CHEMISTRY OF MATERIALS
Article

Chem. Mater. **2010,** *22,* 3259–3264 3259
DOI:10.1021/cm100500d

Robust Plasma Polymerized-Titania/Silica Janus Microparticles

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Received February 17, 2010. Revised Manuscript Received April 16, 2010

We report on the universal fabrication of Janus microparticles from a wide variety of organic and inorganic components. The Janus particle fabrication described in this study details the synthesis of the highly cross-linked polymer nanocoatings on top of the partially embedded particles via plasma enhanced chemical vapor deposition. Here we conducted the plasma enhanced polymerization of different organic functionalized, reactive, responsive, and biomolecular materials ranging from acrylic compounds to organometallic molecules and aminoacids all directly on silica and titania microspheres, while using a masking technique to ensure that only a controlled fraction of the total particle surface area will be covered. This facile, fast, and scalable selected polymerization approach allows for single-face polymerization, generating organic−inorganic Janus particles which are robust and can be further converted into a variety of interesting mesoscale structures. Half-fluorescent, half-metal-decorated, and half-shelled structures were all demonstrated here as particular examples.

Introduction

Janus particles result from the assembly of two different components combined into a single unit along an interface which allows the design of multifaceted microparticles with unique directional interactions.[1,2] The dual nature of the particle's surface chemistry allows for their use in hierarchical assembly and is currently the subject of experimental studies which exploit Janus-guided assembly.[3−6] Many methods for creating Janus particles have been explored, covering a wide range of fabrication techniques from wet chemistry to microstamping.[7] These methods include both chemical and physical means of construction utilizing both self-organization and top-down fabrication. Some of the recent fabrication methods include deposition of modification layers to substrates via grafting to/from polymerization, self-assembly of copolymer and micelllar systems, vapor deposition techniques, layer-by-layer (LbL) assembly, microfluidic coflow, wax emulsion and microcontact printing, all of which are capable of creating a wide variety of Janus particles in different sizes and chemical compositions.[8−16]

Additional types of particles, such as amphiphilic Janus particles, can be obtained via ligand-exchange reactions.[17] These particles can spontaneously assemble in solution as a result of interactions between their functional groups.[18] Reversible self-aggregation into regular monodispersed supermicelles has also been observed in amphiphilic Janus particles.[19] Another example involving the self-assembly of zwitterionic Janus particles in aqueous solutions showed the formation of charge-equilibrated aggregates caused by the charge asymmetry of individual particles.[20] Asymmetric functionalization was applied to polystyrene particles coated with multilayered films and stamped with polycations on the negatively charged particles. After dissolution from the polystyrene core,

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this yielded zwitterionic hollow Janus microcapsules.[21] In addition to spherical Janus particles, discs, cylinders, and other biphasic structures have also been fabricated.[22,23] Other intriguing examples of complex, structured particles and "patchy" microparticles decorated with gold nanodots have been assembled by Grzybowski and Möhwald.[24,25]

Janus particles with a distinct biphasic chemistry combined in a single structure, are of interest since they possess both the physical and chemical properties of each phase present and thus display interesting assembling behavior not only in mixed solutions but also at interfaces.[17,26−29] Assemblies of Janus particles result in minimized interfacial energy and corresponding spontaneous aggregation of particles into clusters with well-defined aggregation numbers and symmetries, not just simple strings.[20,30] These unique anisotropic interactions and assembling properties offer Janus particles great potential in a wide range of applications which require mesoscale ordering of microparticles such as prospective drug carriers, emulsion stabilizers, electronic paper matrices, anisotropic plasmonic materials, and anisotropic imaging probes for both diagnostic and therapeutic purposes.[16,31−37]

Toposelective modification methods have been previously used to coat microparticles, and are commonly used with a surface masking technique to prepare Janus particles.[13,15,38−40] While all of these techniques are able to create bifunctional particles of a variety of sizes, some processes suffer from tedious multistep fabrication, low yields of functional particles, and problematic stability of these particles. It is our aim to provide a toposelective method for the facile fabrication of Janus particles. Certain inherent material characteristics may result in a limited range of applicable chemistries and surface functionalities which can limit the general applicability of a specific fabrication technique.

