Green Photocatalytic Synthesis of Au and Ag Nanoparticles: Size and Shape Control

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Green chemistry synthetic approaches must be designed for reduced environmental impact; waste reduction; process safety; materials, and energy efficiency. This is seldom the case in the synthesis of nanoparticles, since the need for a high control of size and size dispersion is usually achieved through the use of high temperatures, and toxic materials. The development of bulk solution synthetic methods in water that can save energy and reagents while allowing high yields of NPs with low size dispersion is of paramount importance for the full implementation of a green chemistry synthetic strategy in NPs, specially intended for biological applications. One promising way to achieve it is to control the formation of nanoparticles by use of a catalyzed reaction.

Herein, we describe a method that relies on a photocatalytic reaction to produce gold and silver NPs with enhanced mono-dispersion in an aqueous medium, at pH 7 and room temperature. [1,2] The use of a photocatalyst allows fast formation of seeds in solution, leading to superior size-dispersion of the final NPs (Figure 1). This one-pot seeding method engages the following green chemistry principles: (*i*) low energy consumption, the reaction is carried out at room temperature and uses a low-power halogen bulb for photocatalysis; (*ii*) short reaction time, the complete synthesis takes in most cases less than 4 minutes; (*iii*) non-toxic reagents, triethanolamine (TEA) is the electron donor and toxic surfactants that are commonly used as capping agents are replaced by water soluble polymers that are physiologically compatible: poly(N-vinyl pyrrolidone) (PVP), starch, acacia gum, and cellulose; (*iv*) no purification is necessary; a mono-dispersed NPs solution is readily obtained. Furthermore, the NPs can be easily functionalized with a thiolated ligand, imparting new functionalities to the NPs that can be explored for biological applications. In comparison to other methods using the same type of capping agents, the present methodology yields a significantly better size dispersion.

A similar strategy was used to control the shape of the nanoparticles. In this case, a shape-directing capping agent was used (CTAB) in conjunction with a stringent control of the reaction kinetics to prepare Au triangular nanoplates (Figure 2) and nanocubes (Figure 3). Adjustment of the experimental conditions, such as concentration of the photocatalyst and concentration of capping agent allows control of the average size of the anisometric nanoparticles. In particular, for the synthesis of triangular nanoplates, it is possible to control the average edge length in the range 50-150 nm by changing the concentration of the photocatalyst. In addition, for each concentration of photocatalyst used it is possible to fine-tune the edge length of the nanoplates by changing the concentration of capping agent. Preliminary kinetic studies show that the photocatalyst and the capping agent influence both the rate of nucleation and the rate of growth of the nanoparticles, but with opposing actions. This behavior may be advantageously used to control the size/size dispersion of the nanoparticles, keeping high yields of the selected shape. In addition, these kinetic studies are useful to further understand the basic principles underneath the control of size and shape in the synthesis of nanoparticles, which represents one of the major challenges in the chemical synthesis of nanoparticles.

References

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[2] P. Quaresma, L. Soares, L. Contar, A. Miranda, I. Osório, P. A. Carvalho, R. Franco, E. Pereira, Green Chem. **11** (2009) 1889.

