Conversion of Pollen Particles into Three-Dimensional Ceramic Replicas Tailored for Multimodal Adhesion

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ABSTRACT: We report the first syntheses of three-dimensional (3D) nanocrystalline all-oxide replicas of pollen microparticles tailored for multimodal (bioenabled and synthetic) adhesion via use of a scalable, highly conformal surface sol–gel (SSG) coating process. High-fidelity replication allowed the pollen-shaped oxide microparticles to be utilized for adhesion via tailorable short-range (∼10 nm) van der Waals (VDW) attraction, with the magnitude of such VDW-based adhesion influenced by the nanoscale topography of surface features retained by the replicas. Conversion of the pollen into ferrimagnetic (Fe3O4) microparticle replicas allowed the use of magnetic attraction at short and long ranges (up to ∼1 mm). By selecting pollen particles with particular surface features and by SSG-enabled conversion of such pollen into 3D nanocrystalline replicas composed of an appropriate type and amount of magnetic oxide, adhesive microparticles with tunable short- and long-range attractive forces can be generated.

KEYWORDS: surface sol–gel coating, pollen, three-dimensional replicas, magnetic oxides, van der Waals, adhesion

INTRODUCTION

Adhesion by or on microparticles plays a critical role in a wide range of developing and mature technologies, including drug delivery, catalysis, water/chemical purification, sensing, anti-fouling coatings and membranes, semiconductor device processing, composite processing, paints, printing, and xerography.1 Although predominant models and mechanistic experimental studies for understanding adhesion have been based on smooth spherical particles,2 microparticles with rough surfaces and nonspherical shapes are desired for a number of such technologies. However, the scalable fabrication of microparticles with well-controlled surface asperities in a variety of three-dimensional (3D) morphologies and with tailorable chemistries to allow for tunable adhesion remains a difficult synthetic challenge.

A rich sustainable source of 3D microparticles, with complex morphologies affecting dispersion and adhesion in nature, is pollen. Pollen particles come in a wide variety of 3D shapes and surface topographies3 and are produced in large and increasing quantities worldwide by plants.4 Atomic force microscopy (AFM)-based adhesion measurements have recently5 shown that the van der Waals (VDW) attraction of pollen particles to various inorganic and organic surfaces scales directly with the contact radii of asperities on the pollen surface; that is, the selection of pollen particles with particular surface structural features may be used to affect such VDW-based adhesion. The purpose of the present article is to show, for the first time, how such pollen particles may be converted into 3D ceramic replicas endowed with tunable multimodal adhesion. In this demonstration, native pollen particles have been converted, via the use of a highly conformal surface sol–gel (SSG)-coating process,6 into 3D replicas composed of ferromagnetic hematite (α-Fe2O3) or ferrimagnetic magnetite (Fe3O4). The nanoscale surface topography and the magnetic oxide content of such high-fidelity replicas can provide for multimodal attraction to surfaces via both short-range VDW and short-to-long-range magnetic forces. Although other authors have used coating or infiltration methods to chemically modify/transform pollen7 and other biological microparticles8 for desired (bio)chemical, optical, electrical, structural, or fluidodynamic properties, the conversion of sustainable biogenic particles (like pollen) into all-inorganic 3D replicas for the purpose of achieving tunable multimodal adhesion has not been reported.

EXPERIMENTAL SECTION

Pollen Preparation. The conversion of sunflower (Helianthus annuus) pollen (Greer Laboratories, Lenoir, NC) into iron oxide replicas has been examined in this work. The pollen grains were first...
cleaned by immersion in a mixture of chloroform and methanol (3:1) for 24 h followed by deposition onto filter paper (PS, Fisher Scientific, Pittsburgh, PA) and drying under vacuum at 60 °C for 12 h. A second immersion was conducted in 1 M hydrochloric acid (VWR, Suwanee, GA) for 1 h to remove residual inorganic material followed by rinsing three times with deionized water and drying by vacuum aspiration at room temperature for 5 min.

