Published in final edited form as:

Langmuir. 2012 September 11; 28(36): 13066–13071. doi:10.1021/la3024056.

Nanoceria facilitates the synthesis of poly(o-phenylene diamine) with pH tunable morphology conductivity and photoluminescent properties

Atul Asati[†], David Lehmkuhl[†], Diego Diaz[†], and J. Manuel Perez^{†,*}

[†]NanoScience Technology Center, Suite 400 Research Parkway 12424, Orlando, Florida 32826, United States

Abstract

Poly(ortho-phenylene diamine) synthesis enabled by the catalytic oxidase-like activity of nanoceria was accomplished for applications in electronics, medicine and biotechnology. The polymer shows unique morphology, conductivity and photoluminescence based on pH of the solution during synthesis. The various poly(ortho-phenylene diamine) preparations were characterized by UV-visible spectroscopy, scanning electron microscopy, fluorescence spectroscopy, fluorescence microscopy, high pressure liquid chromatography and cyclic voltammetry. Poly(ortho-phenylene diamine) synthesized at pH 1.0 by nanoceria was selected to be extensively studied based on the fast synthetic kinetics and the resulting conductive and photoluminescent properties for various applications.

Keywords

Nanoceria; oxidase-like nanoceria; o-phenylene diamine; photoluminescence

INTRODUCTION

Conductive polymers are of great interest for the design of improved and more efficient sensors, devices, coatings, displays, batteries, electro-catalyst and electro-optic devices.^[1–10] Among these polymers, polymerized o-phenylenediamine (pOPD) has attracted recent attention due to its unique mechanical and conductive properties and its ability to form 1-D nano- and micro-structures.^[11,12] These unique 1-D structures result from the self-assembly of small chain o-phenylenediamine (scOPD) oligomers in solution, which are typically synthesized by either oxidative electropolymerization of o-phenylenediamine (OPD) monomers^[13,14] or chemical oxidative polymerization using an oxidizing agent such as H₂AuCl₄ or AgNO₃.^[15,16] The resulting scOPD are composed of water soluble dimer and trimers of monomeric o-phenylenediamine that eventually self-assemble in solution forming these 1-D nano- and micro-structures of pOPD. A cost effective and high yield solution-based approach for the oxidation of monomeric OPD is preferred over the electrochemical-based approach that for the most part tends to be low yield. Particularly, a facile synthetic

*Corresponding Author Prof. J Manuel Perez, Nanoscience Technology Center, 12424, Research Parkway, Suite 400, Orlando, Florida 32826 (USA), jmperez@ucf.edu.

ASSOCIATED CONTENT

Supporting Information

Demonstration of enzyme like-behavior of nanoceria and kinetics; non-conductive behavior of electrochemically oxidized OPD monomer; photoluminescent/optical properties of OPD via nanoceria pH 1.0 and pH 7.0. This material is available free of charge via the Internet at <http://pubs.acs.org>.

method that can yield 1-D *p*OPD structures of different morphologies and physical properties by changing the reaction conditions, such as pH, would be ideal as it could facilitate further studies about this unique polymer and result in new applications for this material.

Recently, we reported the oxidase activity of cerium oxide nanoparticles (nanoceria) and demonstrated the nanoparticle's ability to oxidize various colorimetric dyes at different rates, depending on the pH.^[17] Particularly, we found that the nanoceria's oxidase-like activity can be easily modulated by changing the pH of the solution as nanoceria can exhibit weak oxidase activity at neutral pH and strong activity at acidic pH. This behavior was demonstrated by studies on the partial oxidation of ampliflu by nanoceria at neutral pH which resulted in the generation of the partially oxidized fluorescent product resorufin as opposed to its completely oxidized non-fluorescent product resazurin, which occurred at acidic pH.^[18] We then hypothesized whether nanoceria's unique pH-dependent oxidase-like activity could be used to modulate the oxidation of OPD monomers at different pH, resulting in the formation *p*OPD structures of different morphologies and physical properties. Moreover, the autocatalysis and autoregenerative properties of nanoceria would allow the production of *p*OPD polymers in high yield for further characterization of their physical properties. Herein, we report the fabrication of 1-D *p*OPD structures of different morphologies and physical properties via the pH modulated nanoceria oxidation of OPD monomers. Particularly, we observed the fast oxidation of monomeric OPD using nanoceria at pH 1.0, yielding brush-like polymeric microstructure with conductive and luminescent properties, including near infrared absorption and emission.