Generally, chemical vapor deposition gives access to a host of different functionalities that can be used in solid microspheres, not available with traditional wet-chemistry approaches.[41] Using a more sophisticated version, plasma enhanced chemical vapor deposition (PECVD), the surface modifying material can be deposited across the entire substrate, coating the microparticles and masking layer. The plasma polymerized coatings are usually chemically grafted to the particle surfaces with a properly selected composition.[42,43] PECVD has been shown to rapidly create robust polymerized coatings of many different materials on a variety of surfaces and thus can be extended as a universal method in the fabrication of many types and compositions of Janus particles simultaneously without tedious prior surface modification, multiple functionalization steps, or a slow buildup of the "second face".[44−48]

Here, we report on universal fabrication of Janus microparticles from a wide variety of organic and inorganic components. Specifically, we utilize plasma polymerization to deposit different monomers onto the exposed surfaces of the partially embedded microspheres of titania and silica to demonstrate facile and robust preparation of organic−inorganic Janus particles. We highlight examples of acrylonitrile, pyridine, and ferrocene materials, all of which are readily able to be deposited by plasma deposition and represent examples of functional nanocoatings with the ability to further covalently graft or tether other materials to the particles and to act as redox-active and responsive coatings.[49,50] This study is based on our previous experience with planar PECVD polymerization, which can be applied to a range of surfaces and generates unique robust conformal coatings.[51] This allows different physical and chemical properties to be imparted to the surface of the inorganic microparticles and microstructures.[52−57]

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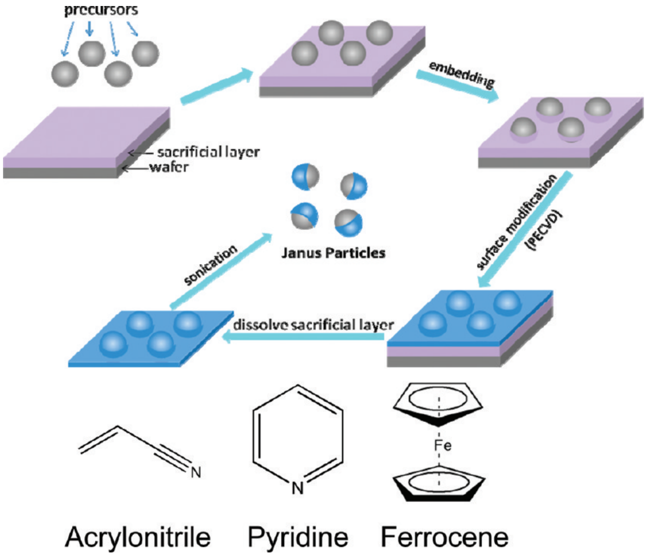

Figure 1. Janus particles fabrication using a sacrificial layer to embed the particles prior to plasma polymerization. Upon dissolution of the PS layer, the particles are released with a characteristic half coating. Chemical structures of selected monomers are presented as well.

Experimental Section

Polystyrene (PS, $M_w = 250\,000$) and toluene were purchased from Janssen Chimica and J.T. Baker. SiO_2 particles with diameter of 3 μm, and TiO_2 particles with diameter of 3 μm were purchased from Microspheres-Nanospheres Corpuscular Inc. The PS was dissolved in toluene at low concentration and spun coated onto a silicon substrate cleaned via piranha solution (caution! 3:1 conc. H_2SO_4 and 30% H_2O_2). Variations in the concentration of the PS solution and spin coating speed were used to prepare sacrificial layers of different thicknesses. A spin speed of 1500 rpm at solution concentration of 12 wt % was used to fabricate layers from 1.4 to 1.6 μm in thickness. The thicknesses of the spin-cast PS films were measured using ellipsometry and an AFM scratch test. The microparticles were suspended in ethanol to form a dilute solution concentration (about 1 mg/mL) which was then cast on the PS film. A drop of the solution (100 μL) was placed on the PS coated wafer and allowed to dry. After casting of particles on the PS film, the system was heated to 135 °C for 3 h and then slowly cooled to room temperature. This process allowed the particles to partially sink into the PS layer (Figure 1). To embed them further in a controllable manner, additional calibrated hydrostatic pressure must be applied uniformly. This procedure was done by placing a clean 5×5 cm^2 silicon wafer with a small weight on top on top of the specimen to distribute force evenly. In this instance, a 150 g mass was evenly distributed through the plate to the particle surface, where the particles were dispersed on a 2×1 cm^2 silicon wafer. However, it is advisible that the pressure applied be determined experimentally for each case as it is highly dependent on the viscosity of a particular PS solution, the size of the particle, and the temperature at which it being heated.

