



Proposed molecular mechanism for the colloidal nanocatalysis of the hexacyanoferrate III–thiosulfate electron transfer reaction: On the involvement of a Prussian blue analogue complex intermediate

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ABSTRACT

Attenuated total reflectance (ATR-FTIR) spectroscopic methods were used to study the mechanism of the reaction between hexacyanoferrate III (HCFIII) and thiosulfate catalysed, by colloidal platinum nanostar (PtNSs). A dynamic flow cell was fabricated and used for in situ FTIR and optical measurements for the reaction near zero-time after mixing the reacting materials. It is proposed here that the mechanism of this reaction takes place *via* a Prussian blue analogue complex intermediate, whereby the HCFIII reacts with the PtNS surface atoms prior to reacting with the thiosulfate reactant. Further, it is proposed here that the complex occurs on the PtNSs surface and that platinum atoms move through multiple redox cycles as they are oxidized and reduced by the reactants. When the reaction is complete, the Pt atoms largely return to their ground state through reduction by excess thiosulfate in solution. In this way, the majority of the Pt atoms are thought to remain associated with the same nanoparticle throughout the reaction, thus providing evidence for a heterogeneous particle surface mediated nanocatalysis.

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1. Introduction

One of the unique properties of the nanoparticles is their high surface area compared with the number of surface atoms [1–3]. When the size of the material decreases to the nanoscale, the surface area of the material largely increases as well as the number of chemically unsaturated thermodynamically active surface atoms. In addition to the high surface to volume ratio, the shape and size of the nanoparticles proved to have a role in the activity of the catalyst [4,5]. An important question that arises in this field is whether catalysis with nanoparticles is heterogeneous [6,7] or homogenous [4,8,9]. The common and acceptable definition of colloidal nanocatalysis is heterogeneous when the reaction occurs on the surface of nanoparticles and formation of a complex on the surface atoms themselves. If a complex forms on the nanoparticles surface, however and dissolves away from the surface the reaction is homogenous.

It has been reported that the activation energy of the hexacyanoferrate III and thiosulfate electron transfer reaction catalysed with platinum nanoparticles was found to be shape dependent. Nanocatalysts possess more catalytic activity when they have more atoms on edges or corners (*i.e.* more valence unsaturated atoms) [4]. Furthermore, it was found that the catalytically active

nanoparticles undergo shape changes [9]. Some research was carried out studying the mechanism of the gas nanocatalysis, *e.g.* the oxidation of CO by O₂ catalysed by palladium nanoparticles supported on the surface of Fe₃O₄, the mechanism of this reaction was found to be size dependent [10], while there is no sufficient work carried out on the mechanism of colloidal nanocatalysis. To make the colloidal nanocatalysis useful, one should understand the mechanism of the reaction and the role of the nanocatalyst. Here, a simple example for colloidal nanocatalysis is discussed, in which the electron transfer reaction between hexacyanoferrate III (HCFIII) and thiosulfate in the presence of platinum nanostars (PtNSs) as nanocatalyst is studied.

Former studies were carried out on the HCFIII–thiosulfate reaction using PtNSs with different shapes and sizes [4,8,9]. Reshaping of the nanocatalyst was observed for all shapes but the mechanism of the electron transfer process is still unclear. In this study, the proposed molecular mechanism for the HCFIII–thiosulfate electron transfer reaction, catalysed by platinum nanoparticles, is discussed.

The attenuated total reflection FTIR (ATR-FTIR) technique is used here to measure the IR of the compounds in aqueous solution, because it depends on the multi-reflection of the IR source through the ATR cell. However, it monitors the adsorbed materials on the surface of PtNSs. The in situ optical and FTIR spectroscopies in steady state and in time-resolved (mixing of the reacting materials during the measurement) technique were applied.

