Synthesis and properties of covalently linked photoluminescent magnetic magnetite nanoparticle-silicon nanocrystal hybrids

Morteza Javadi, Tapas Purkait, Lida Hadidi, John Washington and Jonathan G. C. Veinot

Link to this article: http://journals.cambridge.org/abstract_S2059852116004655

Request Permissions : Click here

Synthesis and properties of covalently linked photoluminescent magnetic magnetite nanoparticle-silicon nanocrystal hybrids

Morteza Javadi,[1] Tapas Purkait,[1] Lida Hadidi,[1] John Washington,[2] Jonathan G. C. Veinot[1],*

[1] Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, Canada. E-mail: jveinot@ualberta.ca; Fax: +1-780-492-8231; Tel: +1-780-492-7206
[2] Department of Chemistry, Concordia University of Edmonton, 7128 Ada Boulevard, Edmonton Alberta, Canada

ABSTRACT

Silicon nanocrystals (SiNCs) are quantum dots that do not contain toxic metals and exhibit a photoluminescent response that may be tailored via changes in particle dimension as well as surface chemistry. Herein, we present a promising hybrid nanomaterial that combines the favourable properties (e.g., photoluminescence, biocompatibility, and surface chemistry) of SiNCs with the magnetic characteristics of Fe_3O_4 nanoparticles (NPs). Linking these two complementary nanomaterials via DCC coupling has yielded a new advanced hybrid material that possesses the characteristics of its constituents and affords a photoluminescent system that responds to permanent magnets.

INTRODUCTION

Si nanocrystals are made up of an abundant biocompatible element and exhibit size/surface chemistry tunable photoluminescence (PL) that can span throughout the visible and NIR spectral regions.[1] These properties alone make SiNCs an attractive candidate for many applications.[2] Combining magnetic and luminescent properties to form hybrid nanomaterials raises the possibility of external control and manipulation that could lead to applications such as targeted biochemical labeling, separation, detection, and medical theranosis.[3]

Examples of cell labelling agents based upon the combination of a magnetic nanoparticle (i.e., iron and its oxides) with molecular dyes,[4, 5] or prototypical CdSe QDs have appeared.[6, 7] Unfortunately, these materials are limited by significant disadvantages that hinder their widespread use. For example, dye-based labels suffer from limited photo-stability,[8–10] while CdSe QDs are cytotoxic. [2, 11–14] Clearly, an attractive alternative to these materials would be to combine the properties of non-toxic, photostable SiNCs with magnetic systems.[15] The

following report outlines the preparation of a new magnetic responsive, photoluminescent nano-hybrid based upon SiNCs and Fe_3O_4-NPs.
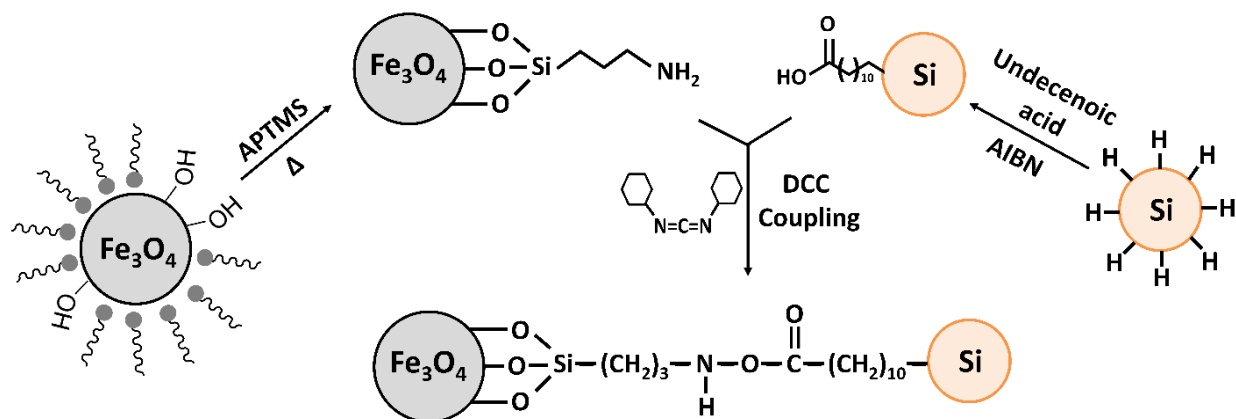
Scheme 1. A summary for the synthesis of Fe_3O_4NP-SiNC hybrid materials.

