IOP Conference Series: Earth and Environmental Science

PAPER • **OPEN ACCESS**

Nickle and Cobalt Spinel Catalyzing Wet Air Oxidation of Refractory Pollutants under Mild Condition

To cite this article: Qi Jing and Huan Li 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **295** 012057

View the article online for updates and enhancements.

This content was downloaded from IP address 110.16.80.106 on 09/10/2019 at 23:39

Nickle and Cobalt Spinel Catalyzing Wet Air Oxidation of Refractory Pollutants under Mild Condition

Qi Jing[1], Huan Li[1*]

[1]Shenzhen Engineering Research Laboratory for Sludge and Food Waste Treatment and Resource Recovery, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

*Corresponding author's e-mail: li.huan@sz.tsinghua.edu.cn

Abstract. Refractory organic pollutants are critical issues in water or wastewater treatemnt, and catalytic wet air oxidation (CWAO) is a common method. To improve the efficiency and decrease the reaction conditions, a type of $NiCo_2O_4$ (NCO) spinel with urchin-like hollow strucutres was synthesized and used in CWAO of organics at low temperature and atmosphere pressure. Both scanning electron microscopy and X-ray photoelectron spectra were used to characterize NCO. The 3-D hierarchical architectures, solid state redox couple M^{2+}/M^{3+} (M represents Ni or Co), and plenty of surface oxygen species were proved. Furthermore, the reaction path of CWAO with NCO as the catalyst was concluded, i.e. consecutive adsorption, surface oxidation, and re-oxidation of reduced NCO by O_2. NCO showed excellent catalytic performance in CWAO of refractory organics, such as alkaline lignin and bisphenol A. The removal rates of total organic carbon exceeded 80% within 3 h. These findings promise a convenient and economical way for the treatment of refractory organics in water or wastewater.

1. Introduction

Hazardous and refractory organic pollutants from industrial wastewater, landfill leachate, and ground-to-drinking water can cause serious environmental problems due to its toxicity, unpleasant color and odor production, and recalcitrance to microbial degradation. In order to eliminate its harm to environment of pollutants, satisfy the stringent water quality regulations and the demand for recycling of water in the process, it is particularly urgent to develop appropriate pollutant removal technologies. Flocculation and filtration can only concentrate these organic substances, while advanced oxidation processes (AOPs) can degrade or mineralize them. Catalytic wet air oxidation (CWAO) is a promising technology to remove refractory organic substances with the capability of generating and exploiting free radicals [1]. Moreover, CWAO is one of the most economically, technologically and eco-friendly viable AOPs for wastewater treatment [1], as it uses O2 as oxidant instead of harmful and expensive oxidants like ozone and hydrogen peroxide in other AOPs. Furthermore, as the dosage of catalysts are allowed to be quite high, usually 1–5 g/L in slurry reactors and several orders higher in fixed-bed reactors, it is a suitable process with great potential for the treatment of wastewater containing high concentration of organics at high flow [1]. However, reaction conditions applied in CWAO are generally quite harsh at present, mostly at oxygen partial pressure of 0.1–3.0 MPa and temperature of 100–280°C [1-3], which increase operational cost and complexity. Hence, it is an essential issue to develop compatible catalysts to reduce the severity of reaction conditions and improve the degradation efficiency of organics.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

There have been an increasing number of novel catalysts with non-noble metals or carbon materials in recent studies. Catalysts with transition metals of Ni, Co, Mn, Mo, etc. are often studied because of their abundant resources, convenient synthetic methods and strong redox properties derived from the d-electron layer of metal cations being easy to lose or capture electrons. Composite metal oxides, hydrotalcite [4], perovskite [5, 6], and spinels [7] for instance, are such catalysts have been used in CWAO and have been found with good performance, robustness and oxygen storage capacity. Nevertheless, reaction conditions in most of the studies are still quite severe. Morphology and structure of catalysts are important factors affecting their performance. Hierarchical hollow structures are been considered with the ability to improve catalytic performance by offering a high specific surface area, short diffusion path for ions or electrons, and efficient channels for mass transport [8]. Hierarchical NiCo2O4 (NCO) with structures of nanorods, nanosheets and microspheres have been verified to have excellent performances of electronic conductivity [8] and catalytic peroxymonosulfate activation [9], and it has been widely applied to lithium-ion batteries, super capacitors, electro catalysts, AOPs, etc [10]. However, the performance of NCO in CWAO has not been investigated before.

