Photothermal effect: application in manipulation of nanoparticles

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Abstract. The optical force, photothermal effect and enhanced electric field induced by the localized surface plasmon resonance (LSPR) of plasmonic nanoparticles have been widely applied in nanomanipulation. Among them, the manipulation based on photothermal effect has attracted increasing interest because of its relatively larger manipulation radius and stronger driven force. In this paper, several typical approaches to manipulate nanoparticles using photothermal properties of metal nanomaterials are concluded, divided into direct ones and indirect ones. Among the indirect ones, taking Au as an example, there exist single Au NP-based schemes, multiple Au NPs-based schemes and Au nano-island-based schemes. At last, some problems unsolved are raised and some outlooks are suggested.

1. Introduction

Recently, the manipulation of polymers and metal NPs with external forces have been widely applied to the fabrication of materials in micro- and nano-scale, which can be realized effectively by optical trapping with highly focalized laser beam [1]. The beam can transport NPs to desired locations where aggregation happens. Under particular condition when the plasmonic properties of NPs match with the optical trapping parameters, the manipulation in nanoscale becomes possible. In another sense, plasmonic based manipulation can finish some tasks that cannot be handled by self-assembly, realizing superior functions [2].

Some latest researches have verified that hot electrons can be created in NPs plasmonic systems due to LSPR [3]. Concurrently the decay of hot electrons will cause heat effect or plasmonic heating, and the brought temperature field is regarded as an effect way to drive the nanoparticles [4]. Approaches taking advantage of this mechanism are attracting intensified interests from researchers with their independence on high optical intensity and their ability to trap NPs with high efficiency [5].

To realize photothermal manipulation, people have explored phenomenon such as surface tension gradient cause by temperature gradient, thermophoresis, Marangoni effect, thermal convection and other kind of flow created by plasmonic heating, and the convert between hydrophobicity and hydrophilicity in some polymer system based on a characteristic temperature. The heating caused by plasmon has shown its potential to fabricate nanomaterials in a bottom-to-top way.

In this paper, several instructive approaches to manipulate NPs based on photothermal effect are concluded and classified in the manner of their manipulation objects and the component of the system. The merits and defects of subsistent approaches are discussed with some suggestions offered. At last, some outlooks on this research area are put forward.

2. Photothermal manipulation

Based on the manipulated objects, photothermal manipulations can be divided into manipulations on
optical heated NPs themselves and manipulations on other nanoparticles in the system induced by those plasmonic heated NPs. The way in which the heated particles themselves are manipulated is dubbed direct manipulation. It is plain to see that this approach is more straightforward with more resources saved. On the other hand, the so-called indirect manipulations are imposed on those non-heated NPs taking advantage of the heated ones. In the following part of this section we will see, every kind of indirect photothermal manipulation corresponding to systems composed in different ways possesses its merits and defects, which is worthy further discussions.

2.1. Direct manipulation

Hidai and coworkers had an instructive exploration on the manipulations of NPs themselves [6]. They found under the irradiation of a horizontal laser beam, a stainless steel particle with a radius of 40um placed on a glass board experienced a force towards the light source. Given the soften process experienced by the glass board due to the plasmonic heated stainless steel particle, the particle could even move towards the light source. The force comes from the change of the surface tension of the interface between the glass board and the particle [7]. According to calculation, the illuminated side of the particle possesses a temperature 320K higher than the other side, creating a driven force up to 100uN, which can completely compensate the viscous resistance.

However, in this circumstance, one laser beam can only drive one NP, which is not feasible in large-scale materials fabrication. What’s more, the moving speed of the particle is approximately 72um/s, which is relatively slow. As a result, people devote more energy to realize manipulation on large-scale nanoparticles using finite amount of NPs.

2.2. Single Au NP-based manipulation

There exist several approaches to realize the photothermal manipulation on large amount of NPs, the most economical one being just optical heating a single Au NP on the substrate. This method employs thermophoresis, Marangoni effect and thermal convection in the solution induced by the temperature gradient.