EXPERIMENTAL

Reagents and Materials. Commercial hydrogen silsesquioxane (HSQ) was purchased from Dow Corning Corp. (Midland, MI). Electronic grade hydrofluoric acid (HF, 49% aqueous solution) was purchased from J. T. Baker and used as received. 1, 2-Hexadecanediol (> 98.0%) was obtained from Tokyo Chemical Industry. All other reagents were purchased from Sigma-Aldrich (iron (III) acetylacetonate (97%), oleic acid (90%), oleylamine (70%), benzyl ether (98%), 10-undecenoic acid (98%), 2,2′-azobis(2-methylpropionitrile) (AIBN, 98%), (3-aminopropyl)trimethoxysilane (APTMS, 97%), N,N′-dicyclohexylcarbodiimide (DCC, 99%) and reagent grade dichloromethane, toluene, ethanol, methanol. They were used as received unless specified otherwise. Ultrapure water (18.2 MΩ/ cm) obtained from a Barnstead Nanopure Diamond purification system was used throughout the present investigations.

Hydride surface terminated SiNCs (H-SiNCs) bearing diameters of ~ 3 nm were prepared using well-established procedures developed in the Veinot laboratory.[16] Briefly, approximately 3 g of solid HSQ was placed in a quartz boat, transferred to a Lindberg Blue tube furnace and heated in a slightly reducing atmosphere (i.e., 5 % H_2/95 % Ar) at 18 °C/min to a peak temperature of 1100 °C where it was maintained for 1 hr. After cooling to room temperature the resulting a composite consisting of oxide-embedded SiNCs (d ~ 3 nm) was mechanical ground to a fine powder using an agate mortar and pestle for 15 min, followed by wrist-action shaker for 12 h. Subsequently, 0.30 g of the composite powder was transferred to a polyethylene terephthalate beaker and 3 mL each of deionized water, EtOH, and 49% HF acid were added sequentially with stirring. *(Caution: Appropriate safeguards must be implemented when working*

with hydrofluoric acid.) After stirring for 1 h in ambient light and atmosphere hydrophobic H-SiNCs were extracted into three 15 mL aliquots of toluene. The resulting suspensions were centrifuged at 3000 rpm for 5 min to obtain a pellet of H-SiNCs that were dispersed in toluene and dried over molecular sieves to remove trace water and the NCs dispersion was centrifuged one more time. The dry H-SiNCs pellet was dispersed in 20 mL of dry toluene and used directly in functionalization procedures described below.

Surface Functionalization of H-SiNCs. Undecanoic acid terminated SiNCs were prepared using established procedures for radical initiated surface hydrosilylation.[17] A 100 ml Schlenk flask was charged with 10-undecenoic acid (1.1 mmol, 200 mg) equipped with a Teflon-coated magnetic stir bar. The flask was attached to an argon charged double manifold and heated to 70 °C under reduced pressure (*ca.* 2 mbar) for 3 h to remove trace water from undecenoic acid. After cooling to room temperature toluene dispersion of H-SiNCs (ca. 25 mg SiNCs in 20 mL dry tolulene) and AIBN (0.061 mmol) were added to the flask and the mixture was subjected to three freeze-pump-thaw cycles. The cloudy reaction mixture was heated to, and maintained at 60 °C under an argon atmosphere for at least 15 h. After cooling to room temperature the crude product mixture were transferred to a 50 mL PTFE centrifuge tube and 20 mL of dry toluene was added followed by centrifuging at 12000 rpm for 20 min. The supernatant was decanted and the pellet containing functionalized SiNCs was re-dispersed in toluene (40 mL) followed by centrifuging at 12000 rpm for 20 min. The centrifugation/re-dispersion process was repeated twice after which the purified undecanoic-acid functionalized SiNCs were dispersed in methanol as clear suspension and further analyzed by TEM, EDX, PL and FT-IR.

