Phase-transfer of oleic acid stabilized rod-shape anatase TiO₂ nanocrystals

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Keywords: TiO₂, nanocrystal, phase transfer, catechol, ligand exchange, decarboxylation

Abstract

Three methods were evaluated for phase transfer of oleic acid stabilized TiO₂ nanorods from non-polar phase to an aqueous phase. Three alkyltrimethylammonium bromide (C₆, C₈, C₁₂) 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.

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 resonance¹²⁻¹⁸ or fluorescence probes,¹⁸⁻²³ tumor annihilation,^{15,22,24-26} or nano-inks²⁷⁻³¹ 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 Shimoizaka 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 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-shape anatase TiO₂ nanocrystals.

Experimental

General considerations. Reagents (oleic acid, titanium(IV) isopropoxide, hexanes, isopropanol, chloroform, THF, poly(isobutylene-*alt*-maleic anhydride), RNMe₃Br (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 CaH₂. Powder X-ray diffraction data were acquired using a Rigaku Ultima IV powder X-ray diffractometer. The X-ray tube produced Cu K α radiation ($\lambda = 1.54 \text{ \AA}$), and the generator was set to 40 kV and 44 mA during data collection. Data was collected from 20–80° (2 θ). Dry TiO₂ NR powders and M,M'-TiO₂ 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 was obtained using a Technai Spirit G² Twin (FEI Company) transmission electron microscope fitted with LaB₆ filament operated at 120kV. 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.

Amphiphilic polymer (I). The preparation has been reported elsewhere.⁴⁴ Briefly, a 250 mL flask under N₂ 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 N₂. The solvent was reduced to ~1/3 volume in vacuo, then the contents were stirred at room temperature for 18 hours under N₂. The remaining solvent was removed in vacuo, leaving a pale yellow residue. The resultant polymer was soluble in THF and chloroform.

Synthesis of rod-shape anatase TiO₂ 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 52.5g 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 shape TiO₂ 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 11000 rpm. The residue was composed of anisotropic TiO₂ nanorods with diameter ~3 nm and aspect ratio of ~13; yield 4.08 g (85%).* Additionally, the supernatant can be processed further to yield TiO₂ 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 TiO₂ nanocrystals (~4 nm diameter). All nanocrystal products can be purified with additional precipitation/redispersion cycles; however, eventually after at least six cycles, the product will not redisperse unless further oleic acid (or other ligand) is added.⁵² All further work

was performed with the high aspect ratio nanorods obtained from the first precipitation step.

* The mass of TiO_2 was determined the following way. The nanocrystal product was dispersed in an arbitrarily chosen, but known volume of hexanes. From the dispersion, an arbitrarily chosen aliquot of known volume was taken, and placed in a fired and weighed ceramic crucible. The solvent was allowed to evaporate and the nanocrystal residue was calcined at 450°C for 6 hours in air to remove organic material. The inorganic material was carefully weighed, which allowed for determination of the mass of the product and the concentration of the product in the dispersion of hexanes.

Interdigitation with RNMe_3Br . In a 20 mL vial, a dispersion of TiO_2 nanorods (0.058 g TiO_2 , 0.73 mmol) in 1 mL hexanes was combined with a solution of 0.73 mmol RNMe_3Br in 5 mL reverse-osmosis purified water. The contents were stirred vigorously for 24 hours at room temperature. After this time, a white clumpy material was found separate from the organic and aqueous layers, and did not redisperse in hexanes or water.

*Interdigitation with **1**.* In a 20 mL vial, a dispersion of TiO_2 nanorods (0.034 g TiO_2 , 0.43 mmol) in 3 mL THF was combined with a solution of **1** (0.146 g) in 3 mL THF. The contents were refluxed for 10 minutes, after which time a precipitate had formed. The contents were brought to room temperature, transferred to a 50 mL polypropylene centrifuge tube, and centrifuged at 1000 rpm for 5 minutes. The supernatant was discarded, and 10 mL of distilled water was added to the precipitate. This was sonicated for five minutes to give a cloudy dispersion.

