Self-Assembly



Nanoparticle Interactions Guided by Shape-Dependent Hydrophobic Forces

Shu Fen Tan, Sanoj Raj, Geeta Bisht, Harshini V. Annadata, Christian A. Nijhuis, Petr Král, and Utkur Mirsaidov*

Department of Physics, Centre for BioImaging Sciences and Department of Biological Sciences, Department of Chemistry, Centre for Advanced 2D Materials and Graphene Research Centre National, NUSNNI-NanoCore, National University of Singapore

Department of Chemistry, Departments of Physics and Biopharmaceutical Sciences, University of Illinois at Chicago, USA

Adv. Mater. 2018, 30, 1707077

Amrita Chakraborty 11-08-2018

Relevance to the group

Langmuir, Vol. 24, No. 9, 2008



Paulami : AgNP + Au NC







Ongoing:

Self assembly of synthesized gold nanocube and cube@cluster composite material



Adv. Mater. **2016**, *28*, 2827–2833

Introduction

- Spontaneous bottom-up self-organization of nanoscale objects into various desired architectures is pivotal for their potential applications in catalysis, sensing, optoelectronics and biomedicine.
- ✓ The solution phase NP self-assembly is driven and controlled by many competing attractive and repulsive interactions which include van der Waals (vdW) attraction, electrostatic interaction, steric repulsion, hydrophobic force etc.
- ✓ During the self-assembly processes, attractive interactions such as vdW (between the metallic cores of NPs) and hydrophobic (between the ligated NP surfaces) forces are responsible for bringing NPs together and stabilizing them against interparticle repulsions.
- ✓ Hydrophobic interactions : the hydrogen bonding network between water molecules around the surface of each hydrophobic NP is interrupted. Increase in the energy of these interfacial water molecules gives rise to an attractive force that drives the NP self-assembly.
- ✓ Hydrophobic interactions between the NPs depend on their surface properties, sizes, and

In this paper

- Small angle X-ray scattering, UV-vis spectroscopy, and optical imaging : bulk methods, lack the resolution needed to describe the interactions between individual NPs at different stages of the self-assembly process.
- In situ liquid cell TEM enable probing the interactions between NPs and their selfassembly by direct nanoscale imaging of their real-time dynamics in thin liquid films.
- Examined how shape-dependent attractive hydrophobic and vdW interactions, and repulsive electrostatic forces guide the NP self-assembly in water.
- Using cuboidal gold NPs capped with a monolayer of CTA+, they have shown that hydrophobic interactions between the nanocubes (NCs) are directional, which promote their aligned face-to-face attachment, and dominate over the vdW attraction and electrostatic repulsion.
- The attractive hydrophobic forces between two NCs are greater than those between a pair of nanospheres (NSs), nanobypiramids (NBPs), and nanorods (NRs) of similar sizes.

Experimental procedure

- Synthesized gold nanocube, commercially purchased gold nanorods, spheres and bipyramids.
- For liquid cell experiments, ≈500 nL of the resulting solution was loaded into a custom microfabricated liquid cell, which is comprised of two ultrathin (≈20 nm) electron translucent SiN*x* membranes separated by ≈200 nm thick spacer. Before loading the solution, these liquid cells were treated with oxygen plasma to make their SiN*x* membrane surfaces hydrophilic.
- TEM image series were acquired at a rate of 25 and 10 frames per second.
- The assembly of NPs was followed in realtime by observing NPs found in a 30 nm *200 nm window of the TEM liquid cell. The movies were recorded when the visible movements of the gold NPs (t = 0 s) were first observed.





Figure 1. Pairwise interaction of CTA+-capped gold nanocubes in an aqueous se



A) A time series of TEM images and a schematic showing an aligned face-toface attachment of two gold NCs capped with CTA+ monolayer. A sequence of TEM images showing the attachment between three NCs into: B) an L-shaped and C) linear NC-trimers. In both cases, all three NCs undergo the face-to-face attachment. D) TEM timeseries images display the assembly of a small NC array from: I) one NC-trimer and II,III) two NC-dimer blocks.

XPS: 1 mM CTAB = monolayer 20 mM CTAB bilayer of CTA+.

In-situ : assemblies that formed inside the liquid cell.

Post-attachment spacing between the NC faces was 1–2 nm whereas the linear length of a fully stretched CTAB molecule is \approx 2.2 nm.

Ex-situ : assemblies formed after dropcasting the NC solution onto a carbon film of a TEM grid.

Spacing is ~2-3 times larger than in the *in situ* case.

For the *ex situ* experiments, CTAB concentration increases when water starts to dry on a TEM grid, multilayers of CTA⁺ can form on the surface of NCs.



