



## Porosity control of nanoporous CuO by polymer confinement effect

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### ABSTRACT

We propose a simple method for fabricating porous CuO, which is elementally abundant, nontoxic, environmentally stable, and a good electrochemical performing material, and easily controlling pore size by using a mixture of Cu precursor and polystyrene solutions followed by heat treatment, which we named polymer-confined direct solution pyrolysis (PDSP). We mixed an ionized metal solution and polymer template with different molecular weights, and then burned out the polymer template in air. The fabrication technique and application of nanoporous CuO produced by PDSP are presented herein. The applications studied were metal oxides for nanoenergetic materials and a non-enzyme glucose sensor.

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Nanoporous materials have pore sizes ranging from several nanometers to several hundreds of nanometers. Since nanoporous materials have unique advantages due to their large ratios of volume to surface area compared to those of bulk materials, their applications, such as adsorption, catalysts, acoustic shielding, insulation, super capacitors, and even for lightweight structural materials, have been studied. The applications of nanoporous materials depend on their porosities and pore distributions. Therefore, research on controlling the pore sizes of nanoporous materials is essential. In previous studies, nanoporous materials have been prepared by vapor deposition, injection of molten gases, dealloying, the sol-gel method, spraying with polymeric materials, etc. [1–5].

In this study, we focused on metal oxide nanoporous structures because oxides are extremely stable and sustainable, even in extreme environments. Metal oxide nanoporous materials are usually fabricated by casting into hard templates, such as silica or anodized alumina, and then removing the templates [6–10]. Another common method is pyrolysis with polymer particles and an ionized metallic source, in which the ionized metal species form metallic oxide networks during burn-out of the polymer particles. In the conventional methods, pore size is dependent on the template properties, which requires pore size control of the template. In the spray pyrolysis method, the nanoporous structures can be dependent on the particle size of the polymer.

Herein, to overcome these limits, we propose a simple technique to produce nanoporous metal oxide networks, which we named polymer-confined direct solution pyrolysis (PDSP). We mixed an ionized metal solution and polymer template with various molecular weights and then burned off the polymer template in air. During burn-out of the polymer template, metal ions react with oxygen to form oxides and diffuse on the surface to form oxide networks.

We mainly focused on the fabrication and application of nanoporous CuO by PDSP in this study. CuO (copper (II) oxide) is a p-type semiconductor with about a 1.2 eV band gap energy, and it belongs to the monoclinic crystal system. The copper atom is coordinated with four oxygen atoms in an approximately square planar configuration [11]. Cupric oxide can be used to produce dry cell batteries [12–14], gas sensors [15], and antimicrobial agents [16], and has many other potential applications. In this study, two applications were considered: 1) metal oxides for energetic materials and 2) non-enzyme glucose sensors.

Toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>) was used as a solvent to dissolve the polymer template (polystyrene), and copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>) in acetone was prepared as the Cu source. Polystyrene, 0.1 g, dissolved in 5 ml of toluene and 0.5 g of copper nitrate in 5 ml of acetone were well mixed using magnetic-bar stirring and ultrasonication. To observe the effect of the molecular weight of the polymer template, we used four different molecular weights (m.w.) of polystyrene, 1300, 13,000, 123,000, 900,000 m.w. (Alfa Aesar, USA), denoted as P1.3, P13, P123, and P900, respectively.

Detailed experimental procedures of the two different methods are shown in Fig. S1. Fig. S1(a) shows a schematic of the conventional spray pyrolysis process. In conventional spray pyrolysis, nanosized