EXPERIMENTAL

Materials

O-phenylene diamine (OPD) monomer and all of the solvents used were purchased from Sigma Aldrich (St. Louis, USA) Polyacrylic acid-coated nanoceria (PNC) preparations was synthesized using the methodology described previously.^[17]

UV and photoluminescent characterization of *p*OPD microcrystals

UV-visible and photoluminescent spectroscopic measurements were done by using solution of *p*OPD microcrystals in water on a Varian Cary 300 Bio UV-visible spectrometer and a Nanolog HORIBA JOBIN YVON spectrometer respectively. Approximately (0.5 mg) microcrystals were dissolved in 1.0 ml of water and a spectrum was recorded.

Michaelis Menten kinetic constants measurement

Steady-state kinetic assays were carried out in 96-well plate using PNC (5.0 μ M) at room temperature with o-phenylene diamine monomer at pH 1.0 and pH 7.0. Reactions were monitored at 570 nm in time scan mode using a Bio- TEK, Synergy HT Multidetector Microplate reader. Color reactions were observed immediate upon addition of nanoceria to substrate, o-phenylene diamine monomer. To study the steady-state kinetics, experiments were carried out using above conditions with varying concentrations of o-phenylene diamine monomer while nanoceria concentration was kept constant (5.0 μ M). The kinetic parameters $V_{\max}$, K_m and K_{cat} were calculated.

Oxidation of OPD with decreasing of nanoceria

UV-visible spectroscopic measurements were done on a Varian Cary 300 Bio UV-visible spectrometer. Briefly, OPD monomer (4×10^{-4} moles) solution was treated with decreasing amount of nanoceria (1.7×10^{-5} to 1.7×10^{-7} moles) and spectra were recorded after each reaction.

Electrochemical instrumentation for OPD oxidation

Electrochemical experiments were carried on a CH Instruments CH760c potentiostat. A 2.0 mm diameter Pt electrode was used. The electrode was mechanically polished using 1-micron diamond paste (Buehler) and electrochemically polished on 0.5 M H₂SO₄. The cleanliness of the electrode prior to experiments was determined by looking at the hydrogen absorption region in 0.5 M H₂SO₄. Samples were purged with high-purity N₂ before each voltametric experiment. Briefly, various oxidized OPD microcrystals obtained via nanoceria and electrochemical oxidation at pH 1.0 and 7.0 microcrystals were subjected to conductivity measurements using buffer solution as supporting electrolyte.

RESULTS AND DISCUSSION

In our first set of experiments, we studied nanoceria's ability to oxidize OPD monomers at acidic and neutral pH. The formation of scOPD units in solution is characterized by the development of an intense yellow color. When nanoceria (5 μ M) was added to a solution of OPD monomer (0.04 μ moles) at pH 1.0, a change in the color of the solution (from clear to pale yellow) was observed within minutes. The intensity of the color increased within 24 hours to an intense yellow color indicating further oxidation of the substrate. At pH 7.0, however, the OPD monomer solution did not turn yellow immediately, but took at least 24 hours for the color to develop, suggesting a slower oxidation kinetics at this pH as expected. Spectrophotometric studies of the nanoceria oxidized scOPD units in solution at pH 1.0 show two absorption maxima at 470 and 490 nm, with a very weak absorption at 615 nm (Figure S1A). Similar results were obtained in solutions at pH 2 through 6. Meanwhile, the OPD monomer oxidized at pH 7.0 only exhibit one-absorption maxima at 417 nm (Figure S1B). Similar results to those obtained at pH 7 were also obtained in basic conditions (pH 8–13). These results indicate a possible difference in the electronic properties of the two oxidized products at acidic and basic pH.