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2. Experimental

Platinum nanostars (PtNSs) were prepared by a seed-growth method [5] where tetrahedral platinum nanoparticles (THPN) were used as a seed, which grew to PtNS. THPN were prepared by dissolving 0.0667 g of PVP (MW 360,000) in 33 mL of deionized water, four drops of 1 M HCl were added and the solution was heated under reflux to boil, and then 3 mL of 0.01 M K_2PtCl_4 was added. After 2 min of boiling, 14 mL of ethanol was quickly injected and the solution was left to cool to room temperature. Forty microlitres of the tetrahedral platinum nanoparticle was allowed to grow to PtNS in a hot solution of: 0.133 g of PVP (MW 360,000) dissolved in 100 mL of deionized water, 9.6 mL of 0.01 M K_2PtCl_6 , and 8 mL of 1 M HCl. The resulting mixture was heated under reflux to boil and then 36 mL of ethanol was injected, followed by 3 h reflux. A JEOL 100C transmission electron microscope (TEM) was used to image PtNS before and after the reaction, while JEOL 4000EX used for the high-resolution TEM measurements.

The setup used in this experiment depends on a continuous flow of two reacting materials through two separate tubes and finally allows them to mix together and react inside the ATR with a germanium crystal [2]. By this method, it is possible to generate and detect short lived compounds formed during or at the early stages of the reaction. FTIR (Nicolet 860 Magna-IR) operating in the range of $4000\text{--}600\text{ cm}^{-1}$ with 4 cm^{-1} resolution is used for the ATR-FTIR measurement in which the ATR was fixed at 45° from the IR source.

Forty-five microlitres of 0.5 M sodium thiosulfate was mixed with different volumes of the PtNSs prepared by the above method, and the volume was raised to 50 mL by deionized water.

The HCFIII was flowed through one tube and freshly mixed PtNSs (0.2 mM) and potassium thiosulfate (0.5 M) was flowed through the second tube using a Cole-Parmer pump (model 77202–60). For the UV-Vis. measurement (Ocean optics, HR4000Cg-UV-NIR) was used; the ATR cell was substituted in this

case with an in-out ($0.2 \times 0.5 \times 2\text{ cm}$) quartz cell. To prepare PtNPs from Pt II, a 5 mL solution of K_2PtCl_4 (0.001 M) and thiosulfate (0.01 M) was mixed and left for 4 h.

3. Results

3.1. Imaging of Platinum nanostar

The TEM image of the platinum nanostar before and after the catalysis reaction is useful to study the mechanism of the reaction. Fig. 1A shows the TEM image of PtNS prepared by the above mentioned method; the particles seem to have multiple arms. The statistical analysis performed for 300 particles taken from three different preparations shows that the particle diameter between two facing arm tips was found to be $11.2 \pm 2.7\text{ nm}$. A good size distribution was observed using the Gaussian fitting of size distribution histogram shown in Fig. 1B. The high-resolution TEM imaging proved the PtNS is a single crystal (Fig. 1C). After the PtNS involved in the reaction, the TEM in Fig. 1D shows that the size of the particles seems larger than the original catalyst (before the reaction); the reason for increasing particle size of the PtNS after the reaction is due to the precipitation of some products on its surface. Further, the electron beam diffraction pattern in Fig. 1E proves that this precipitate is crystalline and similar to the reported results by Zhang et al. [11]. It shows that the Prussian blue analogue complex crystallizes on the surface of the nanoparticle.

3.2. Effect of thiosulfate and hexacyanoferrate III on PtNSs

In order to understand the mechanism of the HCFIII–thiosulfate reaction catalysed by PtNSs, one should study the effect of each reactant on the PtNSs. Optical and IR measurements were used to monitor the reaction of each reactant separately with the PtNSs surface.

