Synthesis and Directional Assembly of Gibbous and Inverse-Gibbous Colloidal Nanoparticles

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ABSTRACT

Due to the absence of anisotropic directional bonds, one of the intriguing aspects of nanoparticle structural organizations is encoding directionally guided arrays. Although van der Waals, electrostatic interactions and geometrical matching were proposed, a controllable assembly of isotropic shapes still remains to be a challenge. These studies show the synthesis of gibbous/inverse-gibbous colloidal nanoparticles that utilized hydrophobic and hydrophilic environments during aqueous emulsion polymerization resulting in the formation of opposite shape matching surface topographies. The topography-matching nanoparticles stabilized by opposite charges are capable of forming directional assemblies facilitated by electrostatic forces and mechanical interlocking. As a result, combining gibbous and inverse-gibbous nanoparticles results in the formation of 2D directional arrays. When the same nanoparticles are deposited on a surface, crack-and defect-free colloidal morphologies develop which form face-center-cubicle (fcc) colloidal assemblies with highest packing densities.

Graphical abstract

Many biological processes rely on shape recognition. The basic mechanism by which enzymes catalyze chemical reactions begins with the physical fit between an enzyme and a substrate, where the substrate fits in a key-like fashion to its lock, the enzyme. While macroscopic analogies of these interactions have been well documented, due to many potential applications in medicine, materials chemistry, and engineering, precisely designed shapes and sizes of organic and inorganic nanoparticles continue to be of scientific interests and technological importance. The synthesis of well-defined nanoparticles with various morphologies, such as cubes,¹ clustered spheres,² dimpled,³ and gibbous particles,⁴ is particularly relevant when designing 2D/3D hierarchical structures, requiring directional guidance.⁵ Due to the absence of anisotropic directional bonds, the most challenging and intriguing aspects of nanoparticle constructs is encoding directional guided arrays. Typically, van der Waals,⁶ electrostatic,⁷ depletion,⁸ and DNA hybridization⁹ offer these interactions, but “lock-and-key” shape matching colloids resulting in the higher organized structures^{8, 10} and assemblies of biotin/DNA decorated particles *via* “patch-patch” interactions⁹ are also important. As a matter of fact, theoretical studies suggested that the attractive interactions between nanoparticles are balanced by the entropy for surface non-adsorbing polymers, whereas adsorbing polymers are of the enthalpic origin,¹¹ and thus to achieve programmable self-assemblies of colloidal nanostructures, two general strategies were proposed: puzzle

and folding approaches, which rely on short-range (such as, electrostatic) and long range (for example, geometrical) interactions, respectively.¹²

Figure 1. TEM, SEM images and graphical representations of gibbous (a-a''') and inverse-gibbous particles (b-b''').

In view of these considerations our previous studies developed methodology for the synthesis gibbous colloidal particles (Figure 1a),⁴ but in this study we focused on the synthesis of inverse-gibbous nanoparticles (Figure 1b). The objective of this effort is to develop shape matching surface topographies and examine if geometrically matching surfaces can facilitate particle mechanical interlocking. As shown in Figures 1a and 1a', TEM and SEM images of gibbous nanoparticles exhibit well-defined bulges which consist of poly(methyl methacrylate) (pMMA) core and poly(pentafluorostyrene(PFS)/n-butyl acrylate(nBA)) shell.⁴ Using the same polymerization procedure involving seed formation, monomer diffusion, and localized polymerization, we synthesized inverse-gibbous particles which consist of polystyrene (pSt) core and poly(heptafluoro-n-butyl acrylate(HFBA)/nBA) shell. TEM and SEM images of the inverse-gibbous nanoparticles