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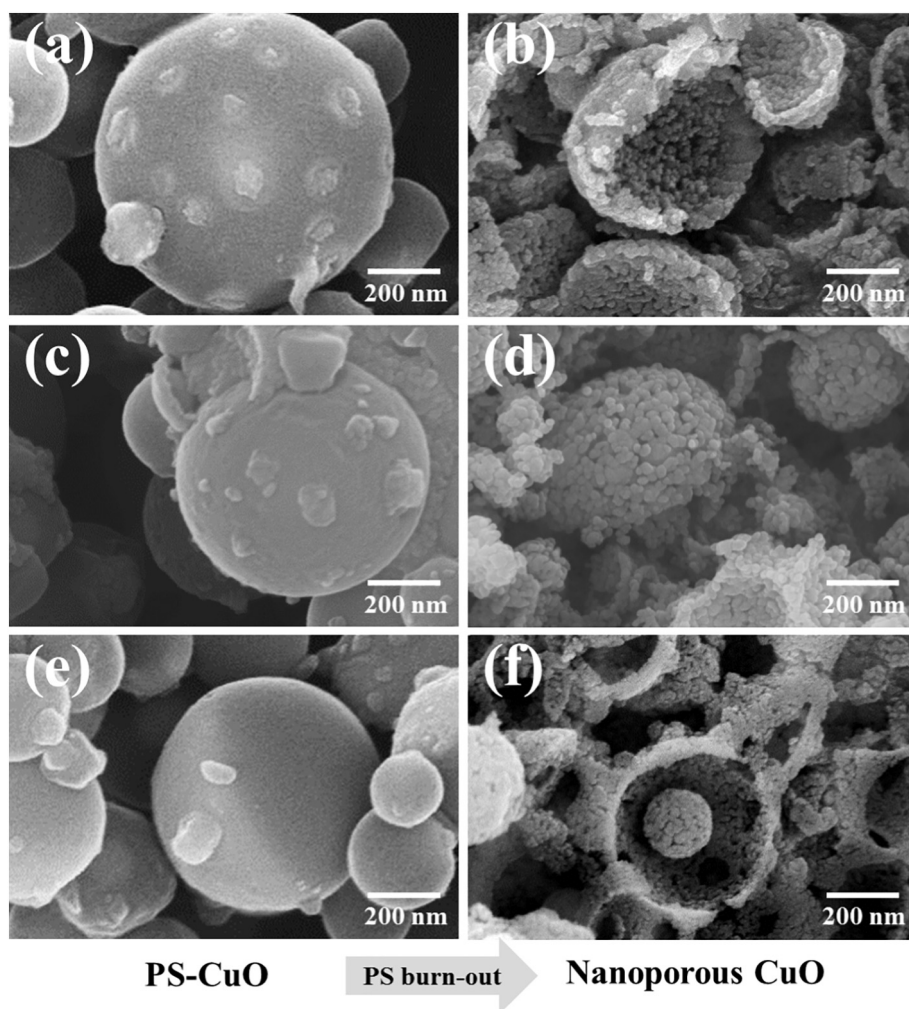
polymer particles are usually used to control pore size. In this work, we used a polymer solution with ionized metal species instead of polymer nanoparticles as the template, which we named polymer solution spray pyrolysis (PSSP). Fig. S1(b) shows a schematic of an alternate method, PDSP, to form nanoporous CuO in a simpler way. We spread a paste, which was a mixture of the polymer solution with aqueous Cu nitrate, on a substrate and then burned off the polymer in a tube furnace. Burn-out of all samples obtained with the two methods was performed in air at 400 and 600 °C for up to for 3 h. Burn-out temperatures were chosen based on TGA analysis (see Fig. S2). The PDSP specimens were placed in an alumina crucible and then heat-treated using a tube furnace for 20 min at 600 °C in air.

The samples were cooled to room temperature after removing them from the furnace, and then the samples were collected with a spatula to investigate their microstructures and crystal structures using scanning electron microscopy (SEM, Hitachi 4500 s) and X-ray diffraction (XRD, Philips Expert™). Application of the nanoporous CuO fabricated by PDSP 1) as metal oxides to control the energy release rate in nanoenergetic materials (nEMs); and 2) non-enzyme glucose sensing substrates were studied. For energetic materials, nanoporous CuO was mixed with commercial Al nanoparticles (80 nm, NTbase, Korea) in a 7:3 weight ratio (see Fig. S1(c)). Two different types of CuO were used to measure the burn rate. The detailed experimental procedures for measuring the

burn rate are in the Supporting Information. For non-enzyme glucose sensing, cyclic voltammetry (CV) and chrono amperometry (CA) techniques were used to measure amount of glucose present. The cyclic voltammetry response from  $-1.0$  to  $1.0$  V was used to investigate and compare the catalytic activities of a bare copper (Cu) film and nanoporous CuO electrodes (see Fig. S1(d)).

