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## Facile synthesis of thermo-responsive Au-polymer hybrid microgels through temperature-induced co-aggregation and self-crosslinking

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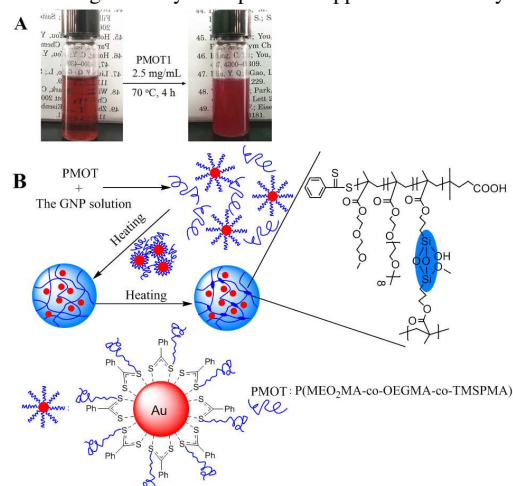
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**Thermo-responsive Au-polymer hybrid microgels were prepared by a facile temperature-induced co-aggregation and self-crosslinking (TICASC) method, needing no complex operations such as preforming of microgels or prior modification of GNPs. The hybrid microgels were utilized as catalysts for the reduction of 4-nitrophenol, which exhibited good activity and recyclability.**

As one of the most widely studied inorganic materials, gold nanoparticles (GNPs) have shown diverse applications in catalysis, sensors and biomedicines, etc.<sup>1</sup> However, because of their high surface energies, GNPs tend to coagulate when some environmental factors (such as pH, solvent and ionic strength) change, which seriously affects their performance.<sup>2</sup> An effective solution to the coagulation is stabilizing GNPs with polymer or inorganic matrix, such as polymer assemblies, microgels and silica nanoparticles.<sup>3</sup> Among these materials, microgels have attracted wide interests for immobilizing GNPs because their structures are not only stable, but also permeable and sometimes stimuli-responsive.<sup>4</sup> There are three major methods for preparing Au-polymer hybrid microgels. The first one is coating GNPs by precipitation polymerization of monomers such as N-isopropylacrylamide and methacrylic acid, forming core-shell or yolk-shell type microgels.<sup>5</sup> Prior surface modification of GNPs is usually necessary in this method, which involves multi-steps and is time-consuming. The second one is in situ reduction of Au<sup>3+</sup> in preformed microgels,<sup>6</sup> however, it's hard to control the size, shape and loading amount of GNPs.<sup>7</sup> The third alternative is to directly incorporate GNPs into microgels via non-covalent interactions (such as electrostatic attraction and

physical entrapment).<sup>7,8</sup> This method is comparatively simple and efficient, while the preforming of certain microgels is still inevitable.

In this work, we report a facile temperature-induced co-aggregation and self-crosslinking (TICASC) method for preparing Au-polymer hybrid microgels, in which no preforming of microgels or modification of GNPs is needed. Thermo-responsive poly-(2-(2-methoxyethoxy)ethyl methacrylate-co-oligo(ethyleneglycol) methacrylate-co-3-(trimethoxysilyl) propyl methacrylate) (P(MEO<sub>2</sub>MA-co-OEGMA-co-TMSPMA)) is employed in this method, and the hybrid microgels are prepared by simply heating the mixture of this polymer and the GNP solution. The loading efficiency of GNPs is close to 100%, and both the size and volume phase transition temperature (VPTT) of the microgels can be easily adjusted. In addition, the catalytic performance of the hybrid microgels for the reduction of 4-nitrophenol has been investigated, indicating that they have potential application in catalysis.



**Fig. 1** (A) Digital photos of the mixture of PMOT1 (5 mg) and the GNP solution (2 mL) before and after being heated at 70 °C; (B) Schematic illustration of the temperature-induced co-aggregation and self-crosslinking process.

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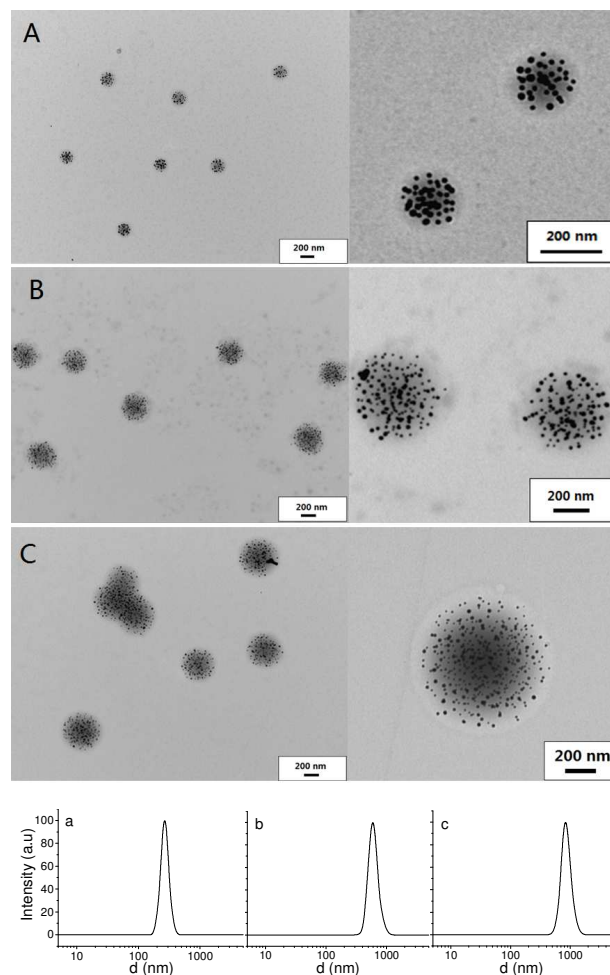
P(MEO<sub>2</sub>MA-co-OEGMA-co-TMSPMA) copolymers with different compositions were synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization (Scheme S1), and the detailed polymerization conditions and results are listed in Table S1. In the <sup>1</sup>H NMR spectrum of the product, signals at  $\delta = 7.4\text{--}8.0$  ppm (a, b, c) are assigned to the proton resonance of aromatic groups, indicating the maintenance of dithiobenzoate groups in the polymer chains (Fig. S2A). Fig. S3 shows the temperature dependence of the transmittance for the aqueous solution of P(MEO<sub>2</sub>MA-co-OEGMA-co-TMSPMA) copolymers, indicating that the products are thermo-responsive. The low critical solution temperatures (LCST) of the products are 36, 41 and 46 °C, respectively, and for distinguishing them in the following sections, they are labeled as PMOT1, PMOT2 and PMOT3.

P(MEO<sub>2</sub>MA-co-OEGMA-co-TMSPMA) can form microgels through a temperature-induced aggregation and self-crosslinking process without need of any surfactant or crosslinking agent, etc. As shown in Fig. S4, upon being heated at 70 °C, the aqueous solution of PMOT1 (2.5 mg/mL) turned opaque within a few minutes. This is because the temperature exceeded the LCST of PMOT1 and led to the aggregation of polymer chains. After 4 h, the dispersion was cooled to room temperature. The cooled suspension didn't turn transparent, indicating that the aggregates had been crosslinked to form microgels. The product was characterized by transmission electron microscope (TEM), and particles of ~300 nm in diameter were observed (Fig. S5).

Generally, the particles formed from temperature-induced aggregation of thermo-responsive polymers will redissolve upon cooling the solution to below the LCST.<sup>10</sup> While in the present work, owing to the existence of TMSPMA units in the polymer chains, aggregates can be gradually crosslinked by the hydrolysis-condensation of methoxysilyl groups.<sup>11</sup> The aqueous medium offers an essential condition for this reaction, because water molecules are involved in the hydrolysis of methoxysilyl groups. According to the Arrhenius empiric equation, the heating can increase the condensation rate of methoxysilyl groups, and on the other hand, the temperature-induced aggregation of polymer chains diminishes the distance between TMSPMA units, which can promote the crosslinking.<sup>11</sup> It was noted that under room temperature, the aqueous solution of PMOT1 (2.5 mg/mL) didn't crosslink even after 12 h. The <sup>1</sup>H NMR spectrum of the microgels is shown in Fig. S2B. Compared with that of P(MEO<sub>2</sub>MA-co-OEGMA-co-TMSPMA), the signals of methoxysilyl groups nearly disappear, which confirms the condensation of these groups.

