

Heterogeneous Gold Nanoparticles Stabilized by Collagen and Their Application in Catalytic Reduction of 4-Nitrophenol

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Heterogeneous catalyst containing gold nanoparticles (AuNPs) was prepared by direct precipitation of collagen of type I as the stabilization reagent. The composite is fibrous and the AuNPs are found to form patterns of long wires, short wires, and dispersed patterns on collagen. The catalytic reduction of 4-nitrophenol to 4-aminophenol by NaBH₄ in the presence of the composite was satisfactory.

In recent years, the gold nanoparticles (AuNPs) have become a star¹ of the catalysts owing to its surprisingly high catalytic activity and mild reaction conditions. The potential uses of AuNPs catalyst cover the fields of hydrogenation, oxidation, hydrochlorination, and others.^{2,3} The AuNPs can be prepared by using stabilization reagents such as surfactants, thiols, polymers, and some other organic ligands.³ AuNPs prepared by using these reagents are often homogeneously suspended in solutions and need to be immobilized for practical uses.

Collagen, coming from skin, tendon, and some other tissues of animals, is one of the most abundant bioresources in the nature.⁴ Like many other polypeptides and proteins,³ collagen also has the ability of stabilizing AuNPs. Kim et al.⁵ studied the hydroxyapatite growth on AuNPs–collagen composite (AuCol). A study of Li et al.⁶ focused on the surface-enhanced Raman scattering of AuCol. But the AuCol prepared by them was homogeneously dispersed in aqueous solutions which were commercial products and were used for other purposes rather than as the heterogeneous catalysts. We found that if using the collagen freshly prepared, heterogeneous AuCol could be formed. Herein, we report a novel method to prepare AuNP heterogeneous catalyst with small size and narrow diameter distribution of nanoparticles by using collagen of type I.

The type I collagen was extracted from bovine skin according to the procedures of the literature.⁷ The collagen obtained was dissolved in the 0.05 M acetic acid solution at 4 °C. 0.3 mL of 2.5 mM hydrogen chloroaurate (HAuCl₄) was added into the solution of collagen. Then, 0.3 mL of 100 mM NaBH₄ used to reduce Au^{III} was added into the mixture dropwise with rapid stirring. The color of the mixed solution changed from nearly colorless to red quickly during the process of the Au^{III} reduction, which indicated the generation of AuNPs. Subsequently, AuCol was aggregated and precipitated in a fibrous state within a few seconds.

It can be suggested that the size and size distribution of AuNPs depend on the reduction process and the stabilization effect of collagen. In the reduction process, Au^{III} was reduced quickly and a number of nuclei of Au⁰ were formed in a short time because NaBH₄ is a strong reductant. Furthermore, the collagen could combine with Au⁰ as soon as Au⁰ is generated

because of the strong affinity of collagen to Au⁰. Both the fast reduction reaction of Au^{III} and the strong stabilization effect of collagen to Au⁰ will retard particle growth of Au⁰. As a result, AuNPs with small size and narrow size distribution were obtained.

The formation of fibrous AuCol should be attributed to the self-assembly of collagen molecules being induced by AuNPs. The fibers could be observed directly by the naked eye (Figure S1A–S1F)¹² or under an optical microscope (Figure S2).¹² It has been recognized that amine groups can bind with AuNPs fairly strongly.⁸ Therefore, it is reasonable to infer that the stabilization mechanism of AuNPs by collagen is due to the interaction between AuNPs and amine groups of collagen. Furthermore, such interaction can induce the aggregation and self-assembly of collagen molecules into fibers. It should be pointed out that the fibrous AuCol can not be obtained under strong alkaline conditions in the reduction process (Figure S1G)¹² as mentioned by Kim et al.⁵

Figure 1 presents the TEM images of AuCol prepared with different molar ratios of collagen and Au^{III}. The largest particle size of AuNPs (6.5 ± 3.1 nm) was observed at the lowest collagen offer in AuCol_{0.05} (the subscript number stands for the molar ratio of collagen to Au^{III}), as shown in Figure 1A and Figure S3A.¹² It is believed that lower content of collagen produces weaker stabilization effects to AuNPs and, therefore, has less ability to prevent the AuNPs from growing. As the molar ratio of collagen and Au^{III} was increased to 0.10, the diameter of AuNPs was decreased to 5.0 ± 0.9 nm (Figure 1B and

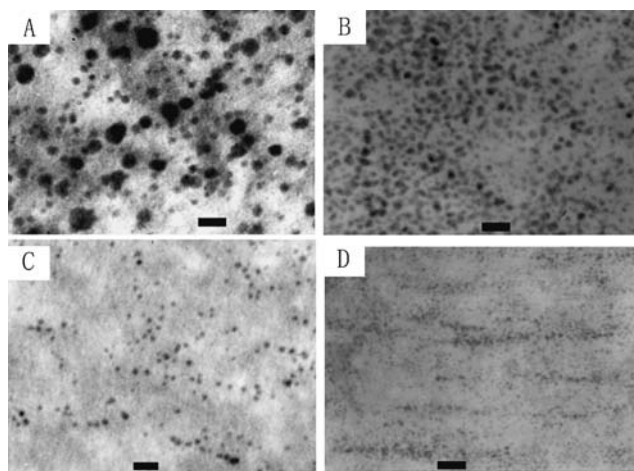
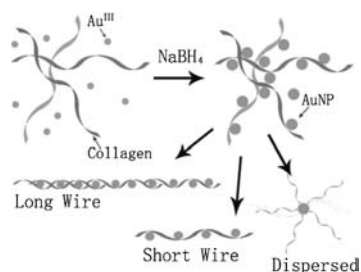


