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Brief communication

General method of synthesis for metal nanoparticles

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Abstract

Sugar-assisted stable monometallic nanoparticles were synthesized by wet chemical method following a general scheme. Judicious manipulation of the reducing capabilities of different sugars has shown to have a bearing on the particle size that corroborates the shift of the absorbance peak positions and TEM analysis. Evaporation of the precursor solutions on the solid surface (strong metal–support interaction), led to the formation of smaller particles. Under the experimental condition, spherical nanoparticles of approximately 1, 3, 10 and 20 nm sizes were prepared reproducibly for gold, platinum, silver and palladium, respectively. Fructose has been found to be the best suited sugar for the synthesis of smaller particles and remained stable for months together.

Introduction

Metallic nanoparticles exhibit unusual optical, thermal, chemical and physical properties that are due to a combination of large proportion of high-energy surface atoms compared to bulk solid and to the nanometer-scale mean free path of an electron in a metal (~10–100 nm for many metals at room temperature) (Valden et al., 1998; El-Sayed, 2001; Feldheim et al., 2002; Murphy, 2002). A challenge in nanotechnology is to tailor the optical, electronic and electrical properties of nanoparticles by controlling their size and shape. Perfectly monodispersed metal nanoparticles are, of course, ideal, but special properties are to be expected even if the ideality is not perfectly realized.

Nanoparticles of gold and other noble metals have attracted much attention because of their potential applications in microelectronics (Schocn,1995; Storhoff, 1999), sensors (Tessier et al., 2000), catalysis (Sau et al., 2001) non-linear optical materials (Collier et al., 1997), etc. Different wet chemical methods have been used for the synthesis of metallic nanoparticles dispersions, the most common involving the use of excess reducing agents such as sodium citrate (Lee et al., 1982) or $NaBH_4$ (Creighton et al., 1979), Ayyanppan et al. (1997) obtained Ag, Au, Pd and Cu nanoparticles by the reduction of metallic salts in dry ethanol. Longenberger et al. (1995) found that metal colloids such as Au, Ag and Pd could be obtained from air-saturated aqueous solutions of poly(ethylene glycol) (PEG). Corresponding mesityl derivatives is also a well-known precursors to synthesize Au, Ag and Cu nanoparticles (Bunge et al., 2003).

In this article, we have reported a general method for the synthesis of different metal nanoparticles (Au, Ag, Pt, Pd) using commonly available sugars, e.g., glucose, fructose and sucrose as reducing agents. We have also addressed the effect of three different sugars as reducing agent on the sizes for different metal nanoparticles syntheses. This approach has several distinct features: (i) sugars (glucose, fructose, and sucrose) are easily available to be used as reducing agents, (ii) upon their exploitation no other stabilizing agent or capping agent is required to stabilize the nanoparticles, (iii) sugars are very cheap and biofriendly and (iv) instead of keeping the nanoparticles in aqueous solution one can safely preserve the particles in a desiccator for months and can be redispersed in aqueous phase whenever required.

Experimental

All the reagents were of analytical reagent grade. Chloroauric acid ($HAuCl_4$), silver nitrate ($AgNO_3$), chloroplatinic acid (H_2PtCl_6) and palladous chloride ($PdCl_2$) [Aldrich] were used as received. Aqueous solutions (10^{-2} M) of all the salts were used as stock solution. Fructose, glucose and sucrose were purchased from S. D. Fine Chemicals, India. Milli-Q water was used throughout the experiment. All absorption spectra were recorded in a Shimadzu UV-160 spectrophotometer (Kyoto, Japan) taking the solutions in a 1 cm quartz cuvette. TEM measurements of the metal sols were performed in a Hitachi H-9000 NAR instrument on samples prepared by placing a drop of fresh metal sols on Cu grids precoated with carbon films, followed by solvent evaporation under vacuum.

A series of solutions were prepared dissolving 0.2 g of sugar in 3.9 ml water in each set and then 100 μl (10^{-2} M) of the corresponding metal salts solution was added to it, so that the final volume of the solution is 4 ml. Three different sugars *viz*., glucose, fructose and sucrose were used individually as reducing agent for the synthesis of each metal nanoparticle. $HAuCl_4$, $AgNO_3$, H_2PtCl_6 and $PdCl_2$ were used for the preparation of Au, Ag, Pt and Pd nanoparticles, respectively. The concentration of the metal salts were 2.5×10^{-4} M in the final solution. The solution was heated on a hot water bath. The temperature of the hot water bath was ~70–75°C. After sometime, for gold and silver, the solution turned pink and yellow respectively and for both Pd and Pt the solution turned black indicating the formation of the corresponding metal nanoparticles. The heating was continued until the solution evaporated to dryness. The total time required to evaporate the solution to dryness take ~2 h time. Then 4 ml of water was again added to it and the solution was sonicated for 30 min. TEM measurements were done for all these solutions.

