Emission enhancement through Nd^{3+} - Yb^{3+} energy transfer in multifunctional NaGdF_4 nanocrystals

Francisco J. Pedraza,¹ Chris Rightsell,¹ G. A. Kumar,^{1,2} Jason Giuliani,¹ Carlos Monton,¹ and Dhiraj K. Sardar¹

¹*Department of Physics and Astronomy, The University of Texas at San Antonio, San Antonio, Texas 78249, USA*

²*Department of Natural and Physical Sciences, Northwest Vista College, San Antonio, Texas 78251, USA*

(Received 7 March 2017; accepted 12 May 2017; published online 31 May 2017)

The growing need for biomedical contrast agents has led to the current development of multifunctional materials such as lanthanide-based nanoparticles (NPs). The optical and magnetic properties these nanoparticles (NPs) possess are important to enhance current biomedical imaging techniques. To increase the optical emissions of the nanoparticles, neodymium (Nd^{3+}) and ytterbium (Yb^{3+}) were introduced into a magnetic host of NaGdF_4 . The energy transfer between Nd^{3+} and the Yb^{3+} was then investigated at multiple concentrations to determine the optimal dopant levels. The $\text{NaGdF}_4:\text{Nd}^{3+},\text{Yb}^{3+}$ nanoparticles were synthesized through a modified solvothermal method, resulting in rectangular structures, with an average side length of 17.87 ± 4.38 nm. A double dopant concentration of 10% Nd^{3+} and 4% Yb^{3+} was found to be optimal, increasing the emission intensity by 71.5% when compared to the widely used Nd^{3+} single dopant. Decay measurements confirm energy transfer from Nd^{3+} to Yb^{3+} , with a lifetime shortening from Nd^{3+} 1064 nm emission and a calculated lifetime of 12.72 ms with 98% efficiency. Despite $\text{NaGdF}_4:\text{Nd}^{3+},\text{Yb}^{3+}$ NPs showing a slight decrease in their magnetic response at the expense of optimizing optical emission, as it is directly dependent on the Gd^{3+} concentration, a strong paramagnetic behavior was still observed. These results corroborate that $\text{NaGdF}_4:\text{Nd}^{3+},\text{Yb}^{3+}$ NPs are viable candidates for multimodal imaging.

Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4984140>]

The next frontier in medical imaging technologies is to develop efficient multimodal contrast agents which in combination with new acquisition systems allow detecting multiple signals. Recent progress in nanotechnology allows for the fabrication of such multifunctional nanomaterials with different physical properties such as optical and magnetic.¹⁻³ Efforts have been made on the development and applications of multifunctional contrast agents such as quantum dots,^{4,5} organic dyes,⁶ graphene,^{7,8} and lanthanide-based nanomaterials;¹⁻³ however, these contrast agents are not favorable for *in vivo* imaging applications. This is due to the inherent photobleaching of organic dyes⁸ and the high toxicity of quantum dots and graphene.⁹⁻¹¹ Lanthanide-based imaging agents lack previously stated drawbacks and present the advantages of low cost of production, multifunctional capabilities,^{1,2} photostability,¹² and an ideal size for biomedical applications.¹³ In addition, their magnetic, optical, and chemical properties can be broadly tuned.¹⁴⁻¹⁷

Lanthanide-based nanomaterials present outstanding optical properties, and in combination with other lanthanide elements, they can also present magnetic behavior.¹⁻³ Lanthanide ions have been in the forefront of the development of photonic-based technologies such as lasers,¹⁸ optical sensors,¹⁹⁻²¹ electrical displays,^{22,23} and solar cells.²⁴⁻²⁶ Lanthanide ions possess high emission and sharp transitions, which arise from the shielding of 4f orbitals by 5s²5p⁶ subshells. This shielding effect facilitates detection due to well-defined emission profiles. Among the lanthanide ions, neodymium (Nd^{3+}) has attracted interest in the medical field for being optically active in the near infra-red (NIR) region

