Self-organization of nanoparticles

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Spontaneous self-organization of nanoparticles has been a topic of intense experimental and theoretical investigations. In this paper, one novel, and simple experiment will be reviewed, where zero-dimensional $CdTe$ nanoparticles self-organize into intermediate pearl necklace-like aggregates, then recrystallize into one-dimensional nanowires. Computational simulation demonstrates that the dipole-dipole interaction is the main driving force for this self-organization process. Similarly, the CA stabilized Au nanoparticles can self-assemble into pearl necklace-like nanostructures by tuning the PH value of the Au solution. The driving force for metal nanoparticle self-assemly will also be revealed.

I. INTRODUCTION

Nanomaterials are becoming more and more important, due to their optical, electric and structural properties which can not be observed in microscopic molecule or macroscopic solid. Assembling nanoparticles(NPs) into nanostructure opens up the possibility of fabricating new nanomaterials with novel or enhanced physical and chemical properties and applications. Recently, variously novel nanostructures have been fabricated either through controlled assembly or through self-assembly. For example, the spherical Cadmium selenide($CdSe$) NPs can be synthesized into rod-like nanostructures through controlled assembly[1]. In this paper, I will focus on the self-assembly of NPs. Here, self-assembly can be defined as a "bottom-up" approach to fabricating large, ordered nanostructures from independent NPs, without being managed by an outside source.

Murray, Kagan, and Bawendi demonstrated self-organization of $CdSe$ nanocrystals(NCs) into three-dimensional superlattices[2]. Liao et al[3], and Wang et al[4] reported Gold(Au) NPs self-organized into one-dimensional pearl necklace-like nanostructures. Two dimensional nanowire(NW) arrays from self-assembled Silver(Ag) NCs have been observed by Korgel and Fitzmaurice[5]. Highly luminescent NWs from self-assembled Cadmium telluride($CdTe$) NPs have been described by Tang, Kotov, and Giersig[6]. The crystal structure of $CdSe$ is wurtzite(Fig. 1 Right). the polar nature of wurtzite lattice brings $CdSe$ NC an intrinsic dipole moment. Zincblende $CdTe$ NC of a specific size would also have a dipole moment(Fig. 1 Middle). This property of semiconductor does not exist in metal NCs, e.x.Au,Ag[7](Fig. 1 Left).
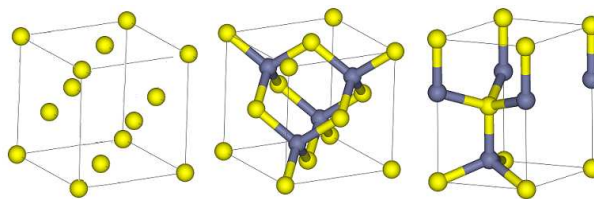

FIG. 1: Crystal structure for metal Au,Ag(Left: FCC), semiconductor $CdTe$(Middle: Zincblende), and semiconductor $CdSe$(Right: Wurtzite). In the crystal structure of Zincblende and Wurtzite, dots of same color represent same type of atoms.

Self organization of zero-dimensional $CdTe$ NPs into one-dimensional chain-like nanos-

tructures is the relatively simple process. In the second section, the experimental procedure of fabricating NWs will be reviewed, and the experimental results will be summarized. Then the modelling simulation will demonstrate that the driving force for $CdTe$ NP self-assembly is the strong dipole-dipole interaction. This explanation would be straightforward for semiconductor NPs, but not obvious for metal NPs. In the fourth section, I will reveal that the driving force for metal Au NP self-assembly is the induced dipole-dipole interaction.

II. EXPERIMENT SECTION

A. Assembly of $CdTe$ NPs

Tang *et al* discovered a simple synthetic method to produce NWs, the fabricated NWs exhibited high luminescence quantum yields[6,8]. The brief experimental procedure is as following: First, The thioglycolic acid-stabilized $CdTe$ NCs of a specific size were produced. In their experiment, four different size samples were generated, whose diameters were $2.5, 3.4, 4.1$, and $5.4nm$ respectively. The corresponding Luminescence maxima were at $520 - 530nm$(Green), $550 - 565nm$(Yellow), $590 - 605nm$(Orange), and $610 - 625nm$(Red), represented by dashed lines in Fig. 2. The next and key step was removing the excess stabilizer. Precipitate $CdTe$ NCs into Methanol addition, then redissolve them in pure water. After partially removing the stabilizer, leave the sample at room temperature for several days, during which self-organization of the $CdTe$ NPs occurred to form pearl necklace-like aggregates. Finally, these linear aggregates recrystallized into NWs. The growth of NWs can be observed by the TEM transmission electron microscopy), and AFM (trapping atomic force microscopy).

