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# Atmospheric pressure plasma-assisted green synthesis of amphiphilic $SiO_2$ Janus particles

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ABSTRACT

A facile green approach for the synthesis of amphiphilic $SiO_2$ Janus particles using low temperature atmospheric pressure plasma is reported in this study. Monodispersed $SiO_2$ particles were masked by embedding half of their surface inside a polystyrene film. The exposed surfaces of the $SiO_2$ particles were readily modified using $He/CF_3CFH_2$ low-temperature atmospheric pressure plasma to obtain amphiphilic Janus particles. Their amphiphilic nature was confirmed using fluorescent microscopy by tagging their hydrophilic part with a fluorescent dye. The present method can be used to generate amphiphilic Janus particles with a variety of functionalities, which may find applications as surfactants and surface modifying agents.

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## Introduction

Janus particles are anisotropic and multifunctional materials (De Gennes, 1992; Panwar, Jassal, & Agrawal, 2015; Zhang et al., 2013). Amphiphilic Janus particles have two faces; one half of their surface is hydrophilic and the other half is hydrophobic. Amphiphilic Janus particles may be used to form kinetically as well as thermodynamically stable emulsions. The hydrophilic-hydrophobic balance of Janus particles can be tuned to suit a particular application. The concept of amphiphilic Janus particles was first mentioned by Pierre Gills de-Gennes in his Nobel lecture (De Gennes, 1992), and was followed by the theoretical and experimental study of amphiphilic Janus particles by Ondarçuhu, Fabre, Raphaël, and Veyssié (1990).

Amphiphilic Janus particles used for the stabilization of emulsions are reported to form a film/layer containing interstitial spaces at the interface of the two solvents, which can lead to chemical exchange in between the two phases (Kumar, Park, Tu, & Lee, 2013). Although homogeneous particles, being surface active, may get adsorbed at liquid–liquid or liquid–air interfaces, Janus particles, being both surface active and amphiphilic in nature, are able to form stable emulsions (Jiang et al., 2010). Further unlike homogeneous particles, Janus particles are reported to be surface active even for contact angles approaching 0° or 180° (Binks & Fletcher, 2001).

There have been several studies in the literature on the synthesis of amphiphilic Janus particles. Takahara et al. (2005) synthesized amphiphilic Janus particles by partial modification of the surface hydroxyl groups of $SiO_2$ particles dispersed in oil using alkylsilylation agents. Janus particles have also been synthesized using directional UV induced selective surface graft-polymerization/coupling reactions (Liu, Ren, & Yang, 2009) and by electrohydrodynamic co-jetting (Yoon, Kota, Bhaskar, Tuteja, & Lahann, 2013). Zhai, Li, He, Xiong, and Wang (2015) synthesized half-cauliflower amphiphilic Janus particles by a one-step emulsifier-free emulsion copolymerization. The Pickering emulsion method (Hong, Jiang, & Granick, 2006; Jiang & Granick, 2008), which is suitable for obtaining higher yields, has also been used for the synthesis of amphiphilic Janus particles. Recently, Wang, Feng, Ma, Yao, and Ge (2016) synthesized amphiphilic Janus particles by a combination of diffusion induced phase separation to form a double emulsion and magnetically driven dewetting. Although amphiphilic Janus particles based on $SiO_2$ have been synthesized by various methods, low temperature atmospheric pressure plasma, which is a green synthesis approach, has not yet been explored.

The use of plasma allows one-step gas phase reaction with small amounts of reactants, which makes it an environment-friendly process. Further, the reactions are limited to the surface, and hence do not affect the bulk properties of the reaction substrate. Among the various types of plasma employed, atmospheric pressure dielectric glow plasma has the ability to impart desired properties at

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rapid reaction rates. It also allows reactions to be carried out under ambient conditions and at low operation cost. However, the use of atmospheric pressure plasma to create functional groups from precursor molecules is a challenging area and has been explored to only a limited extent. Some studies have used plasma to carry out the modification of organic substrates to impart hydrophobicity or hydrophilicity (Panda, Jassal, & Agrawal, 2015, 2016; Samanta, Joshi, Jassal, & Agrawal, 2012; Surucu, Masur, Sasmazel, Von Woedtke, & Weltmann, 2016), improve dyeability (Elabid et al., 2016; Panda, Rastogi, Jassal, & Agrawal, 2012), and polymerize monomers on various surfaces (Garcia-Torres et al., 2014).

In the present study, we have synthesized micro- and nano-sized amphiphilic $SiO_2$ Janus particles using $He/CF_3CFH_2$ low-temperature atmospheric pressure plasma. This approach is versatile in nature and could also be used for the synthesis of other types of Janus particles by immobilizing base materials such as $SiO_2$ particles in various polymeric substrates.

## Experimental

### Materials

Tetraethyl orthosilicate (TEOS, ≥99%) and ethanol were purchased from Merck, Germany. Ammonia (25% aqueous solution) and toluene (≥99%) were purchased from Merck (Mumbai, India). 1,1,1,2-tetrafluoroethane ($CF_3CFH_2$, 99.999%), also commercially known as Floron, was supplied by SRF Ltd., India, and helium (99.999%) was supplied by Sigma Gases, India. Dibutyl tin dilaurate (95%), fluorescein isothiocyanate (FITC, 90%), and $SiO_2$ microparticles (5% aqueous suspension) of 3 μm in diameter were procured from Sigma Aldrich (Steinheim, Germany). Polystyrene (PS) of molecular weight ~68000 was procured from Supreme Petrochem Ltd. (Mumbai, India). Hydrophilic $SiO_2$ (Aerosil 200) and hydrophobic $SiO_2$ (Aerosil R 972) nanoparticles were procured from Evonik Industries (Essen, Germany). All of the reagents were used without further purification.