**Computer-Automated LBL SSG Deposition.** Fe−O-bearing coatings were applied to cleaned pollen grains via a computer-automated, layer-by-layer (LBL) SSG-deposition process. For the first step of a given SSG cycle, pollen grains were immersed for 10 min with stirring in a solution of 0.0125 M Fe(III) isopropoxide (Alfa Aesar, Ward Hill, MA) in anhydrous 2-propanol (>99.8% purity, Acros Organics, Geel, Belgium) to allow the chemisorption of a Fe−O-bearing layer. After rinsing three times with anhydrous 2-propanol and vacuum filtration, the pollen grains were immersed in deionized water (DIW) with stirring for 5 min to allow for the hydrolysis of the chemisorbed alkoxide layer. The grains were then rinsed three times with anhydrous 2-propanol, vacuum filtered, and dried by vacuum aspiration for 5 min. This process (alkoxide exposure, 2-propanol rinsing, DIW exposure, 2-propanol rinsing, and drying) was repeated for a total of 30 cycles to build up a Fe−O-bearing coating.

**Thermal Processing.** The coated pollen particles were heated in air at 0.5 °C min−1 to 600 °C and held at this temperature for 4 h to allow for organic pyrolysis and oxide crystallization. The resulting hematite replicas were converted into maghemite via thermal treatment with a Rhines pack11 powder mixture of Fe (99% purity, Acros Organics) and Fe3O4 (99.5% purity, Alfa Aesar). The hematite pollen replicas were sealed along with the Fe/Fe3O4 powder mixture (Fe/Fe3O4/Fe2O3 replica mole ratio = 14:14:1) inside a mild steel ampule. The sealed samples were then heated at 3 °C min−1 to 550 °C and held at this temperature for 2 h. After cooling to room temperature, the ampules were cut open, and the magnetite pollen replicas were extracted.

**Substrate Preparation and Characterization.** Six types of substrates were utilized for adhesion studies: silicon (Si), poly(vinyl alcohol) (PVA), poly(vinyl acetate) (PVAc), polyurethane (PS), nickel (Ni), and a nickel-coated neodymium (Ni−Nd) alloy. The Si substrates (Silicon, Inc., Boise, ID) were piranha-etched using a solution of 75 vol % sulfuric acid (97% purity, BDH Chemicals Ltd., Radnor, PA) and 25 vol % hydrogen peroxide (30 wt %, BDH Chemicals Ltd.) at 80 °C for 1 h. The polymer substrates (PVA, PVAc, and PS) consisted of blade-cast polymer films on the cleaned Si substrates. For blade casting, solutions composed of 15 wt % PS (MW = 100,000, Avocado Research Chemicals, Lancashire, UK) in toluene (Sigma-Aldrich, St. Louis, MO), 20 wt % PVAc (MW = 50,000, Alfa Aesar) in tetrahydrofuran (THF, BDH Chemicals Ltd.), or 3 wt % PVA (MW = 89,000–98,000, Sigma-Aldrich) in hexafluoropropionic anhydride (HFIP, TCI America, Portland, OR) were used. Blade casting (3540 Bird Film Applicator, Elcometer, Rochester Hills, MI) was conducted using a gap height of 1.2 mm followed by slow drying under a saturated solvent environment for 2 days at 23 °C. The films were then air-dried for 2 days at 23 °C followed by annealing in a vacuum oven for 1 day at 100 °C. The resulting polymer films possessed thicknesses ranging from 20 to 100 μm and completely covered the underlying Si substrate. Ni substrates were prepared by polishing (PMS System, Logitech Ltd., Glasgow, Scotland) nickel foil (0.150 mm thickness, grade 200, 99.5% purity, Shop-Aid, Inc., Woburn, MA) to a surface roughness of 0.06 μm using a colloidal SiO2 suspension (Metlab Corp., Niagara Falls, NY). The Ni−Nd substrate consisted of an axially poled, neodymium−iron−boron alloy permanent magnet disk (ND022N-35, 5 mm diameter, 1.5 mm thick, Master Magnetics, Inc., Castle Rock, CO) onto which was attached the polished nickel foil.

The substrate roughness of each type of substrate was evaluated with a scanning probe microscope (Dimension 3100 SPM equipped with a Nanoscope V Controller, Veeco Instruments, Inc., Plainview, NY) operated in tapping mode at 200−400 kHz using a pyramidal tip silicon cantilever (Applied NanoStructures, Inc., Santa Clara, CA). For each particular substrate, three randomly located scans (10 × 10 μm2) were conducted, with each scan area split into four sectors. The average roughness value for a given substrate was obtained from analysis of these 12 sectors.