Ligand exchange with catechols. A dispersion of TiO_2 nanorods (0.058 g TiO_2 , 0.73 mmol) in 5 mL hexanes was prepared in a 20 mL vial. Separately, an aqueous solution (5 mL) of catechol (0.73 mmol) and sodium hydroxide (0.2 g, 5 mmol) was prepared. The organic TiO_2 nanocrystal dispersion was added to the aqueous catechol solution, and the contents were stirred for 18 hours. The organic layer was decanted. To recover the nanocrystals from the aqueous layer, 10 mL of isopropanol were added and the contents centrifuged at 3500 rpm for 7 minutes. The sample was redispersed in 5 mL water with vortex mixing.

Results and Discussion

Experiments were designed to test the efficacy of organic to aqueous phase transfer of oleic acid stabilized TiO_2 nanorods using three methods: interdigitation with molecular alkyltrimethylammonium bromide surfactants, interdigitation with amphiphilic polymer, and ligand exchange with catecholate molecules. First, the TiO_2 nanorods were prepared according to the method reported by Hyeon.³⁶ The synthesis is advantageous in being simple, scalable, and reproducible. In our hands, we could recover uniform samples of high aspect ratio TiO_2 nanorods in multigram quantities. The samples were characterized with TEM and powder XRD (figure 1). The nanocrystals readily disperse in non-polar solvents such as hexanes, toluene, chloroform, and THF. The dispersions exhibit strong absorbance in the UV wavelengths due to $\text{O } 2\text{p} \rightarrow \text{Ti } 3\text{d LMCT}$, and the absorbance is

significantly blue-shifted compared to bulk anatase TiO₂ due to quantum confinement⁵³ and transition from indirect to direct semiconductor in the dimension limited crystal.⁵⁴

Figure 1. TiO₂ nanorods were characterized with powder X-ray diffraction (top left; JCPDS file 21-1272 for anatase shown for comparison) and transmission electron microscopy. The scale bar = 50 nm (top right) and 5 nm (lower left). An FFT of the boxed region in the high-resolution image is shown (lower right).

Combination of alkyltrimethylammonium bromide with oleic acid stabilized TiO₂ nanorods in a water-hexane biphasic mixture did not lead to clean phase transfer of the TiO₂ to the aqueous phase. We tested three alkyltrimethylammonium cations with R = hexyl, octyl, and dodecyl in order to observe whether the alkyl chain length was important in the phase transfer reaction. In all cases, the experiment led to formation of insoluble white clumpy material. The isolated solids were not soluble in water or hexane. Heating or sonication of the mixtures did not have a significant visible effect, and insoluble white clumpy material remained. Potentially, the oleic acid stabilized nanorods aggregated within large hydrophobic assemblies surrounded by alkyltrimethylammonium cations.

With the negative result of the phase transfer experiment using molecular surfactant, we sought to compare the activity of an amphiphilic polymer (**1**) derived from combination of dodecylamine with poly(isobutylene-*alt*-maleic anhydride). The ratio of dodecylamine:anhydride was kept at ~0.7 to maintain significant fraction of carboxylic acid groups in the amphiphilic polymer product. The neutral polymer was soluble in THF, and could be combined with dispersions of oleic acid stabilized TiO₂ nanorods in the same solvent. The mixture of **1** and TiO₂ nanorods in THF showed no immediate visual change. Upon reflux of the mixture for 10 minutes, a precipitate formed and was isolated using centrifugation. The precipitate formed a cloudy dispersion in water with

ultrasonication, and separation occurred after sitting for more than 24 hours. A transmission electron micrograph (figure 2) shows that the nanorods deposited from aqueous phase are somewhat aggregated compared to the parent oleic acid stabilized nanocrystals deposited from its dispersion in hexanes. In comparison with the molecular interdigitation method, the polymer interdigitation appeared substantially more effective. We note the latter process is more thermodynamically favored due to the less negative entropic term. However, we were concerned with the observation of increased aggregation as evidenced by the lack of clarity in the aqueous dispersion and aggregated material as found with electron microscopy.

Figure 2. TEM of polymer-oleic acid-TiO₂ nanorods.

