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Rapid Synthesis of Gold and Platinum Nanoparticles Using Metal Displacement Reduction with Sonomechanical Assistance

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We present a new route for preparation of metallic nanoparticles by sonomechanical-assisted metal displacement reduction. Au and Pt nanoparticles with sizes around 10 and 6 nm, respectively, and narrow size distributions were synthesized via the displacement reduction of precursor salts of $HAuCl_4 \cdot 3H_2O$ and $H_2PtCl_6 \cdot 6H_2O$ by Cu and Fe foils, respectively. With the effective dislodgment of acoustic cavitation, rapid reduction induced instantaneous nucleation produces a large amount of nanoparticle colloids with small size and uniform size distribution in an astoundingly short period of time (usually a couple of minutes). On the basis of preliminary experiments, this new strategy is applicable to a variety of metallic nanoparticle syntheses upon suitable pairing of precursors and reductive metal foils.

Metal displacement reduction refers to the spontaneous electrochemical reaction in which a metal ion is reduced to the corresponding zerovalent atom state with the concurrent oxidation of a more electropositive metal placed in the same solution. The reaction usually terminates because of the deposition and blanketing of the reduced metal onto the surface of the oxidizing metal. An analogous displacement reduction was employed by Xia and co-workers to generate gold nanoboxes[1] and nanocages[2] with hollow structure by using silver nanocubes synthesized during a polyol process as sacrificial templates. Unlike conventional metal displacement, their reaction is somewhat homogeneous, and plating of gold on the silver nanocubes is desirable. We take advantage of ultrasonic vibrations to successfully overcome plating hindrances and bulk formation. In the synthesis, when atoms are being generated by reduction, ultrasonic vibration effectively ejects them from the foil surface into the bulk solution, and the dispersed atoms nucleate and grow into a uniform nanoscale colloidal suspension.

The ultrasound effect has been explored in sonoelectrochemical and sonochemical syntheses of various metallic nanoparticles including Au,[3−5] Ag,[6] Cu,[7,8] Zn,[9] and Fe.[10] The sonoelectrochemical reduction, initiated by Reisse et al.,[11] is characterized by an electrolysis cell consisting of a power supply, cathode (a titanium horn pulsed sonoelectrode), anode, and electrolyte solution. Sonochemical reduction is

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usually realized by a direct immersion of a continuous high-intensity ultrasound titanium horn into the metal ion solution. The whole sonochemical process typically lasts for several hours.[3,5,7,8,10] Usually alcohol molecules such as propanol[3,4] are added for a higher yield of ultrasound-induced secondary reducing radicals. The particle size and particle formation efficiency is dependent on the presence, type, and concentration of the alcohol. In these reactions, electrons from the external power supply and the ultrasound induced free radicals were attributed to be the reducing source in sonoelectrochemical and sonochemical reduction,[7,11] respectively, while ultrasound was speculated to be aiding in removing the electrodeposited particles on the sonocathode surface.[9]

In fact, the electrochemical reduction itself can produce atoms. For example, the Au and Pt atoms can be generated by using the following metal displacement reactions,

$$[AuCl_4]^-(aq) + Cu(s) \rightarrow Au^0(s) + Cu^{2+}(aq) + Cl^-(aq)$$
$$E_{[AuCl_4]^-/Au^0} = 0.93\ V \qquad E_{Cu^{2+}/Cu^0} = 0.34\ V$$

$$[PtCl_6]^{2-}(aq) + Fe(s) \rightarrow Pt^0(s) + Fe^{2+}(aq) + Cl^-(aq)$$
$$E_{[PtCl_6]^{2-}/Pt^0} = 0.7\ V \qquad E_{Fe^{2+}/Fe^0} = -0.44\ V$$

What is needed is to dislodge the formed atoms from deposition on the surface of the metal (in the above two reactions, the metals are Cu and Fe). We propose to apply the above displacement (electrochemical) reaction to generate Au and Pt atoms and to use ultrasound to dislodge atoms from the metal foils. Ultrasound is a good means to perform just such a function. Under ultrasonication the propagation of pressure waves in solution causes the formation of acoustic microstreaming and acoustic cavitation. The acoustic microstreaming can then dramatically enhance mass transfer at the foil−liquid interface by reducing the ionic concentration gradient.[12] The extreme high temperature and pressure inside the cavitation bubbles initiate the formation of reducing free radicals, which are responsible for the sonoreduction.[7] Collapsing or imploding of the bubbles creates physical effects such as shear forces and shock waves[11] and the formation of liquid jets. All these effects help to impinge and pit against the foil surface through a scrubbing action to dislodge the particles so as to prevent bulk formation. Instead of a powerful Ti horn that is generally used in sonoelectrochemical and sonochemical reduction, we employed a common laboratory ultrasonication cleaner to facilitate the continuous reduction of atom species from the bulk metal foils.