**Pollen and Pollen Replica Characterization.** Scanning electron microscopy was conducted with a field-emission gun instrument (Carl Zeiss SMT, Ltd., Thornwood, NY) equipped with an energy-dispersive X-ray spectrometer (INCA EDS, Oxford Instruments, Abingdon, Oxfordshire). The average spine tip radii of cleaned sunflower pollen particles and of oxide replicas of sunflower pollen particles were obtained from secondary electron (SE) images of particles attached to cantilever probes (described below). For each particle-bearing probe, five spine tips located closest to the position where the particle made contact to the substrates were evaluated (for a total of 15 analyzed spine tips for all three similar types of particle-bearing probes). X-ray diffraction (XRD) analyses were conducted with Cu Kα radiation using a diffractometer (X-Pert Pro Alpha , PANalytical, Almelo, The Netherlands) equipped with an incident beam Johannsen monochromator (PANalytical) and an Xcelerator linear detector (PANalytical).

**Adhesion Measurements.** Adhesion measurements were conducted using colloidal probes consisting of a single particle (a native sunflower pollen particle or oxide replica particle) attached to an atomic force microscope (AFM) cantilever. A small amount of epoxy resin (Epoxy Marine, Locctite, Westlake, OH) was used to attach a given particle to a tipless silicon AFM cantilever (FORT-TL, Applied NanoStructures, Inc.). For each type of pollen-shaped particle (cleaned sunflower pollen, α-FeO2 replica, or Fe3O4 replica), three single-particle-bearing cantilever probes were prepared (for a total of nine particle/cantilever probes). The spring constants, as determined with the scanning probe microscope, of the sunflower-pollen-bearing, α-FeO2 replica-bearing, and Fe3O4 replica-bearing cantilever probes fell in the ranges of 1.84−2.34, 1.19−1.91, and 1.63−1.69 N/m, respectively. The adhesion force between an individual sunflower pollen particle or an oxide replica particle and a particular substrate was evaluated with the scanning probe microscope operated in contact mode. For each particular particle/cantilever probe and particular substrate, 20 separate force−distance scans were randomly obtained, and the depth of adhesion wells upon retraction were averaged. The load force applied during the contact adhesion measurements was 2.5 nN. The ambient relative humidity in the laboratory during the adhesion measurements ranged from 30 to 35%.

## RESULTS AND DISCUSSION

Sunflower pollen particles were converted into magnetic oxide replicas via use of a computer-automated LBL SSG-coating process. Secondary electron (SE) images of a starting cleaned pollen grain are shown in Figure 1a. The sunflower pollen grains were roughly spherical in shape and possessed echini (spines) of relatively high aspect ratio (height/width-at-midheight ratio of ~5:1). Because the exine (outer layer) of such pollen grains is composed of sporopollenin (a complex polymer consisting of carboxylic acids and aromatic moieties cross-linked with aliphatic chains), the pollen surfaces were enriched with hydroxyl groups that provided an abundance of reaction sites for the chemisorption of alkoxide precursors during the SSG-coating process. Repeated, alternating exposure of the pollen particles to an iron(III) isopropoxide precursor and to water allowed for the progressive buildup of a conformal Fe−O-bearing coating on the pollen grains. A SE image and energy-dispersive X-ray (EDX) analysis of a sunflower pollen particle after exposure to 30 SSG-deposition cycles are shown in Figures 1b and 2b, respectively. Comparison of the EDX analyses in Figures 2a and 2b confirmed that the SSG-coated particle was enriched in iron and oxygen. The highly conformal nature of the SSG Fe−O-bearing coating was evident from the preservation of the echini and the fine pores at the base of the echini (as indicated by the arrows in Figure 1b).
The coated pollen particles were then heated in air at 600 °C for 4 h to allow for pyrolysis of the pollen template and crystallization of the oxide coating. Complete pyrolysis of the sporopollenin during this treatment was confirmed by thermogravimetric (TG) analysis (Figure 3). (Note that TG analyses, presented in Figure S1 in the Supporting Information, conducted on Fe–O-coated sunflower pollen specimens revealed that the amount of oxide retained after complete pyrolysis increased linearly with an increase in the number of SSG deposition cycles, which was consistent with a progressive linear buildup in the amount of Fe–O deposited with each SSG cycle.) EDX analyses (Figure 2c) also revealed the loss of carbon and retention of iron and oxygen after such pyrolysis. X-ray diffraction (XRD) analysis (Figure 4a) indicated that these fired particles were composed of phase-pure nanocrystalline hematite (α-Fe2O3). Scherrer analyses of the XRD peaks yielded an average hematite crystallite size of 35 nm. Although smaller in diameter than the starting as-coated pollen particles (by about 40%, Table S1), these hematite particles retained the