with one of the highest emission cross sections for the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ emission band. Similarly, ytterbium (Yb^{3+}) is one of the most important of the lanthanide ions because it possesses the highest absorption cross section. Yb^{3+} is commonly used as a synthesizer in the production of higher energy emission, commonly referred to as upconversion, and as a generator of NIR light.^{14,27} Although switching its role from the synthesizer to the emitter is unconventional, it is possible to induce energy transfer from Nd^{3+} exciting at 808 nm, generating Yb^{3+} emission at 1000 nm. Little work has been performed in this area, with the majority focusing on single crystal systems²⁸⁻³⁰ and some nanoparticle (NP) systems for applications in nanothermometry.³¹ However, to make these materials appropriate for biomedical applications, the energy transfer process needs to be optimized at sub-50 nm size of particles.

In this work, we explore the fabrication of sub-25 nm size $\text{NaGdF}_4:\text{Nd}^{3+},\text{Yb}^{3+}$ NPs and present a systematic study of the optical and magnetic properties of these NPs, monitored as a function of Gd^{3+} substitution by Nd^{3+} and Yb^{3+} dopants. NaGdF_4 was chosen as the host crystal due to its low phonon energies which promote high emission intensities. The inclusion of gadolinium (Gd^{3+}) in the host matrix provides paramagnetic properties, contributing to the multifunctional nature of the material¹⁻³ and opening its use to multimodal optomagnetic imaging.

$\text{NaGdF}_4:\text{Nd}^{3+},\text{Yb}^{3+}$ NPs were synthesized through a modified solvothermal (ST) method. The ST method requires inexpensive precursors, low temperatures, and non-inert atmospheres. In general, this method is a low cost and scalable

process that allows for fine size tuning which yields narrow size distributions. The modified ST method was implemented to optimize the resultant NPs, where stoichiometric amounts of $L(\text{NO}_3)_3$ ($L = \text{Gd}, \text{Nd}, \text{and Yb}$) were magnetically stirred until dissolved in 30 ml of ethylene glycol along with 1 g of polyvinylpyrrolidone (PVP) used as a surfactant. A separate solution of 0.4199 g of sodium fluoride and 1.1112 g of ammonium fluoride in 20 ml of ethylene glycol was prepared. After thoroughly stirring each solution at room temperature, the two solutions were combined and stirred for approximately an hour, until a thin gel was formed. The combined solution was placed in a Teflon-lined stainless steel autoclave and heated at 200 °C for 24 h. Following the synthesis process, the NPs were washed to remove unreacted precursors and freeze-dried to prevent agglomeration and obtain a NP powder. A range of Nd^{3+} (1, 2, 4, 6, 8, 10, 12, 15, and 20%) and Yb^{3+} (0.5, 1, 2, 4, 6, and 8%) concentrations were prepared to explore the energy transfer kinetics between Nd^{3+} and Yb^{3+} ions.

One of the mechanisms that affect optical emission is phonon generation arising from crystalline imperfections. As a result of dopant lanthanide ions favoring locations near NP surfaces, absorbed energy can easily migrate to the crystal surface or lattice defects.^{22,32} To reduce its impact, NPs were heat treated using a double-crucible method at 800 °C to improve crystallinity. The optimal heat-treating duration was investigated by heating the NPs over different time periods (5, 10, 20, 40, and 60 min) and recording emission spectra. The study revealed that 10 min produces the highest optical emission intensity.

