The influence of alkanolamine in the formation of Pt nano- and microstructures

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Abstract. Start your abstract here. Pt nano- and microstructures have been produced by a solvothermal technique in the presence of diethanolamine (DEA) as a reducing and capping agent. The effect of DEA concentration on Pt properties (structural and morphological) was discussed in detail. A lower DEA concentration produces nanoscale size particles while at higher concentration results in micro-flower structures. Pt crystallinity is enhanced with respect to the increment of DEA concentration in the order of 0.43 M > 0.29 M > 0.14 M. The presence of amino groups is confirmed by the intense band at ~1087 cm⁻¹ and absorption peak at 1446 cm⁻¹ corresponds to C-N and N-H bending vibration mode of the amine group. The UV-Visible adsorption peak at 282 nm, due to adsorption of Pt (IV) disappeared implying that the Pt (IV) species has been reduced to Pt (0) valent confirming that DEA acted as a reducing agent. A possible reaction mechanism has been proposed.

1. Introduction

Platinum nano- and microstructures have raised much attention in the development of chemical sensor [1], electrocatalyst in fuel cell [2], medical appliances [3], and biosensors [4]. The reason for this attention is due to its outstanding chemical, physical and catalytic properties. However, the price of Pt is extremely expensive due to the rare reserve on the earth, thus limiting its technological viability. To solve this, it is crucial to promote a highly efficient Pt and producing Pt in a simple and economical technique. It is generally accepted that the solution-based protocol promotes inexpensive and uncomplicated method, as well as capable of tailoring the size and shape of particles. Various simple shapes including nanoframes [5], concave octopod [6], nanocubes [7], and truncated octahedral [8] have been produced by the solution-based method. Recently, a class of complex flower-like structures have emerged as a compelling material owing to their three-dimensional (3D) structure. The flower-like structures generally consist of several sharp tips branching out in three dimensions which are capable of focusing electromagnetic field of excitation light at their ends to produce extremely large field enhancement for surface-enhanced Raman spectroscopy (SERS) [9,10]. Moreover, the surface roughness and high index facet of the particles provides active sites (corners, edges, steps, etc.) for applications in catalysis [11]. Despite these fascinating benefit, synthesis of Pt flower-like structure with a high degree of anisotropy still remains a challenge.
Several synthesis strategies on flower-like geometries have been reported. Recently, Mazzotta et al. [12] produced uniform 3D flower-like nanostructures with the size ranging from 250 to 500 nm on polypyrrole nanowires matrix using electrochemical approach without using any seed, template or surfactant. An ordered array of Pt flower-like nanostructure was produced by Dandapat et al. [13] via ethanol reduction of chloroplatinic acid at 85 °C, employing PVP as a structure directing agent. The group demonstrated that the presence of PVP influenced the generation and growth of the flower-like Pt with ordered structures. Sun et al. [14] demonstrated an environmentally friendly route of single crystal 3D flower-like nanostructures with diameters in the range of 150 – 400 nm via reduction reaction of chloroplatinic acid with formic acid. Similarly, Ye et al. [15] synthesized Pt nanoflower via chemical reduction reaction of chloroplatinic acid with ascorbic acid instead of formic acid. Despite the successful production of nanoflower structures, the use of a high volume of acid in the reaction can cause hazardous. Therefore, it is crucial to find an alternative to the acid solution that serves as a reducing agent.

In recent years, the alkanolamine compound such as ethanolamine and diethanolamine has been investigated for its properties similar to methylamine and ethylene glycol which capable of reducing the metal salts. The reducing power of alkanolamine is derived from the terminal hydroxyl groups at the ends of the molecule. These hydroxyl groups are able to donate an electron to the metal ion and simultaneously reduce the metal to zero oxidation state [16]. However, the reducing power of alkanolamine is much slower than ammonia, thus kinetically-controlled growth becomes more favoured and the shape of the final product will vary from the thermodynamic shape.

Previously, we have investigated the influence of diethanolamine (DEA) in reaction with chloroplatinic acid. Significant growth transformation with respect to synthesis time was observed from the experiment [17]. Nonetheless, more studies are required to understand the function of DEA in the synthesis of Pt structures. In the present work, we extend the studies by investigating the relationship of varying DEA concentration towards Pt properties emphasizing on shape distribution, crystallinity and spectra absorption as well as proposing the possible reaction mechanism.