Figure 1. SE images of sunflower pollen particles at various stages of conversion into Fe3O4: (a) the exine of a natural grain, (b) an Fe–O-coated grain after 30 SSG-deposition cycles, (c) an α-Fe2O3 replica of the same grain in panel b after pyrolysis at 600 °C for 4 h in air, and (d) a Fe3O4 replica of the same α-Fe2O3 grain in panel c generated by partial reduction using a Rhines pack (Fe/Fe3O4 powder mixture) at 550 °C for 3 h. (Note that the Al peak was obtained from the underlying aluminum stub used to support the particles during EDX analyses.)

Figure 2. EDX analyses of (a) the exine of a natural sunflower pollen grain, (b) an Fe–O-coated sunflower grain after 30 SSG-deposition cycles, (c) an α-Fe2O3 replica of a sunflower grain generated by pyrolysis at 600 °C for 4 h in air, and (d) a Fe3O4 replica of a α-Fe2O3 grain generated by partial reduction using a Rhines pack (Fe/Fe3O4 powder mixture) at 550 °C for 3 h. (Note that the Al peak was obtained from the underlying aluminum stub used to support the particles during EDX analyses.)

Figure 3. TG analysis of Fe–O-coated sunflower pollen during pyrolysis by heating in air at 5 °C min\(^{-1}\) to 600 °C.
3D shapes and surface features of the starting pollen grains (Figure 1c). Indeed, the high-fidelity nature of such replication was revealed by SE images of the same particle before (Figure 1b) and after (Figure 1c) the 600 °C/4 h treatment. (Note that the arrows in Figure 1b,c reveal the same spine and fine pore present before and after this thermal treatment.) SE images of fracture cross sections of hematite pollen grain replicas (Figure S2) revealed that the walls of such replicas were porous and were composed of interconnected oxide filaments. The interconnected nature of the oxide filaments running through the wall thickness and the absence of a distinct hollow core within the replica wall indicated that the sporopollenin wall of the native pollen grains had been infiltrated by the iron isopropoxide precursor during surface sol–gel deposition. The average thickness of the porous wall of the hematite replicas was 540 nm.

Conversion of the hematite replicas into magnetite was conducted via use of a thermal treatment with a Rhines pack. An excess powder mixture of iron and magnetite was sealed along with hematite pollen replicas within a mild steel ampule. The ampule was then heated at 550 °C and held at this temperature for 2 h. The oxygen partial pressure established within the ampule by the Fe/Fe3O4 equilibrium at 550 °C (note that wüstite, Fe1−xO, is thermodynamically unstable below 570 °C) allowed for complete conversion of the replica particles into phase-pure nanocrystalline magnetite, as confirmed by XRD analysis (Figure 4b). Scherrer analyses yielded an average magnetite crystallite size of 34 nm. SE images (Figure 1d) indicated that the 3D morphology and sharp echini of the sunflower pollen were retained by the magnetite replicas. (Note that the arrows in Figure 1c,d show the same spine and fine pore before and after this Rhines pack thermal treatment.) No detectable change in replica particle size was detected upon conversion of the hematite into magnetite, which was consistent with the similarity in the volumes of these oxides on a per mole of iron basis (15.2 cm³ Fe₂O₃/mol Fe; 14.9 cm³ Fe₃O₄/mol Fe).

To allow for quantitative evaluation of the adhesion of the sunflower pollen and oxide pollen replicas to various substrate surfaces, the pollen and replica particles were attached to AFM cantilevers (Figure S) using a procedure described previously. Six substrates were chosen to analyze the effects of substrate surface chemistry and magnetic properties on particle attraction. Poly(vinyl alcohol) (PVA) and poly(vinyl acetate) (PVAc) were selected as model proton-donor and proton-acceptor substrates, respectively. Polystyrene (PS) was chosen as a model apolar hydrocarbon substrate. Piranha-etched silicon (Si), which possessed a thin (~2–10 nm) hydroxylated oxide layer, acted as a hydrophilic substrate. Unpoled, polished nickel (Ni) foil served as a weakly ferromagnetic substrate. An axially poled, neodymium–iron–boron alloy was used as a strongly magnetized ferromagnetic substrate (residual induction = 12 300 G). The polished nickel foil was attached to this
permanent magnet to provide a substrate (Ni–Nd) with the same roughness as the Ni substrate. The measured average surface roughness values of the six substrates fell within a range of 0.2–2.8 nm (Table 1).

