# Potential-controllable green synthesis and deposition of metal nanoparticles with electrochemical method†

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**A controllable and environmentally friendly electrochemical method for task specific synthesis and deposition of metal nanoparticles was first demonstrated by simply adjusting the potentials for the reduction of metal precursors in ionic liquids.**

Considerable interest has been drawn both by the synthesis of metal nanoparticles in a bulk solution and by the deposition of metal nanoparticles onto a conducting substrate because the distinct physicochemical properties of metal nanoparticles have largely enabled them to be either solubilized in a bulk solution or deposited onto conducting substrate with promising applications in various research and industrial areas, such as catalysis, sensing, environmental processing and energy conversion and storage.[1] To this end, many methods have been demonstrated for both purposes,[2] of which the electrochemical method remains advantageous in terms of its ease-of-operation and cost-effective properties.[3] More importantly, this method utilizes electrons as the reductants to replace chemical reductants for metal precursors and is thus more environmentally benign than the chemical methods.[4] As a result, ever increasing interest has been drawn by the development of effective electrochemical methods for the synthesis/deposition of metal nanoparticles. In this context, research into the parameters that can efficiently control the growth of metal nanoparticles to form task specific electrosynthesis or electrodeposition process remain central, because such research essentially offers a guide to screen and establish the conditions for synthesis or deposition of metal nanoparticles in different electrochemical systems or in the same electrochemical systems in a switchable manner.

Activated by the formation of metal nanoparticles with controllable size and morphology using the electrochemical method, much effort has been devoted to the investigations on the association between the parameters employed for electrosynthesis or electrodeposition and the properties of the as-formed nanoparticles.[5] However, research on the parameters involved in the electrochemical reduction of metal precursors to efficiently control the nanoparticles' growth have not been reported so far.

This communication describes the first study on the association between the parameters employed for the reduction of metal precursors and the growth of metal nanoparticles, by using Pt nanoparticles as an example. The study undertaken here is very useful for establishing the conditions to efficiently control metal nanoparticles to solubilize into the bulk solvents (electrosynthesis) or to deposite onto electrode surface (electrodeposition) and paves a versatile way to task specific formation of metal nanoparticles either in the solution or onto the electrode surface in the different electrochemical systems or in the same electrochemical systems in a switchable manner.

Investigations undertaken here were carried out with ionic liquids (ILs) as the solvents because earlier efforts have revealed that the excellent physical and chemical properties of ILs, such as high polarity, low vapor pressure, good chemical stability and capability to solubilize the organic and inorganic compounds substantially make them very useful in the formation of metal nanoparticles.[6] More importantly, ILs are involved in the combined intrinsic high charge plus the steric bulk, which could create an electrostatic and steric colloid-type stabilization of metal nanoparticles, without requirement of addition of any capping materials.[7] The use of ILs as the solvents for electrochemical synthesis/deposition of metal nanoparticles is believed to facilitate the controllable task specific formation of nanoparticles with less environmental pollution and simplified experimental procedures.

The formation (*i.e.*, synthesis/deposition) of Pt nanoparticles was carried out in 1-n-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$) containing 20 mM $H_2PtCl_6$ with a three-electrode system by polarizing ITO substrate at different potentials (Scheme S1†). A silver wire was used as a quasi-reference electrode. For a convenient comparison, the potential of the silver quasi-reference electrode was calibrated to that of Ag/AgCl (KCl-sat.) with ferrocenecarboxylic acid as the redox probe. When the substrate was polarized at a high overpotential of −2.8 V (*vs.* Ag/AgCl), Pt nanoparticles were only deposited onto the substrate, with no production in the bulk solution. This was directly evident from the almost unchanged color of the IL solution and the color change of ITO substrate from initially colorless to black (Fig. 1A, B). The deposition of Pt nanoparticles onto ITO substrate was further confirmed by XPS (Fig. S1 A†). Two well-defined peaks in the XPS spectrum were recorded with binding energy of 71.2 and 74.4 eV, which were ascribed to the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ doublet in $Pt^0$, respectively.[8] This demonstration reveals that, at a high overpotential, the as-formed Pt nanoparticles tend to deposit onto electrode surface, rather than to solubilize into the IL solvent. The Pt 4f XPS spectrum recorded for $Pt^0$ was symmetric and was unable to be resolved into different peaks by a nonlinear regression (Fig. S1 A†), implying that the reduction of $PtCl_6^{2-}$ precursor into $Pt^0$ was efficient, with no major reactions under the present condition.

