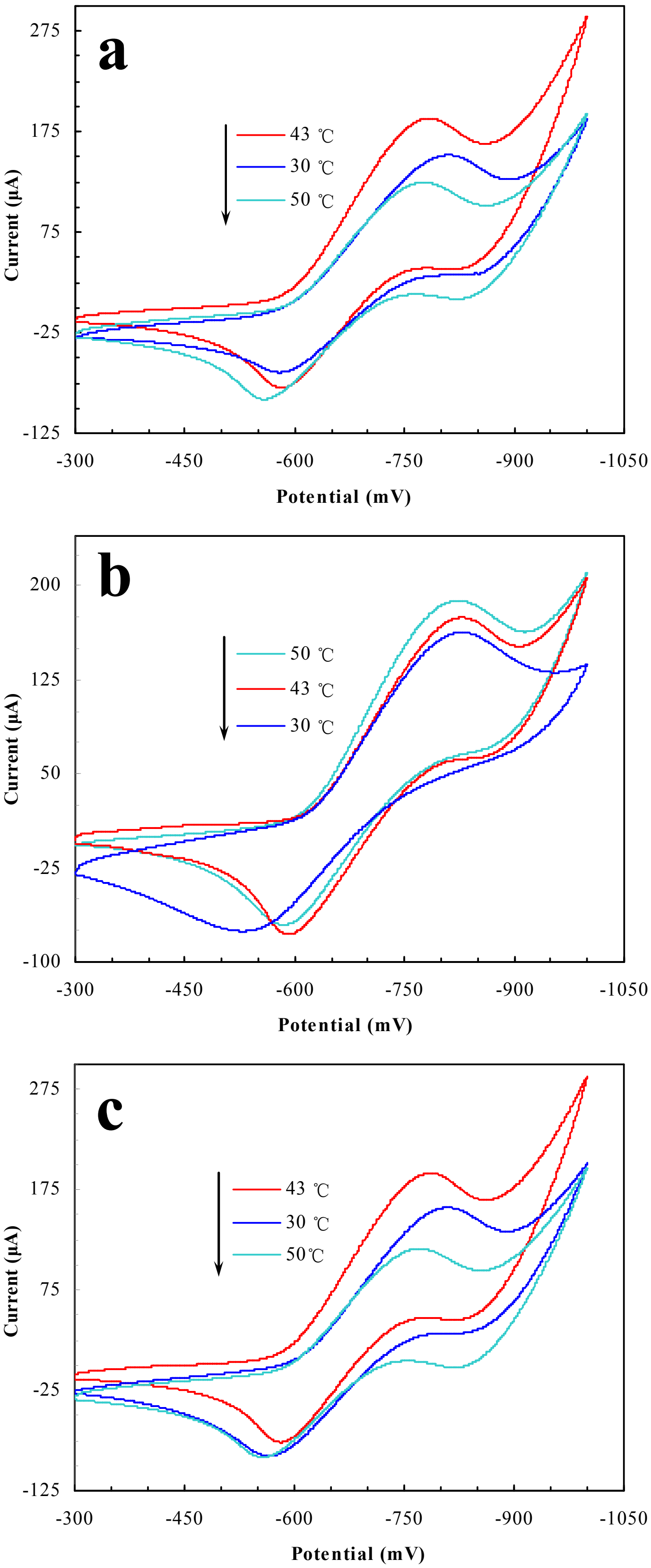

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Graphical Abstract

An originally designed autonomic "off-on-off" polymer microreactor is reported. This unique polymer reactor was made of nickel nanoparticles and an elaborate shape-memory polymer consisting of poly(acrylamide) and pendent dodecyl side chains that exhibited switchable domains. The molecular chain mobility in the switchable domains acted as a molecular switch for fine tuning of the access of substrate to the encapsulated metal nanoparticles, causing an autonomic "off-on-off" catalytic behavior.

TOC figure: