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Gold nanoparticles stabilized by amphiphilic hyperbranched polymers for catalytic reduction of 4-nitrophenol



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ABSTRACT

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1. Introduction

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low-molecular-weight polyethylenimine (PEI) conjugated to commercial aliphatic hyperbranched polyesters (Boltorn Hx) were used to stabilize gold nanoparticles (AuNPs) at the interlayer between the core and the shell. It was found that low generations of Hx-PEI-PEG such as H20-PEI-PEG and H30-PEI-PEG cannot effectively stabilize AuNPs. However, H40-PEI-PEG was both the reduction agent and the stabilizer for the formation of AuNPs, which was confirmed from the solution color change and UV-vis absorption spectra. Spherical nanosized AuNPs (below 10 nm) with narrow particle size distributions were observed from the TEM images. The H40-PEI-PEG-stabilized AuNPs solution could be shelf-stored at room temperature for more than 1 month. In addition, H40-PEI-PEG-stabilized AuNPs showed high catalytic activity for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP).

Amphiphilic hyperbranched polymers (Hx-PEI-PEG) with polyethylene glycol (PEG) chains and

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Sub-10 nm gold nanoparticles (AuNPs) show high catalytic activity and good selectivity for organic reactions such as reduction, oxidation, and coupling [1]. However, AuNPs in colloidal solution tend to aggregate, resulting in poor performance [2]. Therefore, the stabilizers of AuNPs face the very challenging task of obtaining stable AuNPs with good size and shape [3]. The stabilizers mainly include inorganic ligands, small organic molecules, linear polymers, and dendrimers [4]. Among these, dendrimers having a spherical structure and a large molecular bore show significant advantages in the synthesis of monodisperse and stable AuNPs [5–7]. However, dendrimers need a tedious multistep synthesis, leading to high cost. Moreover, due to their open structure at low generations, the reactants escape from the interior before contact with AuNPs. The high generations inhibit movement of

Hyperbranched polymers are a class of alternatives to dendrimers and can be synthesized by a one-step reaction from monomers [9]. Use of hyperbranched polymers in the synthesis of AuNPs has also been attempted [10]. However, either hydrophobic or hydrophilic hyperbranched polymers affect their stability in water or organic solvents. Amphiphilic modification is a workable way to solve this problem [11]. Amphiphilic hyperbranched polymers self-

substances into the interior of the dendritic structure [8].

* Corresponding author. E-mail address: zhangxj@whu.edu.cn (X. Zhang). assemble in water or organic solvents and prevent the agglomeration of AuNPs to obtain more uniform and stable AuNPs [12–15]. Conventional amphiphilic hyperbranched polymers also have steric hindrance and the reactants have difficulty in entering the interior to undergo the catalytic reaction. It has been one of the most important topics in the research of AuNPs catalysts to both effectively disperse AuNPs and easily contact the reactants with AuNPs [16–19].

Here we describe the use of unique amphiphilic hyperbranched polymers (Hx-PEI-PEG) to support AuNPs, which are dispersed at the interlayer. More importantly, the reactants easily reach the interlayer and contact AuNPs for catalytic reaction. Hx-PEI-PEG were synthesized through conjugating polyethylene glycol (PEG) chains and azide groups to commercial aliphatic hyperbranched polyesters (Boltorn Hx) after altering hydroxyls to carboxyls with succinic anhydride and then connecting low-molecular-weight polyethylenimine PEI to the polymer via click chemistry (Scheme 1). We hypothesized that metal precursors (AuCl $_4$) can be adsorbed by PEI and then reduced to AuNPs at the interlayer.

2. Experimental

2.1. Materials

Polyethylenimine (PEI, M_w 800 Da), polyethylene glycol methyl ether (PEG, M_w 2000 Da), hyperbranched bis-MPA polyester (H20: 16 hydroxyl, H30: 32 hydroxyl, and H40: 64 hydroxyl), and 4-





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Scheme 1. Schematic illustration of the synthesis of amphiphilic hyperbranched polymers Hx-PEI-PEG.

nitrophenol (4-NP) standard solution (10 mM) were purchased from Sigma-Aldrich and used as received. Hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O) was purchased from Shaanxi Kaida Chemical Engineering Co., Ltd. in China and used as received. Other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. in China and used as received. Hx-PEI-PEG was synthesized as described elsewhere [20].