Thermophoresis is the phenomenon that under the temperature gradient the solute and solvent migrate in a particular direction, which is represented by thermal diffusion coefficient $D_T$[8]. When $D_T > 0$, it is referring to solute moving from warmer side to cooler side, while $D_T < 0$ stands for solute transmitted from cooler side to warmer side. Thermal convection comes from thermal nonequilibrium state caused by the temperature gradient, driven by the difference in density of the liquid subject to gravitational force [9]. Marangoni effect refers to that the surface tension gradient along the surface of the Au NP caused by the temperature gradient (warmer in the lower part and cooler in the upper part) will induce a flip flow along the surface of the Au NP to the substrate [10].

Enders and colleagues illuminated and heated a single Au NP with a diameter of 100nm lied on sapphire substrate using a laser beam [11], and found the polyethylene glycol or lauryl sodium sulfate moved towards the Au NP and finally stick on it, forming an Au core-polymer shell structure in tens of seconds. As substrate, sapphire enjoys its high thermal conductivity and can create a strong temperature gradient around the Au nanoparticle, helping the forming of thermophoresis. Thermophoresis, together with thermal convection and Marangoni effect direct the migration of polymer NP towards the Au NP.

In fact, this approach still has its intrinsic limitations because it only works when the $D_T$ of solute is negative, otherwise the solute will move away from the heat source, never forming a cluster. For another thing, the whole process takes tens of seconds, which is slow.

Similarly based on single Au NP, some merits of particular polymer i.e. PNIPAM such as phase transition under characteristic temperature [12] can make it faster to manipulate nanoparticles photothermally, as well as realize irreversible assembly under irradiation with high power density. At room temperature, PNIPAM exist in the form of a homogeneous coil state in its water solution, while heated to the characteristic temperature 305K it will experience a phase transition to globule state. The globule molecules will aggregate due to the hydrophobic interactions, causing the phase separation in
the solution.

Aibara and coworkers in one of their works optical heated single Au NP with a diameter of 100nm in PNIPAM solution on a transparent substrate [13]. With the thermal conduction, medium around was heated above 305K, which permitted PNIPAM to aggregate around the Au NP forming a shell structure with a radius around 1-10um in seconds to tens of seconds. With the inflation in the volume of this structure, the refraction index of the medium adjacent to the Au NP will change, causing the red shift of LSPR [14]. As a result, independent of SEM analysis, spectroscopic monitoring on the forming of the assembly is feasible. It is worthy saying that when the intensity of the laser is relatively low, the aggregation is reversible, while when the intensity is higher than $2.6 \times 10^5 W cm^{-2}$, with the sapphire board as substrate, the shell will not decompose even after the laser is removed, which presents a permanent assembly has been given birth [15]. In this approach, we could get a kind of firm enough nanomaterial in such an irreversible form that cannot be adjusted once it shapes up.

2.3. Multi-Au NPs-based manipulation

Ding and his coworkers explored a way that can make the assembly fast and tight with unconditional reversibility [16]. They prepared large amount of PNIPAM shell--Au NP core mentioned in last section as elements in solution and had them optically heated by laser. When the temperature of PNIPAM is above 305K, Au NPs enveloped will aggregate due to hydrophobic interactions, forming a tightly bounded cluster because of the strong van der Waals force (several nN) between Au NPs. Then if the laser is removed and the temperature decreases below 305K, PNIPAM will absorb water and overcome the van der Waals force, returning to the inflated state. In this sense, all the PNIPAM shell--Au NP core will disperse in the solution again so that the aggregation is reversible.

However, the position of the assembly cannot be determined precisely in this way because it is difficult to locate the aggregation center using laser along its optical axis. It may also be the collective defect of photothermal manipulation based on nonlocal multiple Au NPs.

