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Research Article

Photocatalysis of Yttrium Doped $BaTiO_3$ Nanofibres Synthesized by Electrospinning

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Yttrium doped barium titanate (BT) nanofibres (NFs) with significant photocatalytic effect were successfully synthesized by electrospinning. Considering the necessary factors for semiconductor photocatalysts, a well-designed procedure was carried out to produce yttrium doped BT (BYT) NFs. In contrast to BYT ceramics powders and BT NFs, BYT NFs with pure perovskite phase showed much enhanced performance of photocatalysis. The surface modification in electrospinning and subsequent annealing, the surface spreading of transition metal yttrium, and the narrowed band gap energy in yttrium doping were all contributed to the final novel photocatalytic effect. This work provides a direct and efficient route to obtain doped NFs, which has a wide range of potential applications in areas based on complex compounds with specific surface and special doping effect.

1. Introduction

Issues related to environmental protection are increasingly important with the industrial advance [1]. Photocatalysis by semiconductor oxides is a significant way to degrade organic and inorganic pollutants [2, 3]. One of the most famous photocatalysts is TiO_2 [4]. It has showed excellent photocatalytic effect as reported [5]. It is generally accepted that surface defects of TiO_2 play an essential part in photocatalysis [6, 7]. In fact, one-dimensional (1D) nanomaterials such as NFs can perform better photocatalysis for their high specific surface area. Electrospinning has been proved to be an effective technique to prepare NFs with the merits of mass production and high continuity [8, 9]. During electrospinning and subsequent annealing, the volatile solvents which containing polymer could experience rapid phase separation and decomposition. So the final NFs usually have rough and defective morphology. Producing NFs by electrospinning can be a practical way to improve the photocatalytic efficiency. In this trend, many researches on the photocatalysis of NFs obtained by electrospinning were carried out [10, 11]. However, famous photocatalysts such as TiO_2 and ZnO were still the main objects in these researches, while many other important compounds received few attentions.

Apart from the famous photocatalysts, many other doped semiconductors also possess brilliant photocatalytic properties. The suitable band gap is another important deciding factor in semiconductor photocatalysts [1–3, 12]. The doping can effectively narrow the band gap to obtain a better photocatalytic effect. As an important material [13, 14], BT has excellent environmental compatibility, since its excellent performance is with harmful elements abandoning. Because BT has a similar band gap with TiO_2, researches on the BT-based photocatalysts are also growing [15]. However, due to the unfitted band gap, the photocatalytic efficiency of BT did not perform as well as famous photocatalysts. So BT was always used as an auxiliary component, while the investigations on its intrinsic photocatalysis did not operate specially [16]. In particular, doped semiconductor BT is a good candidate to exploit novel properties for its adjustable composition. To improve the original properties of BT, transition metal yttrium was usually doped to tailor the properties, especially in the semiconductor BT with narrowed band gap [17, 18]. Moreover, it is well known that transition metal elements spread easily on the surface of oxides [19, 20]. Actually the distribution of doping elements is a key reason to achieve interesting photocatalysis in doped semiconductor. Researches on doped TiO_2 pointed out that transition metal elements surface doping could produce more efficient photocatalysts than traditional bulk doping [21]. So the transition metal yttrium doping can enhance a desirable surface reaction. Considering the morphology features of NFs, the narrowed band gap of yttrium doping, and the surface spreading of yttrium ions, semiconductor BYT NFs with modified surface could be obtained by electrospinning. It is reasonable to believe that this can cause novel photocatalysis effects which are based on surface defects and band gap. This can provide an unexplored method in the doped semiconductor photocatalysis.

In this paper, we will report observing photocatalytic behavior in BYT NFs, which were synthesized by electrospinning. Results show the photocatalytic efficiency of BYT NFs has been greatly improved in this method. Besides, BYT ceramics powders and undoped BT NFs are also discussed.