X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) were used to obtain the NP composition, crystallinity, and morphology. The XRD spectra of as-prepared and heat treated samples are displayed in Fig. 1(a). A mixed phase of 20% α - NaGdF_4 (cubic) and 80% β - NaGdF_4 (hexagonal) was observed. This mixed phase is due to the high-temperature treatment since a phase change, from hexagonal to cubic, is induced when fluoride materials are heated to high temperatures.³³ Remaining peaks not present in the reference are attributed to unreacted precursors (NdN , GdN , YbN , and NH_4F). Heat-treated samples produced sharper peaks, indicating higher crystallinity, calculated by the following equation:

$$\chi_c = \left(\frac{0.24}{\beta_{[hkl]}} \right)^3, \quad (1)$$

where χ_c represents the degree of crystallinity and $\beta_{[hkl]}$ accounts for the full width at half maximum value of the calculated crystal planes. The increase in crystallinity was calculated to be from 17.64% (as-prepared) to 44.97% (heat treated), resulting in an average increase of 27.33%. Figures 1(b) and 1(c) show TEM images of the $\text{NaGdF}_4:\text{Nd}^{3+}(10\%), \text{Yb}^{3+}(4\%)$ NPs with lattice fringes in the [110] plane and the corresponding selected area electron diffraction pattern shown in the inset of Fig. 1(c). The NPs are cubic in shape with a side length of 10.5–28 nm and an average length of $17.87 \text{ nm} \pm 4.38 \text{ nm}$; hence, the synthesized NPs are suitable for biomedical applications.¹³ The inset of Fig. 1(c) shows the selected area electron diffraction of the NPs, containing primarily a β -pattern with traces of α - NaGdF_4 . The elemental composition of the NPs was confirmed by means of Electron Dispersion Spectroscopy (EDS) in a Hitachi STEM-5500 scanning electron microscope, in agreement with XRD results, Fig. S1 (see [supplementary material](#)).

Stable colloidal properties of NPs in water and physiological media are important when considering a NP for biological applications. Dynamic Light Scattering (DLS) was utilized to measure the hydrodynamic size of the NPs in water and Phosphate Buffer Saline (PBS) solution, Fig. S2 (see [supplementary material](#)). The DLS results show that NPs are stable in water and have a hydrodynamic radius of 205 nm. When suspended in PBS, $\text{NaGdF}_4:\text{Nd}^{3+}/\text{Yb}^{3+}$ NPs agglomerate, causing an increase in the hydrodynamic radius to 1810 nm and a decrease in dispersion. Surface modification, through the use of a hydrophilic and biocompatible shell, has been shown to improve solubility and dispersion in physiological media.^{34,35}

A typical optical limitation of lanthanide-based materials is emission quenching. This process occurs as a result of cross-relaxation between dopant ions, leading to energy loss through non-radiative processes. To find the concentration threshold that minimizes quenching, emission spectra were obtained from all samples of varying dopant concentrations by exciting the NPs at 808 nm while maintaining identical settings throughout all runs (Table SI in the [supplementary material](#)).

FIG. 1. (a) XRD patterns of as-prepared and heat-treated samples compared with the NaGdF_4 reference. Heat treatment had a positive effect on the NPs by increasing the crystallinity, noted by sharper and more distinct peaks. (b) TEM and (c) HRTEM images of $\text{NaGdF}_4:\text{Nd}^{3+}(10\%)/\text{Yb}^{3+}(4\%)$ NPs, showing their rectangular morphology and size distribution. The inset in (c) shows the selected area electron diffraction pattern, confirming a mixed phase between α - and β - NaGdF_4 .

FIG. 2. Emission comparison between the most efficient single dopant (Nd^{3+} 0.5%) in black and double dopant (Nd^{3+} 10% and Yb^{3+} 4%) in red. A 71.5% increase was achieved by simply introducing Yb^{3+} and carefully doping Nd^{3+} . The inset shows the normalized emission intensity of Nd^{3+} 10% and Yb^{3+} 4% doped NPs as a function of the Nd^{3+} concentration.