The aim of our work is to develop a novel CWAO with mild operational conditions by using NCO as the catalyst. Urchin-like hollow NCO spinel was synthesized at first, and its performance was tested using glucose as model substance under different parameters including pH, temperature, concentration and the existence of O2. Finally, humic substances (HS), alkaline lignin (AL), and bisphenol A (BPA) were chosen as the models of refractory organics, and their decomposition was investigated with the assistance of NCO.

2. Experimental Sections

2.1. Materials

The reagents and solvents used were of analytical reagent grade, and they were not further purified. Commercial HS (sodium humate), AL, and glucose were purchased from Aldrich Chemistry, U.S.A., and BPA was supplied by Anpel Laboratory Technologies Inc. (Shanghai). The chemicals used for NCO synthesis, i.e. $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, urea, and isopropanol (IPA), were also supplied by Aldrich Chemistry, U.S.A..

2.2. Synthesis and Characterization of NCO

The urchin-like NCO hollow microspheres were synthesized by a solvothermal method followed by calcination according to the literature [8]. $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, and urea were dissolved in a mixture of isopropanol (IPA) and water, and the mass ratio was 0.58:0.29:3.6:11.78:3 for $Co(NO_3)_2{\cdot}6H_2O$: $Ni(NO_3)_2{\cdot}6H_2O$: urea: IPA: H_2O. The resulting mixture was stirred thoroughly and then transferred into Teflon-lined stainless steel vessels. The vessels were heated at 120°C for a period of 12 h in an electric oven. After that, the vessels were cooled naturally to room temperature, and then the mixture in the vessels was centrifuged to collect the precipitate. The precipitate was washed using deionized water and ethanol several times and then dried at 105°C overnight. All of the synthesized products were calcined at 350°C in air for 2 h at a ramping rate of 1°C/min.

Morphological and chemical composition of the synthesized NCO were studied by scanning electron microscopy (SEM, FEI APREO S, Netherlands). X-ray diffraction (XRD, RINT2000 V/PC, Bruker DS, Germany) was used to obtain crystallographic information and chemical states of the used NCO. X-ray photoelectron spectra (XPS) were measured by using an ESCALAB-MKII spectrometer (UK) with Al Ka radiation (1486.6 eV), and the raw spectra were curve-fitted by non-linear least squares fittings with a Gauss-Lorentz ratio (80:20) through the XPS PEAK41 software.

2.3. CWAO Procedures

CWAO was carried out in two modes including anaerobic batch mode, aerobic batch mode and aeration mode. Anaerobic batch mode was used to explore the interaction between NCO and organics

without external oxygen. Experiments were carried out in airproofed bottles. For glucose, 10 mL 1.8 g/L glucose solution and 1.25 g NCO were added into each bottle. The bottles were first blew with nitrogen in advance to get rid of the initial air in head space, and then placed in a water bath for reactions. After 3 h reaction, the bottles were taken out and placed in an ice-water bath to stop the reactions. After cooling, the mixtures in the bottles were centrifuged at 5800 g for 20 min. The supernatant was collected and then filtered with a 0.45 μm aqueous membrane. The filtrate was used for further analysis. The used NCO precipitation in centrifuge tubes was washed using ultrapure water to remove the residual solution; while the filtration residual of NCO was freeze-dried.

The procedure of aerobic batch mode was similar except for the initial step where the bottles were blew with O_2 in head space and then sealed tightly. Same operations for HS and AL in anaerobic batch mode and aerobic mode.

Experiments in aeration mode was carried out in a series of 2-L glass reactors, each of them was equipped with a reflux condenser, a magnetic stir-heater, an aeration device and a sampling valve. In a typical run, a group of reactors were used, and 1 L solution and 5 g NCO were added into each reactor. These reactors were heated from room temperature to a certain reaction temperature. After that, magnetic stirring started, and oxygen was immediately bubbled into the solutions continuously at 250 mL/min to ensure excessive oxygen in the reaction. For convenient discussion, this moment was defined as the "zero time" of the run. Solution samples containing used NCO were collected from different reactors at regular intervals. The samples were treated with the same methods as described in anaerobic mode.

Total organic carbon (TOC) was determined by a TOC IR analyzer (TOC-LCSH, Shimadzu, Japan).