Results and discussions

For Au and Ag nanoparticle evolution we have monitored the progress of the reaction following their plasmon absorption bands at their respective λ_{max} values. On the other hand, Pt and Pd particle evolutions were followed from the growth of the featureless absorption bands those monotonically increase in the visible region. Representative UV–Vis spectra of the samples for fructose reduction cases are shown in Figure 1. We obtained the characteristic plasmon band for gold and silver with λ_{max} values at 514 and 404 nm, respectively. For both Pd and Pt we recorded the spectra without any characteristic peaks.

During the evolution of the metal nanoparticles we have recorded the UV–Vis spectra of the metal sols at different time also. It was found that as the time progresses the absorption bands for Au and Ag narrowed down and shifted continuously to the shorter wavelength regions with the successive increase in the absorbance values for sucrose and glucose reduction cases. Finally the λ_{max} reaches constancy. Prolong heating caused slow decrease of the absorbance values because the metal particles layer adheres onto the glass surfaces. After complete evaporation of the

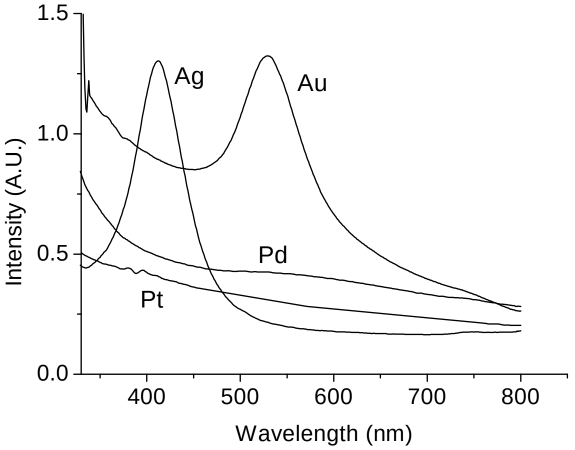

Figure 1. The UV–Vis spectra of the nanoparticles (Au, Ag, Pd and Pt) prepared by fructose reduction. Condition: [metal salt] = 2.5×10^{-4} M; [fructose] = 2.8×10^{-1} M.

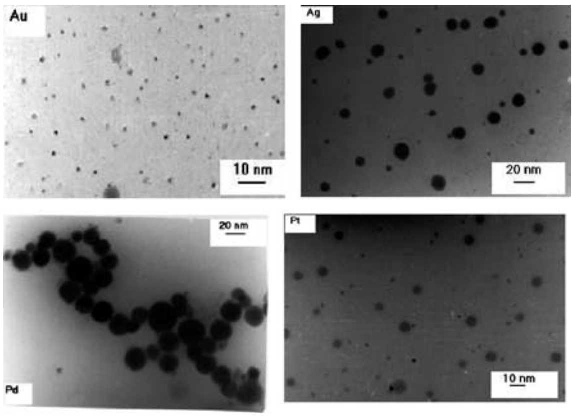

Figure 2. The TEM images of the metal nanoparticles (Au, Ag, Pd and Pt) formed by fructose reduction. Condition: Same as in Figure 1.

aqueous phase from the container metal nanoparticles was stored in a vacuum desiccator for months together. Again the stored particles on sonication with water redispersed the metal nanoparticles to regenerate sol with blue shifting of the λ_{max}. A broad banded spectrum was obtained for all the sucrose reduction cases. However, for fructose and glucose cases the spectra for Au and Ag naoparticle evolutions were rather sharp. The continuous blue shifting of the peaks for sucrose and glucose reductions cases were noticed and the blue shifting was very much pronounced while these two sugars are involved.

Interestingly, the λ_{max} remains constant from the very beginning while fructose mediated reductions were conducted for the metal salts. Therefore, we can conclude that if we use fructose we are able to produce nanoparticles of almost same size but glucose and sucrose on the other hand generate particles of variable sizes. Under the prescribed condition the different types of particles slowly break down into smaller particles. Hence the blue shifts were observed for these two sugar reduction cases.

Among all the three sugars, sucrose is a typical non-reducing sugar and between glucose and fructose, glucose is a stronger reducing agent than fructose. In the experimental salt solutions sucrose hydrolyses to glucose and fructose. Then metal salts are reduced by glucose and fructose. Sucrose is a disaccharide and non-reducing sugar and it hydrolyses to glucose and fructose in the presence of an acid. So we are unable to synthesize silver and palladium nanoparticles by sucrose as we used $AgNO_3$ and $PdCl_2$, respectively for the corresponding particle synthesis. On the other hand gold and platinum particles were synthesized by sucrose. This is because chloroauric acid, $HAuCl_4$ and chloroplatinic acid, H_2PtCl_6 were used as the metal salts which can easily hydrolyze sucrose. The hydrolyzed products (glucose and fructose) then reduce the metal salts into metal particles. So, it takes longer time and therefore, the particle sizes were quite larger. We could not synthesize any silver or palladium nanoparticles using sucrose as the reductant even in the lower pH range. Between glucose and fructose since glucose is a stronger reducing agent it gives smaller particles initially, the smaller particles do not generate sufficient repulsion for colloid stability, and coalescence will be reasonably rapid (Mulvaney et al., 2000). In normal Derjaguin-Landau-Verwey-Overbeek (DLVO) system (Hunter et al., 1989), such particles cannot repeptise, and coalescence is irreversible. Therefore, we ultimately get the particles of larger diameter for glucose reduction cases though they are smaller than the particles obtained using sucrose (authenticated by absorption studies as described earlier).