In a typical synthesis, upon placing the metal foils into the ultrasonicating precursor solutions, observable nanoparticle slurry streams are ejected from the foil surface into the bulk solution within a few seconds, and in a couple of minutes, the bright red/purple Au and gray/black Pt nanoparticle colloids are achieved. Only minor plating for Cu foil and almost no plating for Fe foil occur when using them as the heterogeneous reducing media for Au and Pt nanoparticles, respectively.

The effect of sonomechanical-assisted dislodgment is obvious by comparing to an experimental control with no sonication. In the latter scenario, severe deposition occurs rapidly and no colloid can be achieved. To demonstrate that the metallic nanoparticles are generated by the metal foils rather than the sonochemical effect, reference experiments were performed under sole ultrasonication in absence of the foils. When no active foil is present, almost no nanoparticles are formed during the first 2 h, indicated by no color change of the reaction solution and no obvious surface plasmon resonance (SPR) response from UV−vis characterization.

Figure 1 shows TEM images of Au and Pt colloidal samples taken from a typical synthesis (see Supporting Information), in which $HAuCl_4$ and H_2PtCl_6 were reduced on the surface of the Cu and Fe foils, respectively, in the presence of poly(vinylpyrrolidone) as a capping agent. Figure 1A,B shows Au colloid samples taken after 5 min of reaction. Clearly a high content of nanoparticles with mean size around 10 nm and good monodispersity is achieved in a short time. The uniform size distribution can be attributed to the fast reduction induced instantaneous nucleation, that is, for a short time interval relative to the duration of particle growth. Furthermore, the hetero-sites on the foil surface and the limited nucleation region promote instantaneous nucleation. With further reaction time, the newly "polished" atoms and nuclei in the vicinity of the foil surface begin to take part in kinetic collisions and aggregate with those species in the bulk solution phase, resulting in a relatively broad size distribution (Figure 1C,D). Figure 1E shows the transmission electron microscopy (TEM) image and electron diffraction pattern of Pt nanoparticles with an average size around 6 nm acquired after 5 min of reaction time.

An important property of some nanoparticle colloids is the SPR, the frequency at which conduction electrons oscillate and scatter/absorb the incident electromagnetic waves. Only metals with free conduction electrons (essentially Au, Ag, Cu, and the alkali metals) possess plasmon resonances in the visible spectrum, which give colloids different intense colors.[13] Figure 2A shows the UV−vis spectra of Au nanoparticle colloids at different reaction stages, with the characteristic maximum absorbance at around 530 nm. The absorbance peak intensifies with increased reaction time, indicating an increase in the particle content. To investigate the sonochemical reduction effect, a reference experiment was performed in absence of Cu foil. No color change of the solution was observed in up to 2 h of ultrasonication. Figure 2B shows weak and broad SPR absorption around 580 nm after 1.5 h of sole ultrasonication, which is probably due to the sparse nanoparticle content and wide size distribution owing to a small amount of free radicals produced and a slow reduction rate in the weak-intensity ultrasonic bath. This clearly confirms the overwhelming function of Cu foil as a heterogeneous reducing medium for the formation of Au colloids rather than ultrasound induced free radicals.

The X-ray diffraction XRD patterns of as-synthesized Au and Pt nanoparticles in the typical synthesis are shown in Figure S1 (see Supporting Information). All the diffraction

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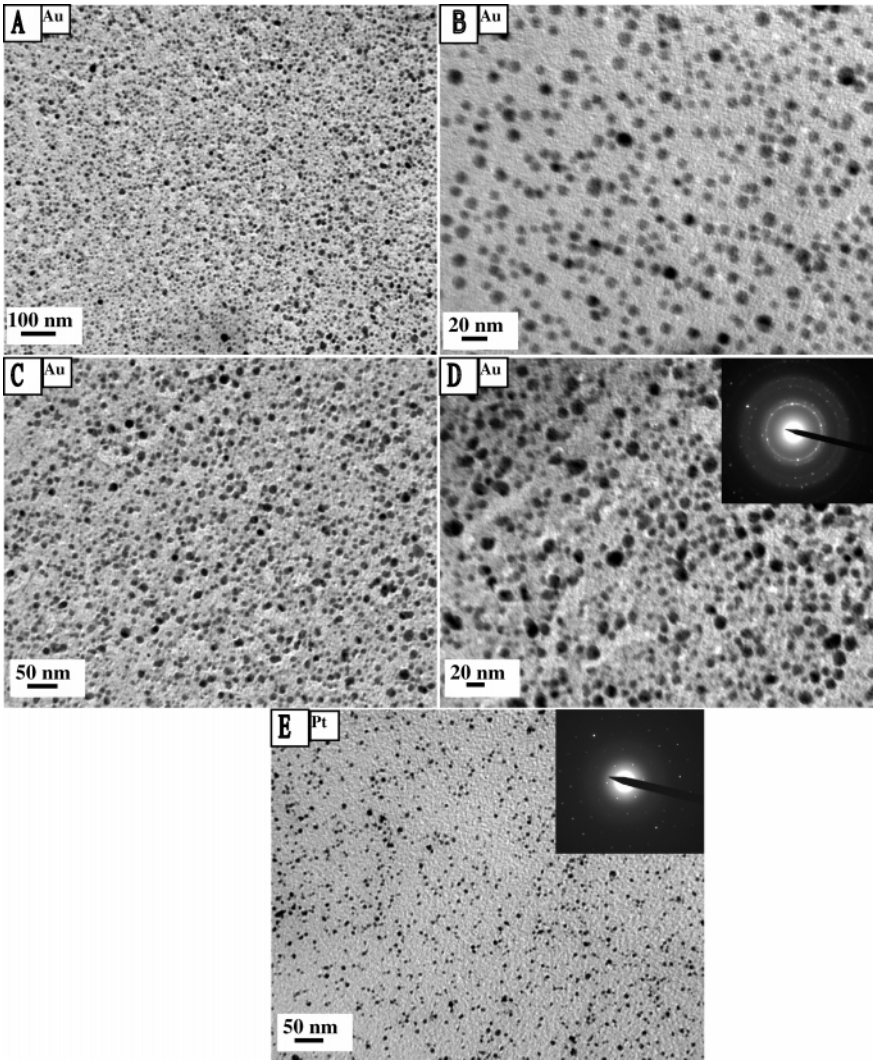

