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Phase transfer of oleic acid stabilized rod-shaped anatase TiO_2 nanocrystals

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ABSTRACT

Three methods were evaluated for phase transfer of oleic acid stabilized TiO_2 nanorods from non-polar phase to an aqueous phase. Three alkyltrimethylammonium bromide (C_6, C_8, C_{12}) surfactants were tested and compared with an amphiphilic polymer as interdigitation agents. Ligand substitutions with catechol derivatives with polar functional groups *para* to the –enediol were evaluated as well. The molecular surfactants were ineffective compared to the amphiphilic polymer in the interdigitation phase transfer approach. Ligand substitution with catechols proceeded efficiently with phase transfer. The ligand substitution reactions were accompanied by gas evolution, which was found to result from decarboxylation of oleic acid in alkaline aqueous conditions.

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1. Introduction

The properties of nanocrystals are strongly dependent on size [1–6], shape [7,8], and surface features [9–11]. To study the effects arising from morphology and surface function of single nanocrystals requires an ability to process and manipulate isolated nanocrystals. This is typically achieved with non-interacting ensembles of dispersed nanocrystals in solution or nanocrystals deposited on a solid surface. New applications that utilize carefully designed nanocrystals are being developed at a rapid pace, with many of these requiring mobile nanocrystals dispersed in solution. For example, in vivo imaging with magnetic resonance [12–18] or fluorescence probes [18–23], tumor annihilation [15,22, 24–26], or nano-inks [27–31] require mobile nanocrystals in solution. Nanocrystals only disperse in solvent when the terminal surface feature introduces a steric and/or electrostatic barrier to particle aggregation and has compatible polarity with the solvent.

Preparation of nanocrystals with precise control of size and shape often requires quite specific conditions, and the surface properties of the nanocrystal may not be compatible with requirements of a final application. For example, many inorganic nanocrystals are prepared in non-polar solvents, yet applications in living tissue require water solubility. Thus, there has been much effort to develop protocols for phase transfer of hydrophobic nanocrystals from non-aqueous solvents to water [32–34]. Some of the strategies include ligand removal (thereby utilizing the surface charge of the nanocrystal to provide electrostatic stabilization and water solubility), ligand substitution, ligand interdigitation, or utilizing responsive terminal functional groups that bind ions.

Ligand removal can be achieved using chemical reactions such as oxidation [35], reduction [36], or protonation of the ligand so that it is no longer able to bind to the nanocrystal surface. Another method for ligand removal is repeated precipitation/redispersion cycles that successively remove ligand from the nanocrystal surface over many cycles. Eventually, the nanocrystal will no longer disperse in solvent due to large loss of stabilizing ligand. A drawback in the ligand removal strategy is that the nanocrystals may be weakly stabilized and highly susceptible to aggregation.

Ligand substitution is a highly effective method for the surface modification of a nanocrystal. Ligand substitution reactions may have high energetic barrier to overcome as the initial ligand dissociates from a surface site. To overcome this, some ligand substitution schemes use a first step of ligand removal followed by introduction of the desired new ligand. Another strategy is to use a strongly binding ligand to replace a more weakly binding ligand, thus the initial kinetic barrier is kept low with the use of a weakly binding ligand. Alternatively, polymers may be used to displace molecular stabilizers. For example, replacement of hydrophobic ligands with polyelectrolytes such as poly(acrylic acid) and poly(allylamine) led to transfer of hydrophobic nanocrystals to water [32]. In this approach, the substitution process is entropy driven. Interestingly, the reverse entropically disfavored substitution of polymer for molecular surfactants was recently demonstrated [37].

