

# Chameleon Multienvironment Nanoreactors

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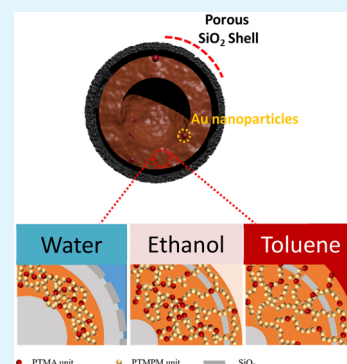


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**ABSTRACT:** Nanoreactors consisting of hydrophilic porous  $\text{SiO}_2$  shells and amphiphilic copolymer cores have been prepared, which can easily self-tune their hydrophilic/hydrophobic balance depending on the environment and exhibit chameleon-like behavior. The accordingly obtained nanoparticles show excellent colloidal stability in a variety of solvents with different polarity. Most importantly, thanks to the assistance of the nitroxide radicals attached to the amphiphilic copolymers, the synthesized nanoreactors show high catalytic activity for model reactions in both polar and nonpolar environments and, more particularly, realize a high selectivity for the products resulting from the oxidation of benzyl alcohol in toluene.



**KEYWORDS:** multienvironment nanoreactors, core–shell nanoparticles, chameleon-like behavior, amphiphilic polymers, self-regulation

## INTRODUCTION

Noble metal nanoparticles are considered to be among the most important catalysts for heterogeneous reactions because of their unique intrinsic properties, large surface-to-volume ratio, and highly active surface atoms.<sup>1–4</sup> Nevertheless, such distinct properties also easily lead to the aggregation of nanoparticles during catalytic reactions, resulting in a rapid decay of catalytic activity.<sup>5</sup> Therefore, maintaining a long-term uniform dispersion of metal nanoparticles and maximizing their surface areas are always the key issues for the application of metallic nanoparticles as highly active heterogeneous catalysts. Until now, two strategies have been widely utilized to suppress the agglomeration of metal nanoparticles: (i) modifying the surface of metal nanoparticles with different kinds of surfactants<sup>6</sup> and (ii) developing carrier systems to load metal nanoparticles, such as core–shell or yolk shell nanoreactors.<sup>7–11</sup> However, most of these systems are designed for only one or a few catalytic environments with similar polarity. Once the environment surrounding the catalysts changes, the stability of the catalytic system is difficult to maintain. Thus, developing multiple environments for stabilizing systems for metallic nanoparticles is still a big challenge.

In 2006, Voronov et al. disclosed an amphiphilic polyester that can be used as a stabilizing agent for metallic nanoparticles in both polar and nonpolar media.<sup>12,13</sup> The synthesized silver nanoparticles based on this system were stable in both acetone (polar) and toluene (nonpolar). Although there is no follow-up report on the application of the synthesized nanoparticles, it provides an option for the development of metallic catalytic systems that are stable in multiple environments. However, the

aim of most of the polymer surfactants developed for catalytic purposes is to generate hydrophobic regions in hydrophilic surroundings.<sup>14–16</sup> To the best of our knowledge, reports on catalytic systems simultaneously achieving high catalytic efficiency in both polar and nonpolar environments with the help of amphiphilic surfactants are still scarce.

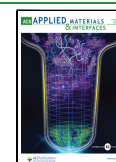
Compared to amphiphilic polymer surfactants, nanoreactors generally contain more complex structures and functions. Therefore, they are considered to be more promising candidates to achieve “one-for-all” environments for efficient catalytic activity. For example, in 2015, Lee et al. developed superhydrophobic hollow silica micelles (SHSMs) with hydrophilic cores and amphiprotic shells.<sup>17</sup> Due to the coexisting hydrophilic poly(allylamine hydrochloride) (PAH) and hydrophobic octadecyltrimethoxysilane (OTMS) domains on the outer shells, the synthesized nanoreactors showed excellent stability in both organic and aqueous environments. Nevertheless, the presence of hydrophobic OTMS still caused the slower diffusion of hydrophilic species through the SHSMs structure, which led to a lower catalytic activity in water compared to that for hydrophilic catalysts.

In the present study, we designed and synthesized novel multienvironment nanoreactors composed of hydrophilic

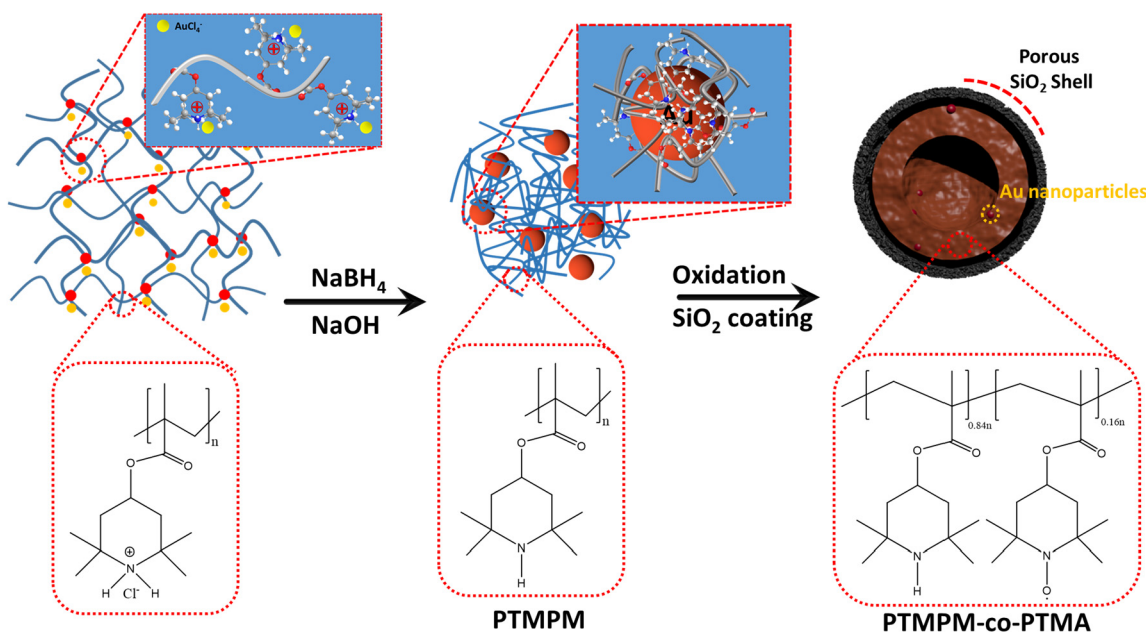
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Scheme 1. Synthesis Process and the Structure of Nanoreactors



