Hyperbranched Polyglycidol Assisted Green Synthetic Protocols for the Preparation of Multifunctional Metal Nanoparticles

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Biocompatible hyperbranched polyglycidol (HBP) has been demonstrated to be an effective reducing and stabilizing agent for the synthesis of highly water-soluble monometallic (Au, Ag, Pt, Pd, and Ru) and bimetallic (Au/Pt, Au/Pd, and Au/Ru) nanoparticles (NPs), which provides a general and green protocol to fabricate metal NPs. The HBP-assisted reduction of metal ions follows an analogous polyol process. The reduction reaction rate increases sharply by increasing the temperature and the molecular weight of HBP. The size of NPs is controllable simply by changing the concentration of the metal precursor. High molecular weight HBP is favorable for the formation of NPs with uniform size and improved stability. By utilizing hydroxyl groups in the HBP-passivation layer of Au NPs, TiO2/Au, GeO2/Au, and SiO2/Au nanohybrids are also fabricated via sol−gel processes, which sets a typical example for the creation of versatile metal NPs/inorganic oxide hybrids based on the as-prepared multifunctional NPs.

Introduction

Metal nanoparticles (NPs) continue to attract considerable interest across diverse areas of science due to their unique physicochemical properties derived from the quantum size effect and single-electron transitions.1,2 To date, a variety of promising approaches such as polyol processes,3−7 phase transfer strategy,8,9 and surfactant-assisted pathways10−13 have been developed to synthesize various metal NPs (Table 1). In those synthetic processes, additional chemicals such as reducing agents, organic solvents, and extra surfactants were generally involved. Moreover, most of those as-prepared metal NPs are devoid of functional surfaces. Therefore, extra ligand-exchange reactions tend to be necessary to achieve metal NPs with functionalities.14,15 All of these unavoidably not only complicate the preparation procedures but also generate environmental hazards, and could result in the formation of harmful chemical-containing metal NPs. Recent studies have demonstrated that the widespread application of such yielded NPs could arouse potential environmental and biological risks.16,17 To conquer these limitations, one of the preliminary alternatives is to develop “green” protocols to synthesize those NPs.18 From the “green” chemistry perspective, the preparation of metal NPs consists of three main steps: the choice of the environmentally benign solvent medium used for the synthesis, the choice of the environmentally friendly reducing agent, and the choice of nontoxic materials for the stabilization of the NPs.18,19

Aimed to prepare metal NPs via “green” protocols, a few synthetic strategies have been explored (see Table 1). For instance, using environmentally benign and renewable materials such as β-D-glucose as reducing agents and starch or ionic polymers as protective agents, Ag and Au NPs have been successfully prepared.18,23 In addition, García-Serrano et al.24 have demonstrated that the environmentally benign poly(o-acyloxyaminophenylarsonic acid) and poly(p-acyloylamino-phenylarsonic acid) could serve as both reducing and stabilizing agents for the synthesis of Au and Ag NPs. However, all these green processes are efficient only for specific metal NPs. Therefore, it is highly desirable to develop more general and green synthetic strategies for synthesizing multifunctional metal NPs. Hyperbranched polyglycids (HBPs) have been proven to be a type of highly biocompatible polymer, which can be conveniently synthesized in a single step and in a high yield.24,25 HBP

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macromolecules consist of dendritic units, linear polymer segments, and numerous terminal hydroxyl groups, which provide a three-dimensionally dendritic globular architecture (Scheme 1). The unique molecular structure of HBP molecules makes them particularly well-suited for synthesizing metal NPs owing to the following reasons: (1) the terminal hydroxyl groups can effectively reduce metal ions to produce metal nanoparticles via an analogous polyol process, and thus, they serve as highly effective reducing agents; (2) the dendritic and void-containing structure allows them to host and stabilize the as-synthesized metal NPs, and therefore, they act as stabilizer; and (3) the hydroxyl moieties bearing on the periphery of HBP-stabilized metal NPs endow such NPs with functional surfaces, which provides promising building blocks to construct a variety of metal NP-based hybrid nanostructures. Note that dendrimeric macromolecules, such as poly(amidoamine) and poly(propylene imine), possessing similar dendritic architectures to HBPs have also been extensively used to synthesize metal NPs. However, in those dendrimer-assisted synthetic protocols, extra reducing agents such as NaBH₄ were generally involved. In addition, HBPs can be easily produced by a one-step ring-opening polymerization reaction, while dendrimers are generally synthesized by rather tedious procedures under harsh conditions. Therefore, compared with dendrimers, the HBP-assisted approach provides a more competitive economic and green alternative to synthesize metal NPs.

Herein, we have explored the use of HBPs as both reducing and stabilizing agents to produce various monometallic (Au, Ag, Pt, and Ru) and bimetallic (Au/Pt, Au/Pd, and Au/Ru) NPs via an analogous polyol process. By utilizing hydroxyl groups in the HBP-passivation layer of NPs, metal NPs/organic oxide hybrids are also fabricated via sol–gel processes. As a means of developing a literally green process, we have used no additional solvents except water and no additional chemicals such as surfactants and reducing agents during the reactions, and employed mild reaction conditions.