2. Experimental Methods

The electrospinning was carried out as follows: 6 g of barium acetate [$Ba(CH_3COO)_2$], titanium butoxide [$C_{16}H_{36}O_4Ti$], and yttrium acetate tetrahydrate [$Y(CH_3COO)_3 \cdot 4H_2O$] were weight and mixed according to stoichiometric ratio of 1 : 1 : 0.02. 40 mL of dichloromethane was used as solvent for its rapid evaporation. To prevent hydrolyzation, 5 mL of acetic acid was added. To adjust the viscosity, 8 g PVP was dissolved into the precursor solution. The electrospinning was conducted through a needle with an inner diameter of 0.5 mm attached to a 20 mL syringe. The flow rate was set at 4 mL/h by a syringe pump. The applied voltage for electrospinning was 1.6 kV and the distance between the tip and the collector was 12 cm. Then as-spun NFs could be deposited on sapphire single crystal substrates which attached to the grounded collector. After annealed in relative high temperature of 1250°C for 2 hours with heating rate of 6°C/min, BYT NFs were obtained. Besides, BT NFs without Y doped were also synthesized in the same procedure. And a group of BYT ceramics powders which were prepared by solid reaction using $BaCO_3$ [99.9%], TiO_2 [99.9%], and Y_2O_3 [99.9%] were also measured in the characterizations. Regents and chemicals in this work were purchased from Sinopharm Chemical Reagents Co., Ltd. (China). Single crystal substrates were from KMT Corporation (Hefei, China).

The structure and microstructure of the NFs were characterized by X-ray diffraction (Philips X-ray diffractometer system), field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F equipped with selected area electron diffraction and an energy-dispersive X-ray spectroscopy). The UV adsorption spectra were measured using a Shimadzu UV-2550 (Kyoto, Japan) spectrophotometer. The photocatalytic activity of the NFs for degradation of methylene blue (MB) was evaluated by agitating the solution and irradiating the samples using a 250 W high-pressure Hg lamp. The initial concentration of MB was 6 mg/L and with a catalyst loading of 1 g/L for measurement.

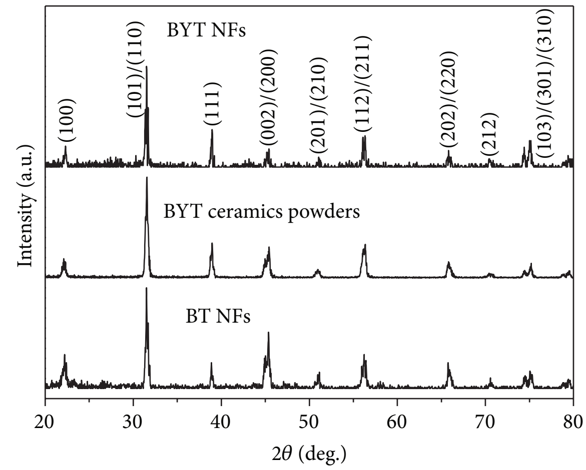
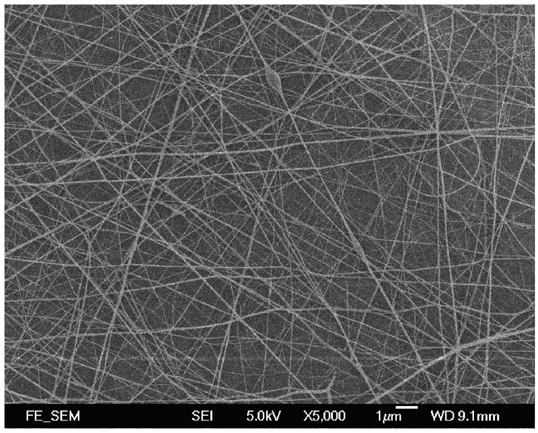


Figure 1: The X-ray diffraction pattern of BYT NFs, BYT ceramics powders, and BT NFs.