3. Results and discussion

3.1. SEM of NCO

Morphology of the synthesized NCO was shown in Figure 1. Figure 1A, 1B and 1C exhibit that NCO particles have hollow microsphere structure with diameters of around 5 μm with a similar shape of hollow urchin shells. Figure 1D shows three dimensional hierarchical architectures of NCO, which is self-assembled from these low-dimensional nanostructured building blocks such as nanorods and nanosheets. The hierarchical architectures can offer more active sites for reaction, high energy adsorption capacity and efficient channels for mass transport [8, 11].

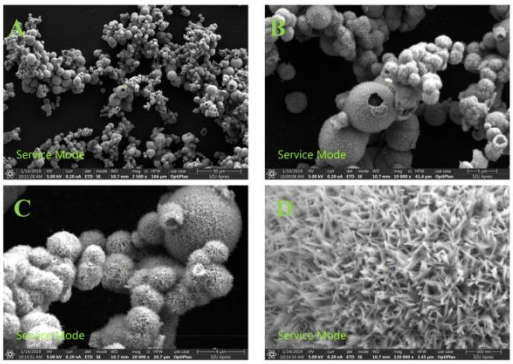


Figure 1. SEM images of the NCO with the amplification times of 2500 (A), 10000 (B), 20000 (C), 120000 (D)

3.2. XPS of NCO

Chemical bonding states and composition of the synthesized NCO were characterized by XPS measurement (Figure 2). The typical signals of O_{1s}, Co_{2p}, and Ni_{2p} core levels were obviously observed from the full scan spectra (Figure 2A). The O_{1s} spectra (Figure 2B) exhibit three oxygen contributions. The fitting peak at 529.5 eV (denoted as O-1) is derived from typical metal-oxygen bonds, i.e. lattice

oxygen. The peak located at 531.8 eV denoted as O-2 is attributed to the oxygen in hydroxyl groups and/or oxygen ions in low coordination sites at the surface. The fitting peak at 533 eV denoted as O-3 is attributed to the multiplicity of physi-/chemisorbed water at and within the surface. The Ni_{2p} spectra and Co_{2p} spectra (Figure 2C and 2D) both consist of two spin-orbit doublets and two shakeup satellites (identified as "Sat."), and the two spin-orbit doublets of these two spectra are ascribed to Ni^{2+} and Ni^{3+} (or Co^{3+} and Co^{2+}). These results showed that the surface of NCO had a composition containing Co^{2+}, Co^{3+}, Ni^{2+}, and Ni^{3+} species. O-1 and O-2 are considered as active and essential oxygen species [12] for oxygen delivery and activation. Besides, the O-2 species with higher mobility have the ability of reacting with organic substance directly or facilitating electron transfer to produce radicals [13].

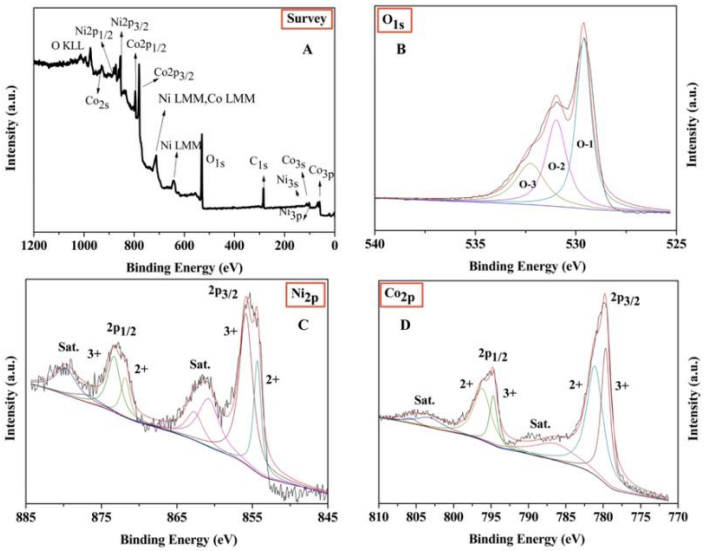


Figure 2. XPS profiles of NCO: survey scan (A), O_{1s} core level (B), Ni_{2p} core level (C), and Co_{2p} core level (D)