Further differences are observed in the fluorescence properties of the two oxidized OPD solutions. The fluorescence properties of scOPD and pOPD have not been fully investigated in the literature and only few reports describe the spectral properties of this polymer.^[16,19] The fluorescence emission spectra of the nanoceria oxidized OPD at pH 1 exhibits two main fluorescence emission at 620 nm and 675 nm, with a minor peak at 525 nm (inset, Figure S1A). In contrast the oxidized OPD preparation at pH 7 show only one broad emission peak at 570 nm, with no near infrared emission (inset, Figure S1B). We also performed transmission electron microscopy (TEM) studies before and after the oxidation reaction to monitor any potential changes in the nanoparticles. Results show that indeed the nanoparticle size and dispersity remained the same after the oxidation reaction (Figure S2), further indicating that nanoceria act as a catalyst and it is not consume in the oxidation process. The observed optical and fluorescence properties of nanoceria oxidized scOPD, allowed us to perform kinetic studies for the oxidation reaction at acidic and neutral pH. Comparison of the Michaelis Menten kinetics corroborates the faster kinetics at acidic pH (pH 1.0, $V_{\max} = 4.4 \times 10^{-9} \text{ M s}^{-1}$, $K_m = 0.2 \text{ }\mu\text{M}$, $K_{\text{cat}} = 4.4 \times 10^{-4} \text{ s}^{-1}$, $K_{\text{cat}}/K_m = 1998.62 \text{ M}^{-1} \text{ s}^{-1}$) in contrast with values obtained at neutral pH (pH 7.0, $V_{\max} = 2.0 \times 10^{-9} \text{ M s}^{-1}$, $K_m = 3 \text{ }\mu\text{M}$, $K_{\text{cat}} = 2.01 \times 10^{-4} \text{ s}^{-1}$, $K_{\text{cat}}/K_m = 66.67 \text{ M}^{-1} \text{ s}^{-1}$) (Figure S1A). The $V_{\max}$ and K_m values for the OPD oxidation at pH 1.0 are comparable to those obtained for the oxidation of other substrates at acidic pH.^[16] Moreover, value of K_{cat}/K_m is a measure of the enzyme efficiency and hence high value of K_{cat}/K_m at pH 1.0 indicates the high enzymatic efficiency of nanoceria at pH 1.0 in contrast to the low K_{cat}/K_m value observed at pH 7.0.^[20] Therefore, nanoceria at pH 1.0 produces more oxidized products of OPD per second (more turnover) than at pH 7.0 (Figure S3A). Moreover, the catalytic and autoregenerative behavior of nanoceria in oxidizing the OPD monomer was corroborated by placing a fixed amount of nanoceria (5 mM) within a dialysis device and allow for

continuous incubation in a pH 1.0 solution of OPD (25 mM) under constant stirring. As expected, the OPD solution turned yellow within 24 hours of incubation, indicating a successful oxidation of OPD by the nanoceria within the device. After taking an aliquot (500 μ L) of the solution to measure its fluorescence emission at 620 nm, the dialysis device containing the nanoceria was washed 3 times over a 24 hours period with fresh buffer (pH 1.0) to get rid of any remaining OPD monomer and oxidized OPD products. Once again, the dialysis device containing the washed nanoceria was incubated for 24 hours under constant stirring with a fresh solution of OPD and an aliquot was taken for fluorescence emission measurements at the end of the incubation period. This process was continued for a total of eight cycles and the fluorescence emission data was graphed against the number of cycles. This data demonstrate the autocatalytic and autoregenerative nature of nanoceria in the oxidation of OPD, as nanoceria is capable of constantly being able to oxidize a fresh batch of OPD for a period of 8 cycles (Figure S3B). In addition, when the oxidation of a fixed amount of OPD (4×10^{-4} moles) was performed with decreasing (catalytic) molar ratios of nanoceria, it was observed that even low nanoceria to OPD molar ratios were able to oxidize OPD, albeit at a lower rate, (Figure S3C). Taken together, these results demonstrate that nanoceria catalyzes the oxidation of OPD in an autoregenerative and autocatalytic manner, confirming the enzyme-like oxidase behavior of nanoceria.