First, we used the spray pyrolysis technique to fabricate nanoporous CuO. A solution of polystyrene dissolved in toluene was mixed with Cu precursors as a template instead of polystyrene nanoparticles, which are usually used in conventional spray pyrolysis to synthesize nanoporous oxide particles [5]. Fig. S3 shows the SEM micrographs of the nanoporous CuO fabricated by spray pyrolysis. For comparison, we also fabricated nanoporous CuO with a polystyrene nanoparticle template, as shown in Fig. S3(a). As shown in Fig. S3, the microstructures of the nanoporous CuO fabricated using the polystyrene solution template and polystyrene nanoparticles were not significantly different, and pores formed more effectively using the polystyrene solution as a confinement template. Spray pyrolysis requires complex equipment, as shown in Fig. S1(a), due to clogging in the ultrasonic spray tube. Moreover, many cycles are required to obtain a sufficient amount of material to use in applications. Thus, we directly burned off the polystyrene template from the mixed solution (Fig. S1(b)).

Micrographs of the polymer solution used as a template to form porous structures by spray pyrolysis (PSSP) are shown in Fig. 1.



**Fig. 1.** SEM micrographs of PSSP for P900: (a) PS/Cu nitrate particle after spraying a mixture of polystyrene (1 wt%) with Cu nitrate (5 wt%). (b) Nanoporous CuO particles after burn-out at 400 °C for 3 h in air of the particle shown in (a). (c) PS/Cu nitrate particle after spraying a mixture of polystyrene (2 wt%) with Cu nitrate (10 wt%). (d) Nanoporous CuO particles after burn-out at 400 °C for 3 h in air of the particle shown in (c). (e) PS/Cu nitrate particle after spraying a mixture of polystyrene (2 wt%) with Cu nitrate (15 wt%). (f) Nanoporous CuO particles after burn-out at 400 °C for 3 h in air of the particle shown in (e).

Fig. 1(a), (c), and (d) show micrographs of the materials fabricated by spray pyrolysis (before burn-out of the polymer template) with various mixing conditions between the Cu precursor and polystyrene. As can be seen in Fig. 1, nanoporous structures were well formed after burn-out of the polystyrene. For comparison, we also used polystyrene nanoparticles as a template for spray pyrolysis, which is shown in Fig. S3(a). As can be seen in Fig. S3, there were no significant differences in the porous structures formed by polymer nanoparticle confinement and polymer solution confinement using spray pyrolysis.

This result shows that fabrication of nanoporous copper oxide structures can be achieved without the expensive polymer nanoparticles used in conventional spray pyrolysis. However, the yield is very low in the production of nanoporous metal oxide structures using spray pyrolysis methods. Therefore, in this study, a metal oxide nanoporous structure with high yield was prepared by directly heat-treating a mixed solution of a metal precursor and polymer without spraying, i.e. the PDSP method. Another merit of PDSP is that nanoporous CuO films are easily formed on substrates for use as sensors.

With PDSP, many experiments were performed under various conditions, such as polymer solutions with different molecular weights and various burn-out temperatures and times. We observed that pore structures were well formed and there were no residual polymers when samples were heat-treated at 600 °C; moreover, the pore size increased with increased annealing time, which is shown in Fig. S4. It is assumed that formation of pore structures occurs through a well-known mechanism involving surface diffusion of the constituents. Interestingly, we observed that pore size also changed with the molecular weight of the polymer used for the template. Fig. 2 shows that CuO structures with larger pore sizes were formed with smaller molecular weight polystyrene as a template (about 230 nm) compared to the pore sizes of structures formed with higher molecular weight polystyrene (about 65 nm). Pore size was measured with the standard metallographic method (ASTM Standard E112).

It was assumed that the molecular weight of the polymer can be a factor for controlling the degree of mixing with the metal precursors in solution. The degree of mixing is affected by the pore distribution.