2.4. Au nano-island-based manipulation

It has been found by Lin and coworkers that when one side of Au nano-island interlayer is irradiated perpendicularly by a laser beam with an intensity even lower than $1 \times 10^4 W cm^{-2}$, the aggregation of Au NTs with a side length of 150nm dispersed in the solution on the heated side can be realized[17], which is also due to thermophoresis. Given that for positive charged CTAC micelles in the solution $D_{T}>0$, together with $D_{T}(CTAC)>D_{T}(Cl^{-})$, under the temperature gradient, CTAC will be transport quickly to the unheated side of the interlayer, forming a temperature-dependent charge distribution thus an electric potential. The positive charged Au NTs will be driven by the electric field force and move to the warmer side to aggregate. When the laser is removed and the temperature gradient disappears, the charge will be uniformly distributed thus the electric field vanishes. The Coulomb repulsion between the Au NTs will tear the assembly apart, making this manipulation approach reversible. Besides, through precise control of the laser they successfully realized manipulation on multiple assemblies as well as accurately localized the assemblies. However, this approach intrinsically depends on thermophoresis, making the process time-consuming.

In another manipulating scheme employing Au nano-island as substrate, utilizing the enhanced photothermal effect of metal substrate induced by laser, micro-bubbles can be created on the interface of the substrate and the solution [18-19] even if a laser beam with a low intensity is used. Thanks to thermal convection, Marangoni effect and the van der Waals force between the NPs and the substrate, nanoparticles can aggregate at the bottom of the bubble in a few seconds. By changing the position of the light spot, bubbles can accordingly move on the substrate, making the assembly form depending on the pattern the bubbles migrate [20].

Because changing the location of a bubble fast is relatively easy to realize, the distinct advantage of this approach is people can flexibly control the location and shape of the assembly. However, the process is still irreversible, for even after the removal of the laser, nanoparticles cannot return to the free state due to the van der Waals force between the NPs and the Au nano-island and the phase
transition of particular nanoparticles [21].

3. Summary
In a word, what we expect is a method to manipulate NPs with large scale, high speed, strong constraint, possibility to locate and reversibility. However, among the existing approaches, direct manipulation has limitations on scale; single Au NP-based manipulation suffers either a low speed or a dilemma between strong constraint and reversibility; Multi-Au NPs-based manipulation has inevitable difficulty in finding an aggregating center; Au nano-island-based manipulation enjoys its superiority in locating aggregation center with the sacrifice of manipulating speed or reversibility as exchange. To conclude, each of the approaches mentioned above has drawbacks at least in one aspect, which remains to be explored.

Here I bring about a method in concept can bring together the merits of the approaches mentioned above, which may be worth trying. We can prepare the system by distributing multiple Au NPs uniformly in the PNIPAM water solution in an Au nano-island interlayer. Then a laser beam parallel to the surface of the layer with an intensity higher than the threshold of irreversibility is employed to optically heat the Au NPs in the solution, which will create a temperature gradient around the NPs. In the area with a temperature higher than 305K PNIPAM will expel water in 1us and irreversibly forming a shell around Au NPs. The next step is to shut down the laser and use another highly focalized one with intensity lower than the threshold of irreversibility to perpendicularly irradiate the substrate, heating the central Au atoms above 305K. Again large amount of Au core-PNIPAM shell elements will very soon aggregate to the heat source due to hydrophobic interactions, tightly bounded by the strong van der Waals force between them. When the laser is removed, the elements will absorb water and return to free state with the van der Waals force overcome, making the assembly reversible. When next time the laser beam is focalized to other positions on the nano-island, the aggregation will happen at that location, so the localization of the assembly is possible.

Of course the approaches mentioned above are based on known phenomenon caused by plasmonic heating without exception. However, people still have long way to go to fully understand the phenomenon such as thermophoresis [22-23]. We can expect with deeper understanding of known phenomenon and continued excavation of brand new properties, a beautiful future is waiting for photothermally nanomanipulation.

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