**Experimental Section**

**Synthesis of HBP and Cyclohexyl Terminated HBP.** HBP macromolecules with different molecular weights (MWs) were synthesized via anionic ring-opening multibranching polymerization. Polymerization was carried out in a reactor equipped with a mechanical stirrer and dosing pump under nitrogen atmosphere. A 50 mM aliquot of glycidol (Aldrich) was slowly added into the reactor containing trimethylolpropane partially deprotected (10%) with sodium methylate solution (3.7 M in methanol, Aldrich) at 95 °C over 12 h. After completion of the reaction (the absence of excess epoxide), the product was dissolved in ethylene glycol, Aldrich at 95 °C, tonated (10%) with sodium methylate solution (3.7 M in methanol and neutralized by filtration over cation-exchange resin. The polymer was triple precipitated from methanol solution into ethyl acetone and subsequently dried for 20 h at 80 °C under vacuum.

Following similar procedures, HBP with different MW could also be obtained by changing the monomer/initiator ratio. The resulting HBPs applied in our current study possess 1000, 1800, and 2000 g/mol of Mn, determined via the ¹³C NMR spectrum of HBP (see Figure S1 of Supporting Information). To synthesize cyclohexyl terminated HBP, 65 mg of cyclohexyl isocyanate was added (the absence of excess epoxide), the product was dissolved in ethylene glycol, Aldrich at 95 °C over 12 h. After completion of the reaction (the absence of excess epoxide), the product was dissolved in ethylene glycol, Aldrich at 95 °C over 12 h. After completion of the reaction (the absence of excess epoxide), the product was dissolved in ethylene glycol, Aldrich at 95 °C over 12 h. After completion of the reaction (the absence of excess epoxide), the product was dissolved in ethylene glycol, Aldrich at 95 °C over 12 h.

Table 1. Summary of the Synthesis of Metal NPs Using Various Approaches

<table>
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<tr>
<th>methods</th>
<th>metal NPs</th>
<th>solvents</th>
<th>temp (°C)</th>
<th>time (h)</th>
<th>reducing agents</th>
<th>stabilizing agents</th>
<th>reaction conditions</th>
<th>functional groups on NPs’ surface</th>
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<tr>
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<td>EG</td>
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<td>EG</td>
<td>PVP</td>
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<tr>
<td></td>
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<td>glycerol</td>
<td>PVP</td>
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<td></td>
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<td>EG</td>
<td>oleic acid</td>
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<td></td>
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<tr>
<td></td>
<td>Au/Pt</td>
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<td>EG</td>
<td>PVP</td>
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<td>Au/Pd</td>
<td>EG</td>
<td>100−190</td>
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<td>PVP</td>
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<td>NaBH₄</td>
<td>OH-terminated PAMAM or PPI</td>
<td>−OH or −NH₂</td>
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<td>Au</td>
<td>water</td>
<td>rt</td>
<td>24</td>
<td>NaBH₄</td>
<td>ionic liquid</td>
<td>11 宝特</td>
<td>PAMAM or PPI</td>
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<td>polythiophene</td>
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<td>rt</td>
<td>NaBH₄</td>
<td>DMP</td>
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<td>β-D-glucose</td>
<td>Starch</td>
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<td></td>
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<td>25−70</td>
<td>2.5−7</td>
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<td>water</td>
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<td>220−243</td>
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<td>water</td>
<td>rt</td>
<td></td>
<td>HBP</td>
<td>HBP</td>
<td>−OH</td>
<td>22</td>
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</table>

AA = Ascorbic acid; AN = acetonitrile; DMF = N,N′-dimethylmethanamide; EG = ethylene glycol; HBP = hyperbranched polyglycidol; PAMAM = poly(amidoamine); PPI = poly(propylene imine); poly(o-AAPHA) = poly(o-acryloylamino phenylarsonic acid); poly(p-AAPHA) = poly(p-acryloylamino phenylarsonic acid); PAAm = poly(amidoamine); PVP = poly(vinyl pyrrolidone).


Preparation of Monometallic and Bimetallic NPs. All the following reactions were carried out in water, at ambient temperature, and under normal pressure. To prepare monometallic NPs, 0.1 mL of metal precursor (10 mM, HAuCl₄, AgNO₃; 40 mM, K₂PtCl₄, Na₂PdCl₄, and RuCl₃) was injected into 1 mL of HBP aqueous solution (Mₙ = 3400 g/mol; 5 mg/mL) under magnetic stirring. After a suitable period of stirring, the resulting metal NPs colloids were purified using cellulose acetate dialysis tubing (MWCO 12 000 g/mol). To produce bimetallic NPs, two methods (co-feeding and sequential feeding) have been employed. (1) Co-feeding route: 0.2 mL of aqueous precursor mixture solution (HAuCl₄:K₂PtCl₄ = 1:1; HAuCl₄:Na₂PdCl₄ = 1:1 and HAuCl₄:RuCl₃ = 1:1) was injected into 1 mL of HBP aqueous solution (5 mg/mL) with vigorous stirring for a suitable period of time. (2) Sequential feeding route: 1.1 mL of Au NPs colloid was first prepared following the procedures mentioned above. Subsequently, 0.1 mL of K₂PtCl₄, Na₂PdCl₄, and RuCl₃ solution (10 mM) was added to as-prepared Au NP colloid with vigorous stirring for a suitable period of time. All the resulting bimetallic NPs were purified using cellulose acetate dialysis tubing.