Synthesis of Fe_3O_4 (magnetite) NPs. A variant of an established literature procedure was employed to prepare magnetite nanoparticles.[18] A round bottom flask equipped with a magnetic stir bar was charged with of Fe(acac)$_3$ (719.5 mg; 2 mmol), oleic acid (2.321 g; 6 mmol), oleyl amine (6 mmol), 1,2- hexadecanediol (2.581 g; 10 mmol) and benzyl ether (20 mL). The mixture was degassed by a three-cycle exposure to vacuum and argon. The reaction mixture was heated with stirring to 140, 200, and 250 °C holding at each temperature for 1 hour. Following this heating profile the crude product mixture was cooled to room temperature yielding a black suspension. Magnetite NPs were separated from reagents by three centrifuge cycles at 12000 rpm for 30 min followed by two cycles of magnetic separation. The particles were re-dispersed in dichloromethane and further analyzed by TEM, EDX and FT-IR.

Surface modification of Fe_3O_4-NPs. The surfaces of the present magnetite nanoparticles were derivatized with (3-aminopropyl)trimethoxysilane (APTMS) using a modified literature procedure.[19] As-synthesized Fe_3O_4 nanoparticles (50 mg) were combined with APTMS (3 mL, 17.3 mmol) in anhydrous toluene (10 mL) and refluxed for 3 hours in an argon atmosphere. The reaction mixture was subsequently cooled to room temperature, transferred to centrifuge tubes

and the black solid was isolated upon centrifuging at 12000 rpm, 20 min. The resulting pellet of APTMS modified was resuspended in ethanol with sonication and isolated by centrifugation (12000 rpm, 20 min.). The sonication/suspension/centrifugation cycle was repeated three times. Following the final centrifugation step the APTMS-functionalized Fe_3O_4 particles were dispersed in purified dichloromethane and stored for further use and characterization by TEM, EDX and FT-IR.

Coupling of undecanoic acid-SiNCs to APTMS-Fe_3O_4 NPs. A dichloromethane solution of DCC (100 μL, 0.1 M) was added to a 5 ml glass vial containing dichloromethane suspension of undecanoic acid functionalized SiNCs (1 mL; 20 mg/mL). The vial was sealed and the reaction mixture as stirred for ca. 20 min, after which the magnetic stir bar was removed and APTMS-Fe_3O_4 NPs in dichloromethane (1 mL; 2 mg/mL) was added. The vial was again sealed and placed on a platform mechanical shaker at 200 rpm for at least 12 h. Finally, the coupled Fe_3O_4NP-SiNC hybrid was drawn to the side of the vial upon exposure to a permanent magnet and the supernatant decanted. Ethanol (~2 mL) was added to the vial and the vial was placed in a bath sonicator for at least 1 min to disperse the Fe_3O_4NP-SiNC hybrid. The hybrid particles were subjected to this magnetic separation/re-suspension procedure six times to ensure free SiNCs were removed. The resulting Fe_3O_4NP-SiNC hybrid particles were stored in ethanol and further analyzed using FT-IR, EDX and PL.

Material Characterization and Instrumentation. Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analyses were performed using a JEOL-2010 (LaB6 filament) electron microscope with an accelerating voltage of 200 kV. High resolution TEM (HRTEM) imaging was performed on JEOL-2200FS TEM instrument with an accelerating voltage of 200 kV. TEM samples were prepared by drop-coating of nanoparticle suspensions in dichloromethane (methanol in case of SiNCs) onto a holey carbon coated copper grid (300 mesh, Electron Microscopy Science). TEM and HRTEM images were processed using ImageJ software (version 1.48 v). Solution photoluminescence (PL) measurements were performed using a Varian Cary Eclipse fluorescence spectrometer. Fourier-Transform Infrared Spectroscopy (FT-IR) was performed on a Nicolet Magna 750 IR spectrophotometer by drop casting of a solution/suspension containing the desired particles in ethanol (for SiNCs) and dichloromethane (for Fe_3O_4-NPs and SiNCs-Fe_3O_4NPs hybrid).