During our initial experiments, we observed that prolonged incubation of the OPD with nanoceria facilitated the formation of reddish needle-like crystals. Interestingly, the speed of crystal formation as well as their morphology varied with the pH at which the oxidation was performed. At pH 1.0, 1-D brush-like microcrystals formed after overnight incubation (without stirring) with nanoceria. These crystals could be easily visualized by brightfield optical microscope (Figure 1A). Meanwhile, at pH 7.0, crystal formation took at least 3 days. The slow rate of crystal formation might be due to the slower oxidation kinetic of nanoceria at neutral pH. The crystals that formed at neutral pH were also visible by brightfield optical microscope but they had a different morphology, forming longer saw-like needle microstructures (Figure 1B). Interestingly, when OPD was electropolymerized on a platinum electrode, belt-like fluorescent OPD microcrystals formed within 3 days at the electrode-solution interface. These microcrystals had to be scraped of the electrode surface for analysis resulting in a low yield compared to those obtained using nanoceria and no significant change in morphology was observed at different pH (Figure 1C–1D). Scanning electron microscopy (SEM) studies confirmed the difference in morphology between the crystals generated by nanoceria oxidation at acidic and neutral pH with those generated by electropolymerization (Figure 1E–1H). Interestingly, the SEM image of the *p*OPD microcrystals generated via nanoceria oxidation at acidic pH 1.0 was obtained without coating or sputtering with palladium/gold (Figure 1E) suggesting that these microcrystals possessed conductive properties in contrast to the other samples that required a palladium/gold coating for SEM imaging (Figure 1F–1H). These results point towards the use of nanoceria's autoregenerative oxidase-like activity to facilitate the fabrication of 1-D *p*OPD microcrystals of different morphologies and physical properties.

Further electrochemical characterization of the *p*OPD microcrystals synthesized with nanoceria at pH 1.0 confirms the conductivity of this material. Cyclic voltametric studies of these crystals show a reversible redox cycle with a sequential increase in current after each cycle. As the polymer film on the electrode grows, the increase in the current can be attributed to the increased surface area of the conductive polymer film on the electrode (Figure 2). This is in stark contrast to studies showing *p*OPD films to passivate electrodes by creating non-conducting films.^[19] Furthermore, the conductive behavior of the nanoceria oxidized OPD at pH 1.0 was confirmed by potassium ferrocyanide oxidation studies at pH 1.0, (Figure S4). Such conductive behavior was not observed in the *p*OPD microcrystals synthesized with nanoceria at pH 7.0 or those generated by electropolymerization of

monomeric OPD (Figure S2). As matter of fact, these samples exhibit an irreversible redox cycle with decrease in the current after each scans, indicating a non-conductive behavior (passivation). In addition, chronoamperometric studies of the electropolymerized *p*OPD microcrystals showed that these samples are not conductive at either pH as indicated by a constant decrease in the current, eventually becoming negligible after 3 days (Figure S5). These results demonstrate that only nanoceria mediated oxidized OPD at pH 1.0 with 1-D self-assembled brush-like microstructures indicated conductivity.

To confirm that the observed 1-D *p*OPD microcrystals were indeed composed of individual short chain dimers and trimers of OPD (*sc*OPD), the crystals were collected and re-dissolved in water for UV-vis/Fluorescence spectrophotometric analysis as well as HPLC-MS characterization. Results show that when the 1-D *p*OPD microcrystals were dissolved in water pH 1.0 or pH 7.0, they displayed similar spectra to those in Figure 1. HPLC-MS of the *p*OPD microcrystals dissolved at pH 1.0 and 7.0 show a prominent peak corresponding to a mass of 268.7, suggesting the presence of fragmented trimers of OPD as reported previously^[21] (Figure 3A–3B). Interestingly, similar results were obtained in aqueous solution of the crystals obtained by electropolymerization (Figure 3C–3D) suggesting that in all these cases the *p*OPD crystals are composed an assembly in solution of 268.7 *sc*OPD fragmented trimers as suggested by others.^[21]