Fabrication of Au NPs/Inorganic Oxide Hybrids. Based on the as-prepared Au NPs obtained by the procedures described above, TiO₂/Au, GeO₂/Au, and SiO₂/Au hybrids were fabricated via sol–gel processes. The typical fabrication procedures are as follows. (1) TiO₂/Au hybrid: 0.5 mL of Au NP colloid was dried under vacuum and then dispersed in 1 mL of absolute ethanol. Subsequently, 20 μL of titanium tetraisopropoxide (TTIP) was directly injected into the solution with vigorous stirring. Stirring was discontinued when the solutions turn slightly turbid. After sitting for 10 min, the TiO₂/Au hybrid was washed via three cycles of centrifugation and redispersion in absolute ethanol. (2) GeO₂/Au hybrid: 20 μL of tetraethyl germane (TEOG) was injected into a vial containing 0.5 mL of Au NP solution and 0.5 mL of absolute ethanol. After stirring overnight, the resulting GeO₂/Au hybrid was purified via three cycles of centrifugation and redispersion in absolute ethanol. (3) SiO₂/Au hybrid: 0.5 mL of Au NP solution was added to a vial containing 1 mL of absolute ethanol. Subsequently, 0.1 mL of ammonia–water (28 wt %) and 20 μL of tetraethyl oxysilane (TEOS) were injected in sequence with vigorous stirring. After continuous stirring overnight, the resulting SiO₂/Au hybrid was collected and washed via three cycles of centrifugation and redispersion in ethanol.

Characterizations. 2D NMR spectra were recorded on a Varian MERCURY plus-400 spectrometer at 400 and 100 MHz for ¹H and ¹³C, respectively. MALDI-TOF-MS measurement was performed with a Bruker Reflex II MALDI-TOF (matrix-assisted laser desorption and ionization time-of-flight) mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. UV–vis absorption spectra of the samples were recorded at room temperature on a UV-1650PC apparatus (SHIMADZU). Samples for transmission electron microscopy (TEM) were deposited onto carbon-coated copper electron microscope grids and dried in air. The size, shape, and fine structures of NPs were investigated using a model H-7600 (HITACHI) low resolution and JEOL 1200 EX high resolution transmission electron microscope. Fourier transform infrared (FTIR) spectra were obtained at a resolution of 1 cm⁻¹ with a Bruker FT-IR spectrophotometer between 4000 and 400 cm⁻¹. The IR measurements of the powder samples were performed in the form of KBr pellets. The structures of the products were examined by X-ray diffraction (XRD) with an automatic Philips powder diffractometer using a nickel-filtered Cu Kα radiation. The diffraction pattern was collected in the 2θ range 15°–90° in steps of 0.02° and with a counting time of 2 s/step. The exact metal contents in the bimetallic NPs were analyzed using an atomic emission spectrophotometer equipped with a Jarrell Ash 955 inductively coupled plasma (ICP) system.

Results and Discussion

Syntheses of HBPs. The HBP molecules with number average molecular weights (Mₐ) of 1000, 1800, and 3400 g/mol obtained from ¹³C NMR spectra of HBPs (see Figure S2 of the Supporting Information) were first synthesized by means of anionic ring-opening multibranching polymerization method.²⁶,²⁷ From the MALDI-TOF mass spectrum of HBP (Figure 1A), the calculated Mₐ is 1000 g/mol, which is in good agreement with the value obtained from the ¹³C NMR spectrum (see Figure S2b of Supporting Information). The mass differences between the peaks represent precisely the molar mass of glycidol (M = 74). Figure 1B shows a section of the HSQC spectrum of 1000 g/mol of HBP. The significant signals of the molecular components of HBP are presented in the marked zones, evidencing that HBPs consist of dendritic units, linear polyether segments, and numerous terminal hydroxyl groups.