are shown in Figure 1b and 1b'. Figures 1a''/a''' and b''/b''' depict the particle's geometrical features obtained from the TEM and SEM images. The radius of the nanoparticles is ~ 145 nm, whereas the bulges (gibbous) and dimples (inverse-gibbous) are ~ 15 nm (r_a and r_b , respectively). In designing and synthesizing these surface topographies, it is critical to utilize experimental conditions (Supp. Docs) enabling the control the r_a and r_b values (Figure 1, a''/b'''). Since it is also important to facilitate phase-separation during polymerization we utilized monomers with specific solubility parameters (Supporting Documents, Table S1) for each polymer/monomer composition. Using previously developed⁴ and modified for the purpose of these studies experiment conditions (Supporting Documents, Figures S1-S3), the solubility parameters of given two polymers should be distinctly apart ($>2 \text{ cal}^{0.5}\text{cm}^{-1.5}$) to obtain phase-separation and controllable surface heterogeneities. Another important factor is the polymerization temperature with respect to the glass transition temperature (T_g); the deformation of forming copolymers during polymerization will significantly influence the resulting particle morphologies.¹³

Figure 2, a and b, depicts the proposed mechanism responsible for the synthesis of gibbous and inverse-gibbous nanoparticles produced by the same synthetic procedures. The only difference is the choice of the starting materials dictated by their solubility parameters and the T_g of the forming copolymers determined by copolymer composition. As shown in Figure 2a, initially, copolymerization of pentafluorostyrene (PFS) and n-butyl acrylate (nBA) (molar ratio 1.5:1) on a pMMA seed results in the formation of phase-separated gibbous bulges with the glass transition temperature (T_g) of 70 °C. The gibbous morphology is attributed to the formation of fluorinated copolymers which are

unable to diffuse into the seed particles and thus become immobilized and form phase-separated bulges. In contrast, when HFBA and nBA in a molar ratio of 1.5:1 are copolymerized onto a hydrophobic pSt seed (Figure 2b and Figure S4-S7), phase-separation leads to the formation of dimples resulting in inverse-gibbous morphologies. Since p(HFBA/nBA) copolymers exhibit the T_g of $\sim -20\text{ }^{\circ}\text{C}$, they will collapse on the seed particle surfaces and maintain their phase-separation to form dimples. Due to low T_g , p(HFBA/nBA) copolymer will adopt the minimum low surface area during polymerization. Furthermore, being hydrophobic, these copolymers will minimize the surface area to lower the interfacial energy. As surfactant-free copolymerization proceeds, localized fluorocopolymer indentations are formed on the surface due to the higher surface tension, resulting in dimple morphologies. The number and the size of the dimples can be tuned by altering the monomer feed ratio as well as the reaction times. This is illustrated in Figures S4-S7 of the Supporting Documents.

Figure 2. Schematic representation of the mechanism responsible for the formation of gibbous (a) and inverse-gibbous (b) nanoparticles using seeded emulsion polymerization. Part a partially adopted from Ref. 4.

In an effort to introduce opposite electrostatic changes on gibbous and inverse-gibbous nanoparticles, in separate experiments, we stabilized their surfaces by introducing opposite surface charges. Specifically, cationic “+” (2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride, AIPD) initiator was utilized to stabilize gibbous, and anionic “-” (potassium persulfate, KPS) was used to stabilize inverse-gibbous nanoparticles. Both nanoparticles were stabilized in such a way that the surface charge density was proportional to the number of polymer chains in each nanoparticle.¹⁴ To verify surface modifications we measured zeta potentials of seeds (control experiment) as well as gibbous/inverse gibbous nanoparticles. The “-” seeds and gibbous nanoparticles have the zeta potential of ~ -35 and -49 mV, respectively. In contrast, the