Figure 1. TEM images and electron diffraction patterns of Au and Pt nanoparticles in typical syntheses: (A and B) Au, 5 min sampling with 100 and 20 nm scale bars, respectively; average particle size around 10 nm, with good monodispersity. (C and D) Au, 10 min sampling, with 50 nm and 20 nm scale bars, respectively; relatively broad size distribution. (E) Pt, 5 min sampling with 50 nm scale bar; average size around 6 nm with good monodispersity.

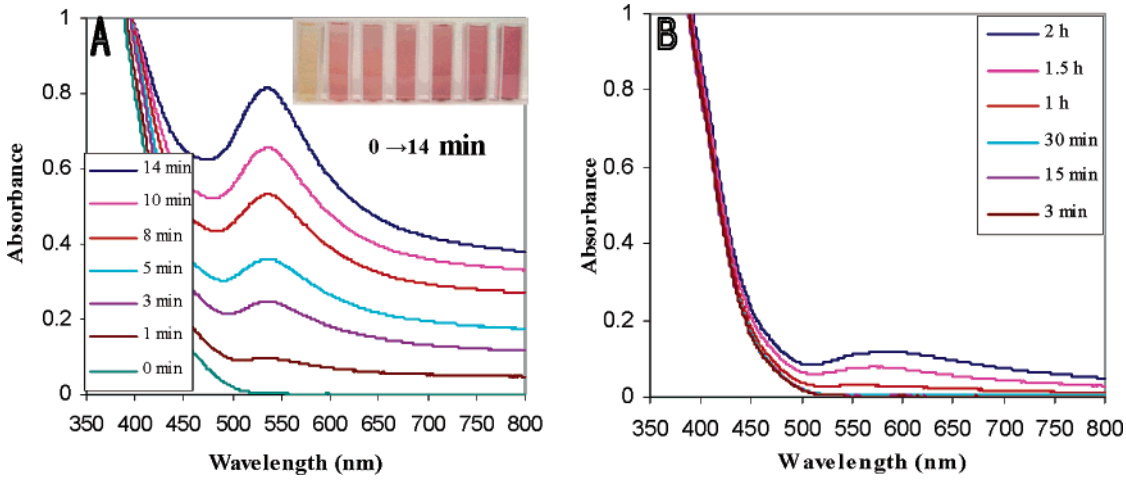

Figure 2. UV−vis absorption spectra of Au nanoparticle colloids sampled at different reaction stages by reducing 0.0025 M $HAuCl_4$ aqueous solutions in 42 kHz continuous ultrasonic cleaner at room temperature and in ambient conditions: (A) in the presence of Cu foil as a heterogeneous reducing medium; (B) in the absence of Cu foil (solely ultrasonication).

peaks index to the pure Au (JCPDS 4-784) and pure Pt (JCPDS 4-802), which confirms the successful preparation of face-centered cubic structured Au and Pt nanoparticles. The calculated average crystallite sizes for Au and Pt, by

the Scherrer formula on the (111) peaks, are 12 and 4 nm respectively, which are in close accord with sizes obtained from TEM images (10 and 6 nm, respectively).

In summary, metal foil as a new reducing medium for metallic nanoparticles synthesis was first presented. Ultrasound as a de-plating tool was proven necessary and highly effective. Preliminary experimental studies presented in this paper have shown the tremendous virtue of this new method for simple and rapid preparation of uniform sized metallic nanoparticles.

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Supporting Information Available: Additional information regarding the typical synthetic process and the XRD patterns of synthesized Au and Pt nanoparticles in the typical experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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