# REPORT

**Title** Reusable Magnetic Janus Particle Scavengers for Environmentally Friendly Remediation of Contaminated Water Bodies

**Project Number** 2011TX393B

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**Abstract:**

Industrial waste containing petroleum products and heavy metals, as well as concern over the fate of oil released from the recent BP Deepwater Horizon rig accident are problems facing the Texan water supply that need to be addressed. One concern with adding small molecule surfactants to the water supply to disperse oil spills or other hazardous materials is the ultimate fate of those small molecules. One proposed solution to this is the fabrication of a retrievable particle for the same purpose. The Janus particle, a compartmentalized colloidal particle with two chemically or physically different sides, can form stable emulsions that can entrap oil or heavy metals depending on the ligands attached to the particle. The emulsion can consequently be destabilized by application of a magnetic field which will allow recovery and recycling of the particles and collection and disposal of oil or heavy metals. Over the course of the sponsored research we have developed solution synthesis for Janus partiles with different functionalities as well as a synthesis for core-shell magnetic nanoparticles. Future work will include the combination of these materials.

**Problem and Research Objectives:**

Oil refineries, pipe-lines and off-shore drilling pose an increased risk to the water supply of the state of Texas. The recent explosion of BP Deepwater Horizon rig released 4,928,100 barrels of oil from the Macondo well into the Gulf of Mexico with an error margin of 10% (1). While a large portion of this oil has been recovered or eliminated, 1,281,306 barrels, or 26% of the total amount (1), is unaccounted for and could potentially wash ashore, contaminating estuaries and wetlands. Marsh cleanup is often suggested as a way to prevent oiling of birds or other animals and to prevent oil from moving to nearby environments (2). Run-off from oil refineries, heavy metal contained in industrial waste and non-point pollution are also an increasing threat to the quality of Texan water supply, and different methods have been used to remedy these problems, one of them being surfactants.

Addition of surfactants, molecules containing a hydrophobic and hydrophilic end, is a common way to approach oil spill and other toxic waste remediation. In the case of oil, surfactant molecules create stable emulsions of non-polar oil constituents by forming micelles that render them water-soluble for easy removal. While introduction of biologically-derived surfactants in recent years helped address some of the concerns regarding environmental toxicity, the inability to recover and recycle surfactant at the end of an operation is still a problem. We propose using Janus particles, or functionalized colloidal particles, to address this issue due to their increased emulsifier potential and possibility of reuse and recycling.

Janus particles are compartmentalized colloidal particles with two sides of different chemistry or polarity (3). It is well-known that small particles can stabilize immiscible liquids forming so-called Pickering emulsions. Unlike surfactants, colloidal particles create more stable emulsions since more energy is required to remove them from the interface (4). Better yet, Janus particles offer a 3-fold emulsifier potential for water-oil emulsions over homogeneous colloidal particles in theoretical studies (5). We will use iron oxide-based particles due to their superparamagnetic properties, along with low cytotoxicity and colloidal stability for environmental advantages (6). Once the oil has been emulsified by the Janus particles and removed from the environment, a simple application of a magnetic field will align the particles into chains or clusters, which will disrupt the emulsion to allow collection of oil and recycling of the Janus particles.

Our long term objectives are to create Janus particles by immobilizing silica-coated magnetite colloidal particles at liquid paraffin/water interface via paraffin solidification and use aqueous/organic chemistry to modify first one, and then the other half of the exposed particles. Different ligands can be attached to the particle surface, and the functional group, length of ligand backbone and pH will influence the ultimate polarity and charge of the particle surface. The attached ligands can also have chelating properties, which can be used to complex and recover toxic heavy metals. The materials synthesis was divided into two parts; the Janus particle synthesis and the synthesis of the core/shell magnetic particles. Core/shell particles with a magnetite core and a silica shell are desired because the silica surface can be more readily modified than magnetite. Also, magnetite nanoparticles are smaller than the optimal particle size, and with the core/shell synthesis