As shown in Fig. 2, the pore size in P1.3 was much larger than those of the other samples. From these results, a pore-forming mechanism is proposed, shown schematically in Fig. 3. This mechanism explains why the lower molecular weight polymer produced structures with larger pore sizes. While the mixed solution of the polymer template solution and the Cu precursor is heat-treated (burn-out process), the solvent is removed, and the polymer is randomly positioned in a bundle. At the same time, the Cu precursor reacts with oxygen in the air and is converted to copper oxide. The lump of the polymer is thermally decomposed after expansion to form an empty space, and simultaneously copper oxide forms in the area surrounding the polymer lump. After, a random network structure of copper oxide can be formed through the surface diffusion of CuO species. Comparing Fig. 3(a) with Fig. 3(b), P1.3, which had a relatively small molecular weight, had a low glass transition temperature. Thus, it expands more at 600 °C than the high molecular weight polystyrene, P900. Larger pores were formed when the molecular weight was small. Therefore, the pore size can be controlled by glass transition temperature differences with the molecular weight of the polymer and time and temperature for surface diffusion of oxide species.

An explosion experiment [17–20] was carried out by mixing the nanoporous copper oxide particles prepared in this study and solid copper oxide particles, which were heat-treated only with the copper precursor solution, with the Al nanopowder. The P1.3 and P900 nanoporous copper oxide samples prepared by PDSP were used for energetic materials tests. For comparison, an energetic materials test was also performed for solid copper oxide particles, which were prepared by a direct oxidation process of a copper nitrate solution mixed with the Al nanopowder. Each copper oxide sample (nanoporous and solid) was mixed with Al nanopowder at a weight ratio of 7:3 using ultrasonic waves and was ignited using a tungsten wire. The explosion characteristics of the solid particles and P900 were not significantly different.

As shown in Fig. 4(a), the explosion propagation time of P1.3 was 11 times faster than that of P900. The burn rates of P1.3 and P900 were 33.33 and 3.03 s, respectively. In the case of P900, the sizes of the Al nanoparticles used were about 80 to 100 nm. Since

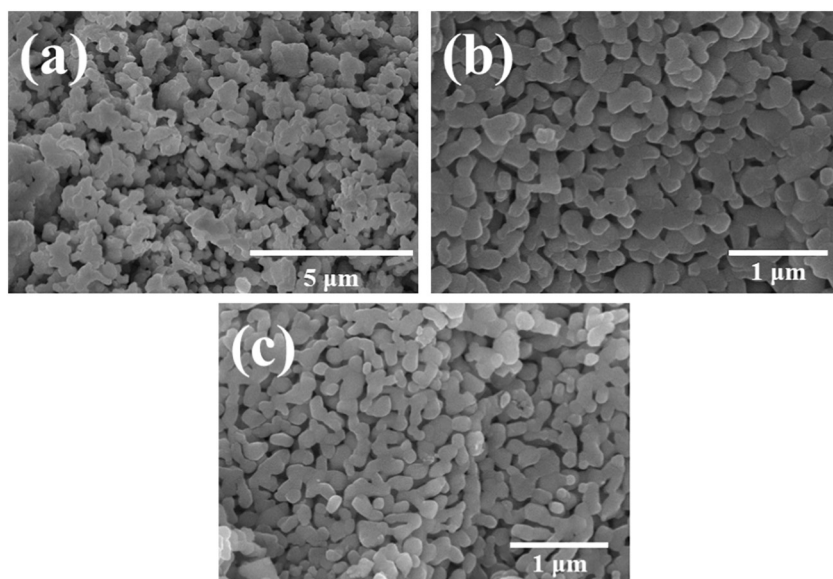


Fig. 2. SEM micrographs of nanoporous CuO formed by PDSP after burn-out at 600 °C for 20 min. (a) P1.3 mixture (231 nm average pore size), (b) P13 mixture (96.2 nm average pore size), and (c) P900 mixture (64.8 nm average pore size).