2.2. Synthesis of hyperbranched polymer-stabilized AuNPs

The in situ formation of AuNPs stabilized by hyperbranched polymers Hx-PEI-PEG was carried out by the addition of HAuCl₄ solution into an aqueous polymer solution and subsequent reduction with NaBH₄. In a typical experiment, an aqueous solution of HAuCl₄ (5.0×10^{-4} M, 2.5 mL) was added to 2.0 mL of an aqueous solution of the polymer (the ratio of nitrogen in the polymer to Au atoms was in the range 0.25–10) with desired pH (4.0, 7.0, and 10.0). The mixture was left at room temperature for 1 h. Subsequently, a fresh aqueous solution of NaBH₄ (2.5×10^{-2} M, 0.5 mL) was added to this mixture at once. The mixture was kept at room temperature for at least 4 h before it was employed in the catalytic reaction.

The Au colloids were characterized by transmission electron microscopy (TEM). TEM was performed on a JEOL-3011 HREM transmission electron microscope operated at accelerating voltage 200 kV. The samples for TEM measurements were prepared by placing a drop of the freshly prepared colloidal solution on a carbon-coated 300-mesh copper grid and allowing it to dry in air naturally. Particle size was calculated by measuring the diameters of samples from the corresponding TEM micrographs and particle distribution was obtained using a Gaussian fit.

2.3. Catalytic reaction of 4-nitrophenol using hyperbranched polymerstabilized AuNPs as catalysts

The catalytic reduction occurred in a standard quartz cell with a 1 cm path length and about 2 mL volume. A fresh aqueous solution of NaBH₄ (0.1 M, 1.0 mL) was mixed with an aqueous solution of 4-nitrophenol (2.0×10^{-4} M, 1.0 mL) in the quartz cell; this led to a change of color from light yellow to yellow green. Immediately after the addition of 2 µL of the prepared AuNPs, the absorption spectra were recorded by a Perkin–Elmer Lambda Bio 40 UV-vis

spectrophotometer in scanning range 200–700 nm at room temperature.

3. Results and discussion

3.1. Synthesis of hyperbranched polymer-stabilized AuNPs

In previous work, Hx-PEI-PEG were synthesized and studied as an effective miRNA carrier. Interestingly, miRNA was combined at the interlayer between the core and shell to form a sandwiched structure, which was confirmed by TEM [20]. As we know, the amino groups of the polymers have the capability of combining metal ions and metal nanoparticles [21]. Therefore, PEI units of Hx-PEI-PEG will tend to absorb $AuCl_4^-$ and AuNPs after chemical reduction [22]. AuNPs are dispersed at the interlayer between the core and the shell. The reactants easily contact AuNPs for catalytic reaction (Scheme 2).

Hx-PEI-PEG series have three different generations of cores with similar composition ratios. The concentration of Au in all the solutions is 250 μ M. The concentrations of Hx-PEI-PEG for C1, C2, C3, and C4 are based on the ratio of nitrogen in the polymer to Au atoms, which is 0.25, 1, 5, and 10, respectively. Amino residues of Hx-PEI-PEG exhibit the ability of Au-ion reduction [21]. The solution color change is observed (Line B in Fig. 1) and the characteristic absorption of AuNPs to the mixture solution of HAuCl₄ and H40-PEI-PEG at low pH is found at wavelengths ca. 536 nm (red line in Fig. 2) in the absence of NaBH₄, which proves the reduction potential of PEI in Hx-PEI-PEG for Au ions at room temperature. The H40-PEI-PEG solution at pH 4.0 exhibits the best reduction capacity. The absence of obvious color change at pH 10.0 indicates that the reduction capacity of PEI in H40-PEI-PEG for Au ions decreases with increased pH. At low pH, amino functional groups are protonated and the acidified ammonium has much greater electron-donating ability for the reduction of Au ions than the unprotonated amino groups at high pH [23]. However, the rate of reduction of Au ions by H40-PEI-PEG at room temperature is low. After the addition of NaBH₄ to the above solution, the mixture immediately takes on a wine red color (Line C in Fig. 1), and the characteristic absorption of AuNPs (blue line in Fig. 2) is observed at wavelengths ca. 536 nm for all pH's, which indicates the formation of AuNPs after the reduction of Au ions. When the solution is



Scheme 2. Schematic illustration of the formation and catalytic reaction of hyperbranched polymer-stabilized AuNPs.