porous SiO<sub>2</sub> shells and poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-*co*-2,2,6,6-tetramethylpiperidin-4-yl methacrylate) (PTMPM-*co*-PTMA) amphiphilic copolymer cores. Thanks to the response of PTMPM-*co*-PTMA to organic solvents with different polarities, copolymer segments can be specifically swollen and pass through the micropores of the SiO<sub>2</sub> shells to rewrap the nanoreactors, thereby realizing the hydrophilic/hydrophobic balance self-regulation without complicated surface modification and a polymer grafting process. The obtained nanoreactors show excellent colloidal stability in most commonly used solvents. In order to demonstrate the catalytic activity of the PTMPM-*co*-PTMA@Au@porous SiO<sub>2</sub> (PPAPS) nanoreactors in different polar environments, the reduction of 4-nitrophenol (Nip) in water (polar) and the oxidation of benzyl alcohol in toluene (nonpolar) have been selected as model reactions. The present approach provides a novel and simple method for the fabrication of multienvironment nanoreactors.

## EXPERIMENTAL SECTION

**Materials.** 2,2'-Azobis(2-methylpropionamidine) dihydrochloride (V<sub>50</sub>), cetyltrimethylammonium bromide (CTAB), sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O), tetraethyl orthosilicate (TEOS), 4-nitrophenol, anhydrous benzyl alcohol, and benzaldehyde were supplied by Sigma-Aldrich. Sodium borohydride (NaBH<sub>4</sub>) and 2,2,6,6-tetramethylpiperidin-4-yl methacrylate (TMPM) were supplied by Tokyo Chemical Industry (TCI). Gold(III) chloride trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O) and H<sub>2</sub>O<sub>2</sub> (35 wt % in H<sub>2</sub>O) were supplied by Acros Organics. Hydrochloric acid (37 wt % in H<sub>2</sub>O), ethanol, methanol, sodium hydroxide (NaOH), toluene, and ammonia solution (32 wt % in H<sub>2</sub>O) were supplied by VWR. All of the reactants were used without further purification. Water was purified by a Milli-Q system.

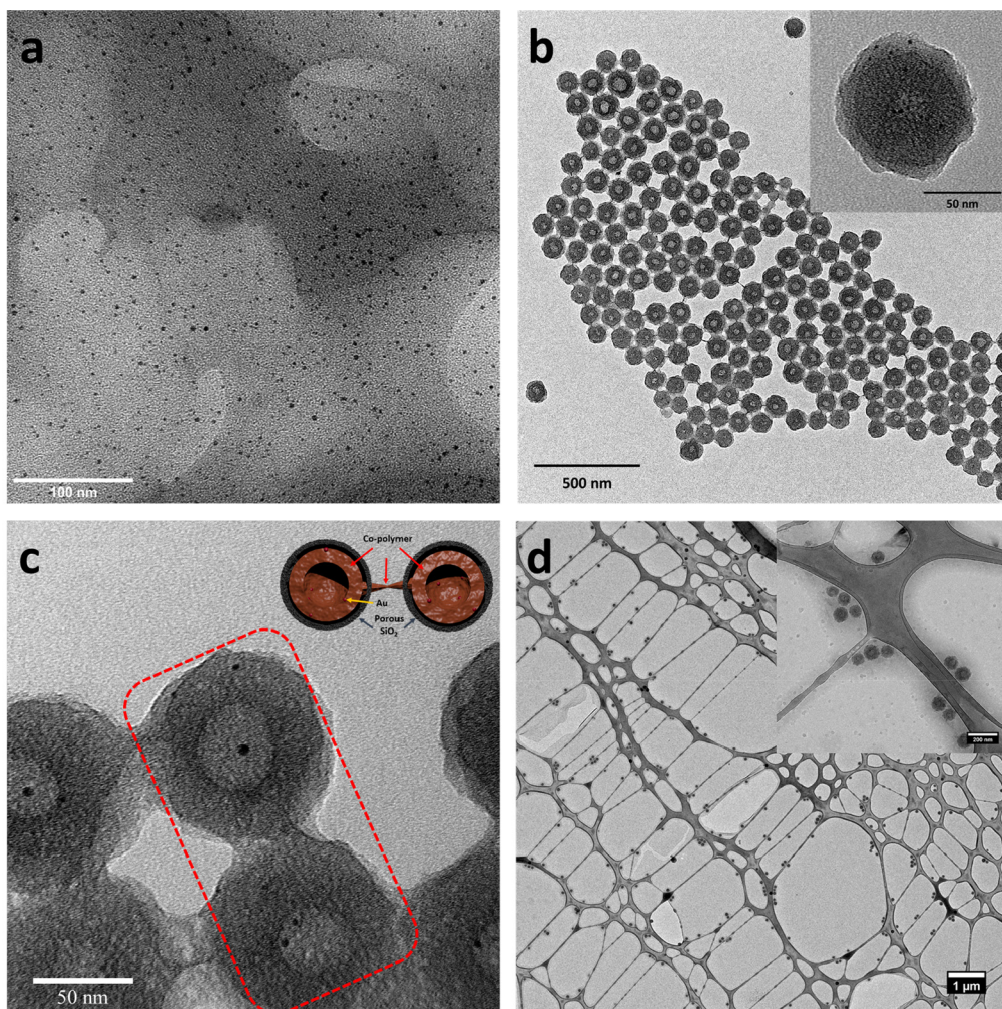
**Characterizations.** Transmission electron microscope (TEM) images were recorded with a LEO 922. The cryogenic transmission electron microscopy (cryo-TEM) micrographs were recorded on a JEOL JEM-2100 operated at 200 kV with a bottom-mounted 4 k × 4 k CMOS camera (TemCam-F416, TVIPS, Gauting, Germany). The total electron dose in each micrograph was kept below 20 e<sup>−</sup>/Å<sup>2</sup>. Cryo-TEM specimens were prepared by applying a 4 μL drop of a dispersion sample to lacey carbon-coated copper TEM grids (200

