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Facile aqueous phase routes to the economical synthesis of metal nanoparticles

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ABSTRACT

The large-scale synthesis of high-quality nanoparticles has attracted tremendous attention, not only in fundamental studies, but also for various industrial applications. The three important components for economic nanoparticle synthesis are inexpensive starting materials, a simple synthetic route, and significant yield. Here, we introduce simple, aqueous-phase routes to the economical synthesis of gold nanoparticles using polyethyleneimine as both reductant and stabilizer.

1. INTRODUCTION

Metal and metal oxide nanoparticles are attracting growing interest due to their potential technological applications in the fields of energy storage and conversion, display devices, bio-imaging and related biomedical applications, data storage media, sensors and electronic devices, and various catalysts. However, such practical applications require the development of an economical synthetic process for the large-scale production of nanoparticles, where the three important components are inexpensive starting materials, a simple synthetic route, and significant yield. While various synthetic methods have already been developed for producing uniform metal and metal oxide nanoparticles, these methods are impractical for large-scale production as they involve extreme synthetic conditions, such as dilute reactant concentrations, high temperatures, and environmentally toxic solvents. For example, hot injection methods, which induce high supersaturation based on the rapid injection of the reactive reactants into a hot organic surfactant solution, require a high reaction temperature of around 200 °C, use expensive organic solvents such as trioctylphosphine, oleylamine, and diacetylene, and produce nanoparticles with a poor dispersibility in water. Meanwhile, water-based methods, which produce metal nanoparticles via the reduction

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of metal salts using reducing agents, require multiple reagents such as reducing agents, capping agents, and/or stabilizers. Furthermore, water-based synthesis typically uses a large amount of solvent to obtain a very small amount of nanocrystals. For example, 1 L of solvent is used to synthesize a sub-gram scale of nanocrystals. Here, we introduce simple, aqueous-phase routes to the economical synthesis of highly concentrated gold nanoparticles using polyethyleneimine (PEI) as both reductant and stabilizer.

2. SYNTHESIS OF HIGHLY CONCENTRATED GOLD NANOPARTICLES USING POLYETHYLENEIMINE AS BOTH REDUCTANT AND STABILIZER

PEI-stabilized Au nanoparticles were synthesized by heating an aqueous solution containing $HAuCl_4$ and PEI at 50 °C for 2 h under magnetic stirring. During the heating process, the color of the solution gradually turned from light yellow to dark red, indicating the formation of Au nanoparticles. A transmission electron microscopy (TEM) image of the Au nanoparticles synthesized when using a high HAuCl4 concentration of 200 mM shows the formation of Au nanoparticles with a nearly spherical profile and average size of 9.4 nm (Fig. 1A). The powder X-ray diffraction (XRD) pattern (Fig. 1B) taken from the as-synthesized Au nanoparticles matched well with the standard pattern of metallic Au (Fm3m, a = 4.078 Å, Joint Committee on Powder Diffraction Standards (JCPDS) file number 04-0784). The nanoparticles exhibited both single-crystal and twinned structures, as shown in the high-resolution TEM (HRTEM) images (Fig. 1C). Fig. 1D shows the UV-vis extinction spectra taken from an aqueous suspension of the as-prepared Au nanoparticles, which reveals a strong plasmon resonance peak at 520 nm, matching well with previous reports on Au nanoparticles with a similar particle size [1]. The as-synthesized Au nanoparticles also exhibited a high stability in the aqueous-phase. The UV-vis spectrum of the Au nanoparticles stored at room temperature for 50 days still showed a strong peak at 520 nm without a red-shift, indicating the absence of any size increase or the formation of aggregates (Fig. 1D).

Fig. 1. (A) TEM image, (B) XRD pattern, (C) HRTEM image, and (D) UV-vis spectra of Au nanoparticles synthesized by reacting $HAuCl_4$ with PEI.

For a better understanding of the action mechanism of PEI on the Au nanoparticle formation, the reaction temperature was varied. When the synthesis was conducted at low reaction temperatures of 10 and 23 °C, the synthesized Au nanoparticles exhibited an average size of around 13 nm and broad size distribution (Figs. 2A and 2B). It is also noteworthy that the Au nanoparticles produced at 10 °C were seriously aggregated, whereas well-dispersed particles were obtained at 23 °C. When increasing the reaction temperature, the size of the Au nanoparticles gradually decreased to 8.9 nm at 50 °C and 6.9 nm at 70 °C (Figs. 2C and 2D). In addition, the

size distribution became narrower when increasing the reaction temperature. However, at 90 °C, the size of the Au nanoparticles increased to 14 nm and the size distribution broadened. The Au nanoparticles also appeared somewhat aggregated (Fig. 2E).