The monomers acrylonitrile, ferrocene, and pyridine were purchased from Aldrich and used as received. Plasma depositions of these monomers were carried out in a custom built PECVD vacuum chamber according to established procedure.[58] Liquid monomers were placed in a sealed tube connected to the reaction chamber and vaporized directly into the plasma stream. Solid monomers were directly sublimed into the plasma stream by heating the monomer in a tantalum crucible in the reaction chamber.[51,59] Plasma depositions were carried out using 13.56 MHz RF plasma in a low pressure argon atmosphere. The pyridine and acrylonitrile were deposited under identical conditions at a chamber pressure of 6.7 Pa, 30 W of power applied to the plasma, and an argon flow rate of 10 cm^3/min. The plasma was run for 5 min. The ferrocene was deposited under modified conditions since it was done via sublimation. A pressure of 2.7 Pa was used with an applied power of 45 W. The argon flow rate was 20 cm^3/min and exposure time was 12 min. The ferrocene was heated to approximately 120 °C for sublimation.

After toposelective modification with plasma polymerization, the microparticles were washed with hot toluene (50 °C) and centrifuged six times, each time removing the supernatant, to remove all PS from the particles. The particles were then sonicated to help separate particles which may have agglomerated. Upon completion of the sonication, the particles were suspended in toluene and cast on a clean silicon wafer substrate for characterization.

The fluorescent dye fluorescein isothiocyanate (FITC) was purchased from Fluka, which was then dissolved in ethanol and used as the dying solution. The SiO_2−ACN Janus particles were placed in the dye solution for 8 h and then washed with ethanol several times. The solution was sonicated for 30 s before washing with ethanol. The silver nanoparticles, with average diameter 30 nm, were prepared according to the literature.[60] The TiO_2−pyridine Janus particles were placed in a solution of silver nanoparticles for 3 h to ensure selective adsorption on pyridine surface and washed with Nanopure water several times.

A Woolam M2000U spectroscopic ellipsometer with WVASE32 modeling software was used to measure the thickness of the PS layers. The measurement was carried out at three incident angles of 65°, 70°, and 75° within a wavelength range from 245 to 1000 nm. Measurements of the morphology of precursor embedded in sacrificial layer and the result Janus particles were carried out on either a LEO 1530 FE or S-3400 N Hitachi scanning electron microscopes (SEM) with operation voltage of 5 kV. All the samples were sputtered with gold. INCA energy dispersive X-ray spectroscopy (EDX) was used in conjunction with the SEM scans to determine the chemical composition. The solution of particles was drop-cast on the surface of a silicon wafer. The samples were sputtered with gold layer before SEM imaging.

AFM imaging was done using a Digital Instruments (DI) 3000 microscope with a Nanoscope IIIa controller.[61,62] Light tapping mode was used in air with triangle cantilevers (MikroMasch) with a nominal resonance frequency of 350 kHz and spring constant of 40 N m^{-1}. The confocal fluorescent microscope images were recorded via a Carl Zeiss Laser Scanning Microscope LSM 510 with FITC reflector and objective of Fluar 40*/13 and plan-Neofluar 63*/1.25 oil.

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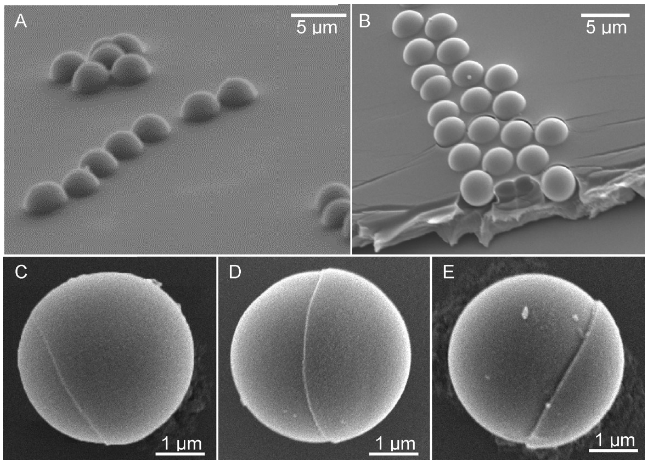

Figure 2. (A) SEM image of 3 μm silica particles half embedded in PS layer. (B) Embedded particles at typical depth in the PS layer. (C−E) Janus particles with controlled coating coverage: 3/4, 1/2, and 1/4 coverage of particles with acrylonitrile on silica microspheres.