mesh, Science Services) and were plunge-frozen in liquid ethane with an FEI Vitrobot Mark IV set at 4 °C and 95% humidity. Vitrified grids were transferred and imaged in the microscope with a cryogenic transfer holder (Gatan 914, Gatan, Munich, Germany). The analysis of Au loading in the nanoreactors was realized with the Varian Vista MPX CCD simultaneous axial ICP-OES. Nanoreactors (50 mg) were analyzed by Medac Ltd., and the samples were digested with HF before the measurement. The content of Au in PPAPS was 246 ppm. UV–visible (UV–vis) spectra were acquired on a Varian spectrophotometer (Cary, 50 Conc). X-band ESR spectra were acquired on an EMXmicro CW-EPR spectrometer from Bruker, Germany (EMX micro EMM-6/1/9-VT control unit, ER 070 magnet, EMX premium ER04 X-band microwave bridge equipped with an EMX standard resonator, and EMX080 power unit). X-ray diffraction (XRD) was performed on a Bruker D8 with a Cu Kα radiation anode. Gas chromatography (GC) was performed on a Shimadzu GC-2010. Dynamic light scattering (DLS) was performed with an ALV/CGS-3 compact goniometer system (ALV GmbH, Germany) and has been repeated at least five times in order to check the reproducibility.

**Conventional Radical Polymerization of TMPM-Cl.** First, 4-(methacryloyloxy)-2,2,6,6-tetramethylpiperidinium chloride (TMPM-Cl) was prepared by protonating the amine functionality of TMPM. TMPM (5 g) was dissolved in ethanol (25 mL), and hydrochloric acid (4.1 M, 6.5 mL) was added dropwise at room temperature. After stirring for 1 h, the solvent was evaporated, and the product was dried in vacuo at 40 °C for 18 h. TMPM-Cl (1 g) was dissolved in a mixture of ethanol (3 mL) and water (2 mL). After the solution was degassed with argon, 1 mL of a V<sub>50</sub> aqueous solution (0.18 M) was added dropwise and the polymerization was started immediately by increasing the temperature to 70 °C. The reaction was run for 2 h. The obtained PTMPM-Cl solution was stored at room temperature for the next step.

**Synthesis of PTMPM-*co*-PTMA@Au Hybrid Polymers.** In the first step, 0.3 mL of the PTMPM-Cl solution was diluted with 9.7 mL of water, and then HAuCl<sub>4</sub> solution (0.001 M, 4.5 mL) was added under vigorous stirring. The excess HAuCl<sub>4</sub> was removed by dialysis for 48 h. Second, the solution was purged with N<sub>2</sub> to remove the oxygen, and a 3-fold excess of sodium borohydride was slowly added to reduce the gold precursors. As the reduction process was completed, sodium hydroxide (1 mL, 1.25 M) was added dropwise to the PTMPM-Cl@Au solution to neutralize the released protons. After 18 h of stirring, a PTMPM@Au hybrid gel was obtained by centrifugation and washed with water until neutral pH was achieved.





**Figure 1.** (a) TEM images of PTMPMA@Au; (b) overview and (c) close-up TEM images of PTMPMA-co-PTMA@Au@porous-SiO<sub>2</sub> core-shell nanoreactors; and (d) a cryo-TEM image of PTMPMA-co-PTMA@Au@porous-SiO<sub>2</sub> core-shell nanoreactors in water.

In the last step, the hybrid gel was dissolved in 4.4 mL of methanol, followed by the partial oxidation of PTMPM into PTMA with hydrogen peroxide (0.85 mL, 35%) in the presence of a NaWO<sub>4</sub> catalyst (0.0158 g) for 72 h at room temperature. The composition of the copolymer was confirmed by ESR measurement, indicating a PTMA content of 16 mol % in the accordingly obtained PTMPM-co-PTMA copolymer.

**Synthesis of PTMPM-co-PTMA@Au@Porous SiO<sub>2</sub> Core-Shell Nanoparticles.** First, the PTMPM-co-PTMA@Au solution was diluted with 4 mL of ethanol and then added dropwise to 20 mL of a CTAB aqueous solution (3.75 mg/mL) containing 0.03 mL of NH<sub>3</sub>·H<sub>2</sub>O (28%). Then, TEOS (200 μL) was added and the mixture was kept at 38 °C for 24 h. The PTMPM-co-PTMA@Au@porous SiO<sub>2</sub> (PPAPS) core-shell nanoparticles were finally collected by centrifugation and washed with water several times.

**Synthesis of CTAB@Au Nanoparticles.** CTAB@Au nanoparticles with a diameter of around 9.5 nm were synthesized by the seed growing method. NaBH<sub>4</sub> solution (0.1 M, 0.6 mL) was added to 20 mL of a mixture of HAuCl<sub>4</sub> (2.5 × 10<sup>-4</sup> M) and trisodium citrate (2.5 × 10<sup>-4</sup> M) to prepare the seed solution. The growth solution was achieved by mixing 0.05 mL of ascorbic acid solution (0.1 M) with 7.5 mL of a mixture of HAuCl<sub>4</sub> (2.5 × 10<sup>-4</sup> M) and CTAB (0.08 M). After adding 2.5 mL of the seed solution, the stirring was continued until the color changed to wine red. The CTAB@Au nanoparticles were washed with water two times before the catalytic reaction.