RESULTS AND DISCUSSION

Oxide embedded SiNCs were prepared via reductive thermal processing of commercial HSQ.[16] Hydride-terminated SiNCs were liberated from the oxide matrix upon etching with ethanolic HF. The surfaces of these H-SiNCs are readily modified using a variety of hydrosilylation protocols.[2],[17],[20],[21] In the current work, functionalization with undecenoic acid was achieved by applying established AIBN initiated radical

hydrosilylation.[17] Figure 1a shows representative TEM images of undecanoic acid functionalized SiNCs (d ~3.5 ± 0.7 nm). As expected for Si NCs of this dimension visible PL with emission maximum at ca. 610 nm is observed.
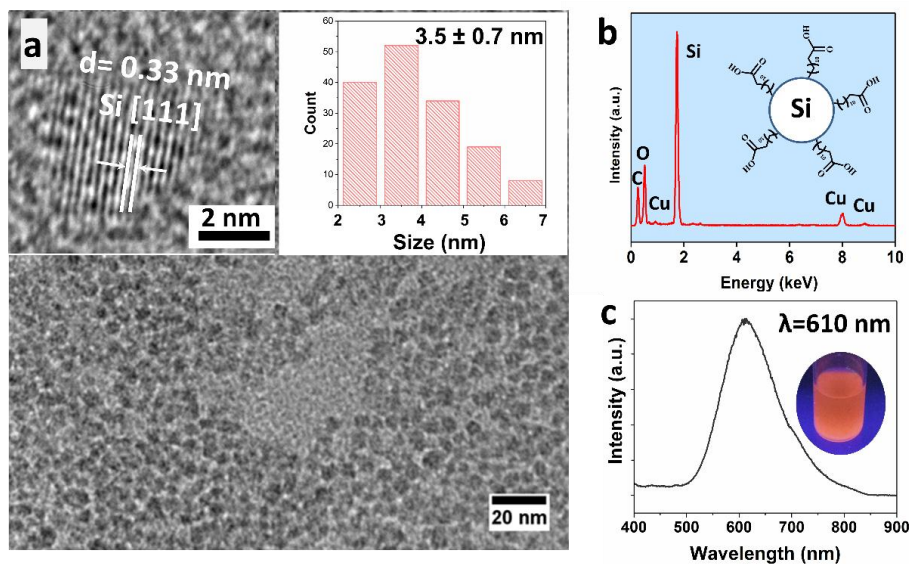

Figure 1. Characterization of undecanoic acid functionalized SiNCs. a) Brightfield TEM image highlighting an average particle diameter = 3.5 ± 0.7 nm. Inset: HRTEM image of a representative NC showing lattice fringes arising from Si [111] planes. b) A representative EDX spectrum of undecanoic acid functionalized SiNCs. c) PL spectrum upon excitation at 350 nm.