At low Nd^{3+} concentrations, the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ (1064 nm) transition dominates. As Yb^{3+} is introduced into the system, the energy transfer to Yb^{3+} ions becomes more prevalent, leading to emission quenching of the Nd^{3+} emission peak at 1064 nm and the enhancement of the 1000 nm transition emission. It is clearly seen in Fig. 2 that the 1064 nm emission intensity reduces drastically and becomes a peak shoulder. Yb^{3+} emission increases as a function of Nd^{3+} up to a concentration of 10%, after which quenching effects were observed. The optimal concentration for 1000 nm emission was found to be 10% for Nd^{3+} and 4% for Yb^{3+} , with a 71.5% peak increase when compared to the highest intensity of single dopant Nd^{3+} , as shown in Fig. 2. An increase of 449% in the number of photons emitted was obtained by integrating the emission profile in Fig. 2.

These results agree with the previously reported work by Jaque *et al.*,²⁸ where in a single crystal system, Nd^{3+} 10% yielded the highest emission intensity with a fixed Yb^{3+} 5% concentration. The energy transfer mechanism between Nd^{3+} and Yb^{3+} is mainly attributed to resonance energy transfer and partly to phonon-assisted energy transfer. Due to the energy level mismatch between Nd^{3+} and Yb^{3+} around 745 cm^{-1} , non-radiative processes such as the generation of two 350 cm^{-1} phonons assist with the energy transfer. This mechanism consists of the absorption of an 808 nm photon by Nd^{3+} , exciting it to the $^4\text{F}_{3/2}$ energy level after which the energy is transferred to Yb^{3+} , exciting it to its $^2\text{F}_{5/2}$ level and

the generation of two 350 cm^{-1} phonons. Finally, Yb^{3+} relaxes to its ground state, $^2\text{F}_{7/2}$, emitting a 1000 nm photon. This process is clearly depicted in Fig. S3 (see [supplementary material](#)). By adjusting Nd and Yb concentrations, near 100% energy transfer can be achieved in the system, which results in a single strong emission at 1000 nm. The strong fluorescent emission enhancement occurs in the biological window located between 600 and 1070 nm; in this spectral region, radiation is less attenuated by soft tissue, allowing deeper imaging and use of lower power densities, decreasing the probability of tissue photodamage.^{36,37}

Fluorescence decay times for 1064 nm and 1000 nm emissions were measured to determine the lifetime of the excited states and energy transfer efficiencies, Fig. 3. Decay curves were fitted with a triple exponential function

$$I(t) = \sum_{i=1}^3 A_i \exp\left(-\frac{t}{\tau_i}\right), \quad (2)$$

where A_i represents fitting parameters and τ_i fluorescence decay times. The decay time for each emission was determined by calculating a weighted average using the expression $\tau_{\text{avg}} = \sum_i A_i \tau_i^2 / \sum_i A_i \tau_i$. For the optimal concentration, Nd^{3+} 10% and Yb^{3+} 4%, the lifetime of the 1000 nm emission was calculated to be 12.72 ms Fig. 3(a). Since $\text{NaGdF}_4:\text{Nd}^{3+}(10\%),\text{Yb}^{3+}(4\%)$ has a lifetime an order of magnitude longer than most other optical materials,³ it can be considered a potential candidate for fluorescence based imaging applications where longer decay times are favored since it is easier to differentiate noise arising from scattered light and autofluorescence from imaged tissue. High energy transfer efficiencies are vital in detection applications due to lower signal loss. A 98.7% energy transfer efficiency was calculated for Nd^{3+} 10% and Yb^{3+} 4%, Fig. 3(b), allowing the use of lower power intensities, suitable for biological applications.