Figure S2. TEM images of gold NC assemblies observed (**A**) *in situ* and (**B**) *ex situ*, respectively.

Figure 2. Mechanism of Face-to-face attachment of NCs in an aqueous solution



A pathway : move toward each other through rotational and translational movements, during which they prealign their faces, and finally attach in a face-to-face configuration.

B pathway : First attach through their edges and then rotate toward each other into a final aligned face-to-face configuration.

A pathway : B pathway = 3:1 => interactions between the NCs are directional, where the face toface attraction is preferred.

Schematics and TEM time series images showing the face-to-face attachment of two gold NCs via two pathways: A) prealigned attachment and B) postattachment alignment of. Molecular dynamics simulations showing two gold NCs (with a 5.3 nm side-length) capped with a monolayer of CTA+ undergoing: C) the prealigned attachment and D) postattachment alignment.

Occasionally found misaligned assembly



A.Edge to edge

B.Edge to face

Reason :

The affinity of CTA+ to {110} gold planes at the edge of the NCs is lower than to {100} face facets. This low capping density at the NC edges makes the NC prone to bonding with the gold face or edge of another NC upon attachment.

The gold-gold bonding between the NCs can be clearly seen when the spacing between the gold NCs in the misaligned attachments is compared with the aligned attachments.



Forces involved:

- Electrostatic force : **repulsive** : acts between the positively charged CTA+ layers of them.
- van der waal force : **attractive** : Acts between the gold cores of 2 adjacent cubes.
- Hydrophobic force : attractive : acts between the ligand and the nearest water layer.
- Molecular dynamics simulations : modeled a system of two NCs capped where CTA+ monolayer (276) in water is partially neutralized by 236 Br-.
- Net charge : +40*e* for each NC.
- This strong net repulsion between the NCs cannot be overcome only by goldgold vdW force. Hydrophobic force plays crucial role.



- 1. The water density at the first water layer (2.8 Å from the CTA+) > the bulk water.
- the water molecules in the first water layer participate on average in ≈3 H-bonds, which is ≈15% less than ≈3.5 H-bonds for bulk water.

These cause the reduction in entropy and increase in the energy of water molecules at the ligand–water interface.

This generates attractive hydrophobic force acting between the NCs because the NC–NC attachment lowers the free energy of the system by eliminating a fraction of NCs' hydrophobic surface exposed to water (i.e., ligand–water interface).

In case of CTA+ bilayer, this hydrophobic force fails to overcome the stronger repulsive force and NCs do not come into contact with each other.

Figure 3. Effect of the different shapes of the Nanopartic



The preferential face-to-face attachment of NCs suggests that their cubic shape influences their pairwise hydrophobic attraction.

For monolayer-capped nanoparticles, strength of attachment : NRs < NBPs < NSs < NCs. The once attached NPs often detach. detachment of NCs is a rare event, which was observed only for NCs contacting edge-to-edge or edge-toface.

NRs and NBPs often come into contact with their tips first because the energy barrier associated with their electrostatic repulsion is the least in the tip-to-tip configuration. However, the attachments between NBPs, which often occurs between their flat sides, as they slide sideways (Figure 3A,B), result in a permanent attachments more frequently than in the case of NRs.

Figure 3. Interaction dynamics between NPs with different shapes



C) Likelihood for the permanent attachments is NC > NS > NBP > NR. Detachment of NCs was observed only for misaligned assemblies.

D) The MD simulations of pairwise attachment of NSs (left) and NCs (right). The overlap of CTA+ is greater for the attached NCs than for the NSs.

The attachments with larger and larger relative surfaces result in the gradual increase in the relevance of the hydrophobic interactions in this sequence.

Effect of the ligand

Ligand	СТАВ		PEG-SH	
NP	cube	sphere	Cube	Sphere
Permanent attachment	84%	52%	100%	67%

PEG-SH

В D Attach Attach-detach Permanent attachment 19.1 s 25.9 s 49.0 s 51.1 s 62.1 s NC **5**0 nm NS NC 1.0 2.7 s 5.9 s 8.0 s 8.1 s 23.2 s 0.8 Normalized count NS 0.6 **5**0 nm 0.4 С Attachment-detachment 19.2 s 20.5 s 20.9 s 21.3 s 21.4 s 0.2 0.0 NS **—** 50 nm

 $H_3C_0 \rightarrow J_9SH \equiv$

А

20 nm

Figure 4. Long-range attractive interactions between the CTA+-capped

From the earlier studies vdW and hydrophobic interactions are expected to be short-range (≤ 20 nm).

in most attachment events the NPs jumped into contact when the separations between their surfaces were 20–100 nm.