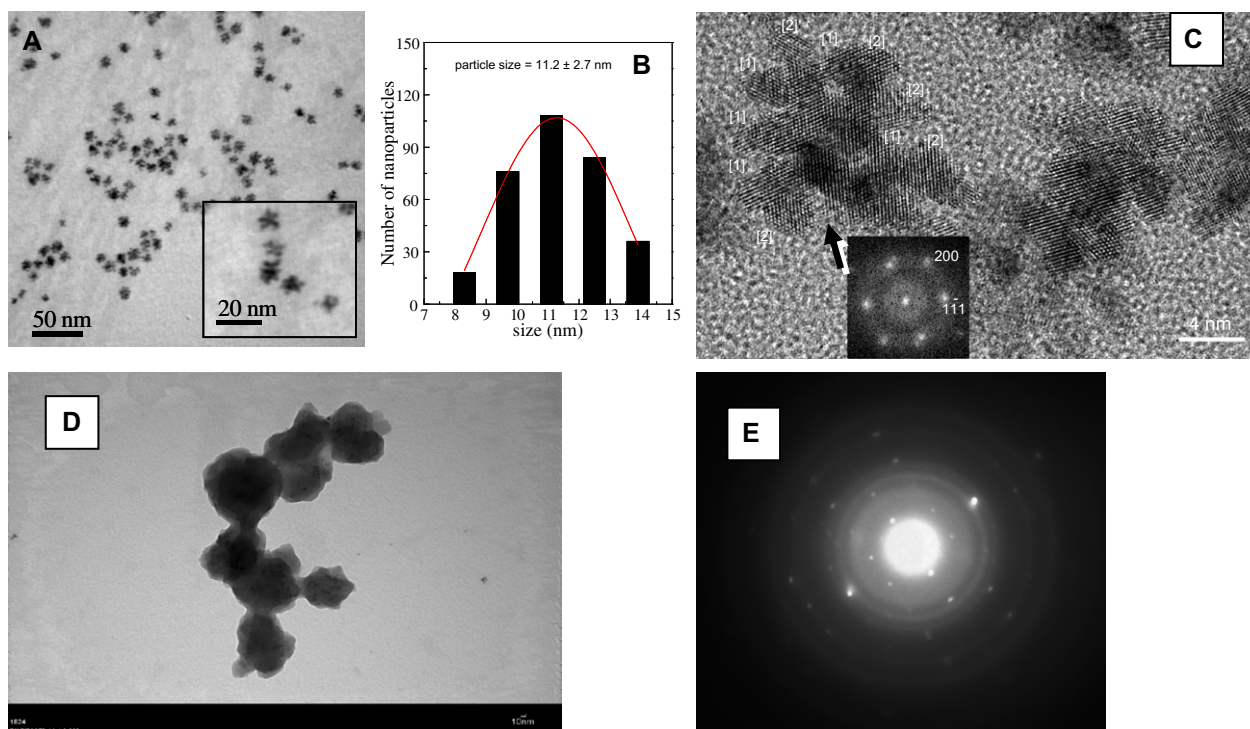
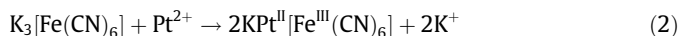
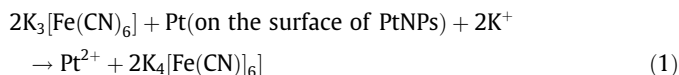


Fig. 1. TEM image of PtNS (A), size distribution histogram with Gaussian fit (B), high-resolution TEM, the inset is the diffraction pattern of the PtNS (C), and TEM of the PtNS after the reaction (D). Electron beam diffraction pattern of the crystalline products, which is deposited on the surface of PtNS (E).

HCFIII is reported to react with PtNSs to form the red Prussian blue analogue according to the following equations [2]:



Two molecules of HCFIII react with the platinum atoms on the surface of PtNSs leading to the formation of Pt II ions, then one molecule of the platinum ion quickly combined with another HCFIII molecule forming a Prussian blue analogue molecule with an optical absorption spectrum peak centred at 560 nm [2]. Zhang et al. have synthesized platinum nanoparticles (PtNPs) modified with Prussian blue by heterogeneous catalytic reaction of HCFIII and

PtNPs, however the PtNPs acts as a catalyst and reactant at the same time [11].

The thiosulfate anion possesses C_{3v} symmetry [12], and it shows two IR vibration bands centred at 996 and 1117 cm^{-1} assigned to the symmetric and asymmetric SO vibrations, respectively [1]. Thiosulfate forms a complex with platinum II through the sulphur atom [13], the coordinated thiosulfate molecules have SO stretching vibration appearing at a higher frequency compared with the corresponding free thiosulfate due to changing the symmetry from C_{3v} to different symmetry. Fig. 2 shows the ATR-FTIR spectrum of thiosulfate after mixing with different amounts of PtNSs. Two IR bands were observed at 996 and 1117 cm^{-1} corresponding to symmetric and asymmetric SO stretching vibration of thiosulfate ions [8,14]. While for all the samples containing thiosulfate mixed with different amounts of PtNSs (5, 10, and 15 mL), three bands were detected. Two corresponding to the symmetric and asymmetric vibration of SO in addition to a new band appear at 1046 cm^{-1} assigned as the symmetric SO vibration for adsorbed thiosulfate on the surface of PtNSs. As the amount of PtNSs increases, the intensity of the band corresponds to the adsorbed thiosulfate increases at the expense of the bands corresponding to the free thiosulfate.