Results and Discussion

This masking technique utilized in this study was adapted from a fabrication process available in the literature (Figure 1).[38] The masking process was begun by spin coating a sacrificial PS layer on a clean silicon substrate to a desired thickness close to the diameter of the microparticles (3 μm), which can be varied from 0.2 to 3.0 μm depending on the embedding level targeted.

By varying the thickness of the PS layer, the masked areas of the spheres can be tailored to cover varying portions of the particles surface (Figure 2). After the silica and titanium dioxide microparticles were embedded in the PS layer, selected materials could be effectively plasma polymerized on open surface areas. The residual PECVD film is removed during rinsing and sonication since the free-standing film is not tethered to a surface. Because the film is thin, the particles can easily break from the free-standing film after the sacrificial layer is dissolved.

These selective plasma polymerized coatings remain firmly attached to the particles as the sacrificial polystyrene layer was dissolved and the Janus particles were released (Figure 2). The coverage areas of the particles with the polymerized coatings can vary over a wide range: from a high ratio of up to 75% of the area coated (Figure 2c) to an equal ratio with approximately 50% coated area (Figure 2d), and to very low, down to 25% coated (Figure 2e). The protect-and-release method proves to be a critical step and can be applied in a number of different fabrication scenarios. Embedding the microparticles into an easily removable sacrificial layer facilitates the protection of the embedded portion while allowing further modification to the exposed portion. This leaves the protected portion of the particle clean for further modification later. By utilizing dissolvable polymer layers of different thicknesses, the microparticles can be easily coated to a controlled degree of surface coverage through toposelective modification before final release of the modified particles through dissolution of the masking layer.

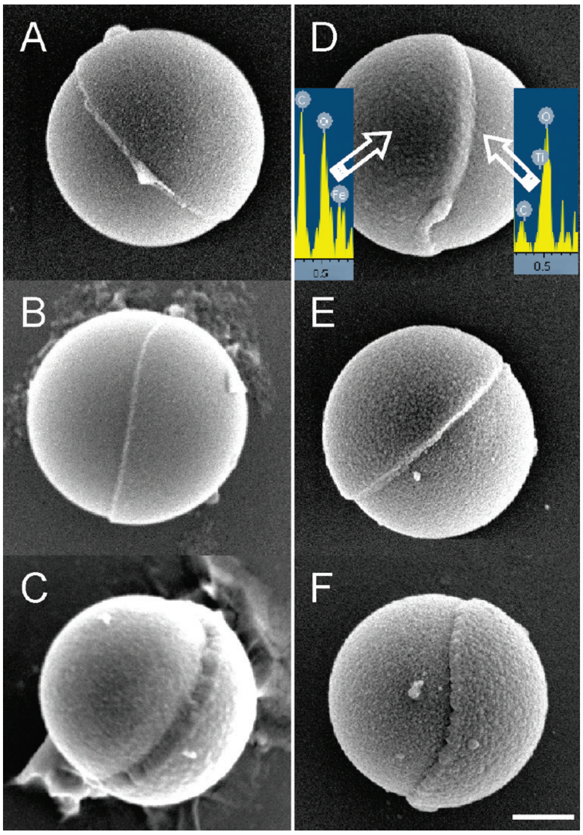

Figure 3. (A−C) SEM images of various coatings on silica and (D−F) titania microparticles via plasma polymerization: (A and D) ferrocene; (B and E) acrylonitrile, and (C and F) pyridine coatings. Representative EDX spectra (insets, D) showing presence of iron and excess carbon on one side of the particle. Scale bar 1.0 μm for all images unless noted.

SEM imaging of individual microparticles shows selective, one-face deposition on their surfaces with half of the particles clearly having additional coatings with distinct morphology and thickness (Figure 3). Images of PECVD-fabricated ferrocene, acrylonitrile, and pyridine on 3 μm silica spheres show a partial plasma polymerized polymer coating covering approximately 50% of the total surface area of the particle with a well-defined boundary (Figure 3). The same monomers were deposited with similar results on 3 μm titania microparticles as well (Figure 3D−F). On both types of particle explored here, the plasma polymerized coating is seen to be conformal to the surface with a sharp delineation between the plasma polymerizaed region and the bare silica/titania region that was masked. Estimation of the thickness of the plasma polymerized layer on the microparticles from the images reports the value of within 200−300 nm, which is consistent with expected film thickness of a typical plasma deposition of the same material on a flat substrate under similar conditions.[54,63,59]

Composition analysis of the plasma polymer coatings on the Janus particles shows the polymerized materials were deposited as expected. EDX shows iron is present on the coated side, along with an increase in carbon from the ferrocene material (Figure 3D; see EDX spectra for all

