Promoting Catalytic Ozonation of Phenol over Graphene through

Nitrogenation and Co$_3$O$_4$ Compositing

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Abstract

Catalytic ozonation is progressively becoming an attractive technique for quick water purification but efficient and stable catalysts remains still elusive. Here we solvothermally synthesized highly-dispersed Co_3O_4 nanocrystals over microscale nitrogen-doping graphene (NG) nanosheets and tested it as a synthetic catalyst in the ozonation of phenol in acid aqueous solutions. Transmission electron microscopy, Powder X-ray diffraction, Fourier transform infrared spectra and X-ray photoelectron spectroscopy were used to determine its morphology, crystallinity, elemental composition and molecular bonds, respectively. The comparative experiments confirmed the highest catalytic activity and oxidation degree (AOSC) of Co_3O_4/NG among four nanocomposites (G, NG, Co_3O_4/G, and Co_3O_4/NG). Co_3O_4/NG has exhibited the highest degradation rate: complete conversion of a near-saturated concentration of phenol (941.1 mg/L) was achieved within 30 min under ambient conditions with only a small dosage of Co_3O_4/NG (50 mg/L) and ozone (4 mg/L, flow rate: 0.5 L/min). It also resulted in 34.6% COD_{Cr} and 24.2% TOC reduction. In this work, graphene nanosheets not only functioned as a support for Co_3O_4 nanocrystals but also functioned as a co-catalyst for the enhancement in phenol removal efficiency. The surface nitridation and Co_3O_4 modification treatment further improved the removal rate of the phenol pollutants and brought in the higher oxidation degree. Our finding may open new perspectives for pursuing exceptional activity for catalytic ozonation reaction.

Keywords: Water treatment; Graphene; Nanocatalysts; Phenol

1. Introduction

The ever-increasing concerns about the quality and safety of water have motivated tremendous efforts in developing advanced waste and drinking water treatment processes.(Camel and Bermond, 1998; Glaze, 1987; Lawrence and Cappelli, 1977; Masten and Davies, 1994) Ozonation has been conceived as a clean and safe oxidation technology. However, high operation cost and energy demand (8–17kWh/kg), selectivity towards organic substrates, and low oxidation efficiency plagued its large-scale industrial applications.(Majumdar and Sproul, 1974) Catalytic ozonation process has then been developed to ameliorate its performance owing to its higher effectiveness in the degradation and mineralization of refractory organic pollutants.(Kasprzyk-Hordern et al., 2003; Li et al., 2015b) Marvelous panoply of nanoparticles has been exploited as ozonation catalysts due to their excellent catalytic activities. Given preventing aggregation and facilitating the post retrieval, macroscopic supports are indispensable. Appropriate choice of supports could also contribute to the enhancement of the reaction rate in various environmental heterogeneous catalytic reactions. Carbonaceous materials, like activated carbons, carbon blacks, carbon fibers, carbon spheres, carbon nanotubes, mesoporous carbons, carbon aerosols and xerogels, benefits from their superb absorption capability and environmentally benignity as supports. (Ikhlaq et al., 2014, 2015; Rodríguez-reinoso, 1998; Shahidi et al., 2015) Moreover, carbon could also function as a metal-free catalyst on its own. Pirkanniemi et. al recognized that supports may also improve the activity of the catalyst by acting as a co-catalyst in liquid phase reaction.(Pirkanniemi and Sillanpaa, 2002) However, carbon materials can be oxidized by ozone, resulting in an unfavorable discrepancy. One feasible and efficient approach to raise the chemical stability and duration of catalysts is compositing carbon with other nanoparticles.

Graphene (G), a 2D honeycomb network of extended sp^2 hybridized carbon atoms, was a good supporting choice taken its tunable micron-scale lateral size and highest specific surface area into account.(Hui et al., 2014) Meanwhile, its oxygenated precursor, graphene oxide (GO), presents plenty of intrinsic hydroxyl,

epoxide, carbonyl and carboxyl groups, allowing the interaction with various original metal ions through physisorption, electrostatic/complex binding or charge-transfer interactions.(Bao et al., 2014) All the interactions favor *in situ* decoration of nanoparticles by providing adequate nucleation sites. (Li et al., 2015a; Wang et al., 2016) Additionally, basic centers produced by nitration and/or amination can play a positive role of active sites for carbon materials.(Devillers et al., 2011) Goncalves et. al demonstrated that the basic nature further enhanced the catalytic activity compared with the acid nature through chemical oxidation for carbon nanotubes.(Goncalves et al., 2013) Cao et al. also evidenced that activated carbons with high basicity and large surface areas were the most active catalyst.(Cao et al., 2014) Thus, exploiting the hybridization of nitrogen functionalized graphene and nanoparticles is an important step in the development of multi-component and multi-phase catalysts with highly-expected synergistic properties.

Herein, graphene nanosheets has been modified with Co_3O_4 nanocrystals, whose excellent behavior as catalysts in ozonation process for degrading refractory organics has been evidenced. (Dong et al., 2010) Nitrogen was also incorporated into graphene using urea as a green and safe nitrogen dopant source to fabricate the basicity centers to further improve the catalytic ozonation reaction. And their superior catalytic ozonation degradation of phenol pollutants in aqueous solutions performance has been investigated. Treatment efficiencies, including averaged phenol degradation rate ($\bar{v}$), total organic carbon (TOC) removal and chemical oxygen demand (COD_{Cr}) abatement, were assessed and compared under the identical conditions to established activity correlations between the introduction and absence of the Lewis basic sites by nitridation.