We evaluated ligand exchange with catecholates for phase transfer of the TiO₂ nanorods. There has been previous work establishing that catecholates and other –enediols bind quite strongly to the TiO₂ surface.⁵⁵⁻⁶¹ The surface monolayer gives rise to LMCT bands in the UV-vis spectrum, and catecholate passivated TiO₂ has been considered for pigment applications. We note that ligand exchange appears to be most effective when the substituting ligand has higher affinity for the surface than the exiting ligand wherein the process is thermodynamically driven by the differences in ΔH for the ligand-Ti bonding. Alternatively, such process can be entropically driven if a polymer displaces a molecular stabilizing layer. In the case of TiO₂ nanocrystals, it has been shown that oleic acid could be removed from the TiO₂ surface upon multiple successive precipitation and redispersion steps that eventually led to TiO₂ nanocrystal precipitate that no longer dispersed in hexanes.⁵² Addition of oleic acid to the precipitate allowed redispersion. Interestingly, addition of alkylphosphonic acid to the oleic acid depleted TiO₂ nanocrystals also led to redispersion; however, the alkylphosphonate stabilized TiO₂ nanocrystals retained the ability to redisperse even after repeated precipitation and redispersion cycles. The observations suggested that alkylphosphate binds the TiO₂ surface more strongly than oleate. Several –enediol ligands have been shown to have high affinity for TiO₂ that is due to the chelate binding mode to the surface.⁵⁵⁻⁶¹ We noted that several *para*-substituted 1,2-benzenediols are commercially available, and evaluated

several candidates (Scheme 1) for ligand substitution and phase transfer of TiO₂ nanorods.

Scheme 1. Substituted catechols selected for ligand substitution and phase transfer of oleic acid stabilized TiO₂ nanorods. **1** = 1,2,4-benzenetriol; **2** = 2,5-dihydroxybenzoic acid; **3** = 4-nitrocatechol; **4** = caffeic acid; **5** = gallic acid; **6** = pyrocatechol violet; **7** = pyrogallol red.

The catechols were dissolved in aqueous alkaline solutions and combined with dispersion of TiO₂ nanorods in hexanes in a biphasic reaction. In each reaction there was a color change of the aqueous phase and evolution of gas. The organic phase was separated from the aqueous phase and was nearly completely depleted of TiO₂ nanorods. The aqueous phase was treated with isopropanol to precipitate the colloid, which was collected after centrifugation. The residue fully redispersed in water with vortex mixing, indicating phase transfer of the TiO₂ nanorods and ability to process the sample. With the exception of 1,2,4-benzenetriol, the catechol stabilized TiO₂ nanorods dispersions in water were very stable, and could be kept for at least one year. UV-visible spectra of the aqueous dispersions of catechol-stabilized TiO₂ nanorods are shown in figure 3. The samples exhibit absorbance features at lower energy than the O 2p → Ti 3d transitions that are consistent with the previously observed LMCT bands found upon adsorption of catecholates to TiO₂.⁵⁶⁻⁶⁰

Figure 3. UV-visible absorption spectra of catechol-stabilized TiO₂ nanorods in water.

In all of the phase transfer reactions, evolution of a colorless, odorless gas was observed. We found that the gas was evolved if the reaction was performed in the presence or absence of light, ruling out a photochemical reaction. The color of the catecholate-TiO₂ dispersion did not change during the course of gas evolution, suggesting the gas did not arise from catechol decomposition. As a control reaction, we combined the hexanes TiO₂ nanorod dispersion with aqueous sodium hydroxide solution and found the same gas evolution reaction. The gas was found to extinguish a glowing splint, and could be confirmed as carbon dioxide (CO₂) with mass spectroscopy. The rate of formation of CO₂ was measured volumetrically by displacement of water. The data was recorded over a temperature range of 31-60°C, and the Arrhenius plot revealed an activation energy of 93±6 kJ/mol (figure 4). The observations are consistent with the evolution of CO₂ gas formed upon decarboxylation of oleic acid. For comparison, the activation energies for the hydrothermal decarboxylation of hydroxyl substituted benzoic acids were found as 90-97 kJ/mol.⁶² Decarboxylation of palmitic acid over activated carbon and Pt/C were found as 125 kJ/mol and 79 kJ/mol, respectively.⁶³

Figure 4. Rate of CO₂ evolution in the phase transfer reaction oleate-TiO₂ → catecholate-TiO₂ and the Arrhenius plot.