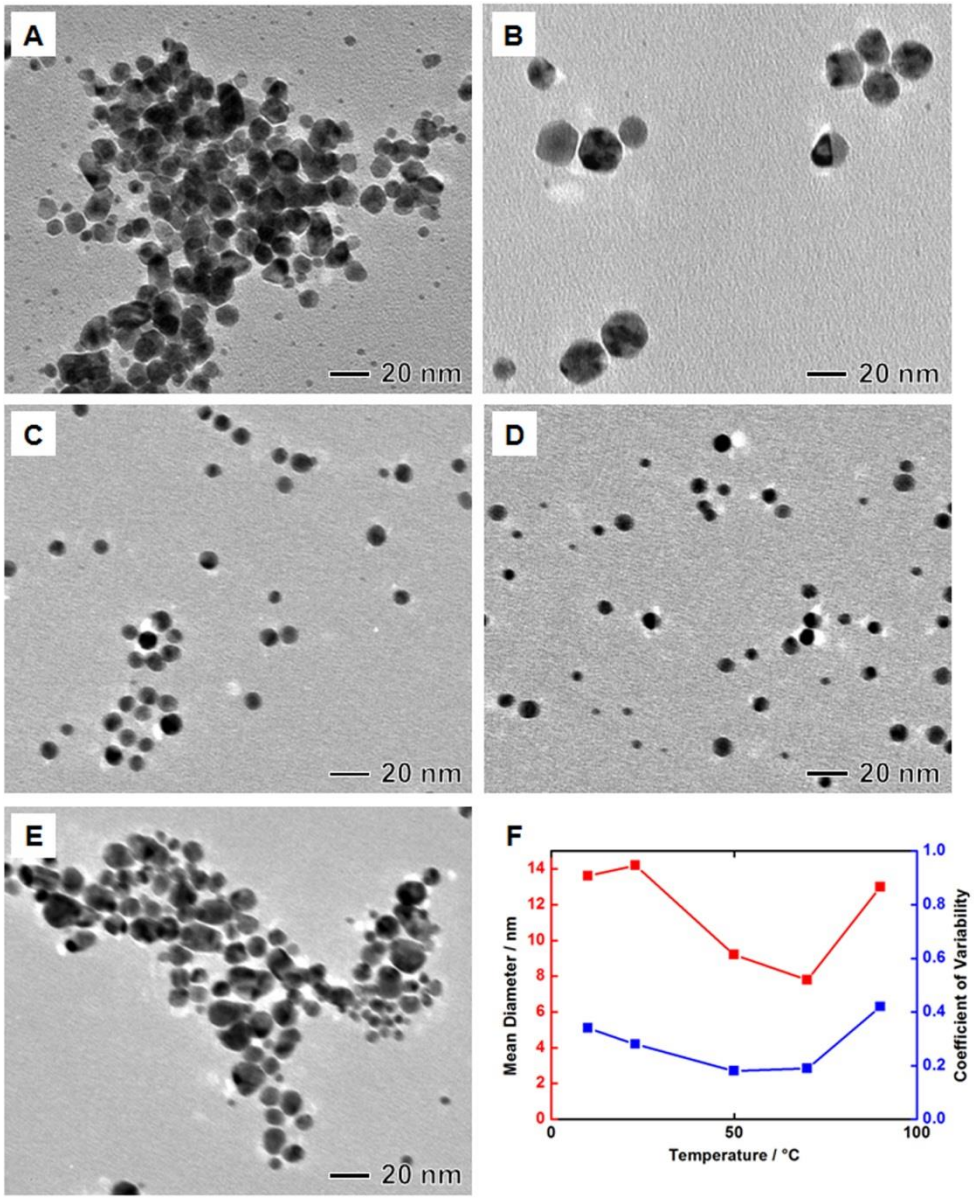

Fig. 2. TEM images (A to E) and particle size distributions (F) of samples prepared under same conditions as those in Fig. 1C, except that synthesis was conducted at various reaction temperatures: 10 °C (A), 23 °C (B), 50 °C (C), 70 °C (D), and 90 °C (E)..

The two dimensional Au nanoplates were also synthesized by addition of urea as a capping agent at a low reaction temperature of 30 °C for 24 h keeping the other experimental conditions unchanged. Fig. 3 is a typical scanning electron microscopy

(SEM) image of the product, showing hexagonal and triangular nanoplates with lateral dimensions of 2 – 8 μm and a thickness of approximately 40 nm.

Fig. 3. SEM image of Au nanoplates synthesized by reducing HAuCl4 with PEI (MW ~ 750,000) in presence of urea in aqueous solution..

3. CONCLUSIONS

Highly concentrated Au nanoparticles and nanoplates could be easily synthesized by reacting $HAuCl_4$ and polyethyleneimine (PEI) in an aqueous phase. In this synthesis, PEI served as both reducing agent and stabilizer. Synthesized Au nanoparticles exhibited long term stability in an aqueous phase, more than 50 days. It is expected that the proposed approach can be extended to the synthesis of other metal nanoparticles.

4. REFERENCES

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