“+” seeds and inverse-gibbous nanoparticles exhibit the zeta potential of +39 and +52 mV, respectively. These data show, that the increase of the absolute values of the zeta potentials are present on the surfaces with the higher charge densities of gibbous/inverse-gibbous surfaces.¹⁵ Having secured electrostatic interactions and shape-matching topologies schematically depicted in Figure 3a in place, we combined gibbous and inverse-gibbous nanoparticles in an aqueous phase. At the nanoparticle concentration levels of $\sim 10^{-7}$ g/mL, the particles link to form 1D directional “gear-like” assemblies. This is illustrated in Figure 3, c and d, which is attributed to geometrical interlocking guided by enhanced electrostatic attractions between “-” gibbous particles and “+” inverse-gibbous nanoparticles. As illustrated in Figure 3b, the attractive forces between oppositely charged particles as well as repulsive forces between the particles with the same charges will favor directional assemblies. At the higher concentration levels $\sim 10^{-6}$ g/mL, gibbous and inverse-gibbous nanoparticles form multi-gear-like assemblies (Supporting Documents, Figure S8), whereas spherical particles and oppositely charged nanoparticles ($\sim 10^{-7}$ g/mL) with spherical, gibbous and inverse-gibbous topographies result in random assemblies (Supporting Documents, Figure S9). The surface charges on the bulges of the gibbous and dimples of the inverse-gibbous nanoparticles will carry higher surface charges than the remaining part of the surface due to both higher surface charge density (higher content of polymer end groups of the initiators) as well as higher effective surface area. While the mirror image surface topographies as well as opposite surface charges of two gibbous and inverse gibbous nanoparticles will initiate the process, thus forming a ‘nanoparticle dipole’,¹⁶ the

remaining nanoparticles will be added to the opposite ends of the dipole, thus resulting in gear-like assemblies shown Figure 3.

Figure 3. Schematic representation of gibbous and inverse-gibbous particles with surface matching geometries and electrostatic double layers (a) and their necklace-like assembly (b), and TEM images of the assemblies of gibbous (-)/inverse-gibbous (+) particles with different concentrations: 10^{-7} g/mL (c), 10^{-8} g/mL (d), respectively. Inset is the close-up image.

Figure 4. SEM images of colloidal films prepared by vertical deposition of (a) mixture of gibbous (0.25 wt%) and inverse-gibbous particle (0.25 wt%) dispersions, (b) spherical pMMA particles (0.5 wt%), (c) gibbous particles (0.5 wt%), and (d) inverse-gibbous particle (0.5 wt%).

One of the challenges in forming 3D nanoparticle assemblies are developing stresses during film formation that result in cracks and defects. The unique feature of gibbous and inverse-gibbous nanoparticles is their ability to interlock during film formation, thus forming 3-D crack-free colloidal assemblies. These conditions are facilitated by vertical deposition of concentrated interlocking nanoparticles stabilized by the same electrostatic charges (anionic) during water evaporation.¹⁷ This is illustrated in Figure 4, a-a". In contrast, self-assemblies of spherical nanoparticles lead to undesired crack formation (Figure 4, b-b") resulting from mechanical stresses developed during drying.¹⁸ Although there are ways to avoid it by using templates,¹⁹ superhydrophobic substrates²⁰ or in-situ reactions,²¹ self-assembly of gibbous particles (Figure 4, c-c") prevents the development of cracks along the horizontal direction. Although mechanistic aspects of this process are likely due to the bulges that fit into the space between neighboring particles, thus alleviating stresses along the horizontal direction, exact

mechanisms are beyond the scope of this study. For self-assembly of inverse-gibbous particles (Figure 4, d-d”), both horizontal and vertical cracking occur due to their spherical shape. However, when gibbous and inverse-gibbous nanoparticles are simultaneously assembled to form colloidal films (Figure 4, a-a”), crack formation is completely eliminated likely due to mechanical interlocking between the bulges on gibbous and dimples on inverse-gibbous nanoparticles as well as electrostatic inter-particle interactions.

In summary, these studies show that the formation of controllable morphology and topography nanoparticles is driven by the surface tension differences at the phase-separated regions during surface polymerization. The gibbous and inverse-gibbous topography can be easily developed as long as solubility parameters, miscibility, and chain rigidity of the forming copolymers are properly adjusted. The topography-matching nanoparticles stabilized by opposite charges are capable of forming directional assemblies due to a combination of electrostatic interactions and mechanical interlocking. Furthermore, topography-matching gibbous and inverse-gibbous nanoparticles are capable of forming 3D crack-free colloidal films.