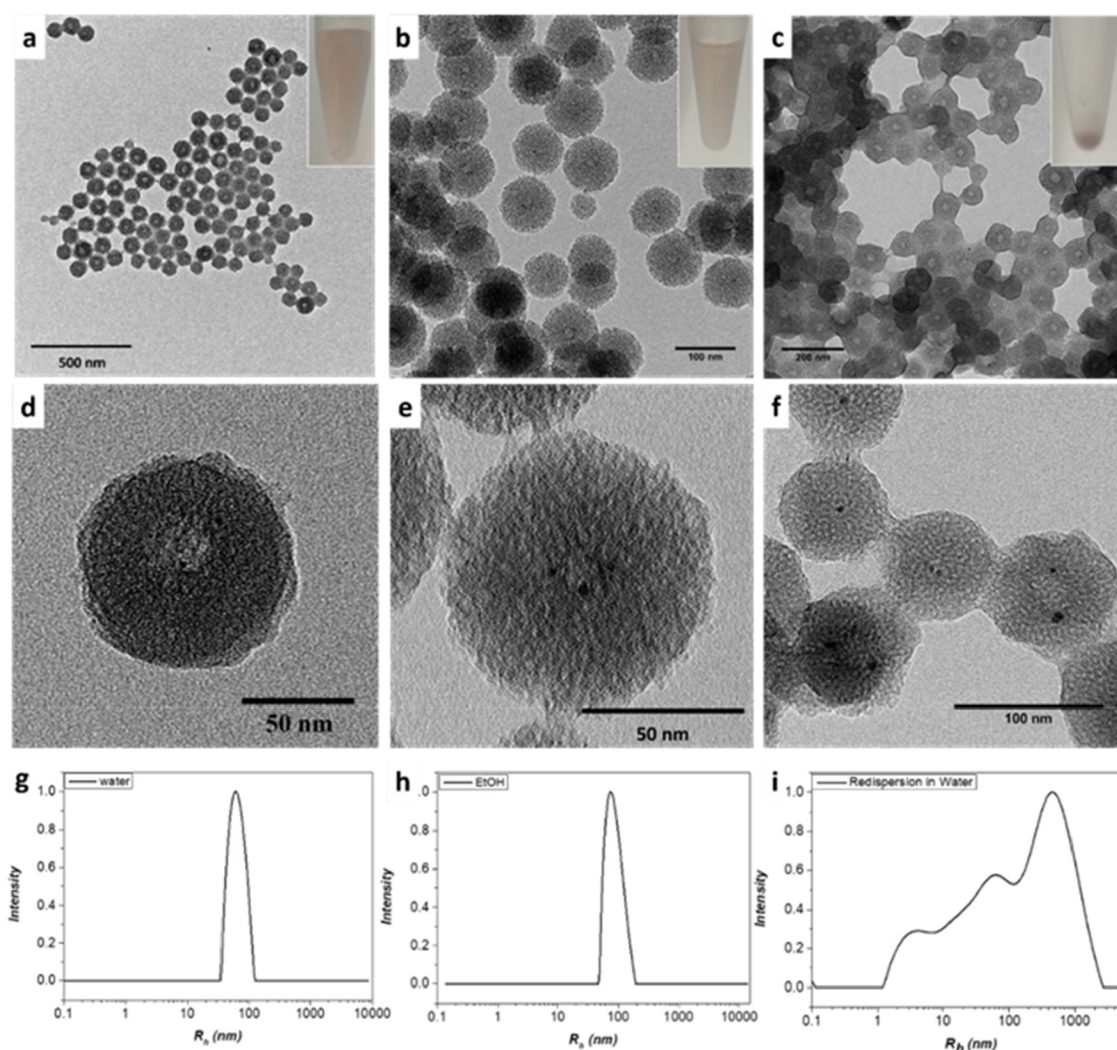
**Catalytic Reduction of 4-Nitrophenol in Water.** Sodium borohydride solution (0.1 M, 0.5 mL) was added to 4.5 mL of 4-nitrophenol solution (0.1 M). Then a given number of PPAPS

nanoreactors were added. UV-vis spectra of the ongoing reaction were recorded every 2 min in the range of 250–550 nm. All solutions were purged with argon before use. The comparative catalytic process for CTAB-Au was carried out under the same conditions.

**Catalytic Oxidation of Benzyl Alcohol in toluene.** Benzyl alcohol (60 μL) was added to 10 mL of toluene. The mixture was stirred for 30 min, and then a given number of PPAPS nanoreactors were added. The catalytic reaction proceeded for 20 h at 110 °C under air. The reaction mixture (20 μL) was added to 1 mL of CH<sub>2</sub>Cl<sub>2</sub> and analyzed by GC. The comparative catalytic process for CTAB-Au was carried out under the same conditions.

## RESULTS AND DISCUSSION

**Synthesis of PTMPM-co-PTMA@Au@Porous SiO<sub>2</sub> Nanoreactors.** The whole synthesis procedure for PPAPS nanoreactors is summarized in Scheme 1. First, thanks to the ionic interaction between AuCl<sub>4</sub><sup>-</sup> and the protonated amine group in PTMPM-Cl, the Au precursors were uniformly localized in the polymer template. Then the in situ generation of Au nanoparticles was achieved via the reduction with NaBH<sub>4</sub>, which was followed by the change in color of the solution from light yellow to wine red and further confirmed by the appearance of a clear plasmon peak at around 530 nm in the UV-vis spectra (see Figure S1). In the next step, the polymer template shrunk in water by the conversion of PTMPM-Cl to more hydrophobic PTMPM, firmly stabilizing



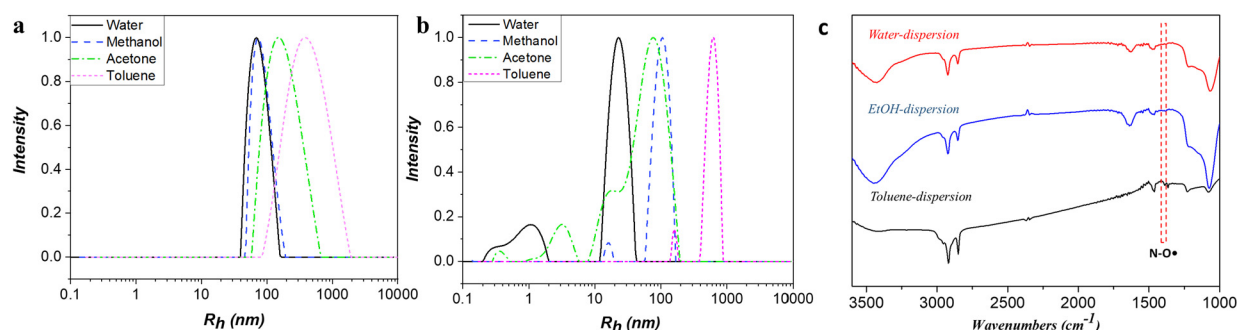
**Figure 2.** TEM images with the related close-up images and DLS measurements of nanoreactors dispersed in water (a, d, g) and in EtOH (b, e, h) and redispersed in water (c, f, i). The inset images are pictures of the corresponding dispersions.