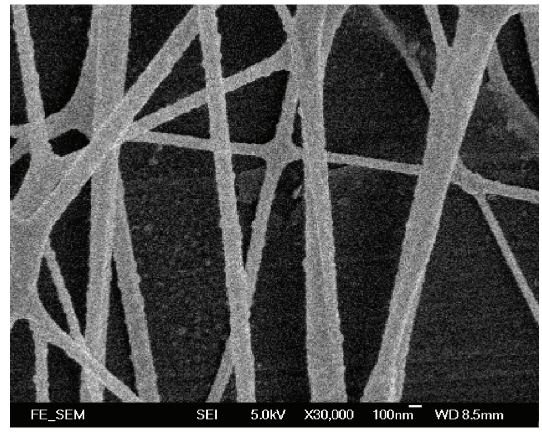
3. Results and Discussion

In the characterizations, we measured three groups of samples: BYT NFs, BYT ceramics powders, and BT NFs. Figure 1 shows XRD patterns of three groups. For BYT NFs and BT NFs, the as-annealed products were using a long collection time for 2 h. Three groups are all of pure perovskite phase. But BYT NFs and BT NFs are with a stronger noise. In the NFs XRD measurement in this work, the annealed products were from as-spun precursor with long collection time of 2 h. After annealing, NFs were obtained and pressed on the sample stage for XRD measurement. However, the flow rate was kept at 4 mL/h and with low metal compound concentration (6 g metal acetates dissolved into 40 dichloromethane which were added with 5 mL of acetic acid) in electrospinning. So even the as-spun NFs had been collected for a longtime, the as-annealed products were not enough to ensure strong diffraction intensity in XRD measurement. So the XRD patterns of NFs are noisy unavoidably. Nevertheless, all the main diffraction peaks in XRD patterns of BYT NFs and BYT ceramics powders have been indexed. They are all matching the BT tetragonal perovskite phase. It draws the dopant Y_2O_3 which has been incorporated into host so no impurity phase is observed. It means that BT-based NFs with high perovskite phase purity and crystallinity can be obtained by electrospinning.

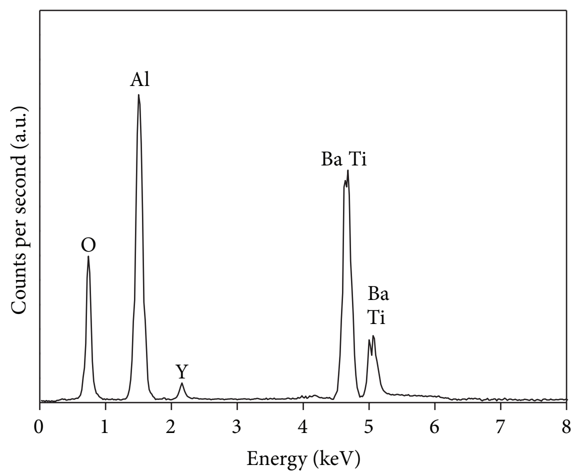
Figures 2(a)-2(b) show the morphology of as-annealed BYT NFs samples. NFs with typical wire-like state with diameter less than 200 nm can be clearly observed in the images. But the diameters are not homogeneous because of the fulmination and multilayer effect in electrospinning. Besides, narrow flat ribbons, branched and broken fibers which formed in electrospinning and annealing can also be detected. Most importantly, it can be seen from Figure 2(b) that all of the NFs have rough surface as expected. Further, to determine the chemical composition of NFs, EDX measurements were taken on a single fibre in Figure 2(b). From the spectrum shown in Figure 2(c), yttrium, barium, titanate, aluminum, and oxygen peaks can be detected. The existing



(a)



(b)



(c)

Figure 2: ((a)-(b)) FE-SEM image of BYT NFs, (c) EDX spectrum of a single BYT NFs.

diffraction peak of yttrium proves that this doping element has been dissolved into host BT. The content of Al is too high because sapphire single crystal was used as substrate.