Interdigitation, also known as bilayer stabilization, has been used to achieve phase transfer of nanocrystals. This method was proposed by Shimoiizaka et al. wherein oleic acid capped magnetic nanoparticles were redispersed in aqueous solution upon treatment with sodium dodecyl benzenesulfonate, poly(oxyethylene)nonylphenyl ethers, or di(2-ethylhexyl)adipate, hypothesizing that the second surfactant coated the primary surfactant-coated particles to form a structured surfactant bilayer [38]. In this scheme, the initial nanocrystal stabilizer

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projects aliphatic hydrocarbon chains outward from the nanocrystal. Addition of a surfactant with aliphatic hydrocarbon chains leads to interdigitation/bilayer formation with the aliphatic surrounding of the nanocrystal that maximizes hydrophobic interactions, much like the action of a detergent. Following interdigitation, the nanocrystal is surrounded by a micelle-like layer, in which the inner polar head groups are bound to the nanocrystal surface and the outer polar head groups interact with solution, and the entity becomes water soluble. Others have prepared bilayer-stabilized nanoparticles in similar ways [39–43]. Amphiphilic polymers have been used to achieve phase transfer upon interdigitation with hydrophobic nanocrystals. For example, poly(isobutylene-*alt*-maleic anhydride) was used to form the hydrophilic backbone of an amphiphilic polymer. Upon addition of long-chain alkylamine in less than equimolar ratio to the anhydride groups, hydrophobic side chains were attached leaving a hydrophilic backbone with carboxylate groups [44]. A dye-modified version of the amphiphilic polymer was used to prepare water-soluble quantum dots [45]. An azide-bearing amphiphilic polymer was used to coat hydrophobic nanoparticles, followed by coupling of DNA to make water-soluble nanoparticles with 'programmable' surfaces [46]. Interestingly, bilayer coating of hydrophobic alkanethiol stabilized Au nanoparticles with triblock copolymer (alkyl-PEG-alkyl) led to amphiphilic nanoparticles that can pass the aqueous/organic interface through conformational change [47]. In aqueous solution, the alkyl caps of the triblock copolymer were associated with the alkanethiol ligands bound to gold and led to bent conformation; whereas in chloroform, the polymer adopted a linear conformation accompanied by phase transfer.

Phase transfer of nanoparticles from non-polar to aqueous phase may result as a response to binding ions. Indeed, bilayer-stabilized nanoparticles typically show a pH-dependent response such that charged headgroups give rise to stable aqueous dispersions and neutral headgroups lead to aggregation and precipitation from aqueous solution or phase transfer to the non-polar phase [42,48]. More broadly, a large number of functionalized nanoparticles have been prepared as scaffolds for molecular recognition [49]. Binding of charged guest species to the host groups on the nanoparticle scaffold has been shown to lead to phase transfer to the aqueous phase [50]. The reverse analogy, in which the stabilizing monolayer molecules serve as guest species to a molecular receptor, has been demonstrated with application of cyclodextrin to monolayer-protected nanocrystals [51]. Though cyclodextrin is not charged, it presents polar functional groups, such that upon formation of the pseudorotaxane motif, the nanocrystal becomes hydrophilic.

In this contribution, we present findings on the use of trimethylalkylammonium bromide salts, amphiphilic polymer, and catecholate ligands to achieve phase transfer of rod-shaped anatase TiO_2 nanocrystals.

2. Experimental

2.1. General considerations

Reagents (oleic acid, titanium(IV) isopropoxide, hexanes, isopropanol, chloroform, THF, poly(isobutylene-*alt*-maleic anhydride), $RNMe_3Br$ (R = hexyl, octyl, dodecyl), sodium hydroxide, 1,2,4-benzenetriol, 2,5-dihydroxybenzoic acid, 4-nitrocatechol, caffeic acid, gallic acid, pyrocatechol violet, pyrogallol red) were obtained from commercial sources and used without further purification unless specifically stated. THF was dried and distilled from CaH_2. Powder X-ray diffraction data were acquired using a Rigaku Ultima IV powder X-ray diffractometer. The X-ray tube produced Cu Kα radiation (λ = 1.54 Å), and the generator was set to 40 kV and 44 mA during data collection. Data were collected from 20 to 80° (2θ). Dry TiO_2 NR powders and M,M′–TiO_2 NR powders were prepared by evacuating the solvent under vacuum at room temperature. UV-visible absorption spectra were recorded with Cary 50-Bio UV-visible spectrophotometer. Transmission electron microscopy (TEM) data were obtained using a Technai Spirit G^2 Twin (FEI Company) transmission electron microscope fitted with LaB_6 filament operated at 120 kV. Samples were dispersed in hexanes, and then drop cast onto carbon film (20–30 nm) on 200 mesh copper grid (Electron Microscopy Sciences) and allowed to dry in the air. Electron micrographs were obtained by projection onto Gatan US1000 or Orius SC200 CCD Digital Camera and recorded with Digital Micrograph software.