the Au nanoparticles in the composite system (the corresponding sample is denoted as PTMPM@Au). As shown in Figure 1a, the prepared Au nanoparticles with an average diameter of 2 to 3 nm (the size distribution is shown in Figure s2a) were homogeneously immobilized in the PTMPM carrier system without aggregation. Both the low dispersity and small size of the templated Au nanoparticles are crucial to guaranteeing a high catalytic activity. The XRD pattern of PTMPM@Au is presented in Figure s2b. The broad diffraction peaks at 38, 44, 64, and 78° correspond to (111), (200), (220), and (311) Bragg reflections of Au, respectively, indicating a face-centered cubic (fcc) structure for the Au nanoparticles and the extremely small size of the nanoparticles.<sup>19</sup> The synthetic process was continued by the partial oxidation of PTMPM to PTMA by using H<sub>2</sub>O<sub>2</sub> as a catalyst at room temperature. The conversion of PTMPM to PTMA was quantified by an ESR measurement and equaled 16 mol %. This results in the formation of a PTMPM-co-PTMA copolymer, in which TPM and TMA units are likely randomly distributed. Thanks to the assistance of CTAB as a surfactant and template, a layer of porous silica was coated around the PTMPM-co-PTMA core, in agreement with our previously reported method.<sup>20</sup> Finally, core-shell nanospheres

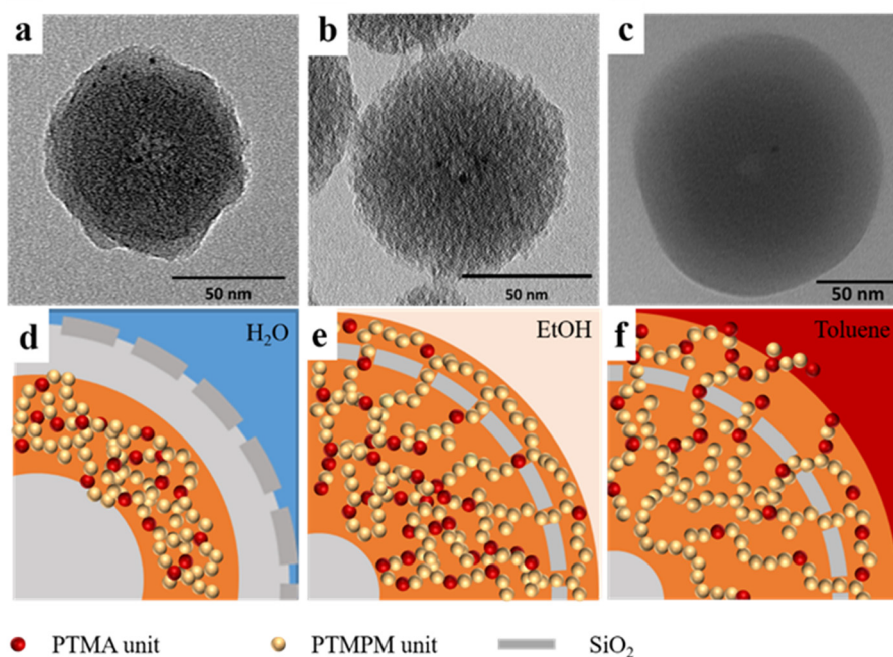
composed of a typical random PTMPM-co-PTMA copolymer core that encapsulates Au nanoparticles and a hydrophilic porous SiO<sub>2</sub> shell were obtained and denoted as PTMPM-co-PTMA@Au@porous SiO<sub>2</sub> (PPAPS). The loading quantity of Au nanoparticles inside PPAPS was confirmed by ICP-OES as detailed in the Experimental Section.

As shown in Figure 1b, PPAPSs core-shell nanoparticles with a uniform diameter of about 80 nm have been visualized by TEM. A thin layer of a porous SiO<sub>2</sub> shell is wrapped around each PTMPM-co-PTMA core. The ring structures observed inside the copolymer cores are attributed to a structural rearrangement of the copolymer which tends to stick on the silica shell as a result of the drying process used for TEM sample preparation. The gold nanoparticles are uniformly dispersed inside the copolymer cores without agglomeration or escaping from the core-shell system, which can be evidenced more clearly from the inset close-up TEM image in Figure 1b. Bridge-like connections can be observed between almost every two adjacent nanoparticles, which are thought to originate from copolymer segments passing through the micropores of the SiO<sub>2</sub> shells. (See the enlarged TEM image in Figure 1c.) Figure 1d shows a cryo-TEM image of the nanoparticles. The nanoparticles are dispersed homogeneously, and no bridge-like





**Figure 3.** DLS of (a) PPAPS nanoreactors and (b) CTAB-Au dispersed in different solvents. (c) FTIR of PPAPS nanoreactors dispersed in different solvents. The peak at 1365  $cm^{-1}$  is associated with nitroxide radicals.

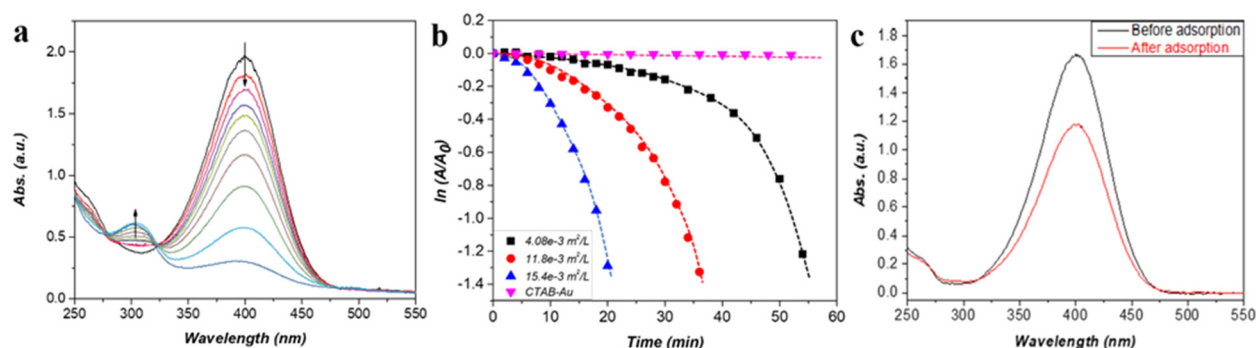


**Figure 4.** TEM images and the corresponding schematic diagrams of the nanoreactors dispersed and swollen in water (a, d), ethanol (b, e), and toluene (c, f).

connection is found, indicating that the formation of the bridges should originate from the drying process for the TEM sample preparation. Indeed, the volatilization of the solvent causes the aggregation of the nanospheres, leading to the connection of the hydrophobic inner cavity through the micropores of the SiO<sub>2</sub> shells and further inducing the bridge connections between hydrophobic copolymer cores. Such a combination of a hydrophilic shell and a mostly hydrophobic core as well as the structural rearrangement ability of the copolymer with the change in external conditions is crucial to the hydrophilic/hydrophobic self-conversion behavior that will be discussed in the next section.