Since, the 1-D *p*OPD microstructures generated at pH 1.0 using nanoceria displayed interesting fluorescence properties, including near infrared emission, we explore the response in fluorescence emission of these microcrystals when dissolved in solvents of different pKa values, increasing polarity and dielectric constant, as well as aqueous solution of increasing pH. First, a blue shift in the fluorescence emission maxima was observed with solvents of increasing pKa value. The emission maxima shifted from 580 nm to 540 nm (Figure S6A) as these crystals were dissolved in solvents of increasing pKa such as methanol, water, ethanol and isopropanol. Images under UV light illumination depicted a green to yellow fluorescent color (Figure S7A). Next, when the *p*OPD crystals were dissolved in solvents of increasing polarity (Figure S6B) or dielectric constants (Figure S6C) a red shift was observed in both cases. Different fluorescent colors from turquoise blue to green fluorescence were observed as a function of increased polarity and dielectric constant, (Figure S7B–S7C). Afterwards, the fluorescence response of the *p*OPD crystals to aqueous solutions of different pHs show that in acidic pH (1–5) the crystals exhibit near infrared fluorescent emission maxima of 630 nm (Figure S6D). In the pH range 6–13, the *p*OPD crystals showed a dramatic blue shift in fluorescent emission with an emission maximum around 565 nm. Images under UV light illumination depicted an orange to yellow fluorescent color (Figure S7E). These results demonstrate the utility of these microcrystals as a photoluminescent optical indicator for pH, polarity, dielectric constant and pKa of various solvents. Finally, we tested whether the 1-D *p*OPD microstructures themselves generated at pH 1.0 using nanoceria exhibited near infrared fluorescence. For these studies, the *p*OPD microcrystals were deposited on a petri dish and imaged using an Odyssey Imaging System using an excitation wavelength of 685 nm and 785 nm. Upon excitation of the crystals, a fluorescence emission of 700 nm was observed when the crystals were excited at 685 nm and 800 nm when excited at 785 nm, allowing visualization of the crystals and the corresponding wavelengths (Figure 4A–4C) and confirming the infrared fluorescence properties of these polymers. At present time, the mechanism for the formation of the various *p*OPD morphologies with unique conductive and luminescent properties using nanoceria is not completely understood. However, the oxidation process seems to takes place in two steps, first nanoceria oxidizes monomeric OPD to OPD oligomers (*sc*OPD) that in second step self-assemble to form 1-D microstructures. It has been reported that *sc*OPD oligomers are rich in π -type bonds facilitating π - π interactions leading to spontaneous self-assembly into 1-D structures.^[15] At acidic pH, OPD oligomers are more protonated and

therefore electrostatic repulsive forces dominate resulting in the formation of small self-assembled microstructures. Furthermore, as reminiscent of other conductive polymers, *p*OPD becomes conductive when doped with protons (H^+) at acidic pH.^[3] It has also been reported that conductivity in most conductive polymers is directly proportional to the degree of protonation (acidic doping).^[22,23] At neutral pH 7.0, OPD oligomers are comparatively less protonated allowing strong π - π interactions to occur and leading to the self-assembly of more scOPD resulting in long microstructures which are not conductive. The unique luminescence properties of *p*OPD crystals, particularly the near infrared excitation and emission of *p*OPD synthesized using nanoceria in acid pH, are quite interesting and will require further studies. However, the *p*OPD crystal morphology is a result of both the pH of the environment as well as the synthetic method (nanoceria vs electropolymerized). Aqueous scOPD solutions have the same optical, electrochemical and photoluminescent properties as the crystals themselves (as crystals were isolated after synthesis and were subjected to optical, electrochemical and photoluminescent characterization) so the observed different morphologies seems not to be the cause of the observed conductive or luminescent properties.