2. Materials and method
Hexachloroplatinic acid (H$_2$PtCl$_6$, 8 wt% in aqueous solution), polyvinylpyrrolidone, (Molecular weight 40 000) were bought from Sigma Aldrich. N, N-dimethylformamide (DMF) from Merck and diethanolamine (DEA) from R&M Chemicals. All of the chemicals were used as received without further purification. In a typical synthesis, 0.50 mL of H$_2$PtCl$_6$ was added into 10 mL of DMF, followed by 0.14 M of DEA and 0.2 g PVP under vigorous mixing to produce a homogeneous yellow solution. Next, the solution was transferred to Teflon-lined stainless-steel autoclave reactors and heated from room temperature to 160 °C for 11 hours. Then, the solution was precipitated with acetone and separated via centrifugation. The product was collected by discarding the yellowish supernatant and washed three times by precipitation/dissolution with acetone/ethanol solvents to remove the unreacted reactants. The product was re-dispersed in ethanol for characterization. Finally, this experiment was repeated using 0.29 M and 0.43 M of DEA for comparison. The morphologies of the synthesized Pt were analyzed using a field emission scanning electron microscope (NOVA Nanosem 45) with an acceleration voltage of 5 kV. The structural properties were characterized using X-ray diffractometer (Bruker D8 Advance Diffractometer) operating at a wavelength of 1.54056 Å by CuKα radiation. The Fourier transform IR (FT-IR) spectroscopy were characterized using FT-IR ATR Perkin Elmer. The absorption spectra were taken using Shimadzu UV 3600 UV-VIS NIR spectrophotometer.

3. Results and discussions
The formation of Pt flower-like structures was confirmed by FESEM observation. Figure 1 presents the FESEM images of samples synthesized with different DEA concentrations, and without DEA as the control sample (Inset Figure 1a). It is evident that the synthesized Pt displayed different morphologies under various concentrations of DEA. The low concentration sample (0.14 M) demonstrated that the synthesized Pt consisted of a high distribution of small and agglomerated nanoparticles with diameters
of 5–10 nm. As the DEA concentration was increased to 0.29 M, the samples exhibited a flower-like structure with sizes of about 500 nm to 1 μm. The high magnification FESEM image revealed that each flower-like structure was composed of close-packed triangular petals constructed by radial triangular arrays growing from the central point to the surface of the structures. When the DEA concentration was further increased to 0.43 M, the synthesized Pt exhibited a network of flower-like microstructures. The sample prepared without DEA produced small agglomerated particles with undefined shape, suggesting the importance of DEA in the formation of flower-like morphology.

Figure 1. FESEM images of the synthesized Pt at different DEA concentrations: (a) 0.14, (b) 0.29, and (c) 0.43 M. Inset Figure 1(a) is Pt synthesized without DEA (control sample).

\[
\text{NH}_2\text{CH}_2\text{O} + \text{PtCl}_6^{2-} \rightarrow (\text{NH}_3)^+\text{PtCl}_4^{2-} + 2\text{H}_2\text{O} + \text{Cl}^- + \text{H}_2 \quad (1)
\]

\[
(\text{NH}_3)^+\text{PtCl}_4^{2-} + 2\text{H}_2\text{O} \rightarrow (\text{NH}_3)^+\text{PtCl}_2^{2-} + 2\text{H}_2\text{O} + 2\text{Cl}^- + \text{H}_2 \quad (2)
\]

\[
(\text{NH}_3)^+\text{PtCl}_2^{2-} + 2\text{H}_2\text{O} \rightarrow \text{Pt} + 2\text{Cl}^- + 2\text{H}_2\text{O} + \text{NH}_4\text{Cl} + \text{HCl} \quad (3)
\]

First, the DEA reacts with chloroplatinic acid to produce amine chloroplatinate complex and ethylene oxide as stated in equation 1. The DEA is weakly adsorbed on the Pt surface via the lone pair electron of the nitrogen atom. The reaction proceeds with reduction of the Pt complex by the nascent releases of the hydrogen molecule as in equation 2 to form Pt atom as stated in equation 3. The equations 1 and 2 are similar to work reported by Meltsner et al. [16]. From the reaction mechanism, it can be deduced that DEA exhibits reducing capability as it produces hydrogen molecules that used as a reductant. This results in the increase of metal reduction rate, which in turn increases the nucleation rate. Therefore, either a continuous or increasing supply of DEA will induce fast reduction kinetics and accelerate the nucleation process. A high concentration of nuclei will increase the nuclei collision frequency and lead to particle agglomeration. During crystal growth, the agglomerate particle is converted into a new bigger particle to form the preferred crystal structure. The formation of flower-like particles began with the reduction of PtCl₆²⁻ to Pt atoms. On the account of the face-centered cubic (FCC) phase, these atoms will cluster into a cuboctahedral (Wulff polyhedron) structure [18]. As amine molecules were present in the reaction, the molecules preferred to bind with the Pt {100} facets and inhibited the growth along the (100) plane [19]. Due to the supply of reductant in the reaction, the nucleation process occurred and the Pt atoms favoured to grow along the {111} and {110} facets. As the reaction prolonged, Pt octapod
structures were produced. Secondary nucleation occurred with the continuous supply of reductant. Secondary atoms subsequently grew on the former octapod to form pyramidal arms with a sharp tip.