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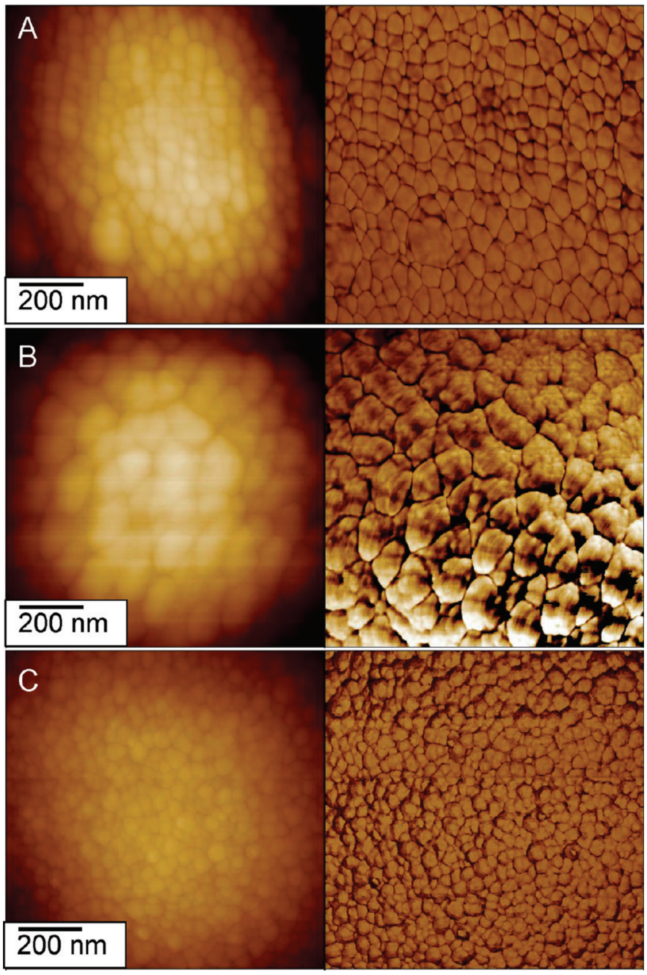

Figure 4. AFM topography (left) and phase (right) of plasma coatings on microparticles. (A) Ferrocene (AFM *z* scale = 200 nm, 50°); (B) acrylonitrile (AFM *z* scale = 100 nm, 50°); (C) pyridine (AFM z scale = 130 nm, 60°).

samples in the Supporting Information). In the case of pyridine, both nitrogen and increased carbon signals were present as expected. Acrylonitrile coating also showed an increased carbon content for polymerized region. AFM topography scans of a $1 \times 1\ \mu m^2$ area are shown for polymerized regions (Figure 4A−C). All images show a uniform surface morphology of the different plasma polymerized coatings with a characteristic fine, grainy surface morphology free of microscopic defects.[51−53] This indicates the presence of a complete, uniform layer, which conformally coats on the designated and highly curved surface areas.

Different plasma polymerized coatings can be employed for the selective reduction of metal nanoparticles, site-selective grafting, potential biological activity, and generating distinct optical response as briefly discussed below. The Janus particles with the ACN coating were placed in a fluorescent dye solution and were seen as half particles under confocal fluorescent microscopy due to the selective grafting of the fluorescent dye molecules to the highly reactive polymer coating (Figure 5A and B). This is seen as regions of bright and dark green on the particles, where the brighter regions fluoresce under the incident light more readily when located on a surface in a higher concentration. The darker region has subsequently less fluorescent dye present and is not illuminated to the degree which the polymer coated regions are. We also demonstrated that the pyridine coated Janus particles can serve as templates for further modification with citrate-modified silver nanoparticles which selectively were adsorbed and firmly grafted to the reactive pyridine surface in greater numbers in contrast to the uncoated silica portion of the Janus particle (Figure 5C; see EDX and comparison with LbL coated Janus particles in the Supporting Information).