**Hydrophilic/Hydrophobic Self-Regulating Behavior of Nanoreactors.** In order to clarify the stability of PPAPS nanoreactors in different polar environments, the core-shell nanoparticles were first dispersed in water and ethanol, respectively. As shown in the photographs embedded in Figure 2a,b, both water and ethanol (EtOH) dispersions of core-shell nanoparticles are stable and translucent, and the corresponding DLS measurements (see Figure 2g,h) show a time-stable (over more than 1 week) and single sharp peak associated with a narrow size distribution, which directly

demonstrates the good colloidal stability of PPAPS in these two solvents. The only difference is that PPAPS nanoparticles in ethanol exhibit a slightly larger hydrodynamic radius than in water ( $R_{h-water} = 63$  nm and  $R_{h-EtOH} = 73$  nm). This difference is thought to mainly originate from the swelling and structural rearrangement of the PTMPM-co-PTMA cores in ethanol. Ethanol is known to be a better solvent for both PTMPM and PTMA segments than water.<sup>21</sup> Therefore, the ethanol-swollen copolymer segments passed through the micropores of the SiO<sub>2</sub> shells, resulting in the external surface rewinding of the nanoreactors by the copolymer. Compared with the water-dispersed sample, the original ring structure disappeared in the ethanol-dispersed sample, and a much smoother coating layer can be observed from the TEM image (see Figure 2d,e). Additionally, the ethanol-dispersed core-shell nanoparticles cannot be redispersed in water. As shown in Figure 2c, obvious precipitation has been noticed in the water redispersion and significantly large areas of agglomerated nanoparticles have been observed in TEM images (see Figure 2c,f), which agree well with the multiple peaks and the broad particle size distribution in the DLS data of the water redispersed sample in Figure 2i.



**Figure 5.** (a) UV-vis absorption spectra of Nip reduced by NaBH<sub>4</sub> in the presence of PPAPS nanoreactors as catalysts at room temperature in water. (b) Kinetic analysis of the Nip reduction in the presence of different numbers of PPAPS nanoreactors (concentrations indicated in the inset) and CTAB-Au ( $15.4 \times 10^{-3} \text{ m}^2/\text{L}$ ) at room temperature. (The induction period of the reaction has been subtracted.) (c) UV-vis spectra of Nip before and after the adsorption by PPAPS nanoreactors.

Those observations are attributed to the rewapping of the PPAPS nanoreactors' surface by the copolymer, which converts the surface of the core-shell nanoparticles from a hydrophilic SiO<sub>2</sub> layer to an essentially hydrophobic PTMPM-co-PTMA layer. Interestingly, such a structural rearrangement of the copolymer is entirely a consequence of the spontaneous selection of the polymer segments with respect to the external polarity change of the solvent, thereby realizing the hydrophilic/hydrophobic self-regulating behavior of the nanoreactors.

PPAPS nanoparticles were further dispersed into other commonly used solvents in order to highlight the stability of the nanoreactors in different environments. As shown in Figure 3a, PPAPS nanoreactors all showed good colloidal stability for the selected solvents with different polarities. For each of the tested systems, the dispersions are stable without precipitation (see Figure s3), and there is only one single peak observed in the DLS spectra, implying the uniform dispersion of the core-shell nanoparticles.

Notably, with the decrease in the environmental polarity, PPAPS nanoparticles exhibit a larger hydrodynamic radius and a broader particle size distribution, which is consistent with the TEM images shown in Figure 4. In contrast, CTAB-stabilized gold nanoparticles exhibit only good colloidal stability in water. When CTAB-Au nanoparticles are dispersed in the less polar organic solvents, the color of the dispersion changes from pink to blue-violet and obvious precipitation is occurring (see Figure s3). Multiple peaks and a broad size distribution can be observed from DLS measurements in Figure 3b. FTIR spectroscopy was also used to study the surface properties of the PPAPS nanoreactors in different polar environments. As shown in Figure 3c, when the polarity of the solvents decreases, the characteristic peak of N-O $\cdot$  at  $1365 \text{ cm}^{-1}$  becomes more obvious, indicating stronger signals of PTMA units in less polar solvents.<sup>22</sup> This implies that the PTMPM-co-PTMA copolymers do not operate the structural rearrangement as a whole but that PTMA and PTMPM units are responding to the change in the external environment on their own, leading to structural rearrangement inside the copolymers. As depicted in the schematic diagrams in Figure 4, when the external environment is water, the PTMA and PTMPM units of the copolymer shrink into a ring shape within the porous shell due to their hydrophobicity (see Figure 4a). When the external environment converts to ethanol, the swelling of the PTMPM units leads to the rewapping of the surface of the nanoreactors as discussed before while PTMA

units essentially stay in the core to minimize exposure to ethanol. This is consistent with the fact that the hydrodynamic radius of the ethanol-dispersed samples measured by DLS does not increase significantly compared to water-dispersed samples (Figure 2g,h) and the relatively weak nitroxide radical signal in the FTIR spectrum (Figure 3c). When the external environment is changed to toluene, both the PTMA and PTMPM units are swollen by the solvent.<sup>23</sup> Compared to the situation observed in ethanol, both PTMA and PTMPM units swell out of the porous shell toward the solvent, leading to the presence of PTMA units on the surface of the nanoreactors. This leads to a larger hydrodynamic radius for the nanoreactor (see Figure 3a) and a more obvious signal of nitroxide radicals in the FTIR spectrum (see Figure 3c). Moreover, a clearly swollen polymer shell can be observed in the TEM image in Figure 4c. Such observation further confirms that, although both PTMA and PTMPM units of the copolymer are swollen in toluene, the copolymer segments are still confined around the nanoreactors without leaking, which may be due to the physical cross-linking of the molecular segments through the pores on the SiO<sub>2</sub> shells.