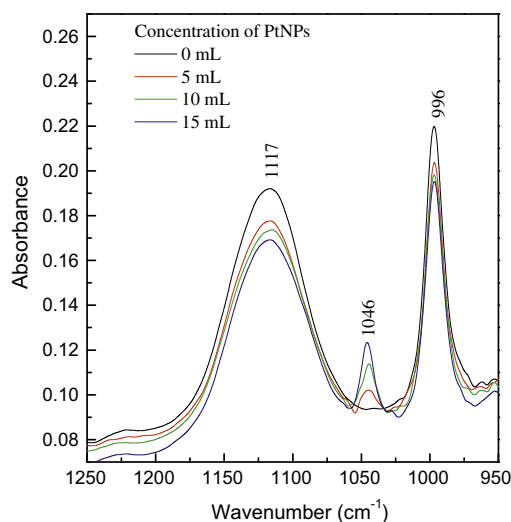


Fig. 2. ATR-FTIR spectral region showing the free symmetric (996 cm^{-1}) and asymmetric (1117 cm^{-1}) S–O stretching of thiosulfate. A shifted vibrational band appears at 1046 cm^{-1} whose intensity is proportional to the concentration of platinum nanoparticles in solution; this band is attributed to the bound symmetric SO stretching of the thiosulfate.

3.3. FTIR measurement for the hexacyanoferrate III–thiosulfate reaction

The reaction of PtNSs and the HCFIII leads to the formation of a red Prussian blue analogue absorbing at 560 nm, as mentioned in the former section [2]. To prove whether this complex is formed during the reaction, HCFIII (0.5 M) was mixed with a solution containing PtNSs and 0.5 M thiosulfate. No optical absorption peak was observed at 560 nm. This could be due to one of two reasons: either the complex forms quickly and takes part in the reaction or it does not form during the reaction. Therefore, its concentration becomes too minute to be sensed. To confirm the formation of the complex during the reaction, the in situ dynamic flow optical measurement was carried out. The thiosulfate–PtNSs solutions mixture was mixed with HCFIII inside a flow quartz cell; this technique made it possible to generate the short lived complexes formed at nearly zero-time of the reaction. An optical peak was observed at 556 nm which was assigned to $\text{KPt}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ Prussian blue analogue complex as shown in Fig. 3A. The rates of flow of