Scheme 1

*Schematic architecture of a hyperbranched polyglycidol (HBP) molecule (a), Mulliken atomic charges on oxygen atoms in backbone of HBP calculated by semiempirical CNDO method (inset of (a), also see Figure S1 in the Supporting Information) and HBP optimized geometry structure (b) obtained by the combination of semiempirical and molecular mechanics method PM1/AMBER using HyperChem release 8.03 for Windows software.
Synthesis of Monometallic NPs. Using HBP (3400 g/mol) as both reducing and stabilizing agent, varied water-soluble monometallic NPs (Au, Ag, Pt, Pd and Ru) have been prepared at ambient temperature (20°C), which can be visualized via the color changes of the resulting colloid solution (for example, from light yellow to wine red color for Au) after mixing the aqueous precursor solution of HBP for a suitable period of time. The evolution of the reduction reactions and the formation of these NPs in the colloid solution were monitored by their UV-vis absorption spectra at different time intervals (see Figure S3 of the Supporting Information). For instance, when the reducing process of AuCl$_4^-$ (1.0 mM) has proceeded for 6 min, a broad plasmon band centered at 515 nm is observed, being associated to the presence of spherical Au NPs.$^{28}$ With the increase of reaction time, the intensity of the surface plasmon resonance (SPR) band increases systematically until it reaches a maximum after 110 min. Thereafter, the intensity of the SPR band approaches an asymptotic value, indicating the completion of reduction (see Figure S3a of the Supporting Information).$^{20,29}$ It is worth noting that the changes in absorbance with time cannot be directly related to the kinetic change in concentration of the as-formed NPs owing to its size changes during the reaction and produces a variation in the extinction coefficient.$^{30}$ Because of this effect, the real value of the concentration of NPs at a given time cannot be directly calculated from the absorbance value. Nevertheless, such changes allow comparison of the global kinetic behavior of reactions and have been frequently used to evaluate NP formation.$^{31,32}$ Similarly, according to the evolution tendency of the absorption bands, it took 5, 22.5, 30, and 32 h to complete the reactions for Ag$^+$, PtCl$_4^{2-}$, PdCl$_4^{2-}$, and Ru$^{3+}$, respectively (see Figure S3b–e of the Supporting Information). These differences in the reduction time of different metal precursors are mainly caused by the different reduction potentials of the metal ions (AuCl$_4^-$/Au$^0$, +1.0 eV vs SHE; Ag$^+$/Ag$^0$, +0.80 eV vs SHE; PtCl$_4^{2-}$/Pt$^0$, +0.76 eV vs SHE; PdCl$_4^{2-}$/Pd$^0$, +0.64 eV vs SHE; Ru$^{3+}$/Ru$^0$, +0.62 eV vs SHE).$^{33–35}$

Figure 1. (A) MALDI-TOF mass spectrum and (B) HSQC NMR section spectrum (measured in DMSO-d$_6$) of 1000 g/mol of HBP.

Figure 2a–e shows the TEM images and the associated particle size distributions of typical samples of Au, Ag, Pt, Pd, and Ru NPs, respectively. Au NPs with good uniformity (Figure 2a, 6.8 ± 1.3 nm) and Ag NPs with relatively broad size distribution (Figure 2b, 11.3 ± 4.2 nm) are usually spherical in shape with smooth surfaces. Pt, Pd, and Ru NPs exhibit ultrafine and nearly spherical morphologies with 1.8, 2.4, and 1.4 nm in average diameter, respectively (Figure 2c–e). Further evidence for the formation of monometallic NPs was achieved by the typical photographs and UV–vis spectra of the resultant metal NPs colloids. Figure 2g exhibits the characteristic color and absorption bands of corresponding NPs. Powder XRD measurements (Figure 2h) confirm the successful synthesis of face-centered cubic (fcc) structured Au (JCPDS 4-784), Ag (JCPDS 4-783), Pt (JCPDS 4-802), Pd (JCPDS 46-1043), and hexagonal Ru (JCPDS 6-663). Note that all the prepared monometallic NPs are stable in aqueous solutions without precipitation for more than 6 months, indicating the HBP molecules serve as not only an effective reducing agent but also a stabilizing agent.

Effects of Reaction Conditions on the Formation of Metal NPs. To get further insight on the HBP-assisted reducing and stabilizing process for the formation of metal NPs, the effect of reaction conditions including temperature, the concentration of metal precursor, and the molecular weight (MW) of HBP on the formation of Au NPs was systematically investigated as a typical example. The corresponding reaction processes were traced by recording the changes in the UV–vis spectra with time. Determined by the evolution of plasmon band intensity as a function of time (Figure 3), it takes 110, 50, and 5 min to finish the reduction reactions when the reactions are carried out at 20, 45, and 70 °C, respectively. With the increase of reaction temperature, the size of Au NPs increases from 6.8, 8.6, to 9.8 nm in average diameter. However, no obvious change in the morphology of NPs is observed (see Figure S4 of the Supporting Information). In addition, these NP colloids are stable in water for more than 6 months at ambient temperature. Therefore, the increase in reaction temperature can greatly increase the reduction reaction rate and yields NPs with larger size. Simultaneously, there are no obvious effects on the morphology and stability of resulting NPs.

A series of experiments were carried out to investigate the effect of the concentration of metal precursor on the formation of Au NPs. From TEM observation shown in Figure 4a, it is found the resulting Au NPs are nearly spherical in shape with 6.1 ± 2.5 nm in diameter when 0.5 mM precursor was used. The Au NPs exhibit regular spherical morphology with more uniform size (6.8 ± 1.5 nm, Figure 2a) with 1.0 mM of precursor. When the concentration of metal precursor is further increased to 1.5 mM, the larger sized Au NPs with irregular shapes and broader size...
distributions are generated (Figure 4b). Further increase of the concentration to 2.5 mM results in the formation of more regular Au nanospheres with 45 nm in average diameter together with some Au nanorods (Figure 4c). More interestingly, the resulting NPs exhibit clear core/shell structure composed of a HBPP shell and Au core (inset of Figure 4c). The changes in the size and morphology cause the changes in SPR properties. Figure 4d demonstrates that the characteristic absorbance bands of Au NPs are red-shifted with the increase of precursor concentration due to the increase of the size of NPs. The sample obtained with 1.5 mM of precursor exhibits a quite broad absorbance band centered at about 555 nm, corresponding to the presence of Au nanospherules with broad size distribution and irregular shapes. In contrast, the sample produced by using 2.5 mM of precursor shows a sharp absorbance band situated at 540 nm accompanied by a quite broad band ranging from about 700 to 950 nm. The sharp band at shorter wavelength might be attributed to the Au nanospheres with relatively regular shape and narrower size distribution, while the broad band at longer wavelength might be derived from the longitudinal electronic oscillation of as-prepared Au nanorods. Based on these results, it can be concluded that the increase in the concentration of metal precursor provides an effective alternative to tune the size of Au NP.