In conclusion, we developed a versatile method to fabricate 1-D *p*OPD microstructures with unique morphological, conductive and fluorescent properties using nanoceria as an oxidase. The enhanced catalytic and regenerative oxidase activity of nanoceria in acidic pH facilitated the fast, cost effective and high yield synthesis of the conductive and fluorescent 1-D *p*OPD microstructures. As the observed morphological, conductive and optical properties of *p*OPD vary with various parameters such as pH, ionic strength and polarity, it gives us the opportunity to create tunable and responsive thin films, conductive materials, and electro-optic devices with potential applications in electronic, medicine and biotechnology.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Authors would like to acknowledge Dr. Charalambos Kaittanis and Dr. Jan Grimm from the Memorial Sloan Kettering Cancer Center, NY, NY for technical assistance with LI-COR two channel Odyssey infrared imaging system.

Funding Sources

The authors acknowledge funding from the National Institutes of Health () and UCF-NSTC Start Up Fund, all to J.M.P.

REFERENCES

1. Nyholm L, Nyström G, Mihranyan A, Strømme M. Toward flexible polymer and paper-based energy storage devices. *Adv. Mater.* 2011; 23:3715.
2. Tran H, Li D, Kaner R. One-dimensional conducting-polymer nanostructures: bulk synthesis and applications. *Adv. Mater.* 2009; 21:1487.
3. Li D, Huang J, Kaner R. Polyaniline nanofibers: A unique polymer nanostructure for versatile applications. *Acc. Chem. Res.* 2009; 42:135. [PubMed: 18986177]
4. Vogelsang J, Adachi T, Brazard J, Vanden D, Barbara P. Self-assembly of highly ordered conjugated polymer aggregates with long-range energy transfer. *Nat. Mater.* 2011; 10:942. [PubMed: 21983890]
5. Aida T, Meijer W, Stupp S. Functional Supramolecular Polymers. *Science.* 2012; 335:813. [PubMed: 22344437]