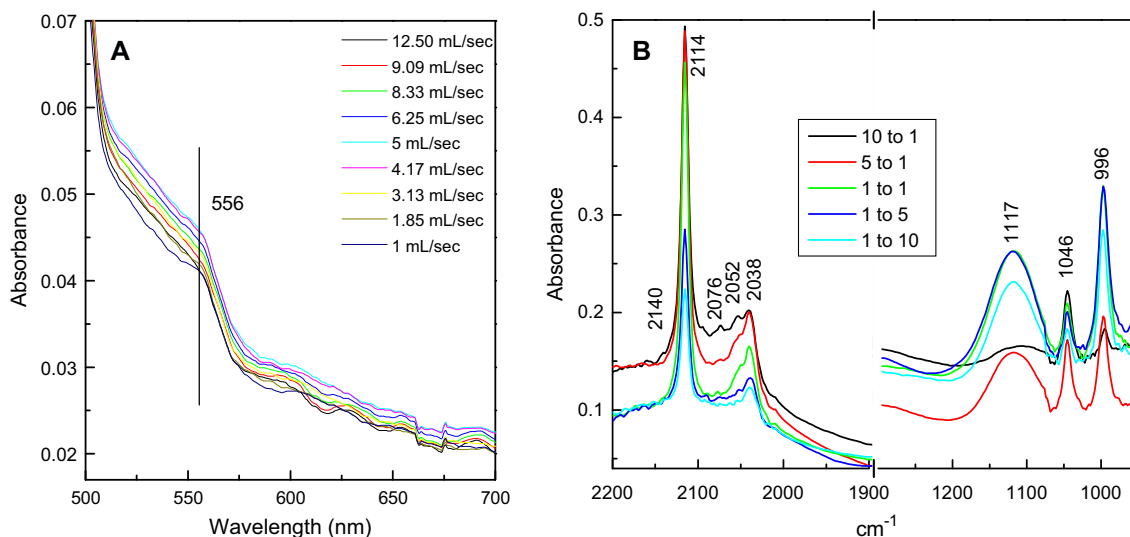


Fig. 3. (A) Visible absorption during the initial mixing of 0.5 M HCFIII and 0.2 M PtNSs at various flow rates (1–12.5 mL/s). The Prussian blue analogue species has an absorption band at 556 nm which forms and quickly disappears. (B) The FTIR spectrum of the hexacyanoferrate III and thiosulfate reaction with ratios of 0.5 M:0.05 M, 0.5 M:0.1 M, 0.5 M:0.5 M, 0.1 M:0.5 M, and 0.05 M:0.5 M at zero-time (mixing the reacting materials inside the ATR cell during the detection).

the reacting materials were changed to obtain the optimum flow that produces the maximum amount of this complex. The optimum flow was found to be 4.2 mL/s.

The reaction of HCFIII–thiosulfate produced short lived species, because the cyanide ligand in HCFIII is capable of binding with two metal ions forming a bridged complex, so the electron transfer could take place through the formation of bridged complex similar to that previously reported [2]. Fig. 3B shows the ATR-FTIR spectra of the HCFIII–thiosulfate reaction at concentration ratios of 10:1, 5:1, 1:1, 1:5, and 1:10 at approximately zero-time (mixing the reacting materials during the IR detection inside the ATR cell). The flow rate was adjusted to 4.2 mL/s (the rate that produced the highest amount of the intermediate see Fig. 3A). The products of this reaction are well known to be tetrathionate and HCFII [15], and the bands at 2114 and 2038 cm^{-1} are assigned to be CN stretching of HCFIII and HCFII, respectively [16]. The band at 2052 cm^{-1} corresponds to the CN stretching of the Prussian blue analogue $\text{KPt}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ complex, while that at 2074 cm^{-1} corresponds to $\text{Pt}^{\text{IV}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ complex formation [2,16] and the band which corresponds to the bridged cyanide appears at 2140 cm^{-1} [16]. The bands at 996 and 1117 cm^{-1} are assigned to the symmetric and asymmetric SO stretching of free thiosulfate, respectively. The adsorbed thiosulfate appears at 1046 cm^{-1} . The intensity of band at 2052 and 2076 cm^{-1} corresponds to the formation of $\text{KPt}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ Prussian blue analogue [2] and was found to be more intense in the case of 10 to 1 (hexacyanoferrate III to thiosulfate) ratio compared to the other concentration ratios.

3.4. Reaction of thiosulfate and the Prussian blue analogue $\text{KPt}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ complex

HCF III reacts with PtNSs and a red Prussian blue complex produces, with a maximum absorption peak around 560 nm. In order to prove that this complex involved in the HCFIII–thiosulfate reaction catalysed with PtNSs, the reactivity of this complex towards the thiosulfate should be examined. This complex was prepared according to the previously reported method [2] (0.2 mM PtNSs mix with 0.5 M HCFIII for 4 h), then 2 mL of the produced red Prussian blue analogue complex allow to react with 2 mL (0.1 M) thiosulfate and the kinetics of this reaction studied optically after the

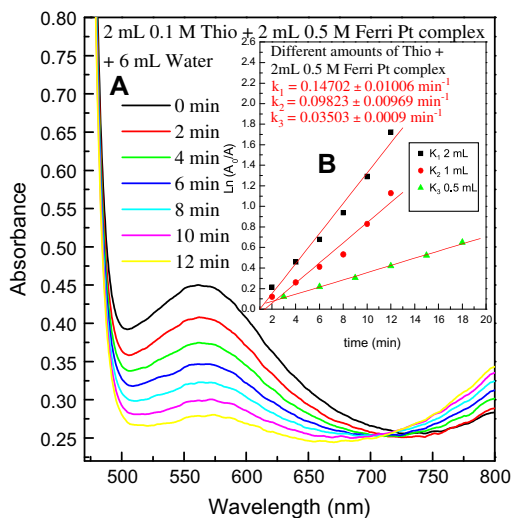


Fig. 4. (A) Absorption spectra showing the disappearance of the Prussian blue analogue complex peak at (556 nm) after mixing with thiosulfate solution. (B) The depletion rate of the Prussian blue analogue complex in the presence of various concentrations of thiosulfate, as the concentration of thiosulfate increases the rate of loss of the Prussian blue analogue complex increases.