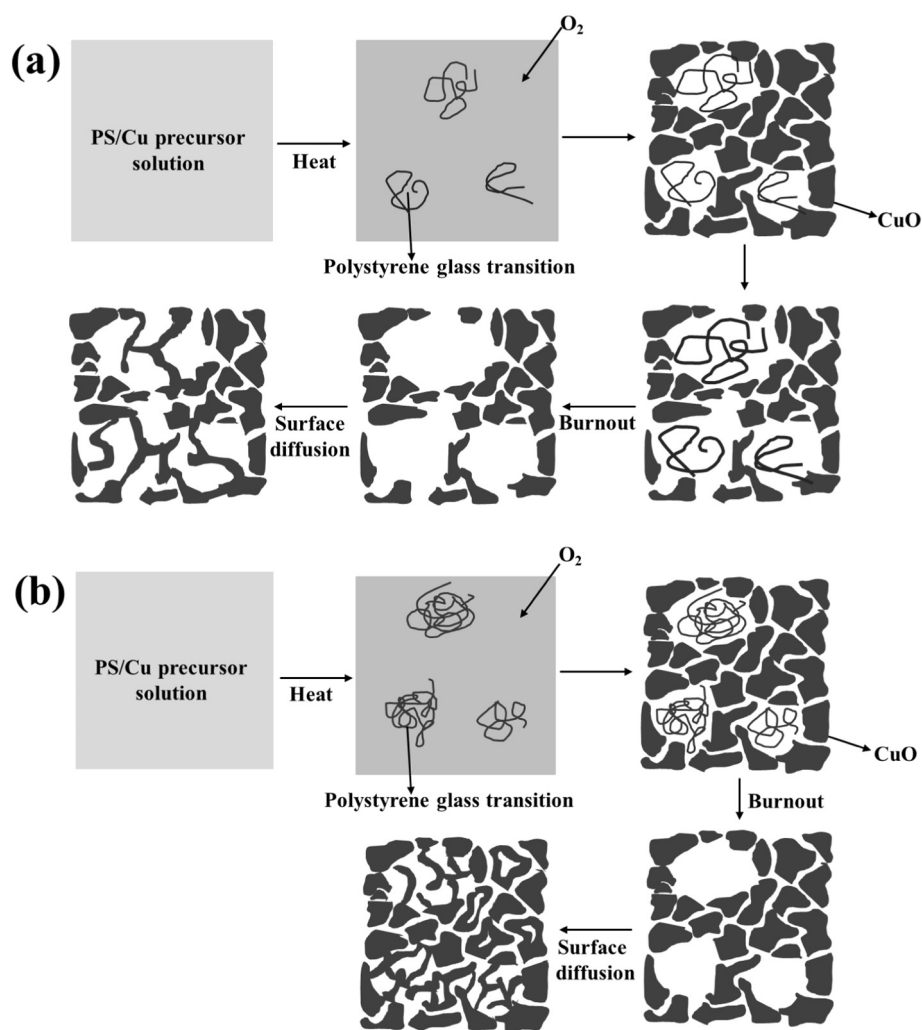


Fig. 3. Schematics of mechanisms to control porosity using PDSP: (a) P1.3 and (b) P900.

the pore size was similar to or smaller than the size of the Al nanoparticles, the advantages of the porous copper oxide could not be realized. However, the larger the pore size samples, e.g. P1.3, had larger contact areas when mixed with the Al nanoparticles. Thus, control of the pore sizes can readily control the explosion propagation speed.

Fig. 4(b) shows the results of the glucose detection by graphite with and without nanoporous CuO films in a solution of 0–5 mM glucose dissolved in 0.1 M NaOH. Cyclic voltammetry was used with a sweep from  $-1$  to  $1$  V at a  $0.05$  V/s of scan rate. According to the literature, glucose will be oxidized around  $0.5$  V to form gluconolactone. As shown in Fig. 4(b), while the activated graphite electrode (no nanoporous CuO, open symbols) did not show any well-defined oxidation peaks other than for water oxidation, the nanoporous CuO/graphite electrode (solid symbols) exhibited significantly increased current density due to oxidation of glucose [21–24].