Fig. 1. Photographs of a mixed aqueous solution of HAuCl₄ and H40-PEI-PEG (A), the mixture left to stand at room temperature for 1 h (B), addition of a fresh aqueous solution of NaBH₄ to the mixture (C), after 4 h (D), and after 24 h (E). The concentration of Au in all the solution is 250 µM. The concentrations of H40-PEI-PEG for C1, C2, C3, and C4 are based on the ratio of nitrogen in the polymer to Au atoms, which are 0.25, 1, 5, and 10, respectively.

kept at room temperature for 4 h (Line D in Fig. 1), there is an obvious black precipitate at low concentrations of H40-PEI-PEG (especially such as C1) and the solution is still a beautiful wine red color at high concentrations of H40-PEI-PEG (especially at C4). Therefore, no symmetrical peak at wavelengths greater than 500 nm could be observed for C1 concentration, and the characteristic absorption of AuNPs is still remarkable for C4 concentration from UV–vis absorption spectra (magenta line in Fig. 2). After being left to stand at room temperature, the color (Line E in Fig. 1) and UV–vis absorption (olive line in Fig. 2) of the solution do not show a clear change, suggesting that 4 h of duration is enough for the reduction of Au ions by NaBH₄ within the H40-PEI-PEG solution. These results confirm that H40-PEI-PEG is both the reduction agent and the stabilizer for the formation of AuNPs.

Interestingly, Hx-PEI-PEG with low generations such as H20-PEI-PEG (Fig. 3) and H30-PEI-PEG (Fig. 4) cannot effectively stabilize AuNPs, and all the solutions at different concentrations and different pH's exhibit the black precipitate. It is suggested that H20-PEI-PEG and H30-PEI-PEG have much a looser space structure than H40-PEI-PEG, resulting in the escape of AuNPs from the stabilizer and then the aggregation of AuNPs. This implies that H40-PEI-PEG with the dense hyperbranched structure is a superior stabilizer for AuNPs. Therefore, only H40-PEI-PEG-stabilized AuNPs were used in the study of stability, morphology, and catalytic applications.

TEM images of H40-PEI-PEG-stabilized AuNPs at different pHs are presented in Fig. 5. The concentration of H40-PEI-PEG based on the ratio of nitrogen in the polymer to Au atoms is 10. The reduction time is 4 h at room temperature. Spherical nanosized AuNPs with narrow particle size distributions are observed from the TEM images. The corresponding particle size distribution histograms of H40-PEI-PEG-stabilized AuNPs at different pHs are shown in Fig. 5. The mean particle diameters statistically calculated are 8.07 ± 1.42 nm, 7.63 ± 0.93 nm, and 6.85 ± 0.82 nm for H40-PEI-PEG-stabilized AuNPs at pH 4.0, pH 7.0, and pH 10.0, respectively. With the increase of pH, more uniform AuNPs with smaller size are formed within the H40-PEI-PEG solution. At pH 4.0, PEI in H40-PEI-PEG exhibits the ability to form Au seeds from Au ions, but the rate of reduction of Au ions by H40-PEI-PEG is low and the residue Au ions continue to grow from Au seeds after the addition of NaBH₄, resulting in bigger AuNPs. At pH 10.0, H40-PEI-PEG has no significant reduction capacity to form Au seeds, and Au ions in the solution are reduced to AuNPs with time.

In our chemical reduction system, only water is used as a solvent and the experiment is easily handled without heating and stirring. More importantly, the H40-PEI-PEG-stabilized AuNPs solution can be shelf-stored at room temperature for more than 1 month and the solution color has no perceptible change (Fig. 6). PEI in H40-PEI-PEG plays a major role in absorbing $AuCl_4^-$ and can partially reduce $AuCl_4^-$ to AuNPs at pH < 7.0. Since



Fig. 2. UV-vis absorption spectra of the solution at pH 4.0 (A-D), 7.0 (E-H), and 10.0 (I-L) in Fig. 1 at a scanning range of 200-700 nm.



Fig. 3. Photographs of a mixed aqueous solution of HAuCl₄ and H20-PEI-PEG (A), the mixture left to stand at room temperature for 1 h (B), addition of a fresh aqueous solution of NaBH₄ (C), after 4 h (D), and after 24 h (E). The concentration of Au in all the solution is 250 μM. The concentrations of H20-PEI-PEG for C1, C2, C3, and C4 are based on the ratios of nitrogen in the polymer to Au atoms, which are 0.25, 1, 5, and 10, respectively.

H40-PEI-PEG is an amphiphilic polymer, which exhibits a strong tendency to self-assemble into core-shell micelles in aqueous solution [20], AuNPs are entrapped at the interlayer between the core and shell, thus resulting in stable AuNPs.

