Preparation and Characterization of Janus Particles

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ABSTRACT:
Research on Janus particles unplugged a new chapter in the field of Colloidal research. They possess dual particle properties like different charges, wettabilities etc. which make them useful in number of applications like targeted drug delivery and emulsion stabilization. They also undergo self assembly into novel structures. They are different from surfactants as small molecules can diffuse through their dense film at air-water interface unlike impermeable nature of surfactant film. Initially, monolayer methods were developed on lab scale and later on in 2006, Granick et al. developed bulk methods to produce Janus particles on commercial scale. This review is highlighting the various methods of synthesis and characterization of Janus nano particles, their behaviour at oil-water interfaces and roadblocks in the preparation methods.

Keywords: anisotropic nano particles, self-assembly, Janus particles, Janus balance, geometry control

I. INTRODUCTION

In 1991, P.G. de Gennes raised the concept of “Janus particles” in his Noble Prize address. This name was borrowed from the name of Roman God who has two faces looking in opposite directions to describe colloidal particles having different chemical properties in their surface segments. The two heads of Roman God signifies beginning and ending of the world respectively. So, they are of different nature. Likewise, two distinct surface segments of Janus particles have different chemical properties like wettability (Contact angle), roughness or surface charge (cationic or anionic)[1].

The name Janus particle was first coined by C. Casagrande in 1989 when he first time fabricated Janus beads on lab scale. The technique was based on spherical particles, half embedded in varnish and silanated on unprotected sites. This produced only micro quantities of material.

In recent years, these type of particles have got very much attention from scientists due to their magical properties. Their inter-particle interactions are very different as compared to homogeneous particles. These interactions are due to the two distinct segments of these particles. External fields are also used to control their movement and orientation. They are characterized by ‘Janus balance’ which means the balance between two segments of a particle.

The dual properties of Janus particles are responsible for their self assembly into various novel structures of variety of shapes and sizes under the proper conditions. The driving forces behind self assembly are the amphiphilic nature of the particles, magnetic dipoles or surface charge variations. Control of these particles in an external field can also lead to the aggregation of particles into interesting structures. The Janus particles can be fabricated by two methods:

1. Monolayer methods (2D methods)
2. Bulk methods (3D methods)

Monolayer methods are restricted to lab scales only. They produce only micro quantities of material. Bulk methods can produce large quantities of material so that production particles can be scaled up for commercial purposes.

Figure 1. Two-faced God Janus

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On 9th December, 1991, P.G. de Gennes talked about Janus grains in his noble prize address. He said that there is an interesting difference between Janus grains and surfactants if we take their films into account. He talked about the film of Janus grains at air-water interface which is quite different from the surfactant film at air-water interface. He said that a dense film of surfactants is quite impermeable. On the other hand, a dense film of Janus grains always has some interstices in between the grains and thus allows some chemical exchange between the two sides. He quoted that “the skin can breathe”. He was sure that this nature of Janus grains might be of some practical interest to scientists[1].

II. REVIEW OF THE PREPARATION METHODS

Simplest methods available in the initial years employed solid substrates as protecting or masking surfaces. A monolayer of particles is formed on the solid substrate and the side of particle towards substrate is protected from any kind of chemical reaction. Unprotected side will undergo chemical modification by some kind of chemical reaction. Different techniques like sputtering, stamp coating, vapor deposition and directed flux of reactive species are used to modify surfaces. These methods provide good control over surface geometry but only a few milligrams of particles can be produced in one batch. This is because of the reason that this approach relies totally on the modification of monolayer, means it’s a monolayer method (2D method).

First method was introduced by C. Casagrande et al., 1988 in which he took glass spheres of equal size which were placed on a plate containing varnish so that one side gets protected. On the other side, they did chemical grafting of octadecyltrichlorosilane due to which outer surface of the spheres became hydrophobic. Then varnish was washed off by acetone and particles were collected. Low yields due to monolayer methods is the disadvantage of this method[2].

A. Simple Method to produce Janus particles in large quantity[7]

Steve Granick et al., 2006 developed this method. To overcome the limitations of monolayer methods, they made pickering emulsions which are the emulsions that are stabilized by solid particles like colloidal silica which adsorb onto the interface between the two phases. It is good to select paraffin wax as oil phase because it has a melting point of 55 °C. The emulsion is made at around 75 °C so that wax remains molten at that temperature. Then it is cooled to room temperature to lock the particles at frozen surfaces of wax water. This locking prevents particle rotation and facilitates chemical modification[7].