Fe_3O_4 (magnetite) NPs were synthesized using an established literature procedure that involved the thermal decomposition/reduction of iron(III) acetylacetonate in the presence of oleic acid and oleylamine.[18] The resulting NPs are hydrophobic and are readily isolated upon addition of ethanol followed by centrifugation. Purification of the present Fe_3O_4-NPs was achieved by magnetic separation. Brightfield and HRTEM analyses (Figure 2a), show the Fe_3O_4-NPs are pseudospherical single crystals with a size distribution of 8.2 ± 1.2 nm. The Fe_3O_4-NPs respond to a permanent magnet (Figure 2b). NPs of these dimensions are considerably smaller than magnetic domains in bulk Fe_3O_4 (128 nm).[22],[23] This leads to well-established superparamagnetic behaviour that has far reaching impacts on biological applications.[24] The EDX spectrum of the present Fe_3O_4-NPs confirms the presence of iron and oxygen (Figure 2c).
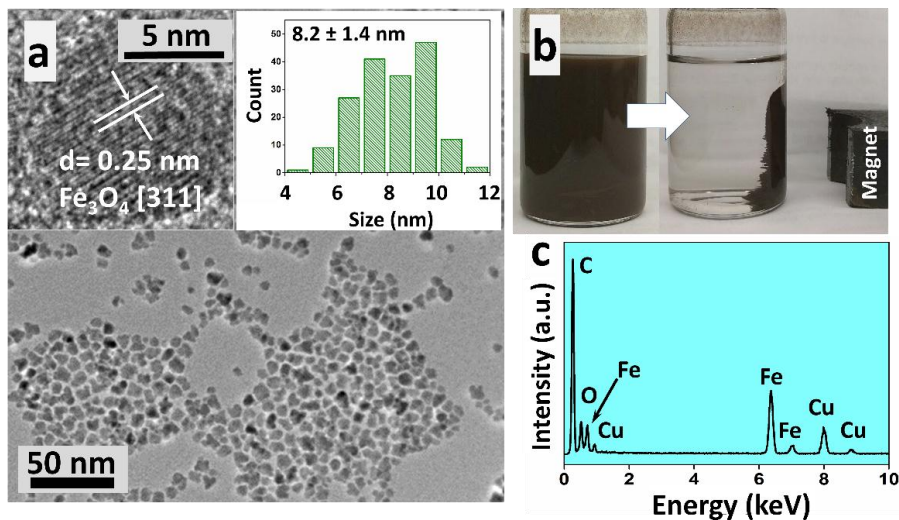
Figure 2. Characterization of Fe_3O_4-NPs. a) Brightfield TEM image showing an average diameter = 8.2 ± 1.2 nm. Inset: HRTEM of a representative NPs showing lattice fringes of 0.25 nm related to Fe_3O_4 [311] planes b) Response of dichloromethane dispersion of NPs upon exposure to a permanent magnet. c) EDX spectrum presented Fe_3O_4-NPs.

To interface Fe_3O_4-NPs with SiNCs it was necessary to introduce appropriate surface reactivity that does not compromise the Fe_3O_4-NP core. Surface pendant (3-aminopropyl)trimethoxysilane (APTMS) functionalities afford the reactivity of amine groups and are frequently used as coupling agents for attaching a variety of substrates.[19],[25] For the present paring of nanomaterials, the amine functionalities on the APTMS-Fe_3O_4 NPs are expected to react with carboxylic acid groups on the surfaces of undecanoic acid functionalized SiNCs via high yielding dicyclohexylcarbodiimide (DCC) coupling (Scheme 1).[26, 27]