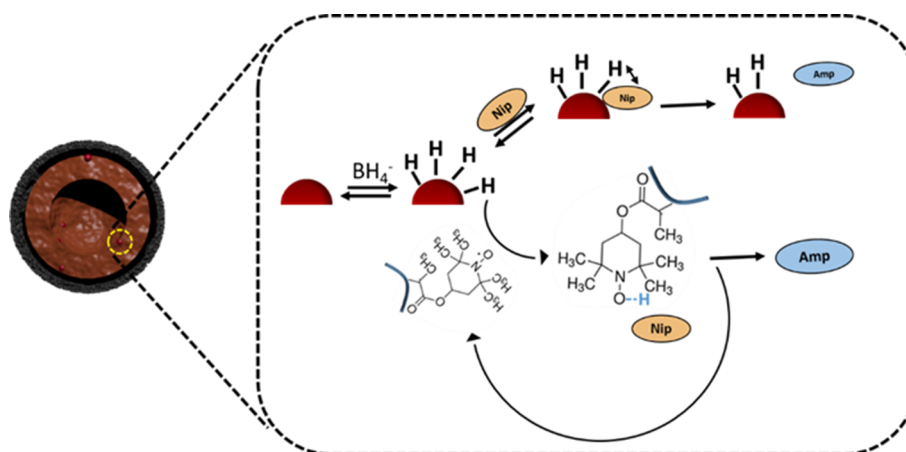
In other words, thanks to the spontaneous response of PTMPM and PTMA units in the copolymer to different external environments, the reversible self-regulation of the surface properties of the nanoreactors can be realized, ensuring their good stability in different solvents. This behavior can be somewhat compared to chameleons adjusting the color of their skin to their environments. This property provides the possibility for nanoreactors to maintain a high catalytic reactivity in different environments.

**Catalytic Activity of Nanoreactors in Multienvironments.** The catalytic reduction of Nip by sodium borohydride in water and the benzyl alcohol oxidation in toluene were selected as model reactions to test the catalytic activity of the PPAPS nanoreactors in both hydrophilic and hydrophobic environments.

As shown in Figure 5a, the reduction of Nip in the presence of PPAPS nanoreactors in water can be easily monitored by UV-vis spectroscopy. As the reduction proceeds, the peak belonging to the 4-nitrophenate ions at 400 nm decreases with time and the peak associated with the product, 4-aminophenol, at 290 nm gradually increases. Since the variation of the concentration (*c*) of Nip with time (*t*) can be directly determined by the ratio of the respective absorbance  $A/A_0$ ,<sup>24</sup> the evolution of  $\ln(c/c_0)$  versus time with different amounts of added catalysts (PPAPS nanoreactors or CTAB-Au nano-



**Scheme 2. Proposed Mechanism for the Reduction of *p*-Nitrophenol (Nip) to 4-Aminophenol (Amp) Catalyzed by PPAPS Nanoreactors in Water**



particles) is depicted in Figure 5b. The amount of catalyst is expressed as the specific surface area of Au per volume unit. From the data reported in Figure 5b, it is obvious that the reaction rate becomes faster with increasing the amount of added PPAPS nanoreactors. As a comparison, with the same specific surface area, the reaction rate with the added CTAB-Au catalyst is much slower. Since both PPAPS and CTAB-Au nanoreactors show good colloidal stability in water (see Figure 3a,b), the difference in the reaction rates could be explained by the following reasons. First, compared to CTAB-Au nanoparticles, the size of the Au nanoparticles loaded in the PPAPS nanoreactors is much smaller (the average diameter of Au nanoparticles in PPAPS nanoreactors is 2 to 3 nm, see Figures 1a and s2a; the average diameter of CTAB-Au is 9 to 10 nm, see Figure s5). Therefore, for a similar Au loading, the available Au surface for the catalytic reaction is higher for the PPAPS nanoreactors. Second, the hydrophobic inner cavity of the PPAPS nanoreactor in water favors the adsorption of the reactant, resulting in a higher reactant concentration around the Au nanoparticles. As shown in Figure 5c, after the addition of the PPAPS nanoreactors (the nanoreactors were removed by centrifugation before the UV-vis measurement), the Nip concentration decreases significantly. In the absence of  $\text{NaBH}_4$ , the decrease in the Nip concentration should be caused by Nip adsorption by PPAPS nanoreactors. This is further supported by the absence of the 4-aminophenol product signal in the UV-vis spectrum, as shown in Figure 5c.

Finally, the PTMA units of the copolymer also participate in the catalytic reaction. As shown in Scheme 2, the reduction of Nip by PPAPS nanoreactors originates from the catalytic combination of Au nanoparticles and PTMA units, and both of them can be recognized as the catalytical sites in this model reaction. According to previous reports, the Au nanoparticles first react with borohydride ions to form metal hydrides.<sup>25,26</sup> A part of the active hydrogens is then reducing Nip molecules adsorbed on the surface of the gold nanoparticles, while the other part of the active hydrogens is reacting with the nitroxide radicals of PTMA units, leading to the formation of PTMA-H bonds (Scheme 2). Such PTMA-H bonds can easily reduce Nip molecules.<sup>27</sup> The involvement of PTMA units in the catalytic reaction makes the reduction of Nip no longer confined to the surface of the Au nanoparticles, leading to the enhancement of the catalytic range and the corresponding

reaction rate. This also caused the deviation of the catalytic curve in Figure 5b from the pseudo-first-order reaction.

The oxidation of benzyl alcohol in toluene was realized by using CTAB-Au nanoparticles and PPAPS nanoreactors as catalysts under mild conditions (ambient air at 110 °C). The reactions were followed by GC, and the obtained results are listed in Table 1. The conversion of benzyl alcohol reached

**Table 1. Different Reaction Conditions for the Oxidation of Benzyl Alcohol to Benzaldehyde in Toluene in the Presence of Either PPAPS or CTAB-Au Nanoparticles**

|   | Catalysts | Au amount (mg)        | Benzyl alcohol ( $\mu\text{L}$ ) | Conversion (%) | Benzaldehyde (%) |
|---|-----------|-----------------------|----------------------------------|----------------|------------------|
| 1 | PPAPS     | $8.65 \times 10^{-3}$ | 60                               | 51             | >99              |
| 2 | PPAPS     | $13.7 \times 10^{-3}$ | 60                               | 73             | >99              |
| 3 | CTAB-Au   | $13.7 \times 10^{-3}$ | 60                               | <5             | >99              |