It has been previously demonstrated that NaGdF_4 NPs possess comparable or greater contrast capabilities to Gd-DTPA at equal concentrations under MRI scans.^{38,39} To assess the viability of the NPs in magnetic-based imaging systems, measurements as a function of the applied field (H) were performed for NPs with different concentrations of Nd^{3+} and Yb^{3+} ions. All samples were measured in powder form using a Vibrating Sample Magnetometer (VSM) at 300 K, see Fig. 4. All NPs show a clear paramagnetic behavior. In the inset of Fig. 4, the magnetization of the NPs is plotted as a function of the amount of Yb^{3+} and Nd^{3+} present in the samples. The result shows

FIG. 3. (a) Lifetime measurements of $\text{NaGdF}_4:\text{Nd}^{3+}$ and $\text{NaGdF}_4:\text{Nd}^{3+}(10\%),\text{Yb}^{3+}(4\%)$. The shortening in the lifetime for the 1060 nm transition (black to blue) indicates an energy transfer from Nd^{3+} to Yb^{3+} . (b) Calculated energy transfer efficiency from decay measurements. The increase in energy transfer efficiency is directly dependent on the Nd^{3+} concentration with the highest efficiency being at 98.7%.

FIG. 4. Magnetic measurements of NaGdF₄ nanoparticles performed at 300 K. The magnetization of the NPs decreases as a function of the Gd³⁺ concentration. At an optimal dopant concentration (Nd³⁺10%,Yb³⁺4%), the reduction in the paramagnetic behavior of the NPs is miniscule.

that the magnetic signal decreases when the content of Yb³⁺ and Nd³⁺ increases. This small reduction in the paramagnetic response of the NPs is due to a reduction in the Gd³⁺ content, which is the magnetic ion in the compound. However, for the optimum NP composition (Nd³⁺10%,Yb³⁺4%), the reduction in the paramagnetic signal is very small. The results of the magnetic characterization show that improvement in the optical properties can be achieved without compromising the magnetic character of the NPs.

In conclusion, we have synthesized sub-25 nm NaGdF₄:Nd³⁺,Yb³⁺ NPs with enhanced emission at 1000 nm when excited at 808 nm. Our modified solvothermal method yielded rectangular shaped NPs with an average side length of 17.87 nm and a standard deviation of ± 4.38 nm. The size and morphology are appropriate for biomedical applications since it has been reported that NPs of approximately 25 nm have the fastest cellular internalization time.¹³ The highest emission intensity was recorded for Nd³⁺ 10% and Yb³⁺ 4% at 1000 nm, which is a 71.5% increase over the highest 1064 nm emission from singly doped Nd³⁺ at 0.5%. Energy transfer from Nd³⁺ to Yb³⁺ was found to be a viable method for improving the emission properties of the NP with over 98% transfer efficiency. Regardless of the Gd³⁺ substitution by Nd³⁺ and Yb³⁺, the NPs present a clear paramagnetic behavior at room temperature. Therefore, the synthesis method reported in this letter allows the fabrication of NPs with optimal optical and magnetic properties. Moreover, due to their optimal size (~ 25 nm), enhanced NIR emission, highly efficient energy transfer, and excellent magnetic properties, the NaGdF₄:Nd³⁺,Yb³⁺ NPs are viable candidates for use as multifunctional contrast agents in multimodal biomedical imaging applications.

See [supplementary material](#) for the highest optical emission intensities as functions of Nd³⁺ and Yb³⁺ dopant concentrations, a detailed energy level diagram containing the energy transfer mechanism between Nd³⁺ and Yb³⁺ under 808 nm excitation, EDS spectra that confirm the elemental composition, and DLS measurements and sedimentation rate studies which depict the colloidal properties of NaGdF₄:Nd³⁺,Yb³⁺ NPs.

The authors would like to acknowledge the financial support from the National Science Foundation Partnerships for Research and Education in Materials (NSF-PREM) under Grant No. NODMR-0934218. This work was partially funded by NIGMS MBRS-RISE GM060655 from the National Institutes of Health, and research reported in this publication was supported by the National Institute on Minority Health and the Health Disparities of the National Institutes of Health under Award No. G12MD007591. The authors would like to acknowledge Dr. Diego Alducin for providing his technical expertise and electron microscopy data.