### Synthesis of amphiphilic $SiO_2$ Janus particles

Highly monodispersed $SiO_2$ particles of ~550 nm in diameter were prepared by the Stöber method, as reported in our previous studies (Panwar et al., 2015, 2016). Almost half of the surface of the $SiO_2$ particles was masked using PS using a method similar to that reported in the literature (Anderson et al., 2010; Jang, Choi, Heo, Lee, & Yang, 2008). A PS solution of 10 wt% concentration was prepared in toluene and spun coated on glass slides at 1200 rpm for 1 min. 50–100 μL of $SiO_2$ particles dispersed in ethanol at concentrations of 0.5 to 1 wt% were coated on the prepared PS films. The samples were dried at 90 °C for 10 min, followed by further heating at 135 °C for 3 h to allow partial embedding of the $SiO_2$ particles inside the PS film. The conditions used were selected based on a literature study by Jang et al. (2008), who reported a direct relationship between heating time and the penetration depth of $SiO_2$ particles in PS film.

The $SiO_2$ particles deposited on the PS film were treated with low temperature atmospheric pressure plasma, using helium and Floron gases. First, the reaction chamber was purged with helium gas at a rate of 0.6 SLPM (standard litre per minute) for 10 min. Thereafter, the flow rate of the helium gas was reduced to 0.3 SLPM and a voltage of 2 kV was applied for 1 min to generate helium plasma. A frequency of 15 kHz was used for the plasma treatment. Next, Floron gas was introduced into the plasma reactor at a rate of 0.05 SLPM and voltage was increased to 5 kV. Floron plasma treatment was carried out for 6 min at a true power of 70 W. The resulting Floron plasma treated $SiO_2$ particles were extracted by dissolving the PS film in toluene.

Similarly, Janus particles were also synthesized using commercially procured $SiO_2$ microparticles of 3 μm in diameter.

### Characterization

The surface morphology of the amphiphilic $SiO_2$ Janus particles was observed under a field emission-scanning electron microscope (FE-SEM) model Quanta 200 F from FEI, Netherlands. Elemental analysis was carried out using an energy dispersive X-ray (EDX) instrument from Oxford Instruments, UK (model X-max 80 $mm^2$) with INCA energy software.

Fluorescence imaging was carried out on an Eclipse E200 fluorescence microscope from Nikon Instruments Inc., New York, USA. The synthesized amphiphilic Janus particles were tagged with FITC for characterization by fluorescence imaging. A FITC solution was prepared by dissolving 10 mg FITC in 5 mL ethanol. 20 mg of amphiphilic $SiO_2$ Janus particles were added to the FITC solution, followed by addition of 10 μL dibutyl tin dilaurate. The sample was left in the dark overnight, after which the FITC tagged amphiphilic $SiO_2$ Janus microparticles were washed and redispersed in ethanol.

## Results and discussion

Monodispersed $SiO_2$ nanoparticles of ~550 nm in diameter were synthesized by the Stöber method. These and commercially obtained $SiO_2$ microparticles of 3 μm in diameter were used in synthesis of amphiphilic Janus particles. The coverage of $SiO_2$ particles on the PS film was controlled by optimizing the concentration of particles deposited. The concentration of the $SiO_2$ particle dispersion was varied from 0.5 to 1 wt%, and the volume of dispersion dropped onto the film was varied from 50 to 100 μL. It was observed that coating with 50 μL of 1 wt% $SiO_2$ particles resulted in a uniform

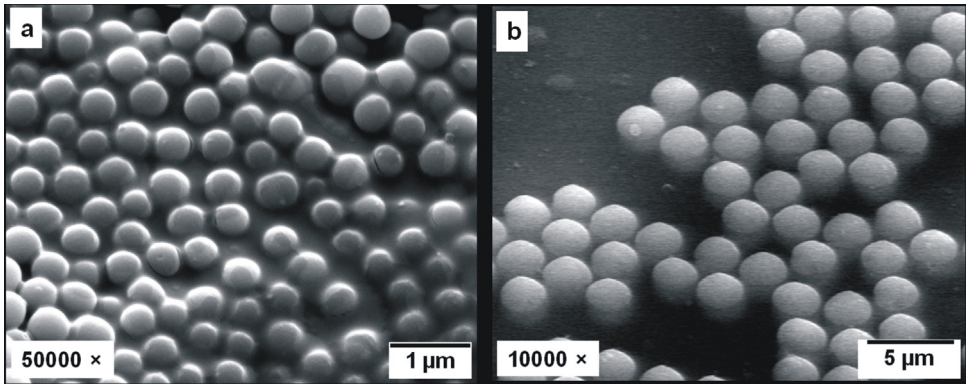


**Fig. 1.** SEM micrographs of $SiO_2$ (a) nanoparticles and (b) microparticles embedded in PS film.

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