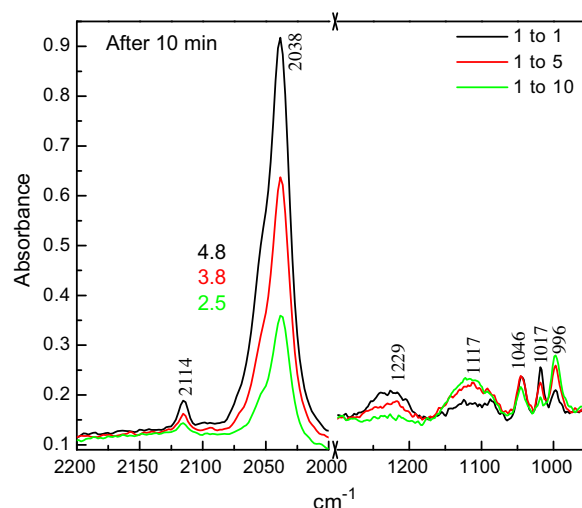


Fig. 5. ATR-FTIR spectrum of hexacyanoferrate III mixed with thiosulfate after 10 min, the hexacyanoferrate III to thiosulfate concentration ratio is 0.5 M:0.5 M, 0.1 M:0.5 M, and 0.05 M:0.5 M.

solution was diluted with deionized water to 10 mL. Fig. 4A shows the decrease in the absorption peak spectra of the Prussian blue analogue complex with time, after mixing with thiosulfate solution. The rate of the reaction of the Prussian blue analogue complex and the thiosulfate solution depends on the concentration of the thiosulfate ions; however, the rate constant of this reaction increases in the following order 0.035, 0.098, and 0.147 min^{-1} for 0.01 M thiosulfate with volume of 0.5, 1, and 2 mL, respectively.

In order to examine the mechanism of the HCFIII–thiosulfate catalysed by PtNSs, the reaction was carried out at different concentration ratios of the reacting materials. The concentration of thiosulfate remains constant and the concentration of HCFIII varied. After ten minutes of mixing, the IR spectrum was measured for each mixture (1:1, 1:5, and 1:10 HCFIII to thiosulfate ratio), a new band appears corresponding to the product formation, but the peaks corresponding to the Prussian blue complexes become minute or even disappear in some cases. Fig. 5 shows the ATR-FTIR spectrum of the HCFIII–thiosulfate reaction. For the three concentration ratios, the bands at 996 and 1117 cm^{-1} , assigned to symmetric and asymmetric SO stretching vibration of free thiosulfate appear with different intensities. As the amount of HCFIII increases, the free thiosulfate bands decrease. While the band corresponds to the bound thiosulfate to PtNSs appeared at 1046 cm^{-1} and was found to have similar intensities. This is because the amount of adsorbed thiosulfate is constant and depends only on the surface area of the catalyst. Since the PtNSs are small compared with the reacting materials, the ATR-FTIR technique can detect both the free and adsorbed reactants and products. In addition to the thiosulfate, two new bands appear at 1229 and 1017 cm^{-1} assigned to be asymmetric and symmetric SO stretching vibration of tetrathionate product, respectively [8]. Since the concentration of thiosulfate used in the experiments is the same, the tetrathionate IR band intensity increases in opposite order compared with the thiosulfate.

The stretching vibration of cyano group in the HCFIII appears at 2114 cm^{-1} , while in HCFII it appears at 2038 cm^{-1} ; however, the band intensity ratio between HCFII and HCFIII was increased in the following order 1:10, 1:5, and 1:1 for the HCFIII to thiosulfate concentration ratio, respectively. The reason for this order is that the rate of the reaction increases as the concentration of HCFIII increases at constant thiosulfate concentration.