Plausibly, the decarboxylation could proceed such that hydroxide ion partially displaces a bidentate bridging oleic acid to give a Ti-OH group adjacent to a monodentate Ti-OOCR group. Nucleophilic attack of the hydroxide on the carbonyl carbon would give rise to a tetrahedral carbon intermediate, stabilized via two Ti-O bonds on the surface. Decomposition of the intermediate to alkane and bidentate bridging carbonate ion, followed by desorption of carbonate ions eventually yields CO₂.

Conclusions

Three methods for phase transfer of oleic acid stabilized TiO₂ nanorods from non-polar to aqueous phase were evaluated. Interdigitation with alkyltrimethylammonium bromide surfactants was found to be ineffective. The amphiphilic polymer formed upon treatment of poly(isobutylene-*alt*-maleic anhydride) with dodecylamine was much more effective for phase transfer of the TiO₂ nanorods. This is likely due to the more favorable ΔS associated with the polymer interdigitation compared to molecular interdigitation. The use of catechol derivatives presenting polar functional groups *para* to the -enediol were found to be effective for phase transfer of the TiO₂ nanorods. The reaction was accompanied by the non-photochemical evolution of CO₂ arising from decarboxylation of the oleic acid on the TiO₂ surface. While we present a plausible mechanism for the reaction, future work is needed to provide the mechanistic details. Interestingly, the observations may suggest a general approach to catalytic decarboxylation on metal oxide surfaces.

Acknowledgements

This work was supported by the National Science Foundation (CHE-0840507, CHE-0722632, CHE-1063000, EPS-0903804). JDH is especially grateful for having had the opportunity to work with Professor Somorjai.