![X-ray diffraction patterns of the synthesized Pt particles at different DEA molarities. Inset figure is Pt prepared without the presence of DEA.](image)

Figure 2. X-ray diffraction patterns of the synthesized Pt particles at different DEA molarities. Inset figure is Pt prepared without the presence of DEA.

The phase structures of the synthesized Pt prepared with different DEA concentrations and without DEA (Inset) are shown in Figure 2. The lack of Pt diffraction peak observed for sample synthesized without DEA implies the absence of Pt formation. This result shows that DEA is essential in producing Pt nanocrystal. On the other hand, samples synthesized with DEA exhibited XRD patterns with face-centered cubic phase at the (111), (200), (220), (311), and (222) reflections. All detectable peaks were matched to the reported JCPDS data card 00-001-1194, which implies that the product has a pure polycrystalline structure. The intensities of the diffraction peak became more prominent as the DEA concentration was increased to 0.29 and 0.43 M. Likewise, the peaks were sharper and stronger with respect to the concentration increment. The increase in intensities was attributed to the excellent crystallinity, while the sharp peaks indicate the formation of bigger crystallites. Taking the strongest line which is the (111) reflection peak (calculate using Scherrer equation), the average crystallite size for sample synthesized with 0.14 M of DEA is approximately 20.14 nm, sample synthesized with 0.28 M of DEA is about 22.00 nm and crystallite size for 0.43 M is approximately 29.80 nm. It can be observed that the average Pt crystallite sizes gradually increased with the increase of DEA concentration. The result is in agreement with other reports that observed crystallites to become bigger in size with the increasing reductant concentration. This is because increasing the reductant concentration increases the rate of reduction of $[\text{PtCl}_4]^{2-}$, thus producing rapid nucleation and inducing fast supersaturation. The high seed concentration will increase the frequency of collision to bind due to the van der Waals force, thus forming bigger crystallites.
Figure 3 showed UV-visible absorption spectra of the synthesized Pt at different DEA concentration. It can be observed that all the synthesized Pt assisted DEA exhibit absorption peak centered at 210 nm corresponds to the presence of Pt atom which confirms fully conversion of Pt salt to Pt atoms. The peak centered at 249 nm is assigned to the ligand-to-metal charge transfer transition of [PtCl₆]²⁻ ion which arises from the ligand field splitting of Pt 5d orbital from the coordination of N and/or O atoms of PVP to Pt atoms [20]. An additional absorption peak centered at 282 nm was observed for the sample prepared without DEA, assigned to the presence of Pt (IV) species, implying that the Pt (IV) species was not fully converted into Pt atoms.

Figure 3. UV-visible spectra of Pt nanocrystal synthesized at different DEA concentrations.

Figure 4 shows the FTIR spectra of the Pt synthesized with 0.43 M of DEA (representing samples synthesized with DEA) and pure DEA for comparison. The broad band at 3322 cm⁻¹ corresponds to the stretching vibration of hydroxyl (O–H) group [21] of ethanol in which the Pt was redispersed. The absorption band in the region of 3000 – 2880 cm⁻¹, 1384 cm⁻¹ and 1055 cm⁻¹ are due to the C–H stretching mode, C–H bending and C–H wagging of methylene (–CH₂–) group respectively [22, 23], which arises from the alkyl group of ethanol and PVP.

The coordination of amino groups on Pt synthesized with DEA is confirmed by the intense band at ca. 1118 cm⁻¹ and absorption peak at 1446 cm⁻¹ which corresponds to C–N and N–H bending vibration mode of the amine group [24]. However, the prominent N–H stretching (~3310–2990 cm⁻¹) band could not be identified as the peak overlapped with the O–H stretching band. The characteristic bond observed at 1660 cm⁻¹ is attributed to the C=O bonds of PVP [21], which confirms the coordination of Pt with O atoms of C=O bonds of PVP.
Figure 4. FTIR spectra of the synthesised Pt structures assisted with DEA and pure DEA as a comparison.

4. Conclusion
In summary, the Pt flower-like structures were synthesized using diethanolamine (DEA) via solvothermal method. Introducing DEA in the reaction induce the production of hydrogen molecules in the system. Increasing DEA concentration results in acceleration of reduction rate and nucleation process. The DEA serves as capping agent by promoting the growth along Pt \{111\} and \{110\} facets forming flower shape structures. The synthesized flower-like Pt particles exhibited a high crystallinity and size enlargement with increasing of DEA concentration. This work shows that DEA has the potential to become an alternative reductant in synthesis of noble metal.

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