The effect of MW of HBPP on the formation of Au NPs was also studied. Herein, HBPP molecules with 1000, 1800, and 3400 g/mol $M_w$ were used. The formation processes of Au NPs were recorded via UV–vis spectra (see Figure S5 of the Supporting Information). From the temporal evolution of the plasmon band peak for different MWs of HBPP (Figure 5a), it takes 45 h, 12 h, and 110 min to reach completion of the reaction in the presence of HBPPs with 1000, 1800, and 3400 g/mol MW, respectively. As is shown in Figure 5b, the corresponding Au NPs present different absorption spectra. By comparison, Au NPs prepared with 3400 g/mol HBPP present one relatively sharp peak centered at 516 nm, characteristic of the formation of uniform spherical Au NPs with small size (Figure 2a).28 For Au NPs obtained with 1000 and 1800 g/mol HBPP, a band centered at $\sim$570 nm accompanied by an extensive absorption at the longer wavelength and a broad band situated at $\sim$565 nm are observed, respectively. These absorption patterns are most probably related to the presence of Au NPs with irregular shape and broad size distribution (Figures 3c and 5d).

The changes in the morphology and size endow NPs with intrinsic anisotropic structures so that the resulting NPs can exhibit multiple absorption bands associated with various resonance modes.20,28 The formation of Au NPs with irregular shape and larger size might be caused by the aggregation of small Au NPs owing to the less-effective protection of HBPP with lower MW. This can be supported by the fact that Au NPs obtained with 1000 g/mol HBPP are easily precipitated within 1 h, and Au NPs prepared with 1800 g/mol HBPP are partially precipitated within 1 week. By comparison, the Au NPs synthesized with 3400 g/mol HBPP can be stored in water for more than 6 months and still no precipitation is visible. These results reveal that the HBPP molecules with higher MW not only possess much stronger reducing ability, leading to the great reduction of reaction time, but also serve as a more effective stabilizer for as-formed NPs, demonstrating the MW of HBPP molecules is one of the decisive factors in the synthesis of regular Au NPs. Note that the number of hydroxyl groups increases as the MW of HBPP molecules increases.

**Proposed Mechanism of HBPP-Assisted Synthesis of Metal NPs.** Although the polyol process has been explored widely for the synthesis of metal NPs since the works done by the Fievet group,37,38 until the recent works reported by Xia group,39 most reported works have been limited to the synthesis of noble metal NPs because of insufficient understanding of their formation mechanism. In typical polyol processes, alcohols (glycerol, ethylene glycol, 2-propanol, etc.) are often used as reducing agents in the synthesis of metal NPs. It was found that the reduction of metal ions occurs only when the employed alcohols are present in high concentrations above a threshold value due to their limited reducing capability.40 From this point of view, in aqueous HBPP solution, each HBPP molecule containing lots of hydroxyl groups provides a “domain” with a certain alcohol concentration. When the metal precursor is added to a HBPP aqueous solution, there exist noncovalent, electrostatic (ion dipole) interactions among the electropositive metal ions, electron-rich oxygen atoms on the ether chains and the adjacent hydroxyl groups of inter- or intra-HBPP molecules (see Figure S1 of the Supporting Information).11,41 Such interactions not only make the metal ions to be tightly trapped within the voids of single HBPP molecules to form metal ions/HBPP complex, but also attract the adjacent HBPP molecules to generate metal ions/HBPP supercomplexes. We proposed each metal ions/HBPP supercomplexes as a “polyol box” (Scheme 2), mimicking an analogous polyol environment due to the space bearing multiple hydroxyl groups. In a “polyol box”, the solubilized metal ions can be in situ reduced to their zerovalent metallic states. Followed by the coalescence of these metal atoms, the metal nuclei are generated. The reported traditional polyol processes generally allow the NPs to be nucleated at the high boiling point of polyol.37–39 However, the formation of metal nuclei in our current process can occur at room temperature. This is attributed to the interactions between metal ions and HBPP molecules, which can effectively lower the mobility of metal ions and thus enhance the formation of metal nuclei.30,41

In order to investigate the effect of alcohol concentration in a “polyol box” on the reducing ability of HBPP, 65% hydroxyl moieties of HBPP (3400 g/mol) were replaced with cyclohexyl terminal groups (see Figure S6 of the Supporting Information).