So, at 75 °C, emulsion is prepared using magnetic stirrer for 1 hour at 1600 rpm. After cooling it to room temperature, they are reacted with APS to render cationic charge to the unprotected segment. After washing with methanol so that the wax is dissolved, the particles are further reacted with OTS to render hydrophobicity to another segment. Solidified emulsions survive multiple washings which show fair mechanical stability. So, emulsion used here are mechanically rigid and stable. This yield of this process is 50%. Emulsion process is easily achievable by magnetic stirring. Monodispersity of particles is better from batch to batch. In SEM images, only a few of the particles are found under wax droplet. The possible disadvantage can be disruption of wax droplet surface by mechanical stirring during chemical modification step. Hence efficiency of this method is also less due to the use of solvent in this method. Further, we can then use vapor instead of solvent to solve this problem. This will be discussed in next method of producing Janus particles. See figure 2.2 to see the schematic of this process.

B. Solvent free method to produce Janus particles[6]

Steve Granick et al., 2008 developed this method to minimize the disrupting surfaces of wax drops at the time of chemical modification step. This method increases the efficiency of chemical reaction or modification as vapors of
dry gas or some inert gas are used to take modifying agent or reactant to the surfaces of wax colloidosomes. This method yields better SEM images of the particles. This method takes place at the ambient temperature because high temperature could melt wax drops. So, dry nitrogen or argon gas is bubbled through the dichloro dimethyl silane (DCDMS) which takes silane vapors with them to react with the silica particles which are locked on the surface of wax drops. Low boiling silanes are much effective for this method because they may then immediately convert into vapors and reach into the funnel in which they put wax colloidosomes. Colloidosomes should rolled over periodically so that vapors of silane reagent should react with every silica particle fixed over wax drops. This method is useful to produce particles having opposite charges on their distinct segments besides amphiphilic particles. We are using inert gases because we don’t want them to react with any of the reagents. Here, they are behaving as carriers only. See figure 2.3 to see the schematic of this process[6].

C. Fabrication of Janus Particles by Microfluidic Approach which Generate Double Emulsion Droplets[8]

Particles with far more different properties can be fabricated by this method by using two different materials which differ in properties. This method results in the production of Janus particles with excellent monodispersity, controlled size and morphology. Two separate streams are co-flowed through same channel of the microfluidic device and they must remain parallel at all times because any disturbance or cross mixing of fluids leads to mixed internal morphology of resultant particles. Microfluidic technique yields the anisotropic particles with monodispersity and controlled dimensions. Relative sizes can be controlled or changed by varying the fluid flow rates in the channel.

Microfluidic device is a nano scale device in which two immiscible monomers are forced to come into contact with each other through junctions in capillary channels forming a droplet that is a mix of both the monomers. In this method, microfluidic device is made up of silicon elastomer of PDMS (Poly dimethyl siloxane) which is developed by soft-lithography techniques. We coat the channels with the layer of sol-gel in which silanes are added which are photoreactive. This leads to the spatial patterning of the channels in order of wettability and it allows the formation of double drops of emulsion. The device is placed on hot plate which is at 225 deg C temperature which leads to evaporation of solvent and curing of sol-gel on walls of the device which thus renders the device wall hydrophobic. In order to do spatial patterning, poly acrylic acid is grafted onto the channel which renders hydrophilicity to the channels.

We use immiscible monomers and they flow through channels to form double emulsion droplets. Firstly, oil monomer gets encapsulated by aqueous monomer medium which is wetting the hydrophilic walls of the channel and forms oil in water emulsion. In the next channel, another oil mainly fluorocarbon oil is flowed by channel so that oil – water – oil double emulsion drops are formed. As these drops are larger than the height of the channel, so they are flattened into a peanut shape and it can be seen in SEM images of the particles formed. Due to the viscous friction inside, inner drop moves towards the back of outer drop due to relative flow and then they are passed through UV chamber in which photo-polymerization solidifies the drop and form anisotropic particles[8].

This method results into mechanically robust particles. The size of the two segments can be controlled by varying the flow rates of fluids. The spherical shape of the caps is due to high surface tension between fluorocarbon oil and acrylamide shell. Main disadvantage of this method is its low yields. Microfluidic device is a nano scale device and hence yields are less.
D. Fabrication of Janus Particles by Plasma Polymerization [9]

It is a flexible method to fabricate Janus particles in which thin films of functional polymers are deposited on substrates. The biggest merit of this method is that chemical and physical properties of the surfaces can be manipulated by this process like thickness, functional group density etc. Janus balance can also be adjusted with the particle size.