3.5. Reduction of Platinum II with thiosulfate

The above measurements involve the formation of Prussian blue analogue based on Pt (II) ions. If it is the case, this means that the PtNSs are not a catalyst but one of the reacting materials and it keeps on dissolving with time leading to size reduction, but what was reported is only reshaping of the platinum nanocatalyst [4,9]. To determine the possibility of the reduction in Pt II ions by the thiosulfate, the potentials of these ions should be studied.

Thiosulfate is well known as reducing agent with reduction potential of 0.304 V while the platinum II is 0.758 V. Therefore, it is electrochemically possible to reduce the Pt II ions to Pt metal by thiosulfate. Fig. 6 shows the TEM image of PtNSs prepared by thio-

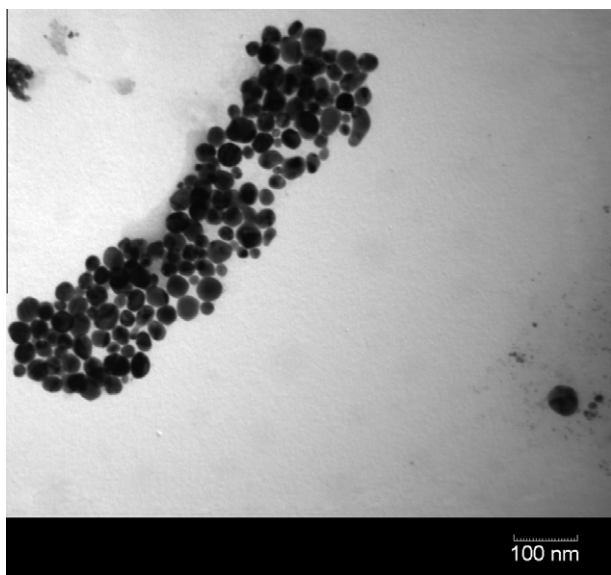


Fig. 6. TEM image of Pt nanoparticles synthesized via K_2PtCl_4 reduction by thiosulfate.

sulfate reduction. The thiosulfate acts here as a reducing agent as well as capping material; this result is supported by what was observed from the ATR-IR measurement which is the thiosulfate adsorbed on the surface of the PtNSs.

4. Discussion

In order to use nanoparticles more effectively to catalyse a chemical reaction, we should understand their role in the mechanism. In other words, determining if it is heterogeneous (in which the reaction takes place on the surface of the nanoparticle catalyst) or homogeneous (in which the reaction takes place wholly in solution). The reason for studying the mechanism is that in some cases the small size of the nanoparticles means that they are close in size of reactants and this question of the reaction mechanism is not easily answered. The mechanism of the HCFIII–thiosulfate reaction catalysed by PtNSs has been investigated using the results obtained here and has been shown to be a heterogeneously catalysed reaction.

The ATR-FTIR measurements for the thiosulfate–PtNSs mixture showed a new vibrational band appeared at 1046 cm^{-1} which corresponds to the adsorbed thiosulfate on the surface of PtNSs, and its intensity increases as the amount of PtNSs increases. Moreover, the in situ UV–Vis. optical detection of HCFIII–thiosulfate reaction catalysed by PtNSs observes an optical spectrum peak at 556 nm corresponding to the Prussian blue analogue. The UV–Vis. optical measurement shows that the Prussian blue analogue complex, prepared by mixing HCFIII with PtNSs for 40 min, reacts with thiosulfate and the rate of the reaction depends on the concentration of thiosulfate. The reactivity of Prussian blue analogue towards the thiosulfate helps to prove its role during the reaction.

The ATR-IR measurements in summary proves that the HCFIII–thiosulfate catalysis reaction takes place through the adsorption of thiosulfate on the surface of PtNSs catalyst and the Prussian blue analogue forms during the reaction.

The thiosulfate has ability to form a complex with platinum II so the Prussian blue analogue will bind to the surface of the PtNSs.