2.2. Amphiphilic polymer (**1**)

The preparation has been reported elsewhere [44]. Briefly, a 250 ml flask under N_2 atmosphere was charged with 3.08 g of poly(isobutylene-*alt*-maleic anhydride). To this flask was added a solution of 2.61 g of dodecylamine dissolved in 100 ml anhydrous THF. A gummy residue formed, then the contents were subjected to sonication bath for 30 seconds followed by reflux for 1 hour under N_2. The solvent was reduced to ~1/3 volume in vacuo, then the contents were stirred at room temperature for 18 hours under N_2. The remaining solvent was removed in vacuo, leaving a pale yellow residue. The resultant polymer was soluble in THF and chloroform.

2.3. Synthesis of rod-shaped anatase TiO_2 nanocrystals

The synthesis was reported previously [36]. We give a detailed account of the procedure in our hands. The synthesis was carried out under nitrogen using Schlenk techniques. A 250 ml round-bottom flask was charged with 52.5 g of oleic acid then evacuated at 120 °C for 1 hour to remove volatiles. The contents were allowed to cool to room temperature, and then the flask was filled with nitrogen and brought into a glove box. The oleic acid was transferred to a 500 ml 3-neck round-bottom flask, and 17 g of titanium (IV) isopropoxide (TTIP) was added. The flask was closed with three rubber septa, brought to the Schlenk line, and under flow of nitrogen was fitted with a reflux condenser under a nitrogen blanket. The flask was fitted with a thermocouple inserted through a Teflon adapter and a heating mantle interfaced with a programmable temperature controller (thus one rubber septum remained on the flask). The contents were heated to 270 °C at a rate of 12.5 °C/min, then held at 270 °C for 2 hours. During the temperature ramp, it was critical to release isopropanol formed in the solvothermal reaction; otherwise, the temperature of the reaction stalls due to internal refluxing of isopropanol and prevents the temperature from reaching the set point. Periodic insertion of a needle through the septum allowed release of the isopropanol vapor, which was performed at temperatures below 200 °C until the vapor no longer condensed in the flask. We found that continuous prolonged venting or venting above 200 °C led to lower yield. After refluxing for 2 hours, the flask was allowed to cool to ambient temperature. To isolate the rod-shaped TiO_2 nanocrystals, the contents were poured into 50 ml disposable polypropylene centrifuge tubes at a volume of ~8 ml/tube, then isopropanol was added to the 35 ml mark on the tube. The tubes were centrifuged for 10 minutes at 3500 rpm. The supernatant was discarded. The residue from all tubes was combined and redispersed in a total of 65 ml of hexanes in a beaker. To this dispersion, 35 ml of isopropanol was added, and the floc was poured into new centrifuge tubes and subjected to centrifugation for 3 minutes at 11,000 rpm. The residue was composed of anisotropic TiO_2 nanorods with diameter ~3 nm and aspect ratio of ~13; yield 4.08 g (85%).* Additionally, the supernatant can be processed further to yield TiO_2 nanocrystals with lower aspect ratio. Thus, addition of 10 ml isopropanol to the combined supernatant followed by centrifugation for 5 minutes at 8000 rpm gave more residue found as low aspect ratio nanorods. Finally, to the combined supernatant after removal of the first two residues, was added 20 ml of isopropanol. Centrifugation for 5 minutes at 8000 rpm led to additional residue that was found to be isotropic TiO_2 nanocrystals (~4 nm diameter). All nanocrystal products can be purified with additional precipitation/redispersion cycles;

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