Contact mode AFM measurements were used to evaluate the short-range (VDW-based) adhesion of the sunflower pollen and the hematite and magnetite replica particles to the Si, PVA, PVAc, PS, Ni, and Ni–Nd substrates. Average values of the VDW-based adhesion for the different particle and substrate combinations are shown in Figure 6. (Note that each average value was obtained from 60 measurements consisting of 20 analyses for each of three similar particle/cantilever probes.) Although the pollen tip radii were considerably larger than the variation in the average surface roughness of the substrates (0.2–2.8 nm), such variation in the substrate roughness could alter the contact area and thereby alter the adhesion force. However, as revealed in Figure 6, similar adhesion forces were found for different particle and substrate combinations involving hematite, magnetite, Ni, or Ni–Nd were calculated on the basis of the Lifshitz theory16 via

\[ F_{\text{vdw}} = \frac{A_{132} R}{6 D^2} \]  

(1)

where \( A_{132} \) is the nonretarded Hamaker constant of material 1 and 2 interacting across a medium 3 (air), \( R \) is the contact radius, and \( D \) is the cutoff separation distance for the VDW interaction \( (\approx 0.165 \text{ nm}) \).16 Approximate \( A_{132} \) values for sunflower pollen on the Si, PVA, PVAc, and PS substrates were calculated from appropriate \( A_{11} \) and \( A_{22} \) values available in the literature5,16,17 and with the assumption that \( A_{33} = 0 \) via

\[ A_{132} \approx A_{11}^{1/2} A_{22}^{1/2} \]  

(2)

The simplified expression in eq 2 is not applicable, however, to media with high dielectric constants. Therefore, interactions involving hematite, magnetite, Ni, or Ni–Nd were calculated from eq 3 using appropriate \( \epsilon_1 \), \( \epsilon_2 \), \( \nu_1 \), and \( \nu_2 \) indices. \( A_{132} \) values for sunflower pollen on the Ni or Ni–Nd substrates as well as for hematite or magnetite replicas on all substrates were calculated from eq 3 using appropriate \( \epsilon_1 \), \( \epsilon_2 \), \( \nu_1 \), and \( \nu_2 \) values

\[ A_{132} \approx \frac{3}{4} \epsilon_1 \epsilon_2 \left( \epsilon_1 - \epsilon_3 \right) \left( \epsilon_2 - \epsilon_3 \right) + \frac{9h_0}{8\sqrt{2}} \mathcal{E} - \left( \frac{n_1^2 - n_3^2}{n_1^2 + n_3^2} \right) \left( n_1^2 + n_3^2 \right)^{1/2} \left( n_1^2 + n_3^2 \right)^{1/2} \left( n_1^2 + n_3^2 \right)^{1/2} \left( n_1^2 + n_3^2 \right)^{1/2} \]  

(3)

Table 1. Average Surface Roughness (Ra, in nm) of the Substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Si</th>
<th>PVA</th>
<th>PVAc</th>
<th>PS</th>
<th>Ni</th>
<th>Ni–Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra (nm)</td>
<td>0.2 ± 0.06</td>
<td>1.3 ± 0.03</td>
<td>0.3 ± 0.06</td>
<td>0.3 ± 0.02</td>
<td>2.7 ± 0.7</td>
<td>2.8 ± 0.4</td>
</tr>
</tbody>
</table>