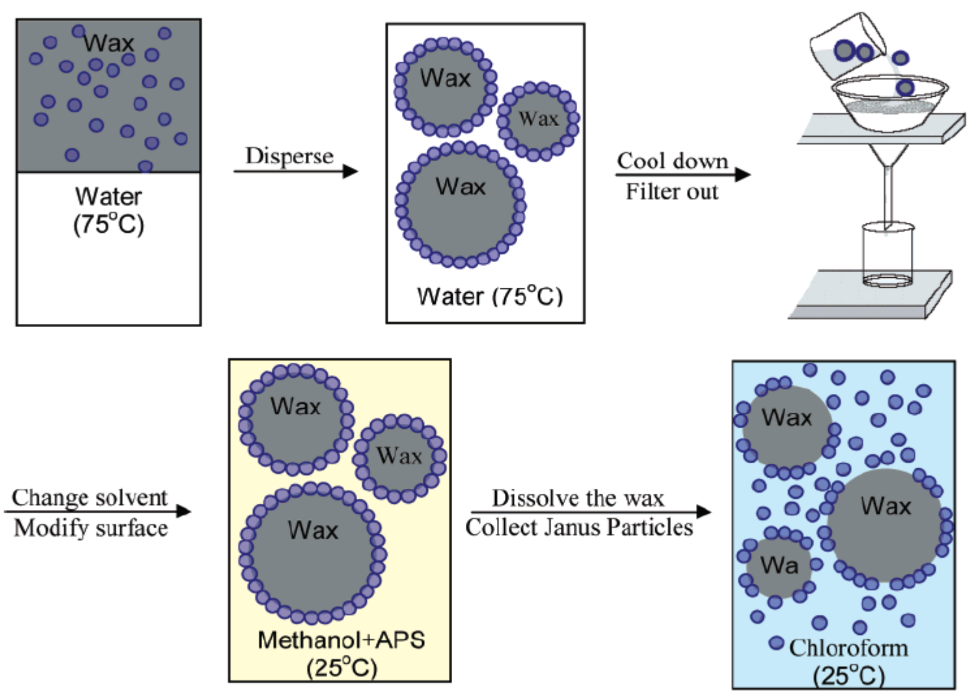


**Figure 1: Schematic process of Janus particle synthesis. A wax drop in water immersion is formed, nanoparticles are assembled at the surface of these drops, which then serve to mask one side of the nanoparticles.**

several magnetic nanoparticles are combined into one core to make an overall larger particle.

One of the problems in the field of Janus particle research is in creating a high yield high synthesis process for their fabrication. We have been working on a synthetic method based on the work of Granick, et al, schematically shown in figure 1 (7). In this method nanoparticles are assembled at the surface of larger wax droplets, which act as a mask to allow one side at a time to be functionalized. In order to characterize the Janus particles their assembly at organic/inorganic interfaces has been observed, and will continue to be observed in future work. Visual observation, rheological changes, sensitivity to turbulence and zeta potential of the emulsion over time, temperature, concentration and pH range are all techniques used for characterization.

## Materials/Methodology

All chemicals were purchased from Sigma Aldrich and used without further purification.

Silica nanoparticles were synthesized with a modified Stober method as according to reference 8.

For the Janus functionalization of the silica nanoparticles paraffin wax and dried silica nanoparticles are added to water at 70°C and sonicated with a probe sonicator to form a good wax in water emulsion. When the emulsion is formed, the temperature is lowered and then the emulsion is filtered to separate thw wax particles from the water. These wax particles are redispersed in a methanol solution of silane of choice to modify the exposed particle surface. Dichloromethane is then added to dissolve the wax and release the Janus particles. Characterization was performed via SEM imaging and Zeta potential measurements.

For the magnetite nanoparticles, iron acetate, 1,2-hexadecanediol, oleic acid, and oleyl amine were mixed and stirred (8). The mixture was heated to 200 °C and then refluxed for an hour. Under ambient conditions, ethanol was added to the mixture and a black material was precipitated and separated via centrifugation.