3.3. Catalytic performance of NCO in oxidative degradation of glucose

This section explored the way NCO worked in CWAO of organics by using glucose as the model, and the experiments were divided into three groups. First group (Figure 3A) was in anaerobic batch mode to investigate the interaction between NCO and glucose at different pH or temperature (Figure 3A). The TOC removal rates were basically the same at initial pH 7.0–12.0, but they tended to decrease under stronger alkaline condition, especially at 60°C. In fact, it was found that the inorganic carbon (IC) contents in most samples increased after reactions. For example, the IC at pH 13.2 and 90°C increased by 240.0 mg/L, and that at pH 12.9 and 90°C increased by 111.6 mg/L. These results verified that NCO had the ability to oxidize, degrade, and even mineralize organics. Besides, pH of the solutions after reaction reduced to some degree (Table 1), indicating some acidic products generated to react with OH^-. Furthermore, when the used NCO was eluted by dilute H_2SO_4, organic carbon was found in the elution, meaning that the interaction between NCO and organics involves consecutive adsorption and surface oxidation. As higher temperatures increased TOC removal, the adsorption of organics by NCO possibly belonged to chemisorption, and neutral pH should be more feasible to chemisorption and activation of organics by NCO.

According to Figure 3B, the actual quantity of organics removed increased as TOC_0 (initial TOC) was higher, which followed reaction kinetics. Figure 3C showed that external O_2 enhanced the removal efficiency of TOC, which verified catalytic oxidation ability of NCO. Thus, a preliminary judgment can be made that in CWAO of organics by NCO, the organics were chemisorbed on NCO at first, then transferred electrons to NCO, and finally decomposed. External O_2 re-oxidized the reduced NCO to make the reactions ongoing. The XRD pattern of the used NCO, which reacted with glucose in aerobic batch mode, was shown in Figure 4. The resultant diffraction peaks identify well with the

standard patterns of cubic spinel NCO (JCPDS No. 20-0781) [8, 14]. This indicated the robust performance of NCO crystal structure.

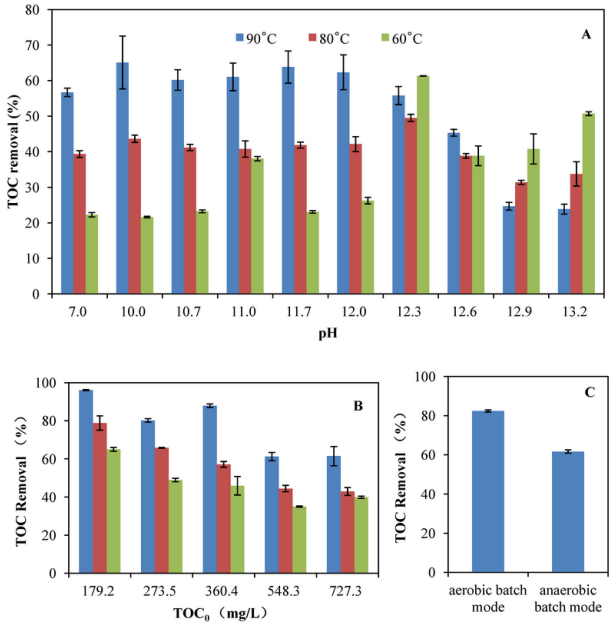


Figure 3. TOC removal after 3 h anaerobic batch experiments (A: 10 mL 1.8 g/L glucose solution (TOC 727.3 mg/L), 1.25 g NCO, and different temperature or pH; B: pH 11.0, 10 mL glucose solution with different initial concentrations, and different temperature; C: compare aerobic batch mode with anaerobic batch mode at 90°C and pH 11.0)

Table 1. The pH of the solution after 3 h reactions

Initial pH	**7.0**	**10.0**	**10.7**	**11.0**	**12.0**	**12.3**	**12.6**	**12.9**	**13.2**
90°C	7.1	7.1	7.1	7.1	7.2	7.3	7.5	8.5	11.6
80°C	7.0	7.0	7.0	7.1	7.2	7.3	7.7	10.3	12.3
60°C	7.1	7.5	7.5	7.5	7.6	7.6	7.8	10.8	12.4