However, when we use fructose we see from the UV–Vis spectra that λ_{max} remains constant. So we conclude that the particles are almost of same size and since fructose is a weak reducing agent than glucose, the initial particle diameter was larger than those obtained from glucose. For the larger particles, the barrier to coalescence is large, and in addition, a secondary minimum form, which means colloid particles, will experience weak flocculation forces (Mulvaney et al., 2000).

From the TEM measurement wherefrom we observed that smallest particles are evolved from fructose reduction then in glucose and largest in sucrose among all the three sugars used. The TEM images of all the metal nanoparticles formed from fructose reduction are shown in Figure 2. The TEM images show indeed the presence nonagglomerated spherical particles (Pal et al., 2004). From this analysis the particles with diameters $\sim$1, $\sim$3, $\sim$10 and $\sim$20 nm were found for gold, platinum, silver and palladium, respectively while fructose was employed as the reducing agent. From TEM measurement we see that the particle size in solution was larger than those obtained after successive evaporation and redispersion. The main factor for the diminution of the sizes of the spherical metal nanoparticles is due to the strong metal-support interaction.

Conclusions

We have described here a general method for the synthesis of metal nanoparticles exploiting different sugars as reducing agent. The process is highly reproducible, easy and surfactantless. Biofriendly reagents are used for the synthesis. Moreover, simply just changing the sugars and evaporating the precursor solution on glass support successfully achieved control over the particle size of metal nanoparticles. Another important point is that the evolved particles can be stored for months in a desiccator without any deterioration of the particle morphology and hence can be used whenever required.

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References

Ayyappan, S., G.R. Srinivasa, G.N. Subbanna & C.N.R. Rao, 1997. Nanoparticles of Ag, Au, Pd, and Cu produced by alcohol reduction of the salts. J. Mater. Res. 12(2), 398–401.

Bunge, S.D., T.J. Boyle & T.J. Headley, 2003. Synthesis of coinage-metal nanoparticles from mesityl precursors. Nanoletters 3(7), 901–905.

Collier, C.P., R.J. Saykally, J.J. Shiang, S.E. Henrichs & J.R. Heath, 1997. Reversible tuning of silver quantum dot monolayers through the metal-insulator transition. Science 277(5334), 1978–1981.

Creighton, J.A., C.G. Blatchford & M.G. Albrecht, 1979. Plasma resonance enhancement of Raman scattering by pyridine adsorbed on silver or gold sol particles of size comparable to the excitation wavelength. J. Chem. Soc., Faraday Trans. 2: Mol. Chem. Phys. 75(5), 790–798.

El-Sayed, M.A., 2001. Some interesting properties of metals confined in time and nanometer space of different shapes. Acc. Chem. Res. 34(4), 257–264.

Feldheim D.L., 2002. In: Fcldheim D.L. and Foss C.A. Jr., eds. Metal Nanoparticles: Synthesis Characterization, And Applications, Marcel Dekker, New York.

Hunter, R.J., 1989. Foundations of Colloid Science, Oxford University Press, New York, Vol. 1.

Lee, P.C. & D. Meisel, 1982. Adsorption and surface-enhanced Raman of dyes on silver and gold sols. J. Phys. Chem. 86(17), 3391–3395.

Longenberger, L. & G. Mills, 1995. Formation of metal particles in aqueous solutions by reactions of metal complexes with polymers. J. Phys. Chem. 99(2), 475–480.

Mulvaney, P., L.M. Liz-Marzan, M. Giersig & T. Ung, 2000. Silica encapsulation of quantum dots and metal clusters. J. Mater. Chem. 10(6), 1259–1270.

Murphy C.J., 2002. Materials science. nanocubes and nanoboxes. Science 298(5601), 2139–2141.

Pal, A., S.K.Ghosh, K. Esumi & T. Pal, 2004. Reversible generation of gold nanoparticle aggregates with changeable interparticle interactions by uv photoactivation. Langmuir 20(3), 575–578.

Sau, T.K., A. Pal & T. Pal, 2001. Size regime dependent catalysis by gold nanoparticles for the reduction of eosin. J. Phys. Chem. B 105(38), 9266–9272.

Schocn, G. & U. Simon, 1995. A fascinating new field in colloid science: Small ligand-stabilized metal clusters and possible application in microelectronics. Part I. State of the Art. Colloid Polym. Sci. 273, 101–117.

Storhoff, James J. & Chad A. Mirkin, 1999. Programmed materials synthesis with DNA. Chem. Rev. 99(7), 1849–1862.

Tessier, P.M., O.D. Velev, A.T. Kalambur, J.F. Rabolt, A.M. Lenhoff, & E. W. Kaler, 2000. Assembly of gold nanostructured films templated by colloidal crystals and use in surface-enhanced Raman spectroscopy. J. Am. Chem. Soc. 122(39), 9554–9555.

Valden M., X. Lal & D.W. Goodman, 1998. Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties. Science 281,1647–1650.