Preparation of Gold and Platinum Nanoparticles Using Visible Light Activated Fe^{III}-complex

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Iron(III)–citrate photochemical system can generate Au and Pt nanoparticles under the visible light illumination with playing the dual role as a precursor of reducing radicals and a stabilizer.

Metal nanoparticles have attracted tremendous interests because of the diverse applications utilizing their unique physicochemical properites.[1–3] Various approaches that include thermal,[4] photochemical,[5] electrochemical,[6] sonochemical,[7] photocatalytic,[8] and radiolytic[9] methods have been tried to make nanoparticles. The essence of these methods is the reductive conversion of metal ion precursors into zero-valent metal nanoparticles, which can be mediated by various chemical mechanisms. In this study, we used the visible light illuminated Fe^{III}–citrate complex system as a new approach to metal nanoparticles. All the previous photochemical[5] or photocatalytic methods[8] of metal nanoparticle preparation are based on the use of UV light.

Direct photochemical excitation of metal ion precursors under 254-nm irradiation can lead to the generation of metal nanoparticles in aqueous solution with surfactant as a stabilizer.[5] For example, the photolysis of $AuCl_4^-$, $PtCl_6^{2-}$, or Ag^+ by 254 nm induced the formation of metal nanoparticles in the presence of surfactants that prevent nanoparticles from agglomerating (reactions 1–3).[5]

$$AuCl_4^- \xrightarrow{h\nu} AuCl_3^- + Cl \qquad (1)$$

$$2AuCl_3^- \xrightarrow{h\nu} AuCl_4^- + AuCl_2^- \qquad (2)$$

$$AuCl_2^- \xrightarrow{h\nu} Au^0 + Cl + Cl^- \qquad (3)$$

In the well-known Turkevich method, Au nanoparticles can be produced by dropping chloroaurate to boiling aqueous citric acid,[4] and citrate ions cap the surface of nanoparticles to prevent the overgrowth of particles.[9b,10] However, at dark room temperature condition, the reduction of $AuCl_4^-$ by citrate occurs very slowly to produce large gold clusters (Figure 1b). Photochemical activation may accelerate the process of metal particle formation. Citrate ions activated by 254-nm light could mediate the formation of tiny spherical gold nanoparticles at highly enhanced rate in the presence of cationic surfactants.[5d]

Figure 1a demonstrated that the photoreduction of $AuCl_4^-$ into Au^0 nanoparticles can proceed even under visible (>420 nm) light. The strong visible absorption band in 500–600 nm range (the surface plasmon band of Au^0 particle) directly indicates the formation of Au^0 nanoparticles. The direct visible light activation of $AuCl_4^-$/citrate is inefficient and slow because the light absorption of $AuCl_4^-$ in the visible region (>420 nm) is very small (see the spectrum of $AuCl_4^-$ in Figure 1a). When ferric ions are present, they form complexes with citrate ions, which absorb visible light. The visible light activation of Fe^{III}–

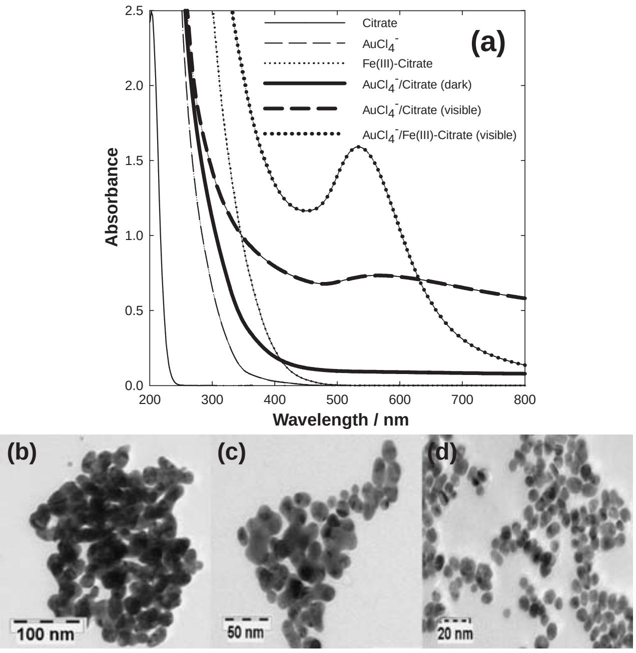
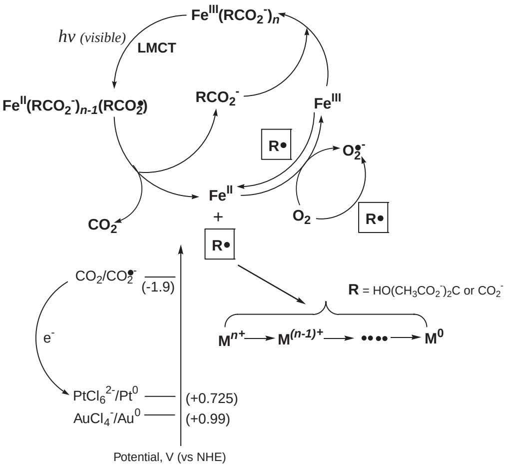


