Interactions of sub-five-nanometer diameter colloidal palladium nanoparticles in solution investigated via liquid cell transmission electron microscopy†

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Inter-particle interactions play important roles in controlling the structures, dispersion state and chemo-physical properties of colloidal nanoparticles (NPs) in liquid media. In this work, we prepared palladium (Pd) NPs with an average diameter of ~4.6 nm in situ inside the liquid cell, and investigated their coupled diffusion and aggregation behaviors through liquid cell transmission electron microscopy (LCTEM). Via analyzing the interaction energies and forces, we derived the effective working range for repulsive double layer interaction experimentally, a value larger than two times the Debye length, suggesting a different interaction behavior of sub-5 nm NPs from that of colloidal NPs in larger sizes. Our results provide insights for the interactions between colloidal ultrafine nanoparticles in solution and will also shed light on the precisely controlled assembly of colloidal nanocrystals for practical applications.

1. Introduction

The inter-nanoparticle (inter-NP) interactions play essential roles on governing a vast of fundamental processes such as the growth, aggregation and self-assembly of colloidal NPs in liquid media. To date, remarkable progress has been achieved on revealing the mechanisms of colloidal NP interactions via different characterization tools, such as small-angle X-ray scattering, zeta potential measurement, UV-Vis spectra, and in situ streaming potential measurements. Recently, liquid cell transmission electron microscopy (LCTEM), as an emerging technique with the capability of imaging at high spatial-temporal resolution, has been demonstrated as an effective and feasible platform for investigating the growth, aggregation, etching, self-assembly, electrochemical reaction, and bio-application of nanosized objects in aqueous solution.

It is well known size matters for NPs. When the diameter of noble metal NPs reduces, i.e., to sub 5 nm regime, the electronic structures and chemo-physical properties may alter due to the intriguing size and quantum confinement effects. As a result, these sub-5 nm NPs hold promising applications in catalysis, optics, and sensor devices. Regarding the inter-particle interactions, scaling down the size of NPs may lead to (i) a weak van der Waals (vdW) interaction as it critically depends on the NP’s radius; (ii) the increased ion–NP interaction and molecule–NP interaction, particularly when size of molecules or ions in solution (typically of a few Ångstrom) becomes comparable with that of the NPs; (iii) the nonadditivity of multiple interactions when the inter-NP separation is smaller than a few nanometers, where the total interaction energy cannot be simply treated as a sum of contributions of all independent interactions. As a result, the strength, range and contribution (or competition) of different interactions between ultra-fine NPs may substantially change. For instance, Anand et al. observed two sub-5 nm Au NPs can form a stable transient dimer before the attachment via LCTEM, and they attributed this finding to the effective force balance between the steric hindrance of water molecules (or surfactant ligands) and the vdW interaction force acting in a short-range (~2 nm). Guerrero-Garcia et al. investigated the interactions of charged NPs in salt solutions via molecular dynamical simulations, and they confirmed that large counterions of ~1 nm in solution can increase the short-range repulsive

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0ra05759b
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RSC Adv., 2020, 10, 34781-34787 | 34781
interaction and hence improve the stability of the colloidal NPs with a diameter of ~5 nm. To date, LCTEM study on the interaction of fine NPs, i.e. <5 nm, still remains limited,26,41,46,49 and the effects of interaction force (or energy) on the resulting NP behaviors need further exploiting.

In this study, we first synthesized sub five nm palladium (Pd) NPs in situ inside the liquid cell via controlling the electron beam dose rate during the radiolysis process, and then investigated the diffusion and assembly behaviors of the as-formed Pd NPs in solution through LCTEM. Via analyzing the aggregation dynamics and calculating the interaction forces and energies acting on the Pd NPs, we unraveled the underlying mechanism for the assembly behaviors, taking the aggregation between an individual Pd NP and a nanocluster as a model. In addition, we also derived out the effective working range of the double layer interaction. Our work provides in-depth insights for the ultrafine NP interactions in liquid.