Figures

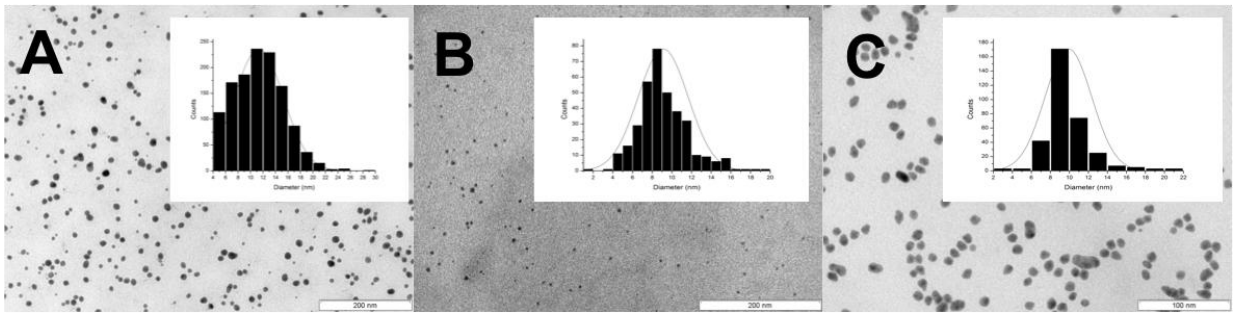

Figure 1: Representative TEM images of A) Au NPs synthesized with acacia gum as capping agent (mean diameter 11.3 ± 3.9 nm); B) Ag NPs synthesized with starch as a capping agent (mean diameter 9.1 ± 2.5 nm); and Au/Ag alloy NPs synthesized with acacia gum as capping agent (mean diameter 9.8 ± 2.5 nm). The insets are the corresponding histograms of size distribution obtained with more than 200 nanoparticles.

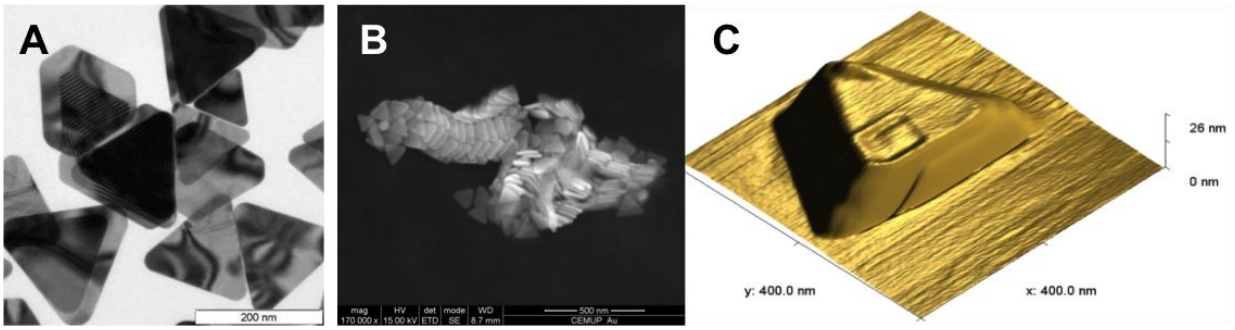

Figure 2: A) TEM, B) SEM, and C) AFM images of gold nanotriangles synthesized photocatalytically.

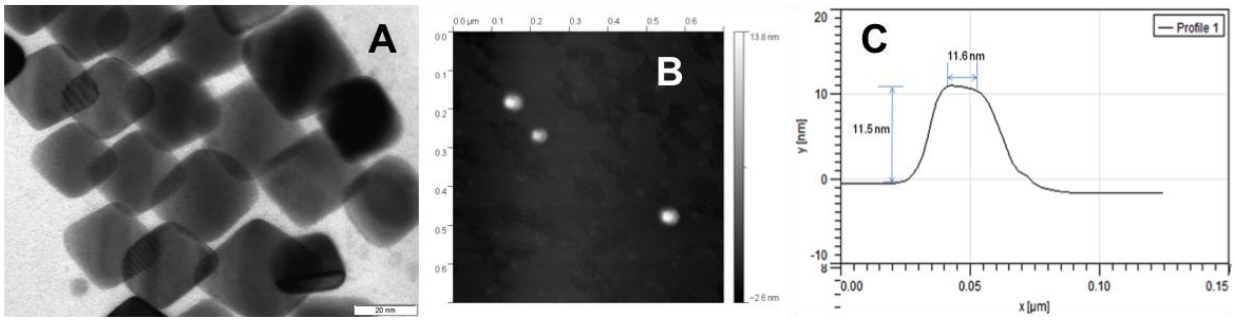

Figure 3: A) TEM image, B) AFM image, and C) AFM height profile of gold nanocubes synthesized photocatalytically.