- ¹L. C. Mimun, G. Ajithkumar, M. Pokhrel, B. G. Yust, Z. G. Elliott, F. Pedraza, A. Dhanale, L. Tang, A.-L. Lin, V. P. Dravid, and D. K. Sardar, *J. Mater. Chem. B* **1**(41), 5702 (2013).
- ²R. Kumar, M. Nyk, T. Y. Ohulchanskyy, C. A. Flask, and P. N. Prasad, *Adv. Funct. Mater.* **19**(6), 853 (2009).
- ³C. Bouzigues, T. Gacoïn, and A. Alexandrou, *ACS Nano* **5**(11), 8488 (2011).
- ⁴X. Gao, Y. Cui, R. M. Levenson, L. W. K. Chung, and S. Nie, *Nat. Biotechnol.* **22**(8), 969 (2004).
- ⁵S. Kim, Y. T. Lim, E. G. Soltesz, A. M. De Grand, J. Lee, A. Nakayama, J. A. Parker, T. Mihaljevic, R. G. Laurence, D. M. Dor, L. H. Cohn, M. G. Bawendi, and J. V. Frangioni, *Nat. Biotechnol.* **22**(1), 93 (2004).
- ⁶P. Sharma, S. Brown, G. Walter, S. Santra, and B. Moudgil, *Adv. Colloid Interface Sci.* **123–126**, 471 (2006).
- ⁷X. Sun, Z. Liu, K. Welscher, J. T. Robinson, A. Goodwin, S. Zaric, and H. Dai, *Nano Res.* **1**(3), 203 (2008).
- ⁸J. Chen, M. Badioli, P. Alonso-Gonzalez, S. Thongrattanasiri, F. Huth, J. Osmond, M. Spasenovic, A. Centeno, A. Pesquera, P. Godignon, A. Z. Elorza, N. Camara, F. J. Garcia de Abajo, R. Hillenbrand, and F. H. L. Koppens, *Nature* **487**(7405), 77 (2012).
- ⁹R. Hardman, *Environ. Health Perspect.* **114**(2), 165 (2006).
- ¹⁰N. V. Vallabani, S. Mittal, R. K. Shukla, A. K. Pandey, S. R. Dhakate, R. Pasricha, and A. Dhawan, *J. Biomed. Nanotechnol.* **7**(1), 106 (2011).
- ¹¹L. V. Efremova, A. S. Vasilchenko, E. G. Rakov, and D. G. Deryabin, *BioMed Res. Int.* **2015**, 869361.
- ¹²Y. I. Park, J. H. Kim, K. T. Lee, K.-S. Jeon, H. B. Na, J. H. Yu, H. M. Kim, N. Lee, S. H. Choi, S.-I. Baik, H. Kim, S. P. Park, B.-J. Park, Y. W. Kim, S. H. Lee, S.-Y. Yoon, I. C. Song, W. K. Moon, Y. D. Suh, and T. Hyeon, *Adv. Mater.* **21**(44), 4467 (2009).
- ¹³S. Zhang, J. Li, G. Lykotrafitis, G. Bao, and S. Suresh, *Adv. Mater.* **21**, 419 (2009).
- ¹⁴F. Wang, Y. Han, C. S. Lim, Y. Lu, J. Wang, J. Xu, H. Chen, C. Zhang, M. Hong, and X. Liu, *Nature* **463**(7284), 1061 (2010).
- ¹⁵F. Wang and X. Liu, *J. Am. Chem. Soc.* **130**(17), 5642 (2008).
- ¹⁶F. Meiser, C. Cortez, and F. Caruso, *Angew. Chem., Int. Ed.* **43**(44), 5954 (2004).
- ¹⁷F. Wang, R. Deng, J. Wang, Q. Wang, Y. Han, H. Zhu, X. Chen, and X. Liu, *Nat. Mater.* **10**(12), 968 (2011).
- ¹⁸R. Reisfeld and C. K. Jørgensen, *Lasers and Excited States of Rare Earths* (Springer, Berlin, Heidelberg, 1977), p. 64.
- ¹⁹J. Lee, P. W. Bisso, R. L. Srinivas, J. J. Kim, A. J. Swiston, and P. S. Doyle, *Nat. Mater.* **13**(5), 524 (2014).
- ²⁰D. Jaque and F. Vetrone, *Nanoscale* **4**(15), 4301 (2012).
- ²¹Y. Cui, H. Xu, Y. Yue, Z. Guo, J. Yu, Z. Chen, J. Gao, Y. Yang, G. Qian, and B. Chen, *J. Am. Chem. Soc.* **134**(9), 3979 (2012).
- ²²T. Jüstel, H. Nikol, and C. Ronda, *Angew. Chem., Int. Ed.* **37**(22), 3084 (1998).
- ²³M. Tzenka, Y. Vladimir, N. Gabriele, and B. Stanislav, *New J. Phys.* **10**(10), 103002 (2008).
- ²⁴X. Huang, S. Han, W. Huang, and X. Liu, *Chem. Soc. Rev.* **42**(1), 173 (2013).
- ²⁵B. M. van der Ende, L. Aarts, and A. Meijerink, *Phys. Chem. Chem. Phys.* **11**(47), 11081 (2009).
- ²⁶G. A. Kumar, M. Pokhrel, A. Martinez, R. C. Dennis, I. L. Villegas, and D. K. Sardar, *J. Alloys Compd.* **513**, 559 (2012).
- ²⁷R. Paschotta, J. Nilsson, A. C. Tropper, and D. C. Hanna, *IEEE J. Quantum Electron.* **33**(7), 1049 (1997).
- ²⁸D. Jaque, M. O. Ramirez, L. E. Bausá, J. García Solé, E. Cavalli, A. Speghini, and M. Bettinelli, *Phys. Rev. B* **68**(3), 249901 (2003).