3.2. Catalytic activity of hyperbranched polymer-stabilized AuNPs

Catalytic reduction is one of the important applications of AuNPs [24]. Here, catalytic activity of H40-PEI-PEG-stabilized



Fig. 4. Photographs of a mixed aqueous solution of HAuCl₄ and H30-PEI-PEG (A), the mixture left to stand at room temperature for 1 h (B), addition a fresh aqueous solution of NaBH₄ (C), after 4 h (D), and after 24 h (E). The concentration of Au in all the solutions is 250 μM. The concentrations of H30-PEI-PEG for C1, C2, C3, and C4 are based on the ratios of nitrogen in the polymer to Au atoms, which are 0.25, 1, 5, and 10, respectively.



Fig. 5. TEM images and the corresponding particle size distribution histograms of AuNP samples obtained within H40-PEI-PEG at pH 4.0 (A and D), 7.0 (B and E), and 10.0 (C and F). The ratio of nitrogen in the polymer to Au atoms is 10. The reduction time is 4 h at room temperature. Scale bar: 20 nm.

AuNPs is tested by the reduction of 4-nitrophenol (4-NP) to 4aminophenol (4-AP), which is a well-known catalytic reaction in industry [25]. After the addition of a fresh aqueous solution of NaBH₄, the absorption peak of 4-NP exhibits a red shift from 317 to 400 nm due to the formation of 4-nitrophenolate ions. The solution color has a significant change from light yellow to yellowgreen [26]. Without the addition of H40-PEI-PEG-stabilized AuNPs, the mixture of 4-NP and NaBH₄ sustains the solution color and the absorption strength at 400 nm for a long time, which indicates that NaBH₄ itself cannot reduce 4-nitrophenolate ions. However, after the addition of H40-PEI-PEG-stabilized AuNPs, the mixture undergoes fading from yellow-green to colorless within about 15 min.

The kinetics of 4-NP reduction was investigated by UV-vis spectroscopy. Since the doses of H40-PEI-PEG-stabilized AuNPs used in the catalytic reduction is very low, the absorption spectra are not affected by the H40-PEI-PEG-stabilized AuNPs. Time dependent UV-vis spectra and the corresponding plot of $\ln(C_t/C_0)$ vs. time are shown in Fig. 7. The concentration of H40-PEI-PEG, based on the ratio of nitrogen in the polymer to Au atoms, is 10. The absorption peak of 4-nitrophenolate ion at 400 nm immediately decreases with time after the addition of H40-PEI-PEG-stabilized AuNPs. Two new peaks at 230 and 300 nm appear in the absorption spectra of reduction products, indicating the formation of 4-AP. The catalytic reduction of 4-NP is complete within 15 min, confirmed from the strength of the absorption peak at 400 nm and the solution color change. As desired, a good linear correction of $\ln(C_t/C_0)$ vs. time is gained and the kinetic reaction rate constants (*k*) at pH 4.0, 7.0, and 10.0 are calculated to be 0.153, 0.196, and



Fig. 6. Photographs of H40-PEI-PEG-stabilized AuNPs in aqueous solution after shelf storage for 2 days (A), 7 days (B), and 1 month (C).



Fig. 7. Time-dependent UV-vis spectra for the reduction of 4-NP and the corresponding plots of $\ln(C_t/C_0)$ vs. time using AuNPs samples obtained within H40-PEI-PEG at pH 4.0 (A and D), 7.0 (B and E), and 10.0 (C and F). The ratio of nitrogen in the polymer to Au atoms is 10.

0.256 min⁻¹, respectively. k increases with the increase of pH. The reason is probably that smaller particles at low pH are more active owing to a larger number of surface atoms available for catalysis. Therefore, H40-PEI-PEG is a good stabilizer in the preparation of AuNPs and shelf-storage H40-PEI-PEG-stabilized AuNPs have high catalytic activity for the reduction of 4-NP.