References

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- ¹ L.E. Brus, *J. Chem. Phys.* 80 (1984) 4403-4409.
- ² H. Weller, *Angew. Chem. Int. Ed.* 32 (1993) 41-53.
- ³ A.P. Alivisatos, *J. Phys. Chem.* 100 (1996) 13226-13239.
- ⁴ R.L. Johnston, *Phil. Trans. R. Soc. Lond. A*, 356 (1998) 211-230.
- ⁵ P. Hapala, K. Kusova, I. Pelant, P. Jelinek, *Phys. Rev. B* 87 (2013) article no. 195420, pgs. 1-13.
- ⁶ A.M. Smith, S.M. Nie, *Acc. Chem. Res.* 43 (2010) 190-200.
- ⁷ R. Van Hardeveld, F. Hartog, *Surf. Sci.* 15 (1969) 189-230.
- ⁸ Y. Xia, Y. Xiong, B. Lim, S.E. Skrabalak, *Angew. Chem. Int. Ed.* 48 (2009) 60-103.
- ⁹ K.E. Sapsford, W.R. Algar, L. Berti, K.B. Gemmill, B.J. Casey, E. Oh, M.H. Stewart, I.L. Medintz, *Chem. Rev.* 113 (2013) 1904-2074.
- ¹⁰ A.B. Descalzo, R. Martinez-Manez, F. Sancenon, K. Hoffman, K. Rurack, *Angew. Chem. Int. Ed.* 45 (2006) 5924-5948.
- ¹¹ E. Katz, I. Willner, *Angew. Chem. Int. Ed.* 43 (2004) 6042-6108.
- ¹² A.K. Gupta, M. Gupta, *Biomaterials*, 26 (2005) 3995-4021.
- ¹³ S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L.V. Elst, R.N. Muller, *Chem. Rev.* 108 (2008) 2064-2110.
- ¹⁴ J.H. Lee, Y.M. Huh, Y. Jun, J. Seo, J. Jang, H.T. Song, S. Kim, E.J. Cho, H.G. Yoon, J.S. Suh, J. Cheon, *Nat. Med.* 13 (2007) 95-99.
- ¹⁵ S. Mornet, S. Vasseur, F. Grasset, E. Duguet, *J. Mater. Chem.* 14 (2004) 2161-2175.
- ¹⁶ J.H. Gao, H.W. Gu, B. Xu, *Acc. Chem. Res.* 42 (2009) 1097-1107.
- ¹⁷ R. Hao, R.J. Xing, Z.C. Xu, Y.L. Hou, S. Gao, S.H. Sun, *Adv. Mater.* 22 (2010) 2729-2742.
- ¹⁸ J. Kim, H.S. Kim, N. Lee, T. Kim, H. Kim, T. Yu, I.C. Song, W.K. Moon, T. Hyeon, *Angew. Chem. Int. Ed.* 47 (2008) 8438-8441.
- ¹⁹ I.L. Medintz, H.T. Uyeda, E.R. Goldman, H. Mattoussi, *Nat. Mater.* 4 (2005) 435-446.
- ²⁰ X.H. Gao, Y.Y. Cui, R.M. Levenson, L.W.K. Chung, S.M. Nie, *Nat. Biotechnol.* 22 (2004) 969-976.
- ²¹ J.K. Jaiswal, H. Mattoussi, J.M. Mauro, S.M. Simon, *Nat. Biotechnol.* 21 (2003) 47-51.
- ²² M. Liong, J. Lu, M. Kovochich, T. Xia, S.G. Ruehm, A.E. Nel, F. Tamanoi, J.I Zink, *ACS Nano* 2 (2008) 889-896.
- ²³ X.H. Gao, L.L. Yang, J.A. Petros, F.F. Marshal, J.W. Simons, S.M. Nie, *Curr. Opin. Biotechnol.* 16 (2005) 63-72.
- ²⁴ D. Peer, J.M. Karp, S. Hong, O.C. Farokhzad, R. Margalit, R. Langer, *Nat. Nanotechnol.* 2 (2007) 751-760.
- ²⁵ X.H. Huang, I.H. El-Sayed, W. Qian, M.A. El-Sayed, *J. Am. Chem. Soc.* 128 (2006) 2115-2120.
- ²⁶ M.E. Davis, Z. Chen, D.M Shin, *Nat. Rev. Drug Discov.* 7 (2008) 771-782.
- ²⁷ M.G. Panthani, V. Akhavan, B. Goodfellow, J.P. Schmidtke, L. Dunn, A. Dodabalapur, P.F. Barbara, B.A. Korgel, *J. Am. Chem. Soc.* 130 (2008) 16770-16777.
- ²⁸ S.B. Fuller, E.J. Wilhelm, J.M. Jacobson, *J. Microelectromech. S.* 11 (2002) 54-60.
- ²⁹ J.M. Meruga, W.M. Cross, P.S. May, Q. Luu, G.A. Crawford, J.J. Kellar, *Nanotechnology* 23 (2012) 395201.
- ³⁰ T. Blumenthal, J. Meruga, P.S. May, J. Kellar, W. Cross, K. Ankireddy, S. Vunnam, Q.N. Luu, *Nanotechnology* 23 (2012) 185305.