EXPERIMENTAL SECTION

Materials. Tetraethoxysilane (TEOS, 98%) and ammonium hydroxide (28–32% in water), methyl methacrylate (MMA, 99%), n-butyl acrylate (nBA, 99%), styrene (St, 99%), anionic initiator potassium persulfate (KPS, 99%), 3-(methacryloyloxy)propyl trimethoxysilane (MPS, 98%), and aluminum oxide (Al_2O_3 , 98%) were purchased from Aldrich Chemical Co. Pentafluorostyrene (PFS, 99%), and heptafluorobutyl acrylate (HFBA, 97%) were purchased from Fisher Scientific Co. Cationic initiator 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (AIPD or VA-44) was purchased from Wako Pure Chemicals Ind. Ltd. MMA, nBA, St, and PFS were allowed to pass through an Al_2O_3 column to remove inhibitors prior to use, and all other chemicals were used as received.

Preparation of Gibbous Nanoparticles. Gibbous nanoparticles were synthesized according to previously reported procedures.⁴

Preparation of “-” and “+” pSt Seed Nanoparticles. In a typical synthesis, 90 g deionized water was placed in a flask and heated to 75 °C under protection of N_2 gas and magnetic stirring at 400 rpm. St (3 g, 28.8 mmol) and 5 mL anionic initiator KPS aqueous solution (0.01 g/mL, 37 mM) (or 5 mL cationic initiator AIPD aqueous solution (0.012 g/mL, 37 mM)) were added, and the reaction was allowed to continue for 15 h. The seed particles were purified by centrifugation at 1500g for 3 h. Upon completion, they were redispersed in 95 mL of deionized water. Conversion > 99 %.

Preparation of Inverse-Gibbous Nanocomposite Particles. In a typical synthesis, 5 g pSt seed particle dispersions were stirred at 600 rpm and 0.16 g HFBA/nBA mixture

(molar ratio 1:1) were added. After the monomers completely diffused into the seed particles (over 15 h), the colloidal dispersion was deoxygenated by purging N₂ for 30 min, and KPS (AIPD for “cationic” seeds) aqueous solution (0.007 mmol) was added. The reaction was continued for 1 h at 75 °C. The inverse-gibbous particles synthesized using this procedure were monodispersed, and agglomerates/aggregates were rarely observed. No separation was needed for TEM/SEM experiments.

Self-Assembly of Oppositely Charged Gibbous and Inverse-Gibbous Particles.

In a typical procedure, negatively charged “-” gibbous nanoparticles and positively charged “+” inverse gibbous particles were diluted by deionized water with a ratio of 1:10,000. Equal amount dispersions were quickly mixed and TEM samples were prepared by putting 2 µL of the colloidal mixtures. The sample was controlled to dry at room temperature and relative humidity of 80 %.

Preparation of Colloidal Films. In a typical procedure, negatively charged “-” gibbous and inverse-gibbous nanoparticle dispersions with topography-matching surfaces (determined by TEM) were diluted to 0.5 wt% using deionized water, respectively. Equal amount (2.5 mL each) of the two dispersions were mixed and put in a 20 mL vial and sonicated for 5 min. Glass slides (pre-cleaned with by sonication in acetone and water) were vertically positioned in these vials. Subsequently, the colloidal particles were self-assembled on the glass slides at 60 °C and relative humidity of 50 %.

Characterization. Particle size measurements were performed using a Malvern Zetasizer Nano ZS at 25 °C. Particle morphologies were examined using a Hitachi H9500 transmission electron microscope (TEM) operated at 300 kV and a Hitachi

HD2000 scanning transmission electron microscope (STEM) with energy-dispersive X-ray spectroscopy function operated at 200 kV. Each colloidal dispersion at ~5 w/w % solids, upon $1:10^4$ dilution, was deposited on a carbon film Cu grid (EMS), and TEM and SEM analyses were performed. Colloidal films were first sputter-coated with Pt (~5 nm thick) and observed by using a Hitachi S-4800 SEM operated at 5 kV. The glass transition temperature (T_g) was measured using differential scanning calorimetry (DSC) (TA instruments Discovery Series) in the temperature range of -55 °C – 150 °C at a heating rate of 10 °C/min.

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Supporting Information Available: Additional experimental figures, tables, and characterizations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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