The previous studies on the reduction of 4-NP using polymerstabilized AuNPs catalysts are summarized together with our work in Table 1. Compared with other reported polymer-stabilized AuNPs catalysts for the reduction of 4-NP, the concentration of AuNPs (0.25 μ M) in our work is very low and the as-prepared H40-PEI-PEG-stabilized AuNPs can catalyzed the fast chemical reduction of 4-NP to 4-AP. For similar catalytic activity, the number of AuNPs that can effectively catalyze the reduction of 4-NP is lower in this work (100-fold or more) than others. Thus, H40-PEI-PEG-stabilized AuNPs exhibit good catalytic performance for the chemical reduction of 4-NP. At low pH, H40-PEI-PEG has much greater absorption and reduction ability for Au ions. But the particle size distribution of AuNPs obtained at low pH is not so good, resulting in unsatisfactory catalytic activity for the reduction of 4-NP. Although H40-PEI-PEG at pH higher than 7.0 does not exhibit significant reduction capacity for Au ions, the catalytic activity of H40-PEI-PEG-stabilized AuNPs for the reduction of 4-NP at high pH is very good. AuNPs prepared at different pHs exhibit different Au particle radii (r_{Au}) and the quality of AuNPs used in the catalytic reduction of 4-NP is identical, so that Au areas (S_{Au}) are different at different pH. In order to examine the quantitative relation between catalytic activity (k) and r_{Au} , excluding the impact of S_{Au} , S_{Au} is calculated as follows:

$$S_{\rm Au} = \frac{C_{\rm Au} \times V_{\rm sol} \times M_{\rm Au}}{\frac{4}{3}\pi r_{\rm Au}^3 \times \rho_{\rm Au}} \times 4\pi r_{\rm Au}^2 = \frac{3 \times C_{\rm Au} \times V_{\rm sol} \times M_{\rm Au}}{r_{\rm Au} \times \rho_{\rm Au}}$$

where C_{Au} is 0.25 µmol/L, V_{sol} is 2 mL, M_{Au} is 197 g/mol, and ρ_{Au} is 19.32 g/cm³. Thus, $S_{Au} = 0.153 \times 10^{-7} (\text{cm}^3)/r_{Au}$. The quantitative relation between r_{Au} and S_{Au} with k at different pHs is listed in Table 2. The r_{Au} decreases with the increase of pH, resulting in an increase of S_{Au} . Higher S_{Au} exhibits higher catalytic activity. After the impact of S_{Au} is excluded, the k/S_{Au} increases with increased pH. Therefore, the concentration of AuNPs and Au particle size, including particle size distribution, are the most important factors influencing the catalytic reduction of 4-NP.

Table 1

Comparison of the reduction of 4-NP using polymer-stabilized AuNPs catalysts.

Entry	Polymer	Size of Au (nm) ^a	C _{Au} (μM)	k (min ⁻¹)	Ref.
1	PAMAM ^b	2.3	40	0.120	[27]
2	PDMAEMA-PS ^c	4.2	436	0.192	[28]
3	PNIPAM-co- P4VP ^d	3.3	20	0.036	[29]
4	Casein ^e	2.6	50	0.233	[26]
5	H40-PEI-PEG ^f	7.6	0.25	0.196	This work

^a Observed by TEM.

^b Poly(amidoamine)-based hollow capsules.

^c Poly(2-(dimethylamino)ethyl methacrylate) grafted onto a solid polystyrene core.

^d Poly(*N*-isopropylacrylamide)-*co*-poly(4-vinyl pyridine).

^e A protein thought of as amphiphilic block copolymers.

^f Aliphatic hyperbranched polyester-polyethylenimine-polyethylene glycol.

Table 2

Quantitative relation of Au particle size (r_{Au}) and Au area (S_{Au}) with catalytic activity (k) at different pH's.

pН	r _{Au} (nm)	S_{Au} (cm ²)	k (min ⁻¹)	$k/S_{Au} ({ m min^{-1}}{ m cm^{-2}})$
4.0	4.035 ± 0.71	0.039 ± 0.0069	0.153	3.9 ± 0.6
7.0 10.0	3.815 ± 0.46 3.425 ± 0.41	0.041 ± 0.0052 0.045 ± 0.0054	0.196 0.256	4.8 ± 0.5 5.7 ± 0.6

4. Conclusions

In summary, we describe a facile preparation of H40-PEI-PEGstabilized AuNPs at room temperature. The preparation route is mild and low-cost. The particle sizes of AuNPs are sub-10 nm, which is adjusted by changing the solution pH. PEI in H40-PEI-PEG can reduce Au ions, and the reduction ability decreases with increased pH. AuNPs are stabilized at the interlayer between the core and the shell due to the absorption of PEI to Au ions and AuNPs. H40-PEI-PEG-stabilized AuNPs at high pH have superior catalytic activity for the reduction of 4-NP. H40-PEI-PEG will hopefully be usable for the preparation of other stable metal nanoparticles such as Ag, Pd, and Pt.

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