Brightfield TEM evaluation of APTMS-Fe_3O_4 NPs (not shown) confirms the Fe_3O_4 core remains intact throughout the APTMS modification procedure. In addition, the EDX spectrum of APTMS-Fe_3O_4 NPs confirms the presence of nitrogen and silicon arising from the surface modification (not shown). Furthermore, FTIR analysis shows the expected features associated with the surface pendant amine moiety. Coupling of undecanoic acid-SiNCs with APTMS-Fe_3O_4 NPs was achieved upon via DCC mediated amide formation. FTIR analysis of the Fe_3O_4NP-SiNC hybrid shows characteristic features (*i.e.*, amide N-H stretch 1650 cm^{-1}) while photoluminescent response of the SiNCs remains intact (Figure 3e). Further highlighting that the Fe_3O_4NPs and SiNC are covalently linked in the present hybrid, exposure to a permanent magnet leads to complete migration/capture of all photoluminescent material (Figure 3)
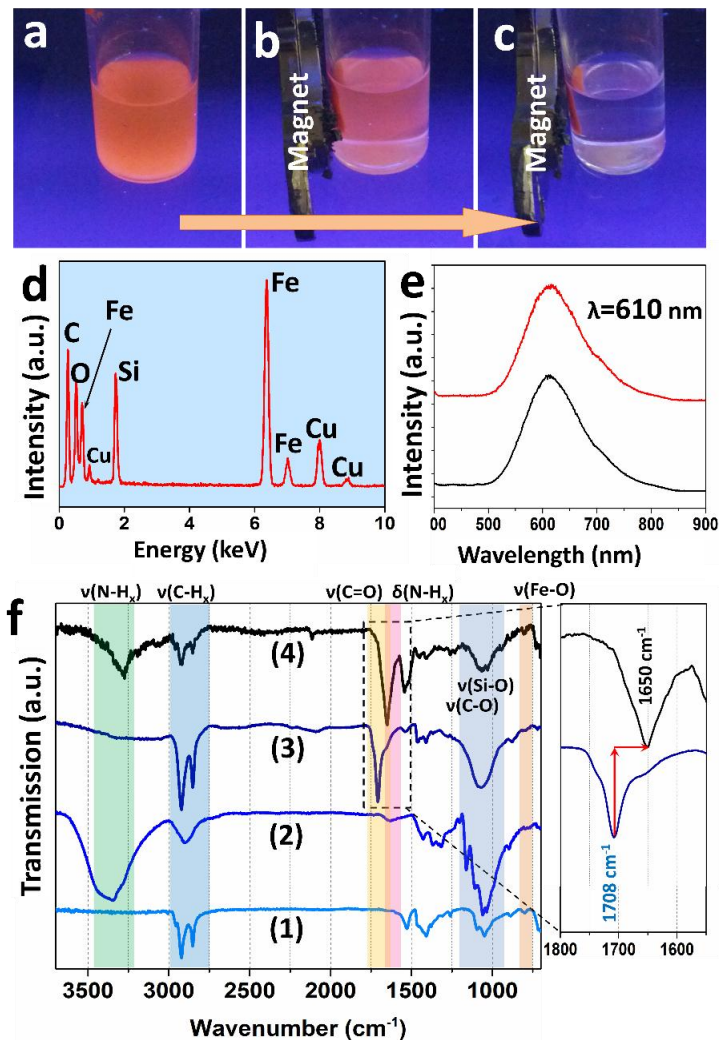
Figure 3. Characterization of the Fe$_3$O$_4$NP-SiNC hybrid. a-c) Response of the Fe$_3$O$_4$NP-SiNC hybrid NPs upon being exposed to a permanent magnet. d) EDX spectrum of Fe$_3$O$_4$NP-SiNC hybrid. e) PL spectra of SiNCs (black) and Fe$_3$O$_4$NP-SiNC hybrid (red). f) IR spectra of as-synthesized Fe$_3$O$_4$ NPs (1), APTMS functionalized Fe$_3$O$_4$ NPs (2), undecanoic acid functionalized SiNCs (3), Fe$_3$O$_4$NP-SiNC hybrid (4).

CONCLUSION

Photoluminescent silicon nanocrystals have been interfaced via direct covalent coupling with magnetic Fe$_3$O$_4$ nanoparticles. Marrying these complementary materials has yielded a luminescent nano-hybrid that exhibits the optical response of benign Si NCs and the magnetic behaviour of magnetite nanoparticles. Furthermore, this is a pivotal example of covalent linking of two nanomaterials and opens possibilities for new hybrid materials.