2. Experimental

2.1 Preparation of precursor solution

All chemical agents including palladium(II) chloride (PdCl₂, 99.9%, Sigma-Aldrich) and cetyltrimethylammonium bromide (CTAB, analytical reagent, Sinopharm Chemical Reagent Co., Ltd) were used as received. 39 mg PdCl₂ was dissolved into 600 μL 2.88 mol L⁻¹ hydrochloric acid (HCl) as a stock solution of H₂PdCl₄, and then diluted to 2 mM. The precursor solution (pH = 2.2) was prepared via mixing 300 μL H₂PdCl₄ solution (2 mM), 100 μL CTAB (1 mM), and 300 μL deionized H₂O together, and then stirred the mixture for 5 minutes to ensure sufficient ion exchange prior to its loading into the liquid cell.

2.2 Liquid cell TEM

In situ liquid cell TEM experiments were carried out in a static liquid cell system (Hummingbird Scientific Inc.). The central part of the cell contains a pair of micro-fabricated silicon chips decorated with a 50 nm thick SiNₓ membrane on each. To remove the organic contamination and render the surfaces hydrophilic, the chips were treated with oxygen plasma (20% vol. O₂ and 80% vol. N₂) for 5 minutes just prior to the loading and sealing of precursor liquid solution (~400 nL). The whole assembled cell was mounted onto a dedicated holder and then loaded into a transmission electron microscope (TEM, FEI Tecnai G² F20) for in situ LCTEM studies. This microscope was operated at an acceleration voltage of 200 kV and the employed electron dose rates ranged 240–1000 e⁻Å⁻²s⁻¹. Time sequenced movies were recorded via a screen capture software (Bandicam) at a frame rate of 3 frames per second.

3. Results and discussion

As learned from the strategy for conventional synthesis of quantum dots,26,31 the ultrafine Pd NPs were prepared via controlling the nucleation kinetics, that is by tuning the electron dose rates during the e-beam radiolysis induced nucleation and growth. As illustrated in Fig. 1a, an intense electron beam with a high dose rate of ~1000 e⁻Å⁻²s⁻¹ was used to illuminate the precursor solution for a short period-23 seconds, leading to the occurring of burst nucleation events.52 Then, the dose rate was reduced to 240 e⁻Å⁻²s⁻¹ and kept unchanged from t = 23.0 s to t = 52.0 s, during which the as-formed Pd nuclei started to grow up gradually either by the direct deposition from the precursor solution or through the inter-nuclei aggregation, as shown in Fig. 1b and Movie S1.† During this period, new nucleation events were rarely observed mainly due to the rapid consumption of local precursors and the limited supply from the nearby environment caused by the greatly restricted diffusivity of PdCl₂₂⁻ within a confined space inside the liquid cell. Size distribution analysis in Fig. 1c gives an average size of 4.6 ± 0.6 nm for the Pd NPs formed at t = 52.0 s in Fig. 1b. Characterization for the as-formed Pd NPs was shown in Fig. S4.†

Notably, the early stage of the assembly of monomer Pd NPs (t = 0 s to 23 s) was hard to capture, due to the limited resolution of our LCTEM. Therefore, we turned to track the dynamics of the aggregation between an individual Pd NP and a nanocluster, as the stability was remarkably improved after nanocluster formed. An example was shown in Fig. 2a and Movie S2,† where the interaction between an individual Pd NP and a Pd dimer (containing two Pd NPs) was investigated. Beginning form t = 36.3 s, the dimer (blue arrowed) and NP (yellow arrowed) gradually approached toward each other, and then the NP suddenly jumped toward the dimer at t = 41.3 s when the inter-NP distance L = 10.5 nm, and a slight rotation was observed on
the dimer. After the aggregation of the NP onto the dimer, the NP can still move around the surface of the dimer, leading to the structural transformation.