B. Experimental results

For each specific size sample, the fabricated NWs would have the same diameter as parent NPs, but high aspect ratio. The Luminescence spectra describe the growth of NWs as shown in Fig. 2. Red shift can be observed for each sample, this is due to the decrease of confinement in one dimension with the growth of NWs along this direction.

Fig. 3 shows a picture of fabricating process. It includes the TEM and AFM images for three different states of $5.4nm$ $CdTe$ NP sample. From left to right, the parent NPs, the
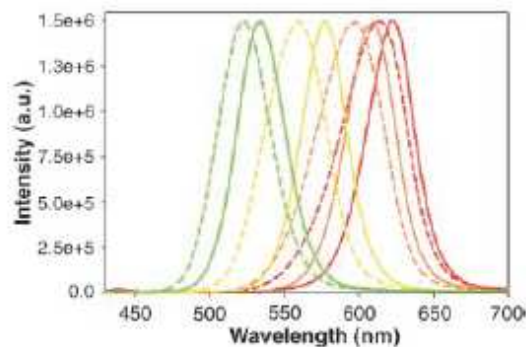
FIG. 2: Luminescence spectra of parent $CdTe$ NPs(dashed lines), and resulting nanowires(solid lines) marked by the corresponding luminescence colors.
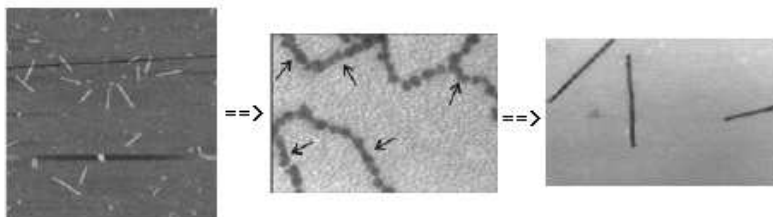

FIG. 3: Left: AFM image of $5.4nm$ $CdTe$ dots; Middle: TEM image of intermediate pearl necklace-like aggregates of NP-NW transition for $5.4nm$ NP; Right: TEM image of fabricated $CdTe$ NW made from $5.4nm$ NP.

intermediate pearl necklace-like aggregates, and finally fabricated NWs are shown. Fig. 3 Middle is an enlarged part of a TEM image, the NPs can be observed to be roughly spherical shape.

III. SIMULATION

To understand the formation, a Monte Carlo simulation was performed, the interaction of $CdTe$ NPs and their aggregation has been studied. It shows that the formation of NWs is due to the dipole moment[9].

A. Modelling

NVT Monte Carlo(NVTMC) method was used to study the equilibrium geometric configuration of the system.

The simulation begins with the randomly arranged NPs. During each step, NPs can either rotate randomly or walk randomly. The new arrangement will be selected by Metropolis criteria. As it is known that $CdTe$ NPs have a cubic zinc blende structure, also from experimental observation(Fig. 3 Middle), the NPs have a spherical shape. Therefore, we can use potential described in Phillies's work[13]. The electrostatic potential between a pair of spherical NPs can be assumed to be the sum of charge-charge, charge-dipole, and dipole-dipole interactions.

$$
\begin{aligned}
V(R) = & \frac{Q_1 Q_2}{\epsilon} \frac{e^{-\kappa R}}{R} C_0^2 + \frac{2 Q_1 D_2 \cos \theta_2}{\epsilon} \frac{e^{-\kappa R}(1 + \kappa R)}{R^2} C_0 C_1 \\
& + \frac{D_1 D_2}{\epsilon} \frac{e^{-\kappa R}}{R^3} [\cos \theta_1 \cos \theta_2 [2 + 2\kappa R + (\kappa R)^2] + \sin \theta_1 \sin \theta_2 \cos (\phi_2 - \phi_1)(1 + \kappa R)] C_1^2
\end{aligned}
$$

Here, Q_i is the net charge of a NP, D_i is the dipole moment of a NP. R is the center-center distance of a NP pair. Coordinates θ_i, ϕ_i are measured with respective to their own NP center, and relative to the center-center line of NP pair. $\frac{1}{\kappa}$ is the Debye screening length. ϵ is the dielectric constant. And where,

$$
\begin{aligned}
C_0 & = \frac{e^{\kappa a}}{1 + \kappa a} \\
C_1 & = \frac{3 e^{\kappa a}}{[2 + 2\kappa a + (\kappa a)^2 + \frac{1 + \kappa a}{\epsilon}]}
\end{aligned}
$$

Another term considered in the potential is the Van der Waals interaction between two spherical NPs[14], which is very weak, and a short range term.