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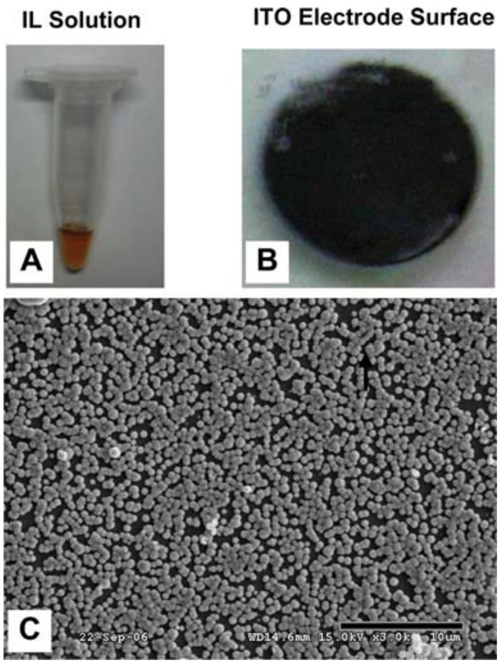


**Fig. 1** Photographs of $BmimPF_6$ solution (A) and ITO substrate (B) after the substrate was polarized at −2.8 V (*vs.* Ag/AgCl) for 1000 s in $BmimPF_6$ containing 20 mM $H_2PtCl_6$. (C) A SEM image of Pt nanoparticles electrodeposited on ITO substrate. Scale bar, 10 μm.

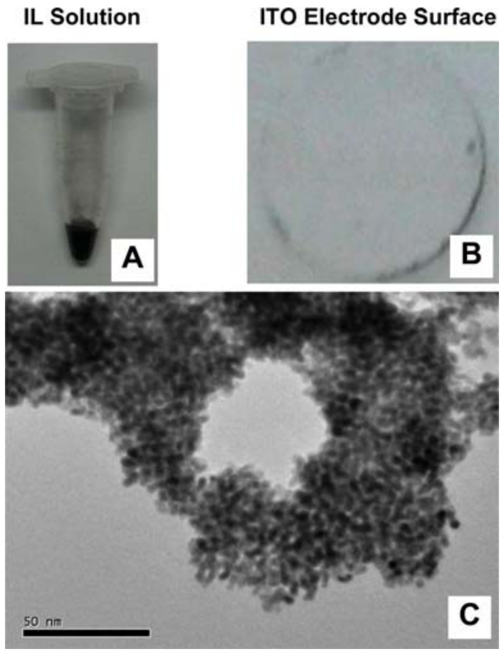


**Fig. 2** Photographs of $BmimPF_6$ solution (A) and ITO substrate (B) after the substrate was polarized at −1.8 V (*vs.* Ag/AgCl) for 4000 s in $BmimPF_6$ containing 20 mM $H_2PtCl_6$. (C) A TEM image of the synthetic Pt nanoparticles. Scale bar, 50 nm.

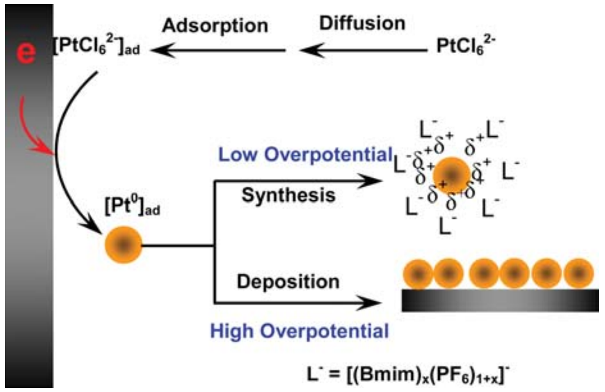
Moreover, the diffraction lines (111, 200, 220) of metallic Pt were clearly observed in the diffraction pattern (Fig. S1 B†), again confirming the formation of $Pt^0$ onto the ITO substrate under the present condition.[7c] Scanning electron microscopy of the as-deposited Pt nanoparticles suggests the nanoparticles almost have a uniform size (*ca.* 100 nm diameter on average) (Fig. 1C). All these demonstrations reveal that when a high overpotential was applied for the reduction of metal precursor, the as-formed nanoparticles tend to deposit onto the substrate surface, rather than to solubilize into IL solvent, to form an electrodeposition process for metal nanoparticles.