REFERENCES

1. J. Heitmann, F. Müller, M. Zacharias, and U. Gösele, *Adv. Mater.* **17**, 795 (2005).
2. M. Dasog, J. Kehrle, B. Rieger, and J. G. C. Veinot, *Angew. Chemie Int. Ed.* **55**, 2322 (2016).
3. M. Mahmoudi and M. A. Shokrgozar, *Chem. Commun.* **48**, 3957 (2012).
4. J. Kim, J. E. Lee, J. Lee, J. H. Yu, B. C. Kim, K. An, Y. Hwang, C.-H. Shin, J.-G. Park, and J. Kim, *J. Am. Chem. Soc.* **128**, 688 (2006).
5. S. A. Corr, Y. P. Rakovich, and Y. K. Gun'ko, *Nanoscale Res. Lett.* **3**, 87 (2008).
6. H. Weller, *Curr. Opin. Colloid Interface Sci.* **3**, 194 (1998).
7. P. Alivisatos, *Nat Biotech* **22**, 47 (2004).
8. J. Kolosnjaj-tabi, C. Wilhelm, O. Clément, and F. Gazeau, *J. Nanobiotechnology* **11**, S7 (2013).
9. S. Jin, Y. Hu, Z. Gu, L. Liu, and H. Wu, **2011** (2011).
10. U. Resch-genger, M. Grabolle, S. Cavaliere-jaricot, R. Nitschke, and T. Nann, **5**, 763 (2008).
11. J.-H. Park, L. Gu, G. Von Maltzahn, E. Ruoslahti, S. N. Bhatia, and M. J. Sailor, *Nat. Mater.* **8**, 331 (2009).
12. X. Gao and S. Nie, *J. Phys. Chem. B* **107**, 11575 (2003).
13. S. T. Selvan, *Biointerphases* **5**, FA110 (2010).
14. S. Jin, Y. Hu, Z. Gu, L. Liu, and H.-C. Wu, *J. Nanomater.* **2011**, 13 (2011).
15. F. Erogbogbo, K.-T. Yong, R. Hu, W. Law, H. Ding, C. Chang, P. N. Prasad, M. T. Swihart, I. I. I. I. Oxide, F. Erogbogbo, K.-T. Yong, R. Hu, W. Law, H. Ding, and C. Chang, *ACS Nano* **4**, 5131 (2010).
16. C. M. Hessel, E. J. Henderson, J. G. C. Veinot, V. Uni, R. V February, V. Re, M. Recei, and V. August, *Chem. Mater.* **18**, 6139 (2006).
17. Z. Yang, C. M. Gonzalez, T. K. Purkait, M. Iqbal, A. Meldrum, and J. G. C. Veinot, *Langmuir* **31**, 10540 (2015).
18. S. Sun and H. Zeng, *J. Am. Chem. Soc.* **124**, 8204 (2002).
19. R. G. Acres, A. V Ellis, J. Alvino, C. E. Lenahan, D. A. Khodakov, G. F. Metha, and G. G. Andersson, *J. Phys. Chem. C* **116**, 6289 (2012).
20. Y. Zhai, M. Dasog, R. B. Snitynsky, T. K. Purkait, M. Aghajamali, A. H. Hahn, C. B. Sturdy, L. Lowary, and J. G. C. Veinot, *J. Mater. Chem. B Mater. Biol. Med.* **2**, 8427 (2014).

21. T. K. Purkait, M. Iqbal, M. H. Wahl, K. Gottschling, C. M. Gonzalez, M. A. Islam, and J. G. C. Veinot, *J. Am. Chem. Soc.* **136**, 17914 (2014).

22. S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L. Vander Elst, and R. N. Muller, *Chem. Rev.* **108**, 2064 (2008).

23. A. Lu, E. L Salabas, and F. Schüth, *Angew. Chemie Int. Ed.* **46**, 1222 (2007).

24. D. L. Huber, *Small* **1**, 482 (2005).

25. S. Photong and V. Boonamnuayvitaya, 453 (2010).doi:10.1007/s11270-009-0268-5

26. J. C. Sheehan, G. P. Hess, A. B. Lerner, and T. E. H. H. Lee, *J. Am. Chem. Soc.* **77**, 1067 (1955).

27. B. Neises and W. Steglich, *Angew. Chemie Int. Ed. English* **17**, 522 (1978).