Table 2. Average Measured Values of Adhesion Force (\( F \), in nN), Calculated Hamaker Constants (\( A_{132} \times 10^{19} \), in J), and Calculated Contact Radii (\( R \), in nm)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Si</th>
<th>PVA</th>
<th>PVAc</th>
<th>PS</th>
<th>Ni</th>
<th>Ni–Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{132} )</td>
<td>0.85</td>
<td>0.84</td>
<td>0.98</td>
<td>0.84</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>F (nN)</td>
<td>57 ± 8</td>
<td>51 ± 9</td>
<td>53 ± 4</td>
<td>56 ± 8</td>
<td>56 ± 10</td>
<td>56 ± 11</td>
</tr>
<tr>
<td>R (nm)</td>
<td>109</td>
<td>98</td>
<td>88</td>
<td>109</td>
<td>78</td>
<td>77</td>
</tr>
<tr>
<td>( A_{132} )</td>
<td>1.7</td>
<td>2.0</td>
<td>1.8</td>
<td>2.1</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td>F (nN)</td>
<td>39 ± 1</td>
<td>32 ± 1</td>
<td>36 ± 7</td>
<td>36 ± 11</td>
<td>38 ± 7</td>
<td>36 ± 5</td>
</tr>
<tr>
<td>R (nm)</td>
<td>37</td>
<td>27</td>
<td>32</td>
<td>28</td>
<td>18</td>
<td>17</td>
</tr>
<tr>
<td>( A_{132} )</td>
<td>1.7</td>
<td>2.0</td>
<td>1.8</td>
<td>2.1</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td>F (nN)</td>
<td>38 ± 4</td>
<td>33 ± 3</td>
<td>33 ± 3</td>
<td>30 ± 3</td>
<td>35 ± 9</td>
<td>33 ± 4</td>
</tr>
<tr>
<td>R (nm)</td>
<td>36</td>
<td>27</td>
<td>30</td>
<td>24</td>
<td>17</td>
<td>16</td>
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</table>
available in the literature, with the assumption that the absorption frequencies of all media are the same. Lacking a literature value for sporopollenin, the $\varepsilon_1$ value for sporopollenin was assumed to be the average of the values for PS, PVAc, and PVA. This assumption was consistent with the organic content of sporopollenin and produced $A_{132}$ values of the expected magnitude. If the substrate is assumed to be flat, then $R$ in eq 1 refers to the contact radius of the spine tip from the probe particle. By inserting the measured average values of adhesion force into eq 1 along with the calculated $A_{132}$ constants, values of contact radii for the cleaned sunflower pollen, $\alpha$-Fe$_2$O$_3$ replicas, and Fe$_3$O$_4$ replicas with the various substrates were calculated (Table 2) to be 93 ± 16, 27 ± 10, and 25 ± 11 nm, respectively. For the native sunflower pollen, the calculated contact radius (93 ± 16 nm) was similar to the average spine-tip radius (120 ± 12 nm) measured by SEM analysis; that is, the VDW-based adhesion force for this native pollen particle was consistent with the contact of a single spine tip to a given substrate. However, the calculated contact radii for the hematite (27 ± 10 nm) and magnetite (25 ± 11 nm) replica particles were significantly smaller than the average spine tip radii of these replicas (i.e., 94 ± 14 and 100 ± 14 nm for hematite and magnetite, respectively) obtained from SEM analyses. Instead, the calculated contact radii for these oxide replicas were not far from the average crystallite radii (17 to 18 nm) of these particles obtained from XRD analyses; that is, the VDW-based adhesion forces of the oxide pollen replicas were consistent with the contact of one or two nanocrystals, located at the spine tips, to the substrates.

The longer-range magnetic forces acting between particle/cantilever probes and the axially magnetized permanent magnet Ni–Nd substrate were evaluated by scanning the probes across the diameter of this disk-shaped substrate at a fixed height of 140 $\mu$m above the substrate surface. As revealed in Figure 7, a noticeable attractive force was detected between the ferrimagnetic Fe$_3$O$_4$ sunflower pollen replica and the disk-shaped Ni–Nd substrate at locations near the outer perimeter of this substrate, which is where the magnetic field intensity associated with this magnetized Ni–Nd substrate was the highest. No appreciable magnetic attraction was detected between the weakly ferromagnetic $\alpha$-Fe$_2$O$_3$ replicas or the nonmagnetic native sunflower pollen at any location across the Ni–Nd substrate (at a distance of 140 $\mu$m from the surface of this substrate). The enhanced magnetic behavior of the magnetite replicas relative to the hematite replicas was also apparent from visual observations of the relative attraction of magnetite and hematite replica particles, dispersed in water, to a permanent magnet (Figure S3).