Expectedly, the reducing capability of the modified HBP molecules decreased sharply, and thus, the reduction of AuCl$_4^-$ ions was not finished within 8 days at room temperature (see Figure S7 of the Supporting Information). This result is agreement with the previous reports.\textsuperscript{40}

To get more insight on the HBP/Au interaction, FTIR spectra were recorded for the HBP and Au NP samples (Figure 6). The spectrum of Au NPs exhibits similar strong peaks situated at 1070 and $\sim$3330 cm$^{-1}$ that are assignable to the vibration modes of C--O and O--H of HBP, respectively. This evidenced the presence of the HBP component in the resultant Au NPs. Interestingly, compared to pure HBP, the Au NP sample shows two new bands centered at $\sim$1600 and 1328 cm$^{-1}$ which are assigned to the stretching modes of C--O complexes to a metal, indicating the presence of Au--O compounds.\textsuperscript{42,43} This results from the reduction process, in which the electrons transfer between the metal ions and hydroxyl groups, leading to the oxidation of metal ions to zerovalent. Concerning the detailed reaction mechanism, the related study is still in process.

Because the as-formed metal nuclei are trapped within the interior voids of the “polyl box”, the HBP molecules serve as host matrix to stabilize them. Owing to the steric effects provided by hyperbranched backbones of HBP, these as-formed nuclei can be confined to migrate freely.\textsuperscript{13} Followed by the continuous supply of metal precursor, more metal atoms are reduced and successively deposit onto the as-prepared nuclei, leading to the in situ growth of these nuclei into NPs in fine grain size. Since the metal NPs are trapped within the HBP matrix, HBP passivates the surface of the metal NPs and endows the NPs with good water solubility. If the HBP molecules provide less efficient stabilizing ability to the as-formed NPs, these NPs tend to aggregate and grow anisotropically, resulting in the formation of NPs with irregular shapes and unstable NP colloid solutions (Figure 5).

\textbf{Synthesis of Bimetallic NPs.} Bimetallic NPs composed of two metal elements have also attracted great interest in the field of catalysis owing to the bimetallic catalyst would make it possible not only to obtain catalyst with improved catalytic activity but also to create new types of catalysts which may not be achieved by monometallic catalysts.\textsuperscript{9,44} Aimed to create such promising metal NPs, the fabrication of various bimetallic NPs was attempted according to a similar synthetic protocol applied for the synthesis of monometallic NPs. Two different approaches have been designed to prepare bimetallic NPs based on the different feeding sequence of two different metal precursors: co-feeding and sequential feeding routes. In the co-feeding route, two different

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Representative TEM images of Au NPs obtained at different AuCl$_4^-$ concentrations: (a) 0.5 mM, (b) 1.5 mM, and (c) 2.5 mM. (d) Typical UV–vis spectra of the corresponding Au NP colloids prepared with varied AuCl$_4^-$ concentrations.}
\end{figure}

aqueous metal precursors were premixed and then directly mixed with aqueous HBP solution. For the sequential feeding route, monometallic NPs were first prepared and the other type of metal precursor solution was subsequently mixed with the as-prepared monometallic NP colloids.

By means of the co-feeding method, a series of bimetallic NPs such as Au/Pt, Au/Pd, and Au/Ru NPs have been obtained successfully. The formation processes of these NPs were traced by UV–vis absorption spectra taken at different intervals after mixing the mixture of HAuCl₄ (1.0 mM) and different metal precursor (K₂PtCl₄, Na₂PdCl₄, RuCl₃, 1.0 mM) aqueous solutions with HBP solution at ambient temperature (Figure 7a, c, and e). In the case of the Au/Pt system, when the premixed metal precursors were added to HBP solution, the color of reaction system rapidly changed from light yellow to brown within 1 min, leading to the rapid emergence of a broad UV–vis absorption band centered at around ∼550 nm (Figure 7a). Thereafter, the maximum absorption band gradually blue-shifted until reaching constant value up to 260 min, indicating completion of the reduction reaction. Figure 7b shows the TEM image of the resulting Au/Pt NPs that exhibit the nearly spherical particles with 4.5 ± 1.7 nm in diameter (Figure 7b).

Similarly, for the Au/Pd system, the gradual UV–vis absorption evolution of the reaction system witnessed the formation process of Au/Pd NPs within 420 min (Figure 7c). Determined by TEM observation (Figure 7d), the resulting Au/Pd NPs exhibit irregular morphologies. From the high resolution TEM image shown in the inset of Figure 7d, the uniform contrast throughout the particle demonstrates the homogeneous mixing of the metallic components. Compared with the Au/Pt and Au/Pd systems, the Au/Ru system exhibits a much faster reduction reaction that takes around 10 min to reach the maximum absorption determined by the UV–vis spectrum (Figure 7e). The yielded NPs exhibit relatively large size with irregular shape (Figure 7f).

Figure 7g shows the typical UV–vis spectra and photographs of the resultant Au/Pt, Au/Pd, and Au/Ru bimetallic NPs colloids, demonstrating quite different absorption bands and colors from the bare Au NPs (Figure 2f and 7g). Powder XRD patterns (Figure 7h) show (111) peaks at 38.8°, 38.9°, and 38.5° for Au/Pt, Au/Pd, and Au/Ru NPs, respectively. Compared with Au NPs with (111) peak at 38.2°, there exist certain shifts in the (111) peaks of bimetallic NPs. ICP analysis of the bimetallic NPs showed that the Au contents of Au/Pt, Au/Pd, and Au/Ru are 50.5, 52.2, and 55.6%, respectively. All of these facts evidenced the successful formation of the bimetallic NPs.