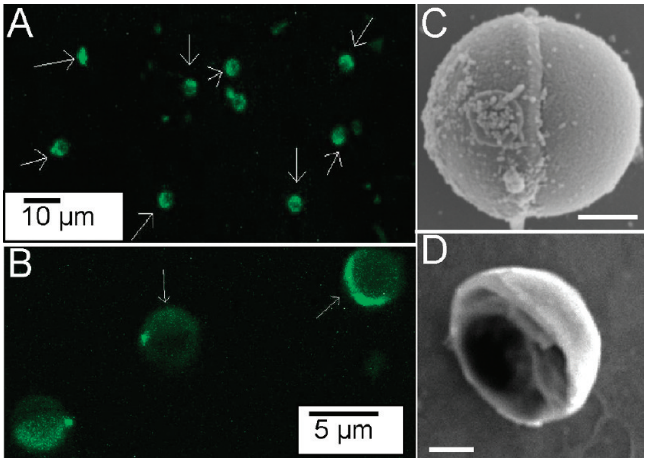

Figure 5. (A and B) Half-fluorescent Janus particles with selectively grafted dye molecules. Arrows indicate fluorescently labeled regions of the particles. (C) Pyridine-coated Janus particle with selectively tethered silver nanoparticles. (D) Free-standing plasma polymerized half-shell of pyridine. Scale bars are 1 μm.

Selective particle absorption and reduction may be extended to include many different inorganic materials mineralized via biologic molecules such as amino acid and protein coatings on the Janus particle.[64] To this end, in our preliminary studies, we successfully polymerized two representative aminoacids, tyrosine, and histidine, thus creating biomolecular Janus particles (see the Supporting Information). Finally, robust half-shell, free-standing polymerized structures can be obtained upon the release of inorganic cores (Figure 5D). This shows that the plasma polymerized coatings covering the microspheres can be released, without damage, as robust half-shells which can undergo release, drying, and transfer to high vacuum without losing their original shape. These half-shelled structures demonstrate the robust nature of plasma polymerized films, showing their ability to be self-supporting and stable through ultrasonication cycles and during release.

General Conclusions

The Janus particles detailed here represent a selected portion of many systems tested and have, thus far, shown the highest potential for further utilization. Further work can been done with other types of coatings providing for biological activities and biomineralization including

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plasma polymerized amino acids on embedded particles. This highlights the universal nature of the plasma polymerization approach to the fabrication of robust organic/inorganic Janus particle covering a broad range of functionalized and biological materials. While this fabrication method is limited to the surface (2D) fabrication regime, we are able to estimate that the simultaneous construction of up to 10^8 particles is possible, based on the size of the particles, substrate, and the density with which the particles are coated on the surface. This shows a significant increase in the number of particles over other methods which are usually used on a smaller or even single particle scale. We demonstrate that this facile, fast, and scalable approach allows for selective, one-face polymerization on embedded particles, generating functionalized organic–inorganic Janus particles which are robust and can be further converted to two-faced structures by covalent grafting and selective nanoparticle adsorption. With the wide range of material species able to be deposited through PECVD, it provides a universal fabrication approach to coated Janus particles. Moreover, PECVD will allow the coverage of a relatively large surface area with complex topologies when compared to conventional microprinting with planar stamps. It also does not require chemical rinsing, solvent compatibility with microparticles, or drying after deposition. By employing a universal toposelective method, we show this as a viable fabrication method.

Plasma coating of many spherical particles at once demonstrates a facile fabrication method for the creation of Janus particles on hard inorganic spheres. While we developed the process described using silica and titanium dioxide microspheres ($\sim$3 μm diameter), this technique can be applied to a wide range of substrate materials since plasma polymerization has been shown to be compatible with a variety of substrates. We have demonstrated the fabrication of Janus particles with many different materials which can be readily deposited on a variety of microparticles and surfaces through the plasma polymerization process. This allows us the means for the fabrication of Janus particles of varying sizes and composition, without the need for extensive and tedious wet chemical synthesis, electrostatic assembling, microprinting, or to modify the microparticles' surfaces.

One-step plasma polymerization on large areas allows us to generate Janus particles rapidly and with multiple coatings of materials as derived from the advanced interfacial structures seen. Using the plasma deposition technique, a wide variety of material systems can be used to create Janus particles with a large range of surface chemistries for different applications. Indeed, examples of five different reactive organic monomers ranging from conventional acrylic compounds to organometallic molecules and aminoacids all were utilized successfully. Finally, half-fluorescent, half-metal-decorated, and half-shelled structures all are demonstrated as examples in the current study.

Acknowledgment. This work was supported by AFOSR, AFRL, and DOE. The authors thank Hao Jiang and Jesse Enlow for technical assistance with plasma depositions and Joseph Slocik, Srikanth Singamaneni, Tolecia Clark, and Eugenia Kharlampieva for useful discussions and assistance.

Supporting Information Available: Additional SEM and XPS data. This material is available free of charge via the Internet at http://pubs.acs.org.