To reveal the underlying mechanism of the aggregation, we derived and analyzed the interaction energy (\(E\)) of the NP following the method proposed by Li et al.\(^\text{1}\) The interaction energy can be written as

\[
E = -\left( F_{\text{net}} \Delta L + \tau \Delta \theta + \int_0^{\Delta L} F_{\text{R}} \text{d}L + \int_0^{\Delta \theta} \tau_{\text{R}} \text{d}\theta \right)
\]

where the net force \(F_{\text{net}}\) is the sum of forces exerted on NP, which can be calculated as \(F_{\text{net}} = ma\), \(m\) and \(a\) are the mass and acceleration of NP, respectively; \(F_{\text{R}}, \Delta L, \tau, \tau_{\text{R}}\) and \(\Delta \theta\) are the viscosity resistive force from solution, change of inter-NP distance, torque of the NP, the resistive torque from solution and the change of rotational angle, respectively (more details can be found in Section 1, Fig. S1 and Table S1 in ESI\(\text{†}\)). In the present study, we only considered the energy related to translation motion \(E_{\text{tra}}\)

\[
E_{\text{tra}} = -\left( F_{\text{net}} \Delta L + \int_0^{\Delta L} F_{\text{R}} \text{d}L \right)
\]

and omitted the contribution related to rotational motion \(E_{\text{rot}}\)

\[
E_{\text{rot}} = -\left( \tau \Delta \theta + \int_0^{\Delta \theta} \tau_{\text{R}} \text{d}\theta \right)
\]

based on two considerations: first, the contribution of \(E_{\text{rot}}\) is negligible when \(\Delta \theta < 2^\circ\) (Section 2 and Fig. S2 in ESI\(\text{†}\)); second, it is hard to measure rotational motion of such a sub-5 nm sphere-like Pd NP. The derived energy was plotted in Fig. 2d. As seen, a minimum of \(E\), namely \(E_m = -1.9 \times 10^{-19} \text{ J}\) occurred at \(L = 10.5 \text{ nm}\), which should correspond to the driving energy for the jump motion of the NP (\(t = 41.3 \text{ s}\) in Fig. 2a). At \(3.0 \text{ nm} < L < 8.6 \text{ nm}\), an energy “valley” existed, indicating the development of an attractive interaction. The associated energy difference between \(E_m\) and the energy “valley” practically acted as an energy barrier, suggesting repulsive interaction force worked at \(8.6 \text{ nm} < L < 10.5 \text{ nm}\). This result was also supported by the finding that the corresponding \(F_{\text{net}}\) increased from negative to positive (Fig. 2d; \(F_{\text{net}} > 0\) means a net repulsive force, while \(F_{\text{net}} < 0\) means attractive). It should be noted that the limited statistics in Fig. 2d may influence the landscape of interaction energy, \(e.g.\) the depth and width of energy “valley”, and possibly introduces considerable errors into the calculation.

Besides jump-to-approach pathway shown in Fig. 2a and S3,\(\text{†}\) the aggregation sometimes can be accomplished in a more complex one, as shown in Fig. 3a and Movie S3.\(\text{†}\) In this case, an individual NP firstly attached to a pentamer nanocluster (made of five Pd NPs) via two discrete jump motions occurred at \(L = 28.0\) and \(13.3 \text{ nm}\) (stage I in Fig. 3c), respectively. The Pd NP detached after the aggregation and underwent oscillated motions (stage II) prior to its second approach (stage III). The evolution of \(E\) and \(F_{\text{net}}\) in this aggregation event (Fig. 3d) were similar to those observed in the previous case (Fig. 2d), except for an additional energy barrier at \(13.3 \text{ nm} < L < 28.0 \text{ nm}\), which was likely generated by the solution fluctuation, due to the corresponding \(F_{\text{net}} < 0\) mainly, \(i.e.\), the net force of NP was attractive.