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- ³¹ J.M. Meruga, A. Baride, W. Cross, J.J. Kellar, P.S. May, *J. Mater. Chem. C* 2 (2014) 2221-2227.
- ³² T. Zhang, J. Ge, Y. Hu, Y. Yin, *Nano Lett.* 7 (2007) 3203-3207.
- ³³ J. Yang, J.Y. Lee, J.Y. Ying, *Chem. Soc. Rev.* 40 (2011) 1672-1696.
- ³⁴ G. Palui, F. Aldeek, W. Wang, H. Mattoussi, *Chem. Soc. Rev.* 44 (2015) 193-227.
- ³⁵ A. Dong, X. Ye, J. Chen, Y. Kang, T. Gordon, J.M. Kikkawa, C.B. Murray, *J. Am. Chem. Soc.* 133 (2011) 998-1006.
- ³⁶ J. Joo, S.G. Kwon, T. Yu, M. Cho, J. Lee, J. Yoon, T. Hyeon, *J. Phys. Chem. B* 109 (2005) 15297-15302.
- ³⁷ N. Dahal, S. Garcia, J. Zhou, S.M. Humphrey, *ACS Nano* 6 (2012) 9433-9446.
- ³⁸ J. Shimoizuka, K. Nakatsuka, T. Jujita, A. Kounosu, *IEEE Trans. Magn. MAG-16* (1980) 368-371.
- ³⁹ S.E. Khalafalla, G.W. Reimers, *IEEE Trans. Magn. MAG-16* (1980) 178-183.
- ⁴⁰ A. Wooding, M. Kilner, D.B. Lambrick, *J. Colloid Interface Sci.* 144 (1991) 236-242.
- ⁴¹ L. Shen, P.E. Laibinis, T.A. Hatton, *Langmuir* 15 (1999) 447-453.
- ⁴² Q. Lan, C. Liu, F. Yang, S. Liu, J. Xu, D. Sun, *J. Coll. Interf. Sci.* 310 (2007) 260-269.
- ⁴³ A. Swami, A. Kumar, M. Sastry, *Langmuir* 19 (2003) 1168-1172.
- ⁴⁴ T. Pellegrino, L. Manna, S. Kudera, T. Liedl, D. Koktysh, A.L. Rogach, S. Keller, J. Radler, G. Natile, W.J. Parak, *Nano Lett.* 4 (2004) 703-707.
- ⁴⁵ M.T. Fernandez-Arguelles, A. Yakovlev, R.A. Sperling, C. Luccardini, S. Gaillard, A.S. Medel, J.M. Mallet, J.C. Brochon, A. Feltz, M. Oheim, W.J. Parak, *Nano Lett.* 7 (2007) 2613-2617.
- ⁴⁶ C. Zhang, R.J. Macfarlane, K.L. Young, C.H.J. Choi, L. Hao, E. Auyeung, G. Liu, X. Zhou, C.A. Mirkin, *Nature Mater.* 12 (2013) 741-746.
- ⁴⁷ S. Sekiguchi, K. Niikura, Y. Matsuo, K. Ijro, *Langmuir* 28 (2012) 5503-5507.
- ⁴⁸ B.P. Binks, J.A. Rodrigues, *Angew. Chem. Int. Ed.* 44 (2005) 441-444.
- ⁴⁹ U. Drechsler, B. Erdogan, V.M. Rotello, *Chem. Eur. J.* 10 (2004) 5570-5579.
- ⁵⁰ J. Liu, J. Alvarez, W. Ong, E. Roman, A.E. Kaifer, *J. Am. Chem. Soc.* 123 (2001) 11148-11154.
- ⁵¹ Y. Wang, J.F. Wong, X. Teng, X.Z. Lin, H. Yang, *Nano Lett.* 3 (2003) 1555-1559.
- ⁵² P.D. Cozzoli, A. Kornowski, H. Weller, *J. Am. Chem. Soc.* 125 (2003) 14539-14548.
- ⁵³ T. Sasaki, M. Watanabe, *J. Phys. Chem. B* 101 (1997) 10159-10161.
- ⁵⁴ N. Serpone, D. Lawless, R. Khairutdinov, *J. Phys. Chem.* 99 (1995) 16646-16654.
- ⁵⁵ Q. Ye, F. Zhou, W. Liu, *Chem. Soc. Rev.* 40 (2011) 4244-4258.
- ⁵⁶ C. Creutz, M.H. Chou, *Inorg. Chem.* 47 (2008) 3509-3514.
- ⁵⁷ L. de la Garza, Z.V. Saponjic, N.M. Dimitrijevic, M.C. Thurnauer, T. Rajh, *J. Phys. Chem. B* 110 (2006) 680-686.
- ⁵⁸ P.C. Redfern, P. Zapol, L.A. Curtiss, T. Rajh, M.C. Thurnauer, *J. Phys. Chem. B* 107 (2003) 11419-11427.
- ⁵⁹ Y. Liu, J.I. Dadap, D. Zimdars, K.B. Eisenthal, *J. Phys. Chem. B* 103 (1999) 2480-2486.
- ⁶⁰ I.A. Jankovic, Z.V. Saponjic, M.I. Comor, J.M. Nedeljkovic, *J. Phys. Chem. C* 113 (2009) 12645-12652.
- ⁶¹ L.M. Liu, S.C. Li, H. Cheng, U. Diebold, A. Selloni, *J. Am. Chem. Soc.* 133 (2011) 7816-7823.

⁶² Brill, T.B.; Li, J., J. Phys. Chem. A 107 (2003) 2667-2673.

⁶³ J. Fu, F. Shi, L.T. Thompson, Jr., X. Lu, P.E. Savage, ACS Catal. 1 (2011) 227-231.