6. Zhou Y, Huang W, Liu J, Zhu X, Yan D. Self-assembly of hyperbranched polymers and its biomedical applications. *Adv. Mater.* 2010; 22:4567. [PubMed: 20853374]
7. Janata J, Joswicz M. Conducting polymers in electronic chemical sensors. *Nat. Mater.* 2003; 2:19. [PubMed: 12652667]
8. Nystrom G, Razaq A, Stromme M, Nyholm L, Miharanyan A. Ultrafast All-Polymer Paper-Based Batteries. *Nano Lett.* 2009; 9:3635. [PubMed: 19739594]
9. Leclerc P, Surin M, Viville P, Lazzaroni R, Kilbiger A, Henze O, Feast W, Cavallini M, Biscarini F, Schenning A, Meijer E. About Oligothiophene Self-Assembly: From Aggregation in Solution to Solid-State Nanostructures. *Chem. Mater.* 2004; 16:4452.
10. Park S, Kang S, Fryd M, Saven J, Park S. Highly tunable photoluminescent properties of amphiphilic conjugated block copolymers. *J. Am. Chem. Soc.* 2010; 132:9931. [PubMed: 20608674]
11. Lu W, Luo Y, Guohui C, Abdullah M, Abdulrahman A, Xuping S. Supramolecular microfibrils of *o*-phenylenediamine dimers: oxidation-induced formation of Au nanoparticle-decorated nanoplates for H₂O₂ detection. *Curr. Nanosci.* 2012; 8:221.
12. Sun X, Xu Y, Zhu W, He C, Xu L, Yang Y, Qian X. Copper-promoted probe for nitric oxide based on *o*-phenylenediamine: Large blue-shift in absorption and fluorescence enhancement. *Anal. Methods.* 2012; 4:919.
13. Del Valle M, Diaz F, Bodini M, Alfonso G, Soto G, Borrego E. Electrosynthesis and characterization of *o*-phenylenediamine oligomers. *Polym. Int.* 2005; 54:526.
14. Losito I, Giglio E, Cioffi N, Malitesta C. Spectroscopic investigation on polymer films obtained by oxidation of *o*-phenylenediamine on platinum electrodes at different pHs. *J. Mater. Chem.* 2001; 11:1812.
15. Sun X, Dong S, Wang E. Formation of *o*-Phenylenediamine Oligomers and their Self-Assembly into One-Dimensional Structures in Aqueous Medium. *Macromol. Rapid Commun.* 2005; 26:1504.
16. Sun X, Dong S, Wang E. Large scale, templateless, surfactantless route to rapid synthesis of uniform poly(*o*-phenylenediamine) nanobelts. *Chem. Commun.* 2004:1182.
17. Asati A, Santra S, Kaittanis C, Nath S, Perez JM. Oxidase-like activity of polymer coated cerium oxide nanoparticles. *Angew. Chem. Int. Ed. Engl.* 2009; 48:2308. [PubMed: 19130532]
18. Asati A, Kaittanis C, Santra S, Perez JM. pH-Tunable Oxidase-Like Activity of Cerium Oxide Nanoparticles Achieving Sensitive Fluorogenic Detection of Cancer Biomarkers at Neutral pH. *Anal. Chem.* 2011; 83:2547. [PubMed: 21370817]
19. Ono T, Kawakami K, Goto M, Furusaki S. Catalytic oxidation of *o*-phenylenediamine by cytochrome c encapsulated in reversed micelles. *J. Mol. Catal. B: Enzym.* 2001; 11:955.
20. Voet D, Voet JG, Pratt CW. *Fundamentals of Biochemistry.* 2008:371.
21. Losito I, Cioffi N, Vitale M, Palmisano F. Characterization of soluble oligomers produced by electrochemical oxidation of *o*-phenylenediamine by electrospray ionization sequential mass spectrometry. *Rapid Commun. Mass Spectrom.* 2003; 17:1169. [PubMed: 12772273]
22. Tarachiwin L, Kiattibutr P, Ruangchuay L, Sirivat A, Schwank J. Electrical conductivity response of polyaniline films to ethanol–water mixtures. *Synthetic Met.* 2002; 129:303.
23. Stejskal J, Hiavata D, Holler P, Trchova M, Prokes J, Sapurian I. Polyaniline prepared in the presence of various acids: a conductivity study. *Polym. Int.* 2004; 53:294.

Figure 1.

Morphology of nanoceria and electrochemically oxidized scOPD. (A) Bright field images of scOPD oxidized via nanoceria pH 1.0. (B) SEM images of scOPD oxidized via nanoceria at pH 1.0 (imaged without any sputtering or coating with palladium/gold). (C) Bright field images of scOPD oxidized via nanoceria pH 7.0. (D) SEM images of scOPD oxidized via nanoceria at pH 7.0. (E) Bright field images of scOPD oxidized via electrochemical polymerization at pH 1.0. (F) SEM images of scOPD oxidized via electrochemical polymerization at pH 1.0. (G) Bright field images of scOPD oxidized via electrochemical polymerization at pH 7.0. (H) SEM images of scOPD oxidized via electrochemical polymerization at pH 7.0.

Figure 2.
Conductivity of nanoceria oxidized scOPD. Cyclic voltammogram of nanoceria oxidized scOPD at pH 1.0 showing constant increase in current.

Figure 3. HPLC-MS analysis of nanoceria and electrochemically oxidized pOPD. (A and B) Trace graph showing fragmented trimer fraction for nanoceria oxidized pOPD at pH 1.0 and pH 7.0. (C and D) Trace graph showing fragmented trimer fraction for electrochemically oxidized pOPD at pH 1.0 and pH 7.0.

Figure 4.

Near IR fluorescence of pOPD microcrystals generated via nanoceria at pH 1.0. (A) Bright field image of pOPD microcrystals (B) Red fluorescent image of pOPD microcrystals upon excitation at 685 nm. (C) Green fluorescent image of pOPD crystals taken upon excitation at 785 nm.