According to the previous reports, the co-feeding route often results in the formation of core/shell bimetallic NPs via a polyol reduction because of the difference in the reduction potentials of the two metal ions: one type of ion with higher reduction potential is reduced more easily and provides seeds for the reduction of the
other metal ion.\textsuperscript{45–47} In our current study, UV–vis and XRD results (Figure 7) show that Au/Pt, Au/Pd, and Au/Ru bimetallic NPs are successfully generated via the co-feeding routes. However, no obvious core/shell structures of the resulting bimetallic NPs were observed by TEM analyses. This might follow additional formation processes. As described above, HBP bearing a large amount of interior cavities presents a mild reducing environment toward varied metal ions with different reduction reaction rates. For the Au/Pd ([AuCl\textsubscript{4}^{−}]/[PdCl\textsubscript{4}^{2−}] = 1:1) system, as an example, Au nuclei can be first generated owing to the higher reduction potential of AuCl\textsubscript{4}^{−} ions, and then the slowly reduced Pd atoms together with newly reduced Au atoms are successively deposited onto the as-formed Au nuclei to form Au/Pd clusters until the consumption of AuCl\textsubscript{4}^{−} ions is completed. Note that these codeposition processes of the two types of metal atoms might cause the anisotropic growth of the NPs, leading to the formation of final NPs with unusual morphologies (Figure 7d). Thereafter, the remaining PdCl\textsubscript{4}^{2−} ions continue to be reduced and deposited onto the formed Au/Pd clusters, leading to the construction of final Au/Pd NPs. These NPs composed of a large amount of Au/Pd clusters with fine grain size are responsible for the failure to form any obvious core/shell structure.

To compare with the co-feeding route, Au/Pt, Au/Pd, and Au/Ru bimetallic NPs have been successfully fabricated by means of the sequential feeding method. The Au NPs with 6.8 nm in average diameter had first been synthesized, and subsequently, various metal precursors (K\textsubscript{2}PtCl\textsubscript{4}, Na\textsubscript{2}PdCl\textsubscript{4}, RuCl\textsubscript{3}, 1.0 mM) were added to the as-prepared Au NP colloid, leading to the formation of different bimetallic NPs after a suitable period of time at ambient temperature. The corresponding reaction processes were investigated by recording the changes in UV–vis spectra with time. Figure 8a shows the evolution of absorption spectra for the Au/Pt reaction system. The absorption bands of the reaction system gradually evolve into broader bands from the starting absorption band of as-prepared Au NPs for 20 h of reaction. The resulting NPs are in nearly spherical shape and with 8.0 ± 1.8 nm in diameter (Figure 8b), which is larger than that of starting Au NPs (6.8 nm in average diameter). The Au/Pd system exhibits a similar evolution in UV–vis absorption to the Au/Pt system (Figure 8c). The reaction takes around 11 h to reach completion. TEM observation (Figure 8d) indicates that the resulting Au/Pd NPs are

in nearly spherical morphology with 7.8 ± 2.0 nm in diameter. In comparison, the Au/Ru system exhibited different UV–vis absorption evolution as shown in Figure 8e. After mixing RuCl₃ aqueous solution with Au NPs colloids, the absorption of the reaction system rapidly red-shifts to 553 nm from 516 nm derived from the starting Au NPs, and at the same time a shoulder absorption peak appears centered at around 400 nm which is assigned to the unreacted Ru³⁺ ions. When the reaction has proceeded for 250 min, this shoulder peak disappears and the absorption peak situated at around 550 nm keeps unchanged, indicating the completion of the reduction. The TEM image shown in Figure 8f indicates that the resulting NPs are in spherical shape and with 7.1 ± 1.3 nm in diameter. Figure 8g shows the typical UV–vis spectra and photographs of the final Au/Pt, Au/Pd, and Au/Ru bimetallic NPs, which are obviously different from the original Au NPs and the corresponding bimetallic NPs prepared by the co-feeding way (Figure 7g). XRD patterns shown in Figure 8h demonstrate the (111) peaks at 38.7°, 38.9°, and 38.4° for Au/Pt, Au/Pd, and Au/Ru NPs, respectively. Considering the (111) peak of Au NPs is observed at 38.2°, the corresponding shifts confirm the formation of bimetallic NPs. Determined by ICP analysis, the Au contents in Au/Pt, Au/Pd, and Au/Ru bimetallic NPs are 51.0%, 50.8%, and 52.5%, respectively.

The preformed Au NPs used in the sequential feeding route consist of a large amount of fine NPs. Among these grain size NPs, there still exit numerous voids owing to the steric effects caused by the backbones of HBP molecules. These voids can allow the subsequently feeding metal ions to be successively reduced and deposited on the preformed fine Au NPs, resulting in the formation of fine core/shell NPs with Au cores. These newly formed core/shell NPs with fine grain size might constitute the final bimetallic NPs with uniform composition. With a careful

Figure 7. Bimetallic NPs obtained by the co-feeding route. Evolution of UV–vis spectra during the reaction and the corresponding TEM images of final NPs: (a,b) Au/Pt, (c,d) Au/Pd, and (e,f) Au/Ru NPs. UV–vis spectra and photographs of the corresponding bimetallic NPs colloids (g). XRD patterns of each obtained bimetallic NPs (h).