## Principal Findings

Our group has developed expertise in synthesizing monodisperse (within %5) silica spheres of different sizes. This was our starting point for developing Janus functionalization of these spheres with a solution state synthesis. The method is to create a wax in water emulsion (the wax droplets are large, hundreds of microns) and then allow the smaller particles of interest (e.g. silica spheres) assemble at the interface, shown in figure 5. The solution is then frozen and filtered, retrieving wax particles with smaller silica spheres embedded on the surface. These wax particles are redispersed and functionalization of the unprotected surface only is possible. Figure 2 shows SEM images of the surface of wax droplets with silica nanoparticles embedded in them. This demonstrates that A simple silanization imparts a different charge or other property to one side of the spheres. Then once the wax is dissolved the unfunctionalized side of the spheres can be functionalized. As an initial trial to begin optimization of this process, aminopropylsilane and octadecyltrichlorosilane were chosen for hydrophilic and hydrophobic functionalizations, respectively. Once Zeta potential measurements confirmed that these funcationalizations had worked, polyelectrolytes were chosen. We successfully functionalized Janus particles to have one hydrophobic face and one charged polyelectrolyte face,

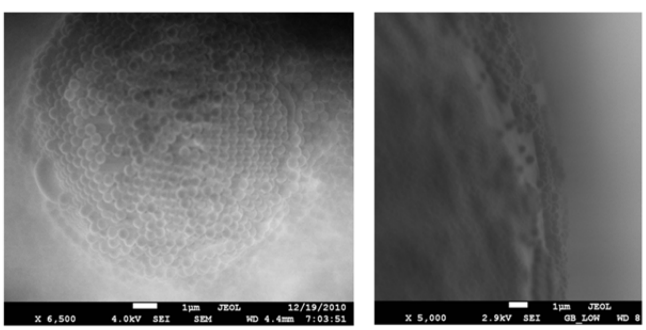

Figure 2: SEM images showing silica particles embedded in the surface of solid wax drops.

either negative or positive. Figure 3 shows the complexation of oppositely charged particles. This demonstrates our control of either face of the Janus particles.

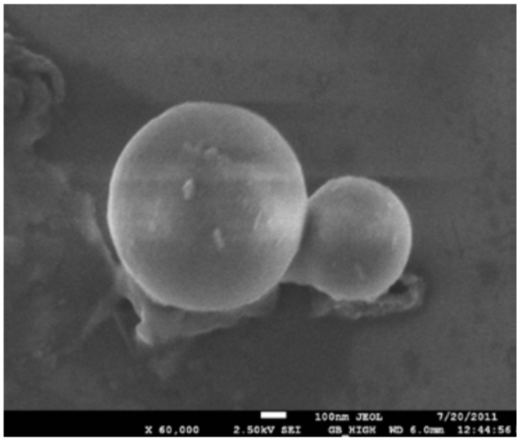


**Figure 3: Doublet particles formed from the complexation of oppositely charged Janus particles.**

Preliminary results show that the particles are more effective at stabilizing a water/toluene mixture than sodium dodecyl sulfate (SDS). Figure 5 shows time lapse images of water and toluene alone (first row), water and toluene with SDS (second row), and water and toluene with an equal wt% of functionalized 400 nm spheres (third row). All three mixtures were initially sonicated to create the dispersion, which explains why the water and toluene mixture doesn't separate more quickly. It can be seen that the unstabilized dispersion separates the most quickly, followed by the surfactant stabilized emulsion, followed by the particle stabilized emulsion. While there is still a great deal of work to be done investigating the effect of particle size and specific ligands used to impart hydrophobicity or hydrophilicity, we have shown that the Janus particles have potential to improve micellization over small molecule surfactants.