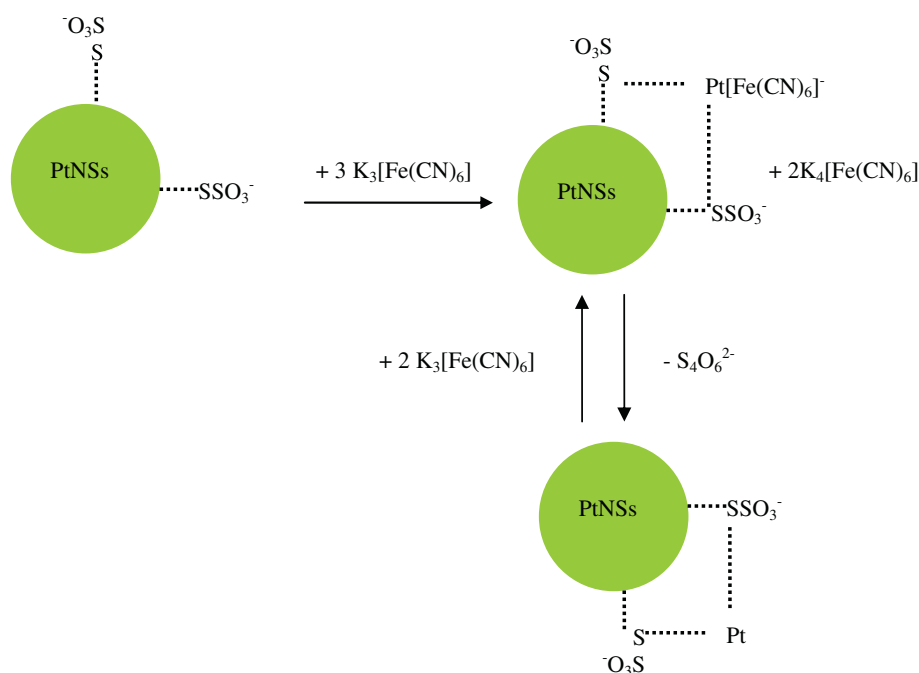


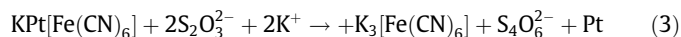
Fig. 7. Schematic diagrams for the mechanism of the reaction of hexacyanoferrate III and thiosulfate catalysed by PtNS.

It has been reported that the shape of the nanocatalyst changes after the catalysis reaction, while the size does not change much [4]. The TEM image in Fig. 1D and E showed a deposition of the Prussian blue analogue complex on the surface of the nanocatalyst after the reaction. On combining these results, one concludes that the reshaping during the reaction is due to the movement of the corner and edge atoms to other sites on the surface of the nanocatalyst. Because if the Prussian blue complex dissolves away in the solution, the size will decrease and small nanoparticles will form. Since no tiny particles were observed after the reaction, therefore the complex forms on the surface the PtNSs and the Pt ion present in the complex reduce to atomic Pt on the surface of PtNSs by the thiosulfate adsorbed on its surface.

The reaction takes place by the attack on the PtNSs by the HCFIII and formation of Prussian blue analogue complex, the complex formed on the surface of the PtNSs. The thiosulfate will reduce platinum II in the $KPt^{II}[Fe^{III}(CN)_6]$ complex to Pt atom and return it back to the surface leading to the reshaping of the particles. Ostwald ripening (size reduction) will take place if some $KPt^{II}[Fe^{III}(CN)_6]$ is leached from the PtNSs surface [4]. This is why the amount of adsorbed thiosulfate does not change on changing the concentration ratio of the reacting materials, but it depends on the concentration of thiosulfate. Pt involved in the reaction will regenerate after oxidation because thiosulfate will reduce Pt II in the Prussian blue complex to platinum atoms.

The above measurements and discussion summarized in Fig. 7; two molecules of HCFIII attacks the PtNS surface and oxidize Pt into Pt II and the HCFIII reduced to HCFII. Then Pt II forms a Prussian blue analogue complex with another HCFIII molecule. The complex binds with two thiosulfate ions on the surface of PtNSs. Therefore, a red Prussian blue analogue forms on the catalyst surface. The electron transfer takes place between the thiosulfate and

the Prussian blue analogue leading to the formation of tetrathionate and Pt atoms which return back to the surface leading to reshaping of the PtNS. The complete reaction is described by Eqs. (1)–(3).



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