Fig. 2 The interaction dynamics between a Pd dimer nanocluster and an individual Pd NP. (a) Time sequenced TEM images and (b) corresponding schematics of the interaction process. Electron dose rate: 240 e\(^{-}\) Å\(^{-2}\) s\(^{-1}\). Blue and yellow arrows point to the dimer and the Pd NP, respectively. (c) The plots of the inter-NP distance (L) vs. time. (d) The change of interaction energy (E) and net force (\(F_{\text{net}}\)) with L. \(E_m\) represents the minimum point of E, and the blue and pink dotted lines are the trend lines of \(F_{\text{net}}\) and E for eye-guiding, respectively. (e) The variation of \(F_{\text{vdW}}\) (purple dots) and \(F_{\text{Br}}\) (blue area) with L.
In principle, Brownian motion and vdW interaction can both provide attractive force to drive the approach motion of Pd NPs in solution. As shown in Fig. 2e (and Fig. 3e), as the inter-NP distance \( L \) decreases, vdW interaction force \( (F_{\text{vdW}}) \) gradually increases and then becomes comparable with Brownian motion force \( (F_{\text{Br}}) \) at \( L = 6.9 \) nm (7.5 nm for Fig. 3e), and hence \( F_{\text{vdW}} \) should serve as the primary driving force for the NP aggregation at short inter-NP separations. The energy barriers (such as the curves for 8.6 nm < \( L < 10.5 \) nm in Fig. 2d and 6.2 nm < \( L < 10.4 \) nm in Fig. 3d) that hindered the NPs approaching should mainly originate from (i) the double layer interaction force between NPs and (ii) the steric hindrance force between CTA\(^+\) ligands.\( ^{6,18,53,54} \) Of them, the effective range of the hindrance force is usually smaller than two times the length of CTA\(^+\), i.e., \( L < 2 \) nm \( \times 2 = 4 \) nm,\( ^{6,46} \) while the working range for the double layer interaction depends on the ionic strength of solution, a parameter reflecting the solution property, which will be discussed later. Via comparing the effective ranges of energy barriers derived experimentally with that of the steric hindrance force (8.6 nm < \( L < 10.5 \) nm or 6.2 nm < \( L < 10.4 \) nm vs. 4 nm), we can infer that the energy barrier should be mainly attributed to the double layer interaction. Under such an approximation, the upper value of the range of \( L \), denoted as \( L_{\text{exp}} \), can be assigned as 10.5 nm from Fig. 2d and 10.4 nm from Fig. 3d, respectively. And this \( L_{\text{exp}} \) can be approximately treated as the effective distance where the double layer interaction started to work. Interaction between SiN\(_x\) membrane and two individual NPs in Fig. 2a and 3a is expected to play minor roles on the aggregation, due to the following two considerations: (i) the NPs kept mobile with a velocity of 0.1–33.2 nm s\(^{-1}\) during the whole process (as shown more clearly in Movies S2 and S3\(^*\)), suggesting a loose bounding of these NPs to the SiN\(_x\) membrane, and (ii) as reported previously,\(^ {17} \) the NP-membrane friction force is rather small.

It is well known that within the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory,\(^{5,55} \) the analysis of double layer interaction is based on the Poisson–Boltzmann equation, where...
ions in the solution are assumed as point-like ions without any volume. However in our system, this approximation may not be valid any more since the diameter of ions can reach ~0.4 nm (ref. 47) for Cl\(^-\) and Br\(^-\), and ~2 nm for CTA\(^+\), which cannot be ignored in comparison with that of the NPs (4.6 nm).

To check the validity of this assumption and figure out if there exists any specific size dependence for the double layer interaction of such sub-5 nm NPs, we compared the effective range of double layer interaction with that predicted by the DLVO theory. Within the framework of DLVO theory, ions in solution distribute surrounding the NP to balance the surface charges (Fig. 4a), leading to the formation of a double layer with a thickness called Debye length \( \kappa \) and written as 1/\( \kappa \), where

\[
1/\kappa = 1/\sqrt{2000\varepsilon^2 N_A I / \pi e_0 k_B T}
\]

where \( N_A \) is Avogadro’s constant, \( \varepsilon \) is the dielectric constant of water, \( e_0 \) is the dielectric permittivity of vacuum, \( e \) is the elementary charge, and

\[
I = \frac{1}{2} \sum_{i=1}^{n} c_i q_i^2
\]

is the total ionic strength of the solution containing \( n \) types of ions with a valence \( q_i \) and a concentration \( c_i \) for each ion. The double layer repelling force arises when two double layers start to overlap with a critical distance \( L_{c,DLVO} = 2/\kappa \), as illustrated in Fig. 4a.