Figure 1. a) UV–vis spectra obtained after 60 min under the dark ($AuCl_4^-$/citrate) or visible-irradiated ($AuCl_4^-$/citrate and $AuCl_4^-$/Fe^{III}–citrate) solutions. TEM images of Au colloids prepared (b) after 17 h under the dark condition with $AuCl_4^-$/citrate, (c) after 120 min under visible-illuminated condition with $AuCl_4^-$/citrate, (d) after 60 min under visible-illuminated condition with $AuCl_4^-$/Fe^{III}–citrate. ($[citrate]_0 = 5$ mM, $[AuCl_4^-] = 0.5$ mM, $[Fe^{3+}]_0 = 0.72$ mM, $pH_i = 6.3$).



Scheme 1. Proposed pathway for the photochemical reduction of $AuCl_4^-$ and $PtCl_6^{2-}$ via carbon-centered radicals generated from the visible-light photolysis of Fe^{III}–citrate complexes.

citrate complexes leads to the generation of reducing carbon-centered radicals through the ligand to metal charge transfer (LMCT) (see Scheme 1).[11–13] Solar photolysis of naturally occurring Fe^{III}-complexes with carboxylate moieties (e.g., oxalate, citrate, and formate) has been reported to generate radical species in the environment.[12,13]

Scheme 1 illustrates the photochemistry of ferric polycarboxylate complexes involved with Fe^{II}/Fe^{III} cycles and in situ formation of carbon-centered radicals. Photoinduced LMCT of Fe^{III}–polycarboxylate complexes generates Fe^{II} and polycarboxylate radicals (e.g., oxyl, citryl radical) that subsequently decompose into carbon-centered radicals (R• in Scheme 1) via decarboxylation. The strong reduction power of carbon-centered radical (e.g., $E^0(CO_2/CO_2{\bullet}^-) = -1.9\,V_{NHE}$[14]) drives the reduction of metal ions, since the reduction potentials of noble metal ion precursors are far more positive ($E^0(PtCl_6{}^{2-}/Pt^0) = +0.725\,V$, $E^0(AuCl_4{}^-/Au^0) = +0.99\,V$ vs. NHE) as shown in Scheme 1. Oxalate and citrate have been reported to be the most efficient as a complexing ligand in the photoreductive generation of Fe^{II} through LMCT.[11] Rapid appearance of purple color (indication of the surface plasmon band of Au^0 particle) was observed within 5 min in the UV-illuminated Fe^{III}/oxalate/$AuCl_4{}^-$ solution (data not shown), while the plasmon absorption band did not appear in $Fe^{III}/AuCl_4{}^-$ under UV light and $Fe^{II}/AuCl_4{}^-$ in the dark. This indicates that the formation of gold nanoparticles needs the presence of organic acid ligands as a precursor of carbon-centered radicals as illustrated in Scheme 1. Au particles generated in the ferrioxalate solution were above 50 nm in diameter and precipitated when left overnight because oxalates do not stabilize gold nanoparticles sufficiently. On the other hand, when citrate was used instead of oxalate,[4,9b,10] the visible light illumination resulted in much smaller gold nanoparticle (Figure 1d). The Au particle formation in the citrate/visible system in the absence of ferric ions occurred at much slower rate with generating larger particles (Figure 1c). Au nanoparticles prepared in the visible-illuminated Fe^{III}/citrate solution remained stable without any precipitation over 5 months.