In similar researches on the electrospinning preparation of 1D nanostructure materials, both NFs and nanotubes (NTs) were obtained. Heating rate and annealing temperature in annealing processes were pointed as key determinants in the formation of these different structures. In the NTs formation [22, 23], metal oxides shell must form firstly when the decomposition of PVP is unfinished. This means that the heating rate and thermal anchoring of precursor must be controlled to minimize sample overheating. In contrast, the formation of NFs needs faster heating rate and higher annealing temperature. They will all lead to sample overheating, which result in the skipping of the oxide shell formation before PVP remove completely. For this reason, we sped up the heating rate and raised the annealing temperature to meet the NFs formation condition. So NFs were fabricated finally.

The photocatalytic activities of BYT NFs, BYT ceramics powders, and BT NFs were evaluated by decomposing MB under irradiation of medium-pressure Hg lamp for 10 hours. Two groups of MB solution with no catalysts and P25 TiO_2 were also treated as contrast. MB is usually used as standard dyes in photocatalytic testing for its photostability. Figure 3 shows photodegradation of MB solutions function of reaction time for different catalysts. In the photocatalysis measurement, we took groups of photodegraded solution after each hour and then used the spectrophotometer to measure the UV adsorption spectra. C_0 and C_t represent the intensity of the maximum absorption peaks of the UV adsorption spectra of solution initially and at time t. Take nature logarithm function of ratio C_0/C_t to obtain the ordinate in Figure 3. It should be noted that the maximum absorption peak wavelength of MB is usually taken at 664 nm [24]. But this wavelength can blue shift to lower value with the degradation of MB. In order to accurately show the photocatalytic effect, we took the intensity of the exact maximum absorption peak at different wavelengths nearby 664 nm every time. MB solution with no catalysts is stable under irradiation. The MB solution used BT NFs as photocatalyst shows a small scale change during the 10 hours' irradiation. Moreover, in the presence of BYT ceramics powders, the MB concentration decreased a little more obviously after 10 hours' irradiation. However, BYT NFs show remarkable photocatalytic efficiency. A much stronger

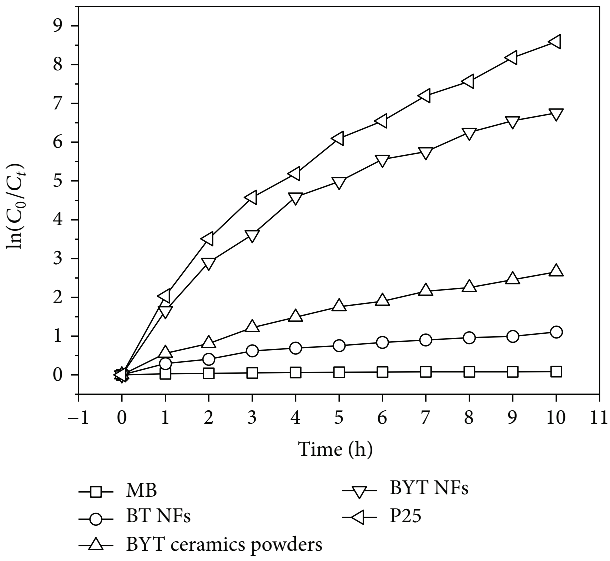


Figure 3: The photodegradation of MB solution with different catalysts: no catalysts, BT NFs, BYT ceramics powders, BYT NFs, and P25 TiO_2.

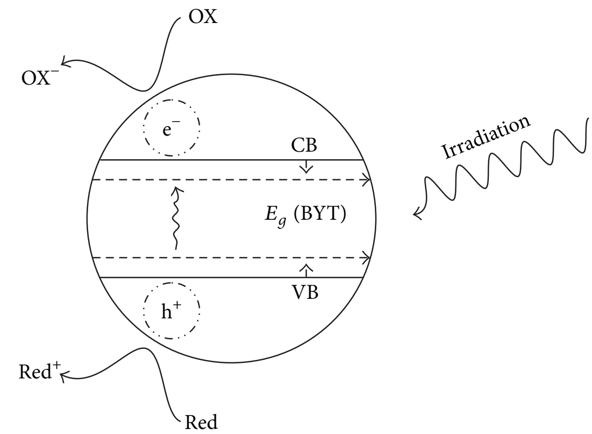


Figure 4: Representation of photodegradation of MB solution with BYT.

degradation is performed in the presence of BYT NFs. Almost all dyes had been degraded after 10 hours, very close to the group with P25. So it can be concluded that BYT NFs have a significant photocatalytic effect, compared to BYT ceramics powders and BT NFs.