Using PDSP, the pore size is readily altered and various types of substrates can be used to create porous oxide structures. We presented a method for fabricating nanoporous CuO easily. Other nanoporous oxide monolithic and complex forms, such as  $Fe_2O_3$  and NiO, can also be fabricated using PDSP (not presented in this study). There are many potential applications of nanoporous CuO, and its uses as an

oxidizer for energetic materials and enzyme-free glucose sensors were successfully demonstrated.

We also suggested a possible mechanism for controlling the pore size with the polymer confinement effect: because the glass transition temperature varies with the polymer (polystyrene (PS) in this study) molecular weight, the amount of volume expansion of the polymer template changes with increased burnout temperature. The ionized metallic species were covered with polymeric materials in solution, and then they reacted with oxygen to form oxides. During the oxidation process, polymeric materials covering the metallic species play a role in controlling the pore size.

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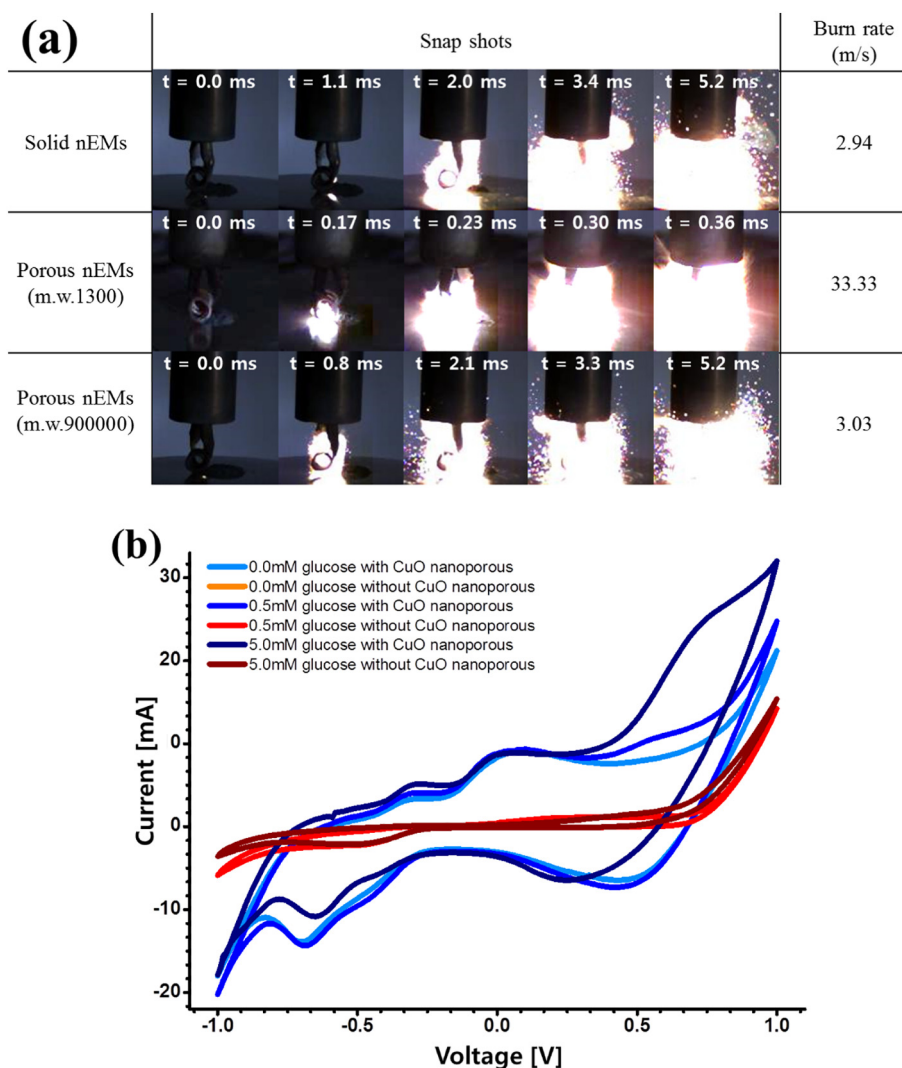


Fig. 4. Examples of possible applications of nanoporous CuO: (a) burn rate control of nEMs with different surface areas of fuel oxides. (b) measurement of enzyme-free glucose sensing ability with various porosities.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scriptamat.2018.10.038>.