RFGD is generated in the presence of Bromopropane. Then, the bromine functionalized plasma polymer is deposited on the monolayer of silica particles. Silica particles are layered on the NaCl crystal so that after chemical modification of the one side of the particle, NaCl can be rinsed through water. Brpp films do not require any separate adhesion treatments. Also, Brpp is responsive to secondary reactions also such as copper catalyzed azide-alkyne cycloaddition which is also known as ‘Click’ reaction having high efficiency and specificity. Further chemical reactions would result in formation of Janus particles [9].

III. BEHAVIOUR OF JANUS PARTICLES AT OIL-WATER INTERFACES

A. Brief Description of Particle Behavior at Oil-Water Interfaces (C. Casagrande et al., 1989) [2], [3]

Particle size is taken so small (of nano-scale), such that capillary forces are dominant over gravity and buoyancy forces which are neglected due to small size of particles. Casagrande first studied behavior of homogeneous beads (either fully hydrophilic or hydrophobic) at oil-water interfaces, and then checked the behavior of Janus beads at same interfaces and observed some interesting things.

For homogeneous particles, successive concentric circles were observed under microscope among which larger one corresponds to equator and smaller to the intersection of sphere with liquid interface. The relative position of the two circles indicates the immersion depth ratio of the sphere in the two fluids.

For Janus beads, totally different behavior was observed. A unique circle was observed under a microscope which shows that Janus bead is symmetrically positioned at the interface. It means, it is immersed equally in water and oil as it has two segments, one hydrophilic which will immerse itself in water and another hydrophobic, which will immerse itself in oil.
If we discuss about the behaviors with respect to the Energy based arguments, then we should first know about total energy of the system.

**Total Energy of System (E) = Interfacial energy between solid and liquid (E_{SL}) + Interfacial energy between liquid and liquid (E_{LL})**

For homogeneous particle, \( E_{SL} \) is minimized when solid is entirely immersed in a preferred liquid (in which it has lowest interfacial energy). \( E_{LL} \), counterbalances the effect as it is reduced when interfacial area intercepted by solid is reduced. From minimization of these two energies, equilibrium position is resulted which results in the trapping of bead at interface or total immersion of bead in one of the two liquids.

For Janus bead, both \( E_{SL} \) and \( E_{LL} \) work together for symmetric configuration. \( E_{LL} \) is minimized as it realizes smallest liquid area and \( E_{SL} \) is minimized as each hemisphere of the bead prefers a different liquid of its choice. So, Casagrande concluded that properties of Janus beads at O/W interfaces suggest two promising directions for future. First is the fact that amphiphilic particles of comparable sizes have an added advantage over homogeneous particles with respect to emulsification process. Second point is about the solid nature of amphiphilic particles due to which constitutive material can be altered easily in order to modulate their applications.

B. A Theoretical Comparison between Spheres of Uniform Wettability and Janus Particles[5], [10]

Colloidal particles are like surfactant molecules. They can spontaneously accumulate on the interfaces of two immiscible liquids and are therefore surface active. Amphiphilic nature of colloidal particles is not a necessary reason for their surface activity. Homogeneous particles have uniform wettability, they are strong surface active but are not amphiphilic. Janus particles are both surface active and amphiphilic. Binks and Fletcher did calculations to show that how particle’s amphiphilicity influences the strength of particle adsorption. They calculated that increasing amphiphilicity would increase the surface activity by a maximum of 3 times for average contact angle of 90°.

**IV. CONCLUSIONS**

Janus particles can be strongly adsorbed on interface as compared to homogeneous particles and hence they can act as very good emulsion stabilizers. They can potentially be used in targeted drug delivery and in making magnetically modulated optical nanoprobes. A large number of methods for fabricating Janus articles are available till now but they are limited to lab scale preparation only. So, scaling them up is very important. We need to use bulk or 3D methods in order to fabricate them instead of using monolayer methods for their preparation. When we’ll be able to produce them in large quantities, then only we can use them commercially for various applications listed above. In addition, the fabrication methods which are available now days are not cost effective. So, we need to develop a fabrication method in which cheap and abundantly available materials such as clay, carbon could be used as precursors. Also, geometry control during the fabrication should be achievable so that we can control and manipulate the surface areas of two distinct regions in a Janus particle according to our requirement. Proper size reduction equipment and process is also needed because achievement of nano-sized reduction will increase the reactivity and specific surface area of the particles making them ideal for large number of applications. So, one should develop a method in which all of these problems could be solved.

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