When the semiconductor catalysts were irradiated with energy higher or equal to the band gap, excited state conduction-band electrons and valence-band holes would form [2]. Then the electrons and holes could be got trapped in metastable surface states to recombine or react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. But the recombination could be prevented if a suitable scavenger or surface defect state is available to trap the electrons or holes. Subsequently, the electrons and holes generated by exciting photons could have redox reaction with dyes in the solutions. It means that suitable band gap energy is a key reason in photocatalysis. As recorded most commonly, the band gap energy for BT is 3.2 eV and for TiO_2 is 3 eV [2, 13, 25, 26]. Considering the unfitted band gap energy, BT NFs show little photocatalysis effect. But for BYT, when Y_2O_3 doped into BT, yttrium will transform BT to semiconductor. The band gap must be narrowed in the semiconductor BYT, just as shown in Figure 4. It means that BYT could become a more suitable candidate in photocatalysis. So the photocatalytic efficiency has been enhanced obviously in BYT ceramics powders.

At the same time, a strong contrast between the photocatalytic activities of BYT NFs and BYT ceramics powders was also obvious in Figure 3. BYT NFs synthesized by electrospinning show almost as high photocatalytic efficiency as P25, while BYT ceramics powders show a little effect. We ascribe this to the modified surface of NFs in electrospinning. As discussed above, the excited state conduction-band electrons and valence-band holes were trapped in metastable surface states in the reaction. Catalysts with surface defects are suitable scavengers to trap the electrons or holes in photocatalysis. It indicates that specific surface plays an important role. In fact, surface defects were pointed as the direct reason in photocatalysis. Oxygen vacancy defects on the surface are not only the oxidizing reagents but also the electron scavengers which ultimately drive surface photooxidation processes experience longer lifetimes due to reducing their recombination rate with electrons [6]. So the most effective way to improve the photocatalytic efficiency of doped semiconductor must be conducted directly on the surface areas.

At first, in electrospinning preparation of NFs, the final morphology and structure of NFs are controlled by many factors, such as volatile solvent, decomposition of the polymer, annealing heating rate, and annealing temperature. When we electrospin the precursor solution, rapid evaporation and following rapid solidification of volatile solvent will induce a rapid phase separation [7]. Phase boundaries may be crossed and structure formation by phase separation sets in. It means the solvent rich and poor regions will transform into different patterns, result in a rough surface of as-spun NFs. Furthermore, the next annealing will further modify the morphology and structure of NFs. Heating rate and annealing temperature were considered decisive factors in the formation of NFs [22, 23]. So we had designed the annealing process carefully. In the NFs annealing, rapid heating rate and/or high thermal anchoring will all lead to a spanking decomposition of polymer. This will make the final NFs have rougher surface and more defects. In this way, electrospinning is a perfect method to prepare NFs with modified surface. So BYT NFs will have more surface defects for photocatalysis. Secondly, the surface spreading of transition metal elements had been proved by both theories and experiments [19, 20]. When transition metal yttrium was doped into BT, the difference in the surface energies of impurities and host could provide a surface segregation energy, which could drive doping elements to the surface areas. This will further strengthen the narrowed band gap effect at surface areas of BYT NFs. Taking into account the high specific surface area of NFs, the photocatalytic efficiency of doped semiconductor BYT NFs can be enhanced in this mechanism.