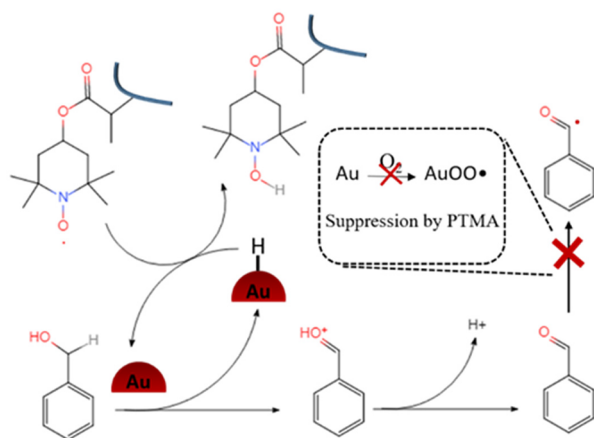
73% by using the PPAPS nanoreactors as catalysts. At the same time, a high selectivity (>99%) for the product (benzaldehyde) was also achieved (see Figure s6). In contrast, the conversion of benzyl alcohol was only 5% by using CTAB-Au as a catalyst, with all other parameters being kept constant. This difference in the catalytic efficiency is attributed to the following two reasons. First, the colloidal stability of the PPAPS nanoreactors in toluene is much better than that of CTAB-Au nanoparticles (see Figure 3a,b), allowing a more effective active surface of Au nanoparticles in the case of PPAPS. Second, the PTMA units in the PPAPS nanoreactors are restoring the surface activity of the Au nanoparticles (see the further discussion of the mechanism of the reaction in the presence of PTMA) and are furthermore suppressing the following oxidation of benzaldehyde into benzoic acid, improving the selectivity of the product.

As shown in Figure s6, PPAPS can be recycled and reused in a new reaction but with a lower catalytic activity, which may be due to the loss of PPAPS during the washing step, the coverage of parts of the active sites by reactants or products, the inactivation of part of the nitroxide radicals after binding with hydrogen, and so on.

The mechanism of alcohol oxidation in the presence of Au nanoparticles has been introduced by Chechik and co-workers.<sup>28</sup> The formation of an Au-H intermediate is observed, and the corresponding hydrogen originates from

the cleavage of the C–H bond in the alcohol molecule, which was further confirmed by isotope labeling. The role of O<sub>2</sub> in the reaction is to remove the hydrogen from the gold surface instead of oxidizing the alcohol. Such a process of reactivation of Au can also be accomplished by nitroxides as hydrogen abstractors. Moreover, the same authors also proved that the initiation step of the aldehyde oxidation is the formation of acyl radicals, which can be efficiently broken by TEMPO.<sup>29</sup> Based on the conclusions of their research, we can speculate on the catalytic reaction process of PPAPS nanoreactors, as shown in Scheme 3. The rate-determining step of the benzyl alcohol

**Scheme 3. Proposed Mechanism for the Benzyl Alcohol Oxidation Catalyzed by PPAPSs in Toluene**



oxidation should be the cleavage of the C–H bond, and the released hydrogen is then captured by the gold surface. The nitroxide radicals on PTMA units have proven to be able to capture the hydrogen from the surface of the Au nanoparticles, leading to the restoring of the surface activity. This promotes the process of the oxidation reaction of benzyl alcohol. Therefore, the Au nanoparticles were considered to be the catalytically active sites, and the PTMA played the role of activating the catalytic reaction sites. Moreover, to the best of our knowledge, alcohol oxidation by using Au nanoparticles as catalysts under an oxygen atmosphere usually proceeds with further oxidation of the aldehyde via a radical pathway.<sup>30</sup> In the presented reaction, due to the utilization of PPAPS nanoreactors as catalysts, the reaction can proceed under milder conditions, which suppress the formation of an acyl radical due to the excess oxygen. Additionally, the nitroxide radicals from PTMA units have proven to be able to efficiently suppress the continued oxidation of benzaldehyde as well,<sup>25</sup> restraining this side reaction and improving the selectivity to the product. Therefore, using PPAPS nanoreactors as catalysts for the oxidation of benzyl alcohol can not only achieve high conversion under mild conditions but also suppress the side reactions, leading to the improvement of the selectivity to the product.

## CONCLUSIONS

We have disclosed novel self-tunable hydrophilic/hydrophobic multienvironment nanoreactors with chameleon-like behavior, consisting of PTMA-co-PTMPM copolymer cores and hydrophilic porous SiO<sub>2</sub> shells. Thanks to the selectivity of PTMA/PTMPM units toward solvents with different polarities, polymer segments can be swollen through the micropores of

the SiO<sub>2</sub> shells to further rewrap the nanoreactors, thereby realizing the hydrophilic/hydrophobic self-regulation with no need for cumbersome surface modification or a polymer grafting process. The structural rearrangement of the copolymer on the surface of the nanoreactors due to the distinct interactions between PTMA/PTMPM units and solvent molecules further helps the nanoreactors to maintain good colloidal stability in a variety of commonly used solvents, and noncovalent interactions of polymer segments with the silica shell prevent the leaking of the copolymer chains out of the PPAPS nanoreactors. Moreover, the PPAPS nanoreactors show a significant enhancement of the reaction rate for the selected model reactions in both polar and nonpolar environments, compared with traditional CTAB-Au catalysts. This is due to not only the excellent colloidal stability of PPAPS nanoreactors in different solvents but also the contribution of PTMA units. Indeed, thanks to the presence of PTMA, the catalytic region and the local reactant concentration around Au nanoparticles are increased, and restoring the surface activity of the Au nanoparticles becomes much faster. The present approach aims to realize the one-for-all catalytic system using the intrinsic physicochemical properties of polymer segments instead of a complex synthetic strategy, which may provide another option for the study of multienvironment nanoreactors.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.3c02185>.

UV–vis spectra of solutions before and after the reduction of Au nanoparticles, size distribution of Au nanoparticles in polymer templates and CTAB-Au, XRD of PTMPM@Au, pictures of nanoreactors and CTAB-Au in different solvents, TEM of CTAB-Au, GC-MS of solutions after oxidation by PPAPS nanoreactors, and CTAB-Au in toluene (PDF)

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## Notes

The authors declare no competing financial interest.

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