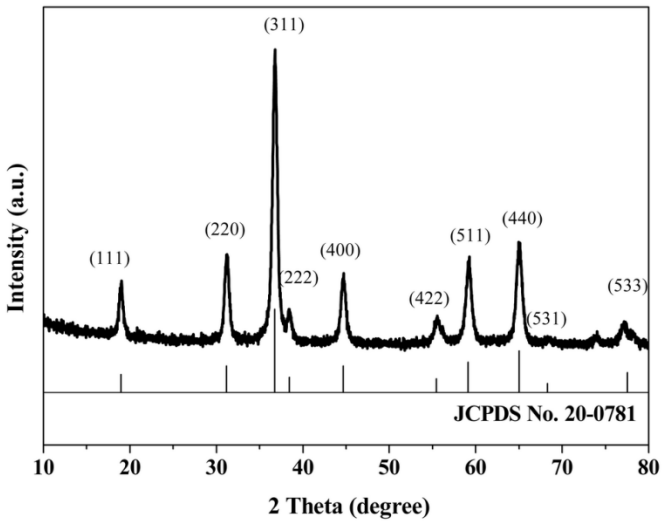


Figure 4. The XRD pattern of used NCO

3.4. Catalytic performance of NCO in CWAO of refractory organics

NCO of 5 g/L was used in CWAO of HS and AL (Figure 5). TOC removal rates kept high level at low concentrations of TOC_0, while the rates decreased at high TOC_0. This should be attributed to the limited external O_2 supply (in the headspace of the vessels). In addition, with the increase of TOC_0, the quantity of organic carbon removed still increased. The possible reason might be that chemisorption was the rate-limiting step, and high concentration of organics enhanced the contact with NCO's active sites. Further experiments were carried out at atmosphere pressure and continuous oxygen supply (Figure 6). TOC of BPA kept decreasing, while TOC of AL decreased at first 3h and then increased slightly. Such difference might be caused by the properities of AL and BPA, and the mechanism needs further investigation. Even so, these results exhibited the excellent catalytic performance of NCO in CWAO at mild conditions with TOC removal higher than 80% within 3 h.

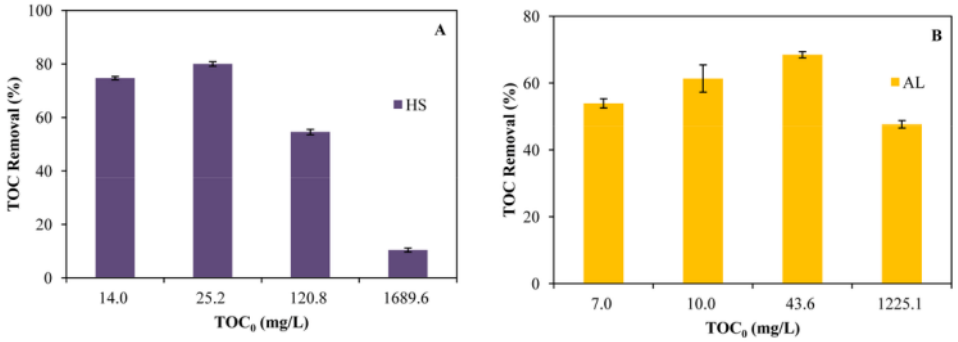


Figure 5. TOC removal after 3 h CWAO reaction of HS (A) and AL (B) with different initial concentrations

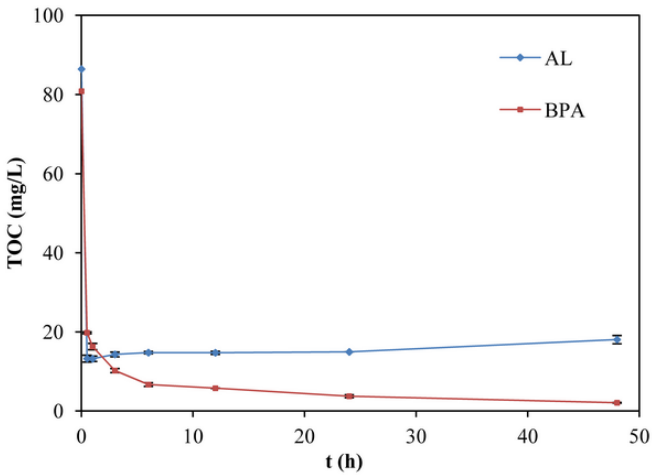


Figure 6. Kinetic tests in CWAO of AL and BPA at 90°C and pH 10 using NCO as the catalyst

4. Conclusion

A novel catalyst with hierarchical structures, urchin-like NCO hollow microspheres, was proposed and applied in CWAO of organics. It can mineralize organics, and its crystal structure was stable after redox reaction. With NCO as the catalyst, CWAO of organics involved consecutive adsorption, surface oxidation, and re-oxidation of reduced NCO by O_2. NCO exhibited excellent catalytic performance of degrading refractory and toxic organics under mild conditions, and TOC removal rate exceeded 80% within 3 h. These results promised an easy and cheap method to clean the water or wastewater rich in refractory organic substances.