Figure 1. TEM images of the AuCol composite prepared at different molar ratios of collagen and Au^{III}. (A) AuCol_{0.05}, (B) AuCol_{0.10}, (C) short wire of AuCol_{0.20}, the bars 20 nm. (D) oriented long wire of AuCol_{0.20}, the bar 40 nm.



Scheme 1. Scheme of the formation and conformations of AuCol.

Figure S3B¹²). The average size of AuNPs was 3.6 ± 0.6 nm when the molar ratio of collagen and Au^{III} was increased to 0.20. The AuNPs are found to form patterns of long wires, short wires, and dispersed ones on collagen, as shown in Figures 1C, 1D, and Figure S4.¹² As presented in Scheme 1, these patterns of AuNPs are determined by the aggregation and self-assembly of collagen molecules. It could be deduced that AuNPs are attached to the outer surface of collagen fiber or that AuNPs are not completely enveloped by collagen molecules. These structures promise high catalytic activity of AuCol. Moreover, as indicated by means of selected area electron diffraction (SAED) as well as X-ray diffraction (XRD), the AuNPs are in face-centered cubic structure (Figure S5¹²). The size of AuNPs calculated from the data of XRD by the Scherrer formula is 3.55 nm, which is consistent with the determination by TEM.

To test the catalytic activity of AuCol, a model reaction of reducing 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by NaBH₄ was undertaken.⁹ A UV-vis spectrophotometer was employed to record the value of the absorption peak at 400 nm during the reaction process. The molar ratio of collagen and Au^{III} was changed from 0.05 to 0.5. The results are summarized in Figure 2. Regardless of the mass transfer, it was found that AuCol_{0.05} exhibited the lowest catalytic reaction rate, while the reaction rate of AuCol_{0.20} was greatly increased. As mentioned above, the size of AuNPs in AuCol_{0.05} is larger than that in AuCol_{0.20}. These facts suggest that the size of AuNPs dispersed in collagen would affect the catalytic activity of AuNPs. In general, the catalytic activity of stabilized AuNPs may be decreased owing to the coverage of stabilization reagents.¹⁰ However, this study indicates that the effect is not evident even though much more collagen is used. The catalytic activity of AuCol is still satisfactory when the molar ratio of collagen to Au^{III} is higher than 0.20. This fact confirms that AuNPs are attached to the outer surface of collagen and that the active sites are exposed outside. Furthermore, the AuCol could be easily recovered by centrifugation after 4-NP reduction reaction performed, and there was no Au nanoparticle leaked out. However, its catalytic activity was significantly decreased at 3rd repeated applications.

In comparison, other linear macromolecules with smaller size, poly(vinylpyrrolidone) (PVP) and poly(vinyl alcohol) (PVA), were used to replace the collagen as the stabilization reagents (see Supporting Information for details).¹² The particle sizes of AuNPs stabilized by these two polymers are not obviously different from those of AuCol.¹¹ However, the catalytic reduction of 4-NP performed for at least 900 s exhibits pronounced differences from that of collagen stabilization (Figure S7).¹² It is believed that these two polymers completely cover the active sites of AuNPs, and thus, the catalytic reaction rates were greatly

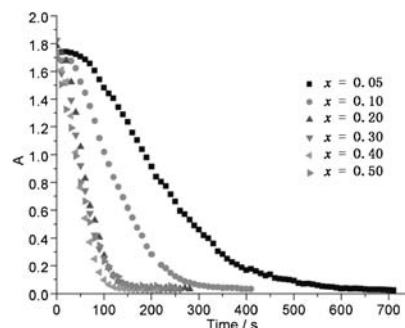


Figure 2. The absorption peak at 400 nm versus time for reducing 4-NP to 4-AP by AuCol_x (x is the molar ratio of collagen to Au^{III}).

decreased. However, the collagen molecule is in “rod-like” shape with 1.5 nm in diameter and 300 nm in length which is different from other stabilization reagents. It could be suggested that AuNPs can only be attached to the surface of collagen rather than being completely covered as mentioned above. Therefore, the catalytic activity of AuCol is much higher than those of AuNPs stabilized by PVP and PVA.

In summary, collagen-stabilized heterogeneous AuNPs with small particle size and narrow size distribution can be prepared based on the affinity of collagen to AuNPs. This catalyst is in the fibrous state, and AuNPs should be attached to the outer surface of collagen. The catalytic activity of AuCol for the reduction of 4-NP to 4-AP by NaBH₄ is perfect. Therefore, the prospective application of this kind of heterogeneous AuCol can be expected.

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