## References

- [1] J. Erlebacher, M.J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, *Nature* 410 (2001) 450.
- [2] E. Detsi, M.S. Selles, P.R. Onck, J.T.M. De Hosson, *Scr. Mater.* 69 (2013) 195.
- [3] J.R. Hayes, G.W. Nyce, J.D. Kuntz, J.H. Satcher, A.V. Hamza, *Nanotechnology* 18 (2007), 275602.
- [4] A. Prakash, A.V. McCormick, M.R. Zachariah, *Chem. Mater.* 16 (2004) 1466.
- [5] G.W. Nyce, J.R. Hayes, A.V. Hamza, J.H. Satcher Jr., *Chem. Mater.* 19 (2007) 344.
- [6] W. Luc, F. Jiao, *Acc. Chem. Res.* 49 (2016) 1351.
- [7] H. Zhang, G.C. Hardy, Y.Z. Khimiyak, M.J. Rosseinsky, A.I. Cooper, *Chem. Mater.* 16 (2004) 4245.
- [8] J. Zhang, C.M. Li, *Chem. Soc. Rev.* 41 (2012) 7016.
- [9] H. Wakayama, H. Itahara, N. Tatsuda, S. Inagaki, Y. Fukushima, *Chem. Mater.* 13 (2001) 2392.
- [10] J. Lee, S. Han, T. Hyeon, *J. Mater. Chem.* 14 (2004) 478.
- [11] J.B. Forsyth, S. Hull, *J. Phys. Condens. Matter* 3 (1991) 5257.
- [12] G. Li, M. Jing, Z. Chen, B. He, M. Zhou, Z. Hou, *RSC Adv.* 7 (2017) 10376.
- [13] X.P. Gao, J.L. Bao, G.L. Pan, H.Y. Zhu, P.X. Huang, F. Wu, D.Y. Song, *J. Phys. Chem. B* 108 (18) (2004) 5547.
- [14] S. Grugeon, S. Laruelle, R. Herrera-Urbina, L. Dupont, P. Poizot, J.-M. Tarascon, *J. Electrochem. Soc.* 148 (4) (2001) A285.
- [15] J. Zhang, J. Liu, Q. Peng, X. Wang, Y. Li, *Chem. Mater.* 18 (2006) 867.
- [16] M.E. Grigore, E.R. Biscu, A.M. Holban, M.C. Gestal, A.M. Grumezescu, *Pharmaceuticals* 9 (2016) 75.
- [17] S.H. Kim, M.R. Zachariah, *Adv. Mater.* 16 (2004) 1821.
- [18] J.Y. Ahn, J.H. Kim, J.M. Kim, D.W. Lee, J.K. Park, D. Lee, S.H. Kim, *Powder Technol.* 241 (2013) 67.
- [19] R. Shende, S. Subramanian, S. Hasan, S. Apperson, R. Thiruvengadathan, K. Gangopadhyay, S. Gangopadhyay, P. Redner, D. Kapoor, S. Nicolich, W. Balas, *Propellants Explos. Pyrotech.* 35 (2010) 384.
- [20] M.R. Weismiller, J.Y. Malchi, J.G. Lee, R.A. Yetter, T.J. Foley, *Proc. Combust. Inst.* 33 (2011) 1989.
- [21] P. Salazar, V. Rico, R. Rodríguez-Amaro, J.P. Espinós, A.R. González-Elipe, *Electrochim. Acta* 169 (2015) 195.
- [22] J. Luo, S. Jiang, H. Zhang, J. Jiang, X. Liu, *Anal. Chim. Acta* 709 (2012) 47.
- [23] Z. Zhuang, X. Su, H. Yuan, Q. Sun, D. Xiao, M.M.F. Choi, *Analyst* 133 (2008) 126.
- [24] Y. Zhang, Y. Liu, L. Su, Z. Zhang, D. Huo, C. Hou, Y. Lei, *Sensors Actuat. B-Chem.* 191 (2014) 86.