Interestingly, when the ITO substrate was polarized at a low overpotential of −1.80 V (*vs.* Ag/AgCl), there was no color change on the ITO surface, while the color of the IL solution was changed from initially somewhat yellow into black (Fig. 2A and B). XPS results show two well-defined peaks on the XPS spectrum with binding energy of 71.1 and 74.5 eV (Fig. S2 A†), which were ascribed to the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ doublet in $Pt^0$, respectively,[8] suggesting that this kind of black solution was the dispersion of Pt nanoparticles. These results reveal that when the electrode was polarized at a low overpotential for the reduction of $PtCl_6^{2-}$ precursor, the as-formed Pt nanoparticles prefer to solubilize into IL solvent to form an electrosynthesis process for Pt nanoparticles. The Pt 4f XPS spectrum recorded for $Pt^0$ was symmetric and the different peaks could not be analyzed by a nonlinear regression (Fig. S2 A†), implying that the reduction of $PtCl_6^{2-}$ precursor into $Pt^0$ was also efficient under the present condition. Furthermore, the diffraction lines (111, 200, 220) of metallic Pt were clearly observed in the diffraction pattern (Fig. S2 B†),[7c] again confirming the formation of Pt nanoparticles dispersion in the IL solution. TEM image of the as-synthesized Pt nanoparticles reveals that the nanoparticles almost have a uniform morphology with a size ranging from 3.5 to 4 nm (Fig. 2C). The small diameter of nanoparticles may result from the low surface tension of ionic liquids.[7a]

As far as we know, this is the first demonstration on the controllable synthesis of Pt nanoparticles with an electrochemical method with IL as the solvent and capping material. In the whole process, the use of reduction agent, additional capping materials, heating, or high pressure was essentially avoided. This study offers a mild, renewable, nontoxic and completely green synthetic route to formation of Pt nanoparticles colloid. The results described above demonstrate that the simple adjustment of the potentials for the reduction of metal precursors could efficiently control the nanoparticles' growth and thus form a task specific process for electrosynthesis or electrodeposition in a same electrochemical system with a switchable manner.

As another important factor that may also determine the nanoparticles' growth and thus control the process for synthesis or deposition of metal nanoparticles, we have studied the effect of the concentration of $PtCl_6^{2-}$ precursor on the nanoparticles' growth. Unlike the potentials employed for the $PtCl_6^{2-}$ reduction, the change of $PtCl_6^{2-}$ concentration (from 20 mM to 100 mM at −2.8 V and from 5 mM to 20 mM at −1.8 V *vs.* Ag/AgCl) did not greatly influence the growth of the as-formed nanoparticles, implying that the task specific electrosynthesis or electrodeposition may not be effectively controlled by such a factor. Presumably, this is due to the low diffusion efficiency of the metal precursor in the viscous IL solvents.

The potential-controllable green synthesis and deposition of Pt nanoparticles is considered to be based on colloid chemistry and unique property of ILs. As shown in Scheme 1, the reduction of the $PtCl_6^{2-}$ precursor diffused onto electrode surface forms so-called Pt adatoms ($[Pt^0]_{ad}$). In this case, on one hand, IL creates electrostatic and steric colloid-type stabilization toward Pt nanoparticles, resulting in the solubilization of nanoparticles in a bulk solution to form Pt nanoparticles colloid. On the other hand, the nanoparticles prefer to deposit onto electrode surface due to the high Gibbs energy of solid surface. The competition between synthesis and deposition of Pt



**Scheme 1** A schematic illustration of potential-controllable task specific electrosynthesis and electrodeposition of metal nanoparticles in IL solvents.

nanoparticles is essentially judged by the relative rate of solvation and nucleation of the as-formed $[Pt^0]_{ad}$, which is basically determined by the rate of the production of $[Pt^0]_{ad}$ at the vicinity of the electrode. The rate of $[Pt^0]_{ad}$ production is simply controllable by the potentials employed for the reduction of $PtCl_6^{2-}$ precursor. When a high overpotential was applied, the nanoparticles prefer to deposit onto the ITO electrode surface since the formation rate of $[Pt^0]_{ad}$ is fast and, as a result, the stabilization and thus solubilization of $[Pt^0]_{ad}$ by IL molecules through the steric and/or electrostatic interaction(s) are suppressed. Conversely, when a low overpotential was applied, the $[Pt^0]_{ad}$ tend to form clusters that are efficiently stabilized by IL molecules through the steric or electrostatic interaction(s) between both components. In this case, the nanoparticles prefer to solubilize into IL solvent to form a homogeneous dispersion. These features substantially make it possible to control the occurrence of both synthesis and deposition of Pt nanoparticles to be task specific either in the different electrochemical systems or in the same electrochemical systems with a switchable manner.

In summary, a controllable and environmentally friendly method for task specific synthesis/deposition of metal nanoparticles has been demonstrated by simply adjusting the potentials for the electrochemical reduction of metal precursors with ionic liquids as the green solvents and with electrons as the reductant. This study essentially paves a controllable and green route to task specific synthesis/deposition of metal nanoparticles with no requirement of reducing agents, capping materials, heating, or high pressure and with no production of toxic substrates. The method is envisaged to be versatile for controllable synthesis/deposition of metal nanoparticles either in the different electrochemical systems or in the same electrochemical systems in a switchable manner, provided the metal precursors are electrochemically redox active.

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