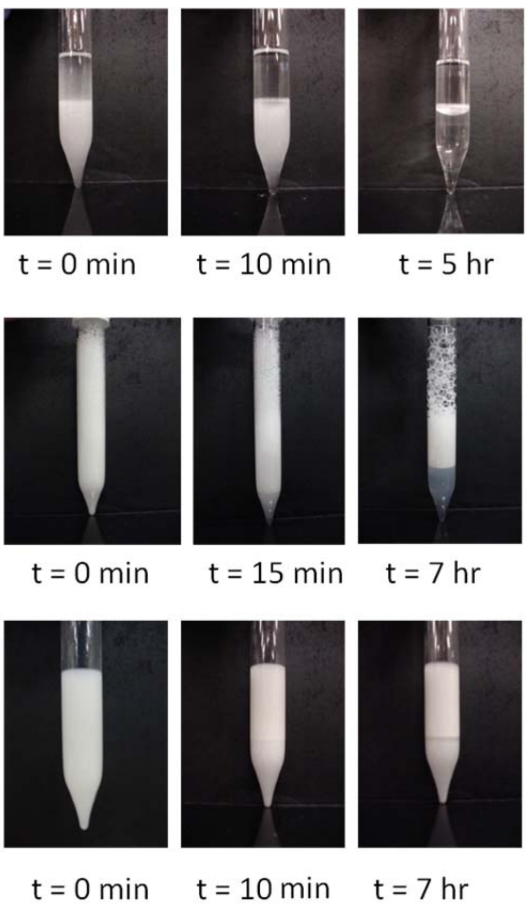


**Figure 4: Top row shows the separation of water and toluene. Middle row shows the separation of the same but stabilized by 0.67 wt% SDS. Bottom row shows the separation of water and toluene stabilized by functionalized silica particles.**

To demonstrate that our functionalized 400 nm particles are well adhered to the oil/water interface, figure 5 shows particles that are stabilizing a dichloromethane/water dispersion, and then after centrifugation for 30 min at 5000 rpm. While non-functionalized spheres would sediment under these conditions, it can be seen that the Janus particles adhere to the interface. The energy required to remove these particles from the interface is large.

In addition to development of the Janus functionalization, our group is working on core-shell colloidal particles with a magnetite core. If we can make particles with a magnetite core and a silica or gold shell, they will be retrievable by magnetic field but the surfaces will also be easily functionalized with either silanes or thiols. Figure 6 shows pictures of magnetite particles suspended in water (a) being attracted to a magnet and (c) SEM images of the same particles. The next steps towards making the core/shell particles involves coating these nanoparticles with a polymer ligand, which we have successfully accomplished, and then attaching silica seeds to the polymer surface.

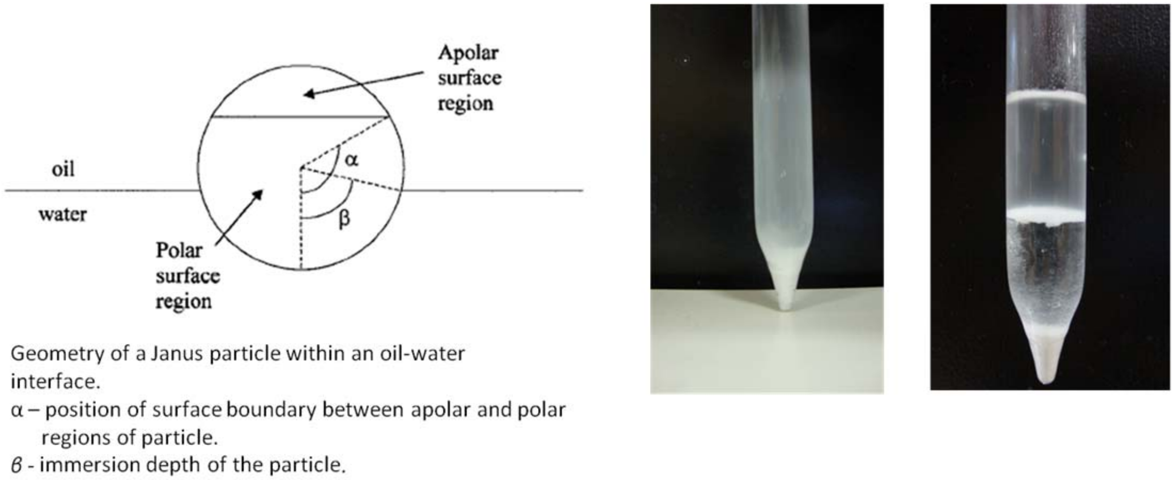


**Figure 5: A schematic showing the geometry of how a Janus particle would sit at an oil/water interface,[16] and 400 nm Janus particles in an oil/dichloromethane dispersion. Even after 30 minutes of centrifugation at 5000 rpm, the majority of the particles stay at the interface and do not sediment.**