On the other hand, the aqueous $PtCl_6{}^{2-}$/citrate solution was completely unreactive both in dark and under visible light unlike the case of Au. The presence of ferric ions was essential for the Pt^0 particle formation under illumination as shown in Figure 2. The red shift of the spectrum observed in the $PtCl_6{}^{2-}/Fe^{III}$/citrate system under UV or visible light illumination indicates the formation of Pt nanoparticles. Under UV illumination, the formation of Pt nanoparticles was observed even in the absence of ferric ions but their presence accelerated the particle formation by more than fourfold. Under visible light, Pt particles did not form at all in the absence of ferric ions. The above result clearly shows that the metal ion reduction and particle formation mechanism are directly related with the photoactivation of Fe^{III}–citrate complexes and the subsequent generation of reducing radicals.

In this work, we propose a new photochemical method for metal nanoparticle synthesis that utilizes the photoactivation of Fe^{III}–citrate complexes under visible irradiation. Fe^{III}–citrate complexes excited by absorbing visible photons subsequently undergo LMCT and release carbon-centered radicals that are powerful enough to reduce metal ions to zero-valent metals. Citrates play the dual roles of a stabilizer that prevents the overgrowth of particles and a complexing ligand that is a precursor of carbon-centered radicals. To the best of our knowledge, this is the first demonstration that visible light can be utilized in metal nanoparticle synthesis.

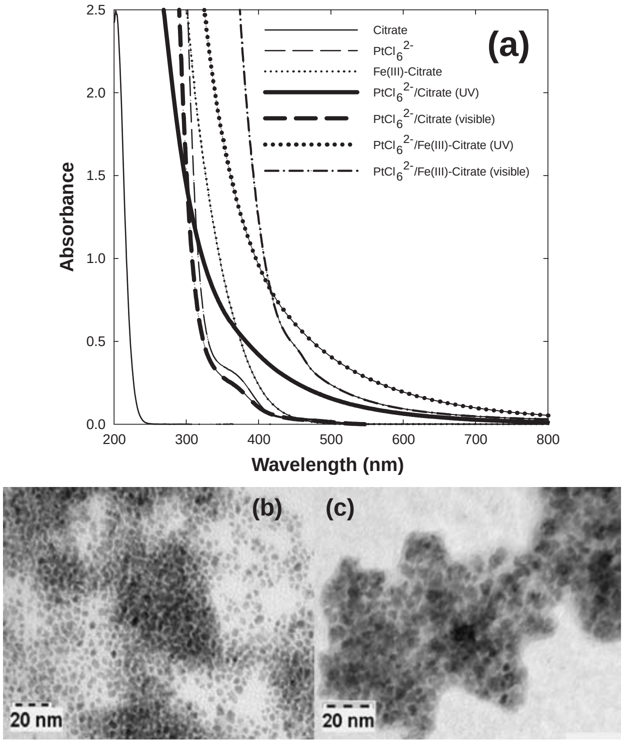


Figure 2. a) UV–vis absorption spectra obtained after 120 min under UV-illuminated condition ($PtCl_6{}^{2-}/Fe^{III}$–citrate) or visible-illuminated condition ($PtCl_6{}^{2-}$/citrate and $PtCl_6{}^{2-}/Fe^{III}$–citrate). TEM images of Pt colloid prepared (b) under UV-illuminated condition ($PtCl_6{}^{2-}/Fe^{III}$–citrate), ($[citrate]_0 = 5\,mM$, $[PtCl_6{}^{2-}]_0 = 1\,mM$, $[Fe^{3+}]_0 = 0.72\,mM$, $pH_i = 6.3$), (c) under visible-illuminated condition ($PtCl_6{}^{2-}/Fe^{III}$–citrate), ($[citrate]_0 = 12.5\,mM$, $[PtCl_6{}^{2-}] = 1\,mM$, $[Fe^{3+}]_0 = 2.5\,mM$, $pH_i = 6.3$).

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