Acknowledgments
Financial support for this project is obtained from the Shenzhen Science and Technology Project (grant number JCYJ20170307152224920).

References

[1] Kim, K.H., Ihm, S.K. (2011) Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: a review, J Hazard Mater, 186: 16-34.
[2] Lopes, R.J.G., Almeida, T.S.A., Quinta-Ferreira, R.M. (2011) Integrated detoxification methodology of hazardous phenolic wastewaters in environmentally based trickle-bed reactors: Experimental investigation and CFD simulation, Journal of Hazardous Materials, 189: 108-118.
[3] Yim, S.D., Dong, J.K., Nam, I.S. (2002) A pilot plant study for catalytic decomposition of PCDDs/PCDFs over supported chromium oxide catalysts, Catalysis Today, 75: 269-276.
[4] Alejandre, A., Medina, F., Rodriguez, X., Salagre, P., Sueiras, J.E. (1999) Preparation and Activity of Cu–Al Mixed Oxides via Hydrotalcite-like Precursors for the Oxidation of Phenol Aqueous Solutions, Journal of Catalysis, 188: 311-324.
[5] Yang, M., Xu, A., Du, H., Sun, C., Li, C. (2007) Removal of salicylic acid on perovskite-type oxide $LaFeO_3$ catalyst in catalytic wet air oxidation process, Journal of hazardous materials, 139: 86-92.
[6] Royer, S., Levasseur, B., Alamdari, H., Barbier Jr, J., Duprez, D., Kaliaguine, S. (2008) Mechanism of stearic acid oxidation over nanocrystalline $La_{1-x}A'_xBO_3$ (A′= Sr, Ce; B= Co, Mn): The role of oxygen mobility, Applied Catalysis B: Environmental, 80: 51-61.
[7] Xu, A., Yang, M., Du, H., Sun, C. (2006) Influence of partial replacement of Cu by Fe on the CWO of phenol in the Cu0. 5− xFexZn0. 5Al2O4 spinel catalysts, Catalysis Communications, 7: 513-517.
[8] Yu, X.Y., Yao, X.Z., Luo, T., Jia, Y., Liu, J.H., Huang, X.J. (2014) Facile synthesis of urchin-like $NiCo_2O_4$ hollow microspheres with enhanced electrochemical properties in energy and environmentally related applications, ACS Appl Mater Interfaces, 6: 3689-3695.
[9] Zhang, W., Su, Y., Zhang, X., Yang, Y., Guo, X. (2016) Facile synthesis of porous $NiCo_2O_4$ nanoflakes as magnetic recoverable catalysts towards the efficient degradation of RhB, RSC Advances, 6: 64626-64633.
[10] Zhao, Q., Yan, Z., Chen, C., Chen, J. (2017) Spinels: Controlled Preparation, Oxygen Reduction/Evolution Reaction Application, and Beyond, Chem Rev, 117: 10121-10211.
[11] Liu, X., Xu, D., Zhang, D., Zhang, G., Zhang, L. (2016) Superior performance of 3 D Co-Ni bimetallic oxides for catalytic degradation of organic dye: Investigation on the effect of catalyst morphology and catalytic mechanism, Applied Catalysis B: Environmental, 186: 193-203.
[12] Ren, Y., Lin, L., Ma, J., Yang, J., Feng, J., Fan, Z. (2015) Sulfate radicals induced from peroxymonosulfate by magnetic ferrospinel MFe_2O_4 (M = Co, Cu, Mn, and Zn) as heterogeneous catalysts in the water, Applied Catalysis B: Environmental, 165: 572-578.
[13] Larachi, F., Pierre, J., Adnot, A., Bernis, A. (2002) Ce 3d XPS study of composite $Ce_xMn_{1-x}O_{2-y}$ wet oxidation catalysts, Applied Surface Science, 195: 236-250.
[14] Ding, R., Qi, L., Jia, M., Wang, H. (2014) Facile synthesis of mesoporous spinel $NiCo_2O_4$ nanostructures as highly efficient electrocatalysts for urea electro-oxidation, Nanoscale, 6: 1369-1376.