- ²⁹F. Liégard, J. L. Doualan, R. Moncorgé, and M. Bettinelli, *Appl. Phys. B* **80**(8), 985 (2005).
- ³⁰J. E. Miller and E. J. Sharp, *J. Appl. Phys.* **41**(11), 4718 (1970).
- ³¹L. Marciniak, A. Bednarkiewicz, M. Stefanski, R. Tomala, D. Hreniak, and W. Strek, *Phys. Chem. Chem. Phys.* **17**(37), 24315 (2015).
- ³²B. S. Richards, *Sol. Energy Mater. Sol. Cells* **90**(9), 1189 (2006).
- ³³K. W. Krämer, D. Biner, G. Frei, H. U. Güdel, M. P. Hehlen, and S. R. Lüthi, *Chem. Mater.* **16**(7), 1244 (2004).
- ³⁴C. Li and J. Lin, *J. Mater. Chem.* **20**(33), 6831 (2010).
- ³⁵C. Mi, J. Zhang, H. Gao, X. Wu, M. Wang, Y. Wu, Y. Di, Z. Xu, C. Mao, and S. Xu, *Nanoscale* **2**(7), 1141 (2010).
- ³⁶A. M. Smith, M. C. Mancini, and S. Nie, *Nat. Nanotechnol.* **4**(11), 710 (2009).
- ³⁷Y.-Y. Huang, A. C.-H. Chen, and M. Hamblin, *SPIE Newsroom* **9**, 1 (2009).
- ³⁸J. Zhou, Y. Sun, X. Du, L. Xiong, H. Hu, and F. Li, *Biomaterials* **31**(12), 3287 (2010).
- ³⁹C. Liu, Z. Gao, J. Zeng, Y. Hou, F. Fang, Y. Li, R. Qiao, L. Shen, H. Lei, W. Yang, and M. Gao, *ACS Nano* **7**(8), 7227 (2013).