GNPs were prepared according to the silver(I)-assisted sodium citrate reduction method,<sup>12</sup> and the obtained GNP solution was utilized directly in the preparation of Au-polymer hybrid microgels. As shown in Fig. 1A, when the mixture of PMOT1 (5 mg) and the GNP solution (2 mL) was heated at 70 °C, the solution turned opaque. After 4 h, the suspension was cooled to room temperature. TEM image shows that microgels of ~530 nm in diameter are obtained, and large amount of GNPs are embedded in the microgels (Fig. 2B). The size of the microgels can be adjusted by varying the polymer concentration. As shown in Fig. 2A-C, when PMOT1 is fed at concentrations of 0.75, 2.5 and 5.0 mg/mL, respectively, the average diameters of the microgels are about 190, 490 and 810 nm,

correspondingly. Evidence for the size control is further provided by the dynamic light scattering (DLS) measurements (Fig. 3a-c), and the hydrodynamic diameters ( $D_h$ ) determined are 267, 593 and 835 nm, respectively. These values are larger than those determined by TEM, which is reasonable because the samples for TEM characterization are in collapsed state while for DLS are in swollen state. It's noted that no free GNPs can be discerned on the TEM images, and all DLS curves are unimodal. These results indicate that the loading efficiency of GNPs is close to 100%.



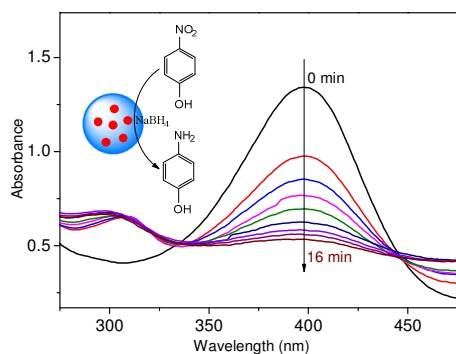
**Fig. 2** TEM images of the hybrid microgels, assembled from PMOT1 of different concentrations in the GNP solution: (A) 0.75 mg/mL, (B) 2.5 mg/mL and (C) 5.0 mg/mL; DLS curves of the above microgels: (a)  $D_h = 267$  nm, (b)  $D_h = 593$  nm and (c)  $D_h = 835$  nm.

It's well known that polymers synthesized via RAFT polymerization can anchor onto the surface of GNPs through the exchange between thioester groups and the citrates.<sup>13</sup> On the other hand, GNPs modified by thermo-responsive polymer usually present aggregation behavior when the environmental temperature exceeds the LCST of the polymer.<sup>14</sup> Based on these points, the formation mechanism of the Au-polymer hybrid microgels is supposed to be a temperature-induced co-aggregation and self-crosslinking (TICASC) process. As illustrated in Fig. 1B, when GNPs are mixed with

P(MEO<sub>2</sub>MA-co-OEGMA-co-TMSPMA), they are combined with a certain amount of the polymer chains on the surface. Upon heating the mixture to above the LCST of P(MEO<sub>2</sub>MA-co-OEGMA-co-TMSPMA), both the surface-modified GNPs and the unbound polymer chains turn hydrophobic and they co-aggregate into hybrid particles.<sup>15</sup> Owing to the hydrolysis-condensation reaction of methoxysilyl groups, these particles are gradually crosslinked in the heating process, forming hybrid microgels ultimately.

The combination between P(MEO<sub>2</sub>MA-co-OEGMA-co-TMSPMA) and GNPs has been confirmed by TEM characterization. In a typical operation, 2 mL of the GNP solution was mixed with 10 mg of PMOT1. The mixture was incubated for 1 h at room temperature and then subjected to 15 min of centrifugation at 13,000 rpm. The precipitate was redispersed in 2 mL of water and then characterized by TEM. As shown in Fig. S6, at the periphery of GNPs, polymer shells of ~4 nm in thickness can be distinguished. The temperature-induced aggregation of GNPs has also been confirmed. When the dispersion of GNPs combined with PMOT1 was heated to 70 °C, the solution turned from red to purple (Fig. S7). TEM image shows that most GNPs are agglomerate (Fig. S8A), and on the surface of them, polymer shells can be also discerned (Fig. S8B).