In sum, producing doped NFs by electrospinning is an excellent method to tailor the properties of materials not only due to the modified surface but also due to the doping effect. This work shows how it improved the photocatalytic properties of doped BT. Furthermore, it has a wide range of potential applications in areas based on complex compounds with specific surface and special doping effect, such as sensor, filter, or absorbed reactant. Much investigation on the properties and applications of doped NFs synthesized by electrospinning is highly desired.

4. Conclusions

Based on electrospinning, a direct and effective method to improve the photocatalysis of doped semiconductor was developed. BYT NFs were fabricated by electrospinning and subsequent annealing. BT NFs and BYT ceramics powders were also prepared as contrast. XRD patterns show that all samples have pure perovskite phase. BYT NFs with inhomogeneous diameter less than 200 nm have been proved by SEM images and EDX measurements. Significant photocatalytic effect of BYT NFs was characterized compared to weaker effect of BYT ceramics powders and little effect of BT NFs. Since specific surface and proper band gap energy were considered key factors in photocatalysis, the strong photodegradation of MB in the presence of BYT NFs was induced by the morphology and structure modification in electrospinning, the surface spreading of transition metal yttrium, and the narrowed band gap energy in yttrium doping. BYT ceramics powders and BT NFs have weaker photocatalytic efficiency for the unmodified surface and unfitted band gap energy. Producing doped NFs by electrospinning is an excellent method to tailor the properties. Much investigation on the properties and potential applications of doped NFs synthesized by electrospinning is highly desired.

Conflict of Interests

The authors declare that they have no conflict of interests regarding the publication of this paper.

Acknowledgments

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References

[1] M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, "Environmental applications of semiconductor photocatalysis," *Chemical Reviews*, vol. 95, no. 1, pp. 69–96, 1995.

[2] G. Palmisano, V. Augugliaro, M. Pagliaro, and L. Palmisano, "Photocatalysis: a promising route for 21st century organic chemistry," *Chemical Communications*, no. 33, pp. 3425–3437, 2007.

[3] A. Mills and S. le Hunte, "An overview of semiconductor photocatalysis," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 108, no. 1, pp. 1–35, 1997.

[4] S. Livraghi, A. Votta, M. C. Paganini, and E. Giamello, "The nature of paramagnetic species in nitrogen doped TiO_2 active in visible light photocatalysis," *Chemical Communications*, vol. 28, no. 4, pp. 498–500, 2005.

[5] J. Zhang, W. K. Chen, J. H. Xi, and Z. G. Ji, "{001} Facets of anatase TiO_2 show high photocatalytic selectivity," *Materials Letters*, vol. 79, pp. 259–262, 2012.

[6] T. L. Thompson and J. T. Yates Jr., "TiO_2-based photocatalysis: surface defects, oxygen and charge transfer," *Topics in Catalysis*, vol. 35, no. 3-4, pp. 197–210, 2005.

[7] A. L. Linsebigler, G. Q. Lu, and J. T. Yates, "Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results," *Chemical Reviews*, vol. 95, no. 3, pp. 735–758, 1995.

[8] M. Bognitzki, W. Czado, T. Frese et al., "Nanostructured fibers via electrospinning," *Advanced Materials*, vol. 13, no. 1, pp. 70–72, 2001.

[9] H. Niu and T. Lin, "Fiber generators in needleless electrospinning," *Journal of Nanomaterials*, vol. 2012, Article ID 725950, 13 pages, 2012.

[10] Z. Liu, D. D. Sun, P. Guo, and J. O. Leckie, "An efficient bicomponent TiO_2/SnO_2 nanofiber photocatalyst fabricated by electrospinning with a side-by-side dual spinneret method," *Nano Letters*, vol. 7, no. 4, pp. 1081–1085, 2007.

[11] D. Lin, H. Wu, R. Zhang, and W. Pan, "Enhanced photocatalysis of electrospun Ag-ZnO heterostructured nanofibers," *Chemistry of Materials*, vol. 21, no. 15, pp. 3479–3484, 2009.