Before we calculate the range of double layer interaction (\( L_{c,DLVO} = 2/\kappa \)) following the DLVO theory, we address that the electron beam induced change of solution characteristics such as pH and the concentrations of PdCl\(_4\)^2− and Cl\(^-\) should also be taken into account. Note that, other electron beam induced effects such as the radiolysis reactions in the presence of Br\(^-\) (from CTA) and the charge re-distribution in the CTA\(^+\)-NPs were not considered. As predicted by Schneider et al., the concentration of H\(^+\) in solution under e-beam irradiation was almost unchanged when initial pH < 3, and thus we treated the initial solution pH = 2.2 as a steady state. During this process, part of Cl\(^-\) ions will also be transformed into hydrochloride ion (ClOH\(^-\)) and chlorine radical ion (Cl\(_2\)^−, Table S3 in ESI†), which may induce an increase of 20% on the derived value of 2/\( \kappa \), as explained in details in Section 4 in the ESI. Since ClOH\(^-\)− and Cl\(_2\)^− ions possess the same ion valence \( q = -1 \) with Cl\(^-\), we can treat them (ClOH\(^-\), Cl\(_2\)^− and Cl\(^-\)) as a whole, and further assume their total concentration equals to the initial concentration of Cl\(^-\) in solution during the calculation of ionic strength and 2/\( \kappa \). The concentration of PdCl\(_4\)^2− during Pd NPs aggregation was hard to measure due to the gradual consumption of PdCl\(_4\)^2− by hydrated electrons for further growth of Pd NPs. Thus, to calculate 2/\( \kappa \) and \( L_{c,DLVO} \), we hypothesized two limiting conditions: the reduction ratio of PdCl\(_4\)^2− was (a) zero and (b) 100%, respectively (more details are in the Section 4 and Table S2 in ESI†). As listed in Table 1, 2/\( \kappa \) = 7.2 nm, indicating the double layer interaction develops at \( L < L_{c,DLVO} = 7.2 \) nm within the DLVO theory. This value was somehow smaller than our experiment results of \( L_{c,exp} = 10.5 \) nm and 10.4 nm, as revealed by the L-dependent variation of \( E \) and \( F_{\text{net}} \) in Fig. 2d and 3d, respectively, indicating the effective range of double layer interaction between sub-5 nm Pd NPs was larger than that of the DLVO theory, and the validity of approximation of the point-like ions was questionable for sub-5 nm NPs. The CTA\(^+\) ligands coated on NPs may extend the “charged surface” of NPs and make \( L_{c,exp} > L_{c,DLVO} \) as illustrated in Fig. 4b. Besides, fluctuation of ion distribution around NPs also possibly increased \( L_{c,exp} \).

### 4. Conclusions

In summary, we synthesized ultrafine Pd NPs with an average size of 4.6 ± 0.6 nm inside the liquid cell through tuning electron dose rate, and then investigated the self-aggregation processes between individual Pd NPs and nanoclusters via LC-TEM. After the attachment, NPs sometimes may diffuse on the aggregation, or detach from the aggregation and then undergo oscillated movement. We also mapped out the effective working range of the double layer interaction, and found it was larger than two times of the Debye length given by the classical DLVO theory. Our findings may offer understanding of the interaction and self-assembly mechanisms of ultrafine NPs in solution.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

We acknowledged Prof. Hui Zhang, Ruikang Tang, Dr Biao Jin and Xiaoming Ma for their fruitful discussions and suggestions. This work was financially supported by the National Natural Science Foundation of China under Grant No. 51772265, 51761165024, and 61721005; the Zhejiang Provincial Natural Science Foundation under Grant No. D19E020002, the 111 Project under Grant B16042, the Shanghai Leading Academic Discipline Project No. B502, and the Shanghai Key Laboratory Project No. 08DZ2230500. The work on electron microscopy was done at the Center of Electron Microscopy of Zhejiang University.

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