Figure 8. Bimetallic NPs obtained by sequential feeding route. Evolution of UV–vis spectra during the reaction and the corresponding TEM images of final NPs: (a,b) Au/Pt, (c,d) Au/Pd, and (e,f) Au/Ru NPs. UV–vis spectra and photographs of the corresponding bimetallic NPs colloids (g). XRD patterns of each obtained bimetallic NPs (h).
investigation of the bimetallic NPs obtained via the co-feeding route, the resultant difference in the microphase composition leads in the differences in UV−vis spectra and colors of final NP colloids. In addition, the more accommodated metal components are responsible for the further growth of the resulting NPs in size (Figure 8). And the involvement of monometallic deposition processes leads the final bimetallic NPs to keep the spherical shape of original Au NPs.

**Fabrication of Inorganic Oxide/Au NP Hybrids.** The HBP-protected metal NPs contain lots of terminal hydroxyl groups (see Schemes 1 and 2), which not only endows the resulting NPs with high water-solubility but also provides alternatives for creation of a variety of metal NPs-based hybrids. For instance, by means of the hydroxyl groups bearing on the periphery of metal NPs, the inorganic oxide can be successively deposited on NPs via a sol−gel process, leading to the formation of metal NP encapsulated oxide hybrids. Herein, a versatile synthetic approach to fabricate inorganic oxide/Au NP composites, such as TiO$_2$/Au, GeO$_2$/Au, and SiO$_2$/Au nanohybrids, has been demonstrated by sol−gel processes in the presence of as-prepared Au NPs. TEM images (Figure 9a−c) directly show the successful formation of TiO$_2$/Au, GeO$_2$/Au, and SiO$_2$/Au hybrid, respectively. In comparison to the UV−vis absorption spectra of resulting hybrids (Figure 9d), it can be observed that the absorbance maxima are at 595, 532, and 524 nm for TiO$_2$/Au, GeO$_2$/Au, and SiO$_2$/Au hybrid, respectively. In comparison to the UV−vis absorption of Au NPs (centered at 516 nm), the corresponding red-shifts in absorption bands might be attributed to the increase in the local refractive index of the Au NPs surrounding matrix (TiO$_2$, 2.5; GeO$_2$, 1.6 and SiO$_2$, 1.5). This fact further is evidence that the Au NPs are encapsulated into the oxide matrix. Further insight into the structural information of these obtained oxide/Au NPs hybrids was achieved by powder XRD analyses. As shown in Figure 9e, XRD patterns of TiO$_2$/Au, GeO$_2$/Au, and SiO$_2$/Au nanohybrids evidenced the successful incorporation of face-centered cubic structured Au NPs (JCPDS 4-784) within the oxide matrixes, while all the oxides exhibited typical amorphous structures. This facile synthetic protocol can also be extended to the fabrication of other inorganic oxide/metal NP composites based on the as-prepared HBP-protected metal NPs. These resulting composites provide promising candidates for applications such as catalysis and bioimaging.

**Conclusions**

Using highly biocompatible HBP molecules as reducing and stabilizing agent, a series of water-soluble and stable monometallic NPs (Au, Ag, Pt, Pd, and Ru) were successfully synthesized. The reaction rate was tunable by the reaction temperature. And the size of resulting NPs was controllable by the concentration of metal precursors. The MW of HBP plays a key role in the formation of NPs: the higher MW of HBP was favorable for the better stability of resulting NPs, and for the formation of NPs with more uniform and regular shape. The electron transfer between the metal ions and hydroxyl groups of HBP results in the reduction of metal ions to zerovalent metal. In addition, by the co-feeding and the sequential feeding of different metal ions, bimetallic NPs such as Au/Pt, Au/Pd, and Au/Ru NPs were also fabricated successfully. By means of hydroxyl groups bearing on the periphery of the HBP-passivation layer of Au NPs, TiO$_2$/Au, GeO$_2$/Au, and SiO$_2$/Au nanohybrids were fabricated via sol−gel and green processes, which sets a typical example for the creation of versatile metal-NP-based hybrids based on the as-prepared multiple functional NPs. In addition, because the biocompatible HBP-passivated metal NPs were produced under completely green conditions, they are potentially useful in the biomedical areas. Particularly, HBPs possess the analogous void-containing and dendritic architectures to dendrimers. Moreover, they can be more conveniently produced

![Figure 9](image_url)
than dendrimers. Thus, HBP-stabilized metal NPs are more competitive catalysts for varied catalytic applications compared with dendrimer-passivated metal NPs.

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**Supporting Information Available:** Mullicken atomic charges on oxygen atoms in HBP molecule (part). $^{13}$C NMR spectra of HBPs with different molecular weight. Evolution of the UV–vis spectra and plasmon band intensity as a function of time for Au, Ag, Pt, Pd, and Ru NPs obtained by using 3400 g/mol HBP at room temperature. TEM images and size distribution of Au NPs obtained at different temperatures. Evolution of the UV–vis spectra of Au NPs obtained by using a HBP with different molecular weight. $^{13}$C NMR and $^1$H NMR spectra of cyclohexyl terminated HBP. Evolution of the UV–vis spectra for Au NPs in the presence of cyclohexyl terminated HBP in tetrahydrofuran. This material is available free of charge via the Internet at http://pubs.acs.org.