[12] J. Zhang, W. Fu, J. H. Xi et al., "N-doped rutile TiO_2 nano-rods show tunable photocatalytic selectivity," *Journal of Alloys and Compounds*, vol. 575, pp. 40–47, 2013.

[13] W. J. Merz, "Switching time in ferroelectric $BaTiO_3$ and its dependence on crystal thickness," *Journal of Applied Physics*, vol. 27, no. 8, pp. 938–943, 1956.

[14] T. Takenaka and H. Nagata, "Current status and prospects of lead-free piezoelectric ceramics," *Journal of the European Ceramic Society*, vol. 25, no. 12, pp. 2693–2700, 2005.

[15] G. M. Madhu, M. A. L. A. Raj, K. V. K. Pai, and S. Rao, "Photodegradation of methylene blue dye using UV/$BaTiO_3$, UV/H_2O_2 and UV/H_2O_2/$BaTiO_3$ oxidation processes," *Indian Journal of Chemical Technology*, vol. 14, no. 2, pp. 139–144, 2007.

[16] P. Ren, H. Fan, and X. Wang, "Electrospun nanofibers of ZnO/$BaTiO_3$ heterostructures with enhanced photocatalytic activity," *Catalysis Communications*, vol. 25, no. 8, pp. 32–35, 2012.

[17] P. Blanchart, J. F. Baumard, and P. Abelard, "Effects of yttrium doping on the grain and grain-boundary resistivities of $BaTiO_3$ for positive temperature coefficient thermistors," *Journal of the American Ceramic Society*, vol. 75, no. 5, pp. 1068–1072, 1992.

[18] J. Qi, L. Li, Y. Wang, Y. Fan, and Z. Gui, "Yttrium doping behavior in $BaTiO_3$ ceramics at different sintered temperature," *Materials Chemistry and Physics*, vol. 82, no. 2, pp. 423–427, 2003.

[19] A. V. Ruban, H. L. Skriver, and J. K. Nørskov, "Surface segregation energies in transition-metal alloys," *Physical Review B*, vol. 59, no. 24, 10 pages, 1999.

[20] P. Afanasiev, "On the metastability of 'monolayer coverage' in the MoO_3/ZrO_2 dispersions," *Materials Chemistry and Physics*, vol. 47, no. 2-3, pp. 231–238, 1997.

[21] S. Ould-Chikh, O. Proux, P. Afanasiev et al., "Photocatalysis with chromium-doped TiO_2: bulk and surface doping," *ChemSusChem*, vol. 7, no. 5, pp. 1361–1371, 2014.

[22] X. Chen, K. M. Unruh, C. Ni et al., “Fabrication, formation mechanism, and magnetic properties of metal oxide nanotubes via electrospinning and thermal treatment,” *Journal of Physical Chemistry C*, vol. 115, no. 2, pp. 373–378, 2011.

[23] Z. J. Shen, Y. Wang, W. P. Chen et al., “Electrospinning preparation and high-temperature superconductivity of $YBa_2Cu_3O_{7-x}$ nanotubes,” *Journal of Materials Science*, vol. 48, no. 11, pp. 3985–3990, 2013.

[24] J. Zhang, L. S. Qian, W. Fu, J. H. Xi, and Z. G. Ji, “Alkaline-earth metal Ca and N codoped TiO_2 with exposed {001} facets for enhancing visible light photocatalytic activity,” *Journal of the American Ceramic Society*, vol. 97, no. 8, pp. 2615–2622, 2014.

[25] S. Saha, T. P. Sinha, and A. Mookerjee, “Electronic structure, chemical bonding, and optical properties of paraelectric $BaTiO_3$,” *Physical Review B: Condensed Matter and Materials Physics*, vol. 62, no. 13, pp. 8828–8834, 2000.

[26] M.-Q. Cai, Z. Yin, and M.-S. Zhang, “First-principles study of optical properties of barium titanate,” *Applied Physics Letters*, vol. 83, no. 14, pp. 2805–2807, 2003.