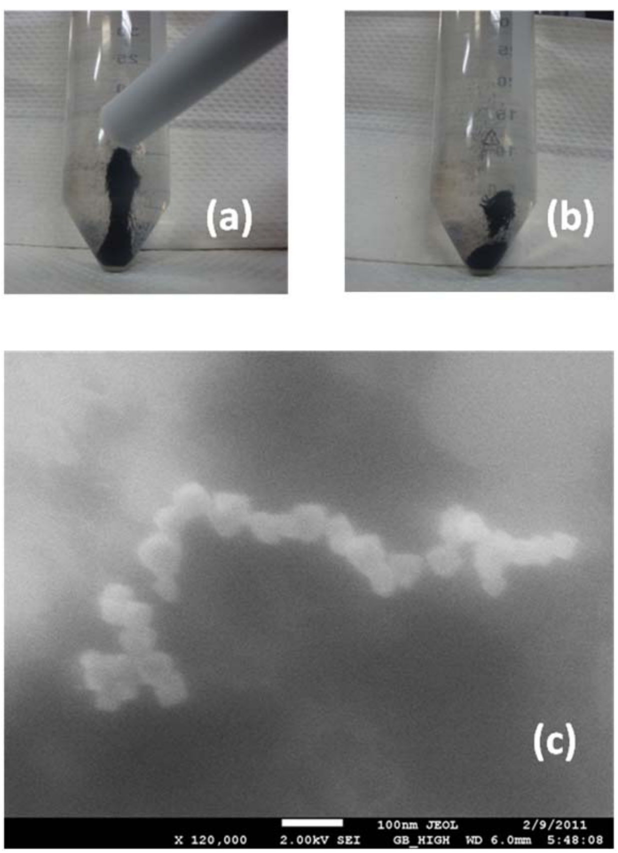


**Figure 6: (a) Magnetite particles in water beingattracted by a magnet and (b) the same particles falling back down in the test tube after the magnet is removed. (c) SEM image showing that the particles are about 50 nm in size.**

## Significance

Over the course of the project, we have made significant gains towards optimizing the functionalization of Janus particles in solution. Our highest scale synthesis has been at the gram level, which is very important for any potential use of these materials. We are able to selectively functionalize one face with either small molecules or polymers. These particles are effective at the stabilization of oil/water interfaces. Future work includes more detailed studies of their assembly at oil/water interfaces.

We are able to successfully synthesize magnetic nanoparticles, and are working on the synthesis of core-shell particles based on these.

## References Cited


1. "The amount and fate of the oil", National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling, Washington D.C., http://purl.fdlp.gov/GPO/gpo185, accessed: 11/30/10

   "Responding to Oil Spills in Coastal Marshes: The Fine Line Between Help and Hindrance", Hazardous Materials Response and Assessments Division National Oceanic and Atmospheric A dministration, http://response.restoration.noaa.gov/book_shelf/965_HelpHind.pdf, accessed: 11/30/10

2. A. Walther and A. Muller, Soft Matter, 2008, 4, 663
3. B. Binks, Current Opinion in Colloid & Interface Science, 2002, 7, 21
4. B. Binks et al., Langmuir, 2001, 14, 4708
5. M. M. Lin et al., Nano Reviews, 2010, 1, 4883
6. Hong, L.; Jiang, S.; Granick, S. "Simple method to produce Janus colloidal particles in large quantity," *Langmuir* **2006**, *22*, 9495-9499.
7. K. D. Hartlen A. P. T. Athanasopoulos and V. Kitaev, "Facile preparationof highly monodisperse small spheres (15 to > 200 nm) suitable for colloidal templating and formation of ordered arrays," Langmuir, vol. 24, pp. 1714-1720, 2008.
8. Jin Xie, Sheng Peng, Nathan Brower, Nader Pourman, Shan X.Wang, and Shouheng Sun *Pure Appl. Chem.*, Vol. 78, No. 5, pp. 1003–1014, **2006.**

# PUBLICATION

### 1. Articles in Refereed Scientific Journals

Ivanova, Nina, Nicole Zacharia, 2012, “Patchy Particle Synthesis via Capillary Condensation,” Colloids and Interfaces B, submitted.

### 2. Dissertations

Ivanova, Nina, 2011, Improved Synthetic Methods for Patchy Particles, "M.S. Dissertation," Mechanical Engineering, College of Engineering, Texas A&M University, College Station, TX, 75 pages.

### 3. Water Resources Research Institute Reports

Ivanova, Nina, Chungyeon Cho, Prasenjit Kar, Nicole Zacharia, 2012, Reusable Magnetic Janus Particle Scavengers for Environmentally Friendly Remediation of Contaminated Water Bodies, Name of WRRI, Texas A&M University, College Station, TX, 7 pages.