A,B) A time series of TEM images showing the pairwise attachment of two CTA+-capped gold NCs (A) and NSs (B). C) Center-to-center separation between four gold NC pairs (red curves) and four gold NSs (black curves) similar to those shown in (A,B). Here, *t*0 is the time point when the NP–NP attachments take place.

MD simulation

Two CTA+-capped gold NCs and NSs were simulated in water within a 34 × 22 × 22 nm3 box,

with an appropriate number of Br- counterions to neutralize the system.

The MD simulations were performed with the Nanoscale Molecular Dynamics (NAMD) software package for an isothermal–isobaric (NPT) ensemble at T = 300 K, using the Langevin dynamics with a damping constant of γ Lang = 0.1 ps-1 and a time step of 2 fs.

The vdW attraction and a steric repulsion, which are part of nonbonding

interactions between the molecules, were described by the Lennard-

Jones (LJ) potential with parameters provided by the CHARMM force field

$$U_{\rm LJ}(r) = \varepsilon \left[\left(\frac{r_{\rm min}}{r} \right)^{12} - 2 \left(\frac{r_{\rm min}}{r} \right)^{6} \right]$$

The vdW interaction energy between two gold NCs was separately described by the formula

$$U(d) = -\frac{Aa^{2}}{12\pi} \left[\frac{1}{d^{2}} - \frac{2}{(d+a)^{2}} + \frac{1}{(d+2a)^{2}} \right]$$

A is the Hamaker constant for a gold–gold interaction in water ($A = 3 \times 10-19$ J), a = 5.3 nm is the side length of the gold NC, and d is the distance between the faces of the gold NCs

in the case of two spherical NPs, the bulk vdW coupling between the gold cores of the NSs (R = 2.65 nm is the radius

of the gold core,)

$$U(d) = -\frac{A}{12} \left(\frac{R}{d\left(1 + \frac{d}{4R}\right)} + \frac{1}{1 + \frac{d}{R} + \frac{d^2}{4R^2}} + 2\ln\frac{d\left(1 + \frac{d}{4R}\right)}{R\left(1 + \frac{d}{R} + \frac{d^2}{4R^2}\right)} \right)$$

For Nanocubes,
$$U_{\text{tot}}(D) = U_{\text{el}}(D) + U_{\text{vdW}}(D) = \frac{(ze)^2}{4\pi\varepsilon_0\varepsilon(D+a)} - \frac{Aa^2}{12\pi} \left[\frac{1}{D^2} - \frac{2}{(D+a)^2} + \frac{1}{(D+2a)^2}\right].$$

For Nanospheres, $U_{\text{tot}}(D) = U_{\text{el}}(D) + U_{\text{vdW}}(D) = \frac{(ze)^2}{4\pi\varepsilon_0\varepsilon(D+2R)} - \frac{A}{12}\left(\frac{R}{D\left(1+\frac{D}{4R}\right)} + \frac{1}{\left(1+\frac{D}{2R}\right)^2} + 2\ln\frac{D\left(1+\frac{D}{4R}\right)}{R\left(1+\frac{D}{2R}\right)^2}\right).$

NCs attract (*i.e.*, approach) even when the gold-gold vdW attraction is absent. This attractive force is a hydrophobic force.

In the case of NSs, once the vdW attraction between the NS gold cores is turned off, the NSs move apart because of the electrostatic repulsion.

The attractive hydrophobic interaction alone is not sufficient to bring the NSs close by for the attachment to take place. Therefore, the vdW attraction between their gold cores is essential for the attachment of the NSs.



Conclusion

- Using in situ transmission electron microscopy imaging combined with atomistic modeling, it is shown that the forces governing the self-assembly of hydrophobic nanoparticles change with the nanoparticle shapes.
- By comparing how gold nanospheres, nanocubes, nanorods, and nanobipyramids assemble, it is shown that the strength of the hydrophobic interactions depends on the overlap of the hydrophobic regions of the interacting nanoparticle surfaces determined by the nanoparticle shapes.
- Specifically, this study reveals that, in contrast to spherical nanoparticles, where van der Waals forces play an important role, hydrophobic interactions can be more relevant for nanocubes with flat side faces, where an oriented attachment between the nanocubes is promoted by these interactions.
- Since the size of NPs are comparable to the size of large protein complexes, these observations can stimulate studies that are important in understanding the biological processes, such as protein folding, site-specific docking, and assembly of biomolecules.
- In general, the ability to monitor self-assembly pathways of NPs can impact the synthesis of new materials, bottom-up nanofabrication, and structural biology.