The total adhesion force acting between a given type of particle and the Si or Ni–Nd substrate is plotted against probe distance from the substrate surface in Figure 8. (Note that for the Ni–Nd substrate, measurements were obtained either at...
the disk center or at a distance of ~300 μm from the disk edge.) Only short-range (~10 nm) attractive forces were detected between the native sunflower pollen or α-Fe₂O₃ sunflower replicas and these substrates (Figure 8a,b). However, both magnetic and VDW attractive forces were detected (Figure 8c) between the Fe₂O₃ sunflower pollen replicas and the magnetized Ni–Nd near the outer edge of this substrate. For this Fe₂O₃ particle/Ni–Nd-edge substrate pairing, the total adhesion force (~70 nN) acting over a short distance (~10 nm) consisted of the sum of the VDW force (~40 nN) and the magnetic force (~30 nN). At distances just beyond the range of VDW-based adhesion, a steady magnetic force (~30 nN) was detected. The magnetic interaction between the Fe₂O₃ sunflower pollen replicas and the magnetized edge of the Ni–Nd substrate persisted out to a separation distance of ~1 mm.

This work demonstrates that a highly conformal SSG-coating process can be used along with controlled modest-temperature thermal treatments to convert sunflower pollen particles into nanocrystalline ferrimagnetic (Fe₃O₄) replicas exhibiting multimodal adhesion via short-range (~10 nm) VDW-based attraction and short-to-long-range (up to ~1 mm) magnetic attraction. Although the work here has focused on generating oxide replicas of sunflower pollen, this process may be generally applied to numerous other types of pollen. Indeed, the wide variety of 3D particle shapes and surface topographies available from pollen generated by different plants and the ability of this LBL SSG-based process to produce high-fidelity nanocrystalline replicas with controlled amounts of magnetic oxide (by adjusting the number of deposition cycles) allows for the syntheses of pollen-derived microparticles with highly tailorable multimodal adhesion.

**CONCLUSIONS**

This work demonstrates, for the first time, the ability to generate high-fidelity, all-oxide replicas of pollen particles exhibiting tailorable multimodal (short-range VDW and short-to-long-range magnetic) adhesion. The hydroxyl-rich nature of the exine of pollen has allowed the use of a computer-automated LbL SSG process to apply highly conformal Fe–O-bearing coatings to pollen particles. For this demonstration, sunflower pollen (Helianthus annuus), with surfaces containing sharp, high-aspect-ratio spines, was coated with 30 Fe–O-bearing layers. Subsequent firing at 600 °C in air yielded high-fidelity replicas composed of nanocrystalline phase-pure ferromagnetic hematite (α-Fe₂O₃). Partial reduction of these hematite replicas, via use of a controlled oxygen partial pressure (Rhines pack-based) heat treatment, yielded nanocrystalline phase-pure ferrimagnetic magnetite (Fe₃O₄) replicas. The Fe₂O₃ replicas were found to exhibit short-range (~10 nm) VDW-based adhesion governed by the contact of oxide nanocrystals present on the sharp spines inherited from the starting sunflower pollen and short-to-long-range (up to 1 mm) magnetic adhesion governed by the ferrimagnetic magnetite. By selecting pollen with particular 3D morphologies and surface features and by using the LbL SSG process to tailor the amount of nanocrystalline magnetite present in the replicas, ceramic microparticles with tunable short-range (VDW-based) and longer-range (magnetic) adhesion can be synthesized.

**ASSOCIATED CONTENT**

Supporting Information

Additional experimental description; TG analyses; SE image of a fractured cross-section of a hematite replica of a pollen particle; optical images of the magnetic attraction of magnetite pollen particle replicas, suspended in water, to a permanent magnet; SE images of the same coated pollen particles on a marked Ni substrate before and after pyrolysis in air at 600 °C; measured values of diameter of the same coated pollen particles before pyrolysis, after pyrolysis in air at 600 °C (as hematite replicas), and after the Rhines pack thermal treatment (as a magnetite replica); and specific values of surface area, micropore volume, and mesopore volume for as-coated pollen particles, hematite pollen particle replicas, and magnetite pollen particle replicas (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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These authors contributed equally.

Notes

The authors declare no competing financial interest.

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**ABBREVIATIONS**

AFM, atomic force microscopy; DIW, deionized water; EDX, energy-dispersive X-ray; LbL, layer-by-layer; Ni, nickel; NiO, nickel oxide; Ni–Nd, nickel–iron–boron alloy; PVAc, poly(vinyl acetate); SEM, scanning electron microscopy; SSG, surface self-assembly; TG, thermogravimetric; 3D, three-dimensional; VDW, van der Waals; XRD, X-ray diffraction

**REFERENCES**