Owing to the thermo-responsiveness of P(MEO<sub>2</sub>MA-co-OEGMA-co-TMSPMA), the hybrid microgels would undergo swollen-to-collapsed state transition upon heating the suspension above the LCST. DLS was employed to characterize the thermo-induced volume change of the hybrid microgels. Take the microgels of 267 nm in diameter for example, upon heating the suspension,  $D_h$  decreases from 267 to 200 nm (Fig. S9A). The VPTT of the microgels is about 35 °C, which agrees with the LCST of the polymer. Compared with the reported methods for preparing thermo-responsive hybrid microgels, an advantage of our method is that products of different VPTTs can be easily obtained, because the LCST of P(MEO<sub>2</sub>MA-co-OEGMA-co-TMSPMA) can be accurately regulated by varying the relative amount of MEO<sub>2</sub>MA and OEGMA.<sup>16</sup> PMOT1, PMOT2 and PMOT3 are copolymers in which the feeding ratios of MEO<sub>2</sub>MA and OEGMA are 90:10, 85:15 and 80:20, respectively. When these copolymers are utilized in the preparation of hybrid microgels, the VPTTs of the products are 35, 40 and 45 °C, respectively, corresponding with the LCSTs of the polymers (Fig. S9).



**Fig. 3** Time-dependent UV-vis spectra of 4-NP reduction in the presence of the Au-polymer hybrid microgels.

Au-polymer hybrid microgels can be used as nanoreactors because GNPs are efficient catalysts for many reactions and the gel networks are highly permeable for small molecules/ions.<sup>17,18</sup> The present Au-polymer hybrid microgels were employed as a nanoreactor system for the liquid-phase reduction of 4-nitrophenol (4-NP) by NaBH<sub>4</sub> to illustrate their potential applications. It was noticed that without catalyst, the color of the reaction solution didn't change even after 24 h. Once a certain amount of the hybrid microgels ( $D_h = 835$  nm) was added, the color of the solution turned from yellow (the color of 4-NP) to pink (the color of the hybrid microgels) within a few minutes (Fig. S10A). UV-Vis spectroscopy was utilized to monitor the reaction. It was found that as the reaction proceeded, absorption at ~400 nm decreased and new absorption at ~300 nm emerged (Fig. 3), indicating the successful reduction of 4-NP into 4-aminophenol (4-AP).<sup>2</sup> After the reaction was finished, the microgels were recovered by centrifugation (5,000 rpm, 10 min), and then characterized by TEM. No leakage or coagulation of GNPs was found on the TEM image, indicating that GNPs were stable in the gel networks (Fig. S11A). The recovered hybrid microgels were utilized in another two courses of the reaction, in which the reaction rate decreased very little (Fig. S12A).

For comparison, we employed naked GNPs as catalysts for the reduction of 4-NP. As shown in Fig. S10B, after being fed with the GNP solution, the mixture of 4-NP and NaBH<sub>4</sub> turned from yellow to black gradually. TEM image shows that GNPs agglomerated seriously during the catalysis (Fig. S11B). The agglomerated GNPs were extremely hard to redisperse after being centrifugated (15,000 rpm, 10 min), which led to a dramatic decrease in the reaction rate in the following courses (Fig. S12B). These results suggest that the protection from gel networks is important for the recyclability of GNPs.

In conclusion, a facile temperature-induced co-aggregation and self-crosslinking (TICASC) method was developed for preparing Au-polymer hybrid microgels. The loading efficiency of GNPs is close to 100%, and the size of the microgels can be easily adjusted. The microgels are thermo-responsive, and products of different volume phase transition temperatures (VPTT) can be facilely obtained. The Au-polymer hybrid microgels can be used as nanoreactors for the reduction of 4-nitrophenol, indicating that they have potential application in catalysis.

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