B. Simulation results

Fig. 4 shows that the equilibrium configuration for a system of 50 NPs change with different dipole values. The MC simulation results give an evidence that a high value dipole favours a more chain-like geometric configuration.
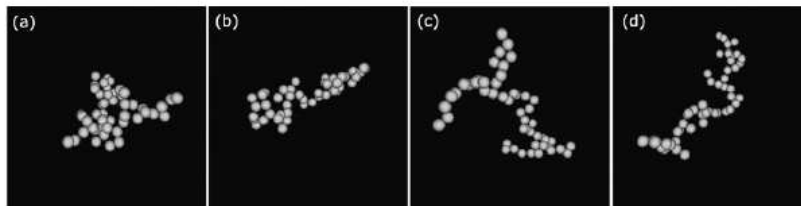
FIG. 4: MC Simulation results for a system of 50NPs with a charge of -1e and dipole moment values as: (a) 0; (b) 25D; (c) 100D; (d) 400D.

IV.   SELF-ASSEMBLY OF Au NPS

In theory, metal Ag NP does not have intrinsic dipole moment. Can it be self-assembled into chain-like nanostructures? Wang *et al* described how Au NPs could self-assemble into chain-like nanostructures under suitable PH conditions.

The experiment can be briefly reviewed as following: First, the solution includes Cinnamic acid(CA), and Tetrachloroaurate($HAuCl_4$), with the ratio of CA to $HAuCl_4$ is 25 : 1. Original PH value of Au NPs solution is about 6. We can adjust the PH value of solution by adding $NaOH$ or HCl aqueous solution.

This experimental environment is different with the one for $CdTe$ self-assembly introduced in the previous sections. Here, environment condition may change the amount of charge on the surface NPs, which eventually change the electrostatic potential. The dipole-dipole interaction is strong and long-ranged in the semiconductor NCs, which leads to the pearl necklace-like nanostructures. The dipole value of Au NP changes with the environment condition. While the PH value of solution decreases, the amount of CA capped on the NP surface decreases. Then the induced dipole moment of NP increases due to the decreasing of screen effect. Therefore, the induced dipole-dipole interaction becomes strong. This can be used to demonstrate that Au self-assembled nanostructure favours more chain-like, within the solution of lower PH value(Fig. 5). In Fig. 5, (a),(b),(c) are the TEM images of self-assembled Au nanostructures prepared in the same ratio of CA to $HAuCl_4$ (25 : 1). The only difference is, (c) solution has lower PH value than (a), (b) solutions. The fabricated nanostructures in (c) solution are relatively longer, and more chain-like.
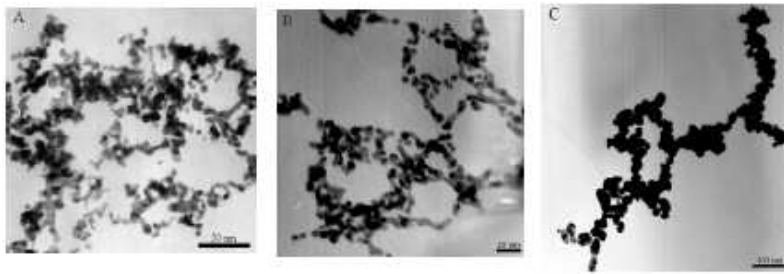
FIG. 5: TEM images of self-assembled Au nanostructures prepared by tuning the PH value of the solution.(a) PH = 11; (b) PH = 7-8; (c) PH = 3.

V.   CONCLUSION

MC simulation demonstrates that the pearl necklace-like configuration is the local-minima of the system, which is in good agreement of the experimental observation of intermediate state of pearl necklace-like aggregates. This chain-like configuration occurs in high dipole value of NP reveals that the fabrication of NW is due to dipole moment of NP.

There are some questions we can continue working on. Firstly, Sinyagin et.al. observe the difference between the nanostructure shape in experiment and the configuration in simulation, they believe there exist some other influence, e.x. short-range interparticle forces. Secondly, Tang et.al. assume that pearl necklace-like aggregates would recrystallize into NWs finally. More theoretical work is needed in explaining this step.

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