2. Experimental

2.1. Materials and Characterization

Graphite powders were obtained from Unichem Chemical Co., Ltd. Cobalt acetate tetrahydrate ($Co(CH_3CO_2)_2 \cdot 4H_2O$), urea ($CO(NH_2)_2$), and phenol (PhOH) were of analytical grade and provided by Guangdong Guanghua Sci-Tech Co., Ltd.

All other chemicals and solvents were purchased from Sigma–Aldrich and used as received without any further purification. All solutions were prepared using ultrapure water (Millipore, 18.2 MΩcm).

The TEM samples were prepared by depositing droplets of the aqueous suspensions onto carbon films supported by copper grids. A Philips Tecnai 12 BioTWIN transmission electron microscope (TEM) operated at an accelerating voltage of 120.0 kV was used to examine the Low resolved morphology of the samples. High resolution transmission electron microscopy (HR TEM) images and selected area electron diffraction (SAED) patterns were obtained on a spherical-aberration (Cs)-corrected JEOL JEM-ARM200FTH (ultra-high-resolution pole piece) Field Emission Transmission Electron Microscope operating at an accelerating voltage of 200 kV with a "Schottky" field emission cathode and an aberration-corrector for the probe forming lens, providing a resolution of 1.9 Å in a high resolution mode. Powder X-ray diffraction (XRD) analyses were carried out on an X-ray diffractometer (X'Pert-MPD System, Philips) with Cu Kα radiation ($\lambda = 1.5406$ Å) at 40 kV and 30 mA in the range of $2\theta = 5-90°$ using a step size of 0.05° and a counting time of 1 s per step. X-ray photoelectron spectroscopy (XPS) data were obtained on a PHI 5802 high resolution X-ray photoelectron spectrometer with a monochromatic Al Kα X-ray source (1486.6 eV). High resolution scans were obtained at a take-off angle of 45° and a step size of 0.1 eV. The C 1s signal at 284.6 eV was utilized for making appropriate charging effect corrections. Each component was fitted with Gaussian–Lorentzian waveforms after performing a Shirley background subtraction. Ultraviolet-visible absorption spectroscopy measurements were recorded on a Perkin Elmer Lambda 35 spectrophotometer with a 1 cm quartz cell. COD values were measured following the standard procedure using a HACH (DRB 200) digestion reactor coupled by COD digestion reagent vials. TOC was determined on a TOC analyzer (Shimadzu 5000A). All pH measurements were carried out on a SevenGo SG2 pH probe. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker spectrometer (Tensor 27) using KBr pellets. The FT-IR samples were freeze-dried and further dried under vacuum to eliminate the

interference caused by oxygen in the air. A Beckman centrifuge (Avanti J-26) has been used to separate the composites from solutions. The BET surface data were collected at 77 K and investigated by N_2 adsorption–desorption isotherms on a physisorption analyzer (ASAP 2020, Micromeritics, USA). The volume of the adsorbed nitrogen was normalized to standard temperature and pressure (STP). Prior to the experiments, the samples were degassed in vacuum oven at 60 ^{o}C for 6 h.

2.2. Catalyst preparation

Synthesis of graphite oxide was conducted following the modified Hummers' method as described in a previous work.(Bao et al., 2011; Hummers and Offeman, 1958) The obtained graphite oxide power was dispersed in ethanol with a concentration of 0.35 mg ml^{-1} and exfoliated into graphene oxide (denoted as GO) monolayer nanosheets by sonication for 45 min. A maximum of 5 ml of cobalt acetate solution at a concentration of 25 mg ml^{-1} was mixed under vigorous stirring with 100 ml of GO/ethanol suspension from the first step. Approximately 5 ml of urea (20 wt.%) solution was introduced into the aforementioned mixture. The reactants were stirred for 10 min and heated at reflux for 12 h. The precursor was transferred into Teflon-lined stainless steel autoclaves with 200 ml volume, and thermal treatment was performed in an electric oven at 160 ^{o}C for 4 h. Then, the autoclaves were naturally cooled to room temperature, and Co_3O_4/NG nanocomposites were obtained by centrifugation, repeated washing with water, and freeze-drying for 24 h. The Co_3O_4/G was synthesized following the identical procedure without the addition of urea, yet with three drops of 1.0 M sodium hydroxide. Similarly, Nitrogen doped graphene preparations were conducted in the absence of Co sources. Undoped graphene was obtained following the same procedure without the addition of N and Co source.

2.3. Experimental procedure

Catalytic ozonation of phenol over the samples were carried out in a semi-batch mode by continuously feeding ozone gas to a home-made glass reactor. The reactor consisted of a cylindrical glass vessel (inner diameter of 50 mm and volume of 100 mL) equipped with a porous ceramic plate to feed the gas. Ozone was generated

from high-purity oxygen gas (99.99%) using an ozone generator (Medozons-BM-02) at a fixed flow rate of 0.5 L/min and the ozone concentration maintained constant automatically. The ozone concentration mentioned was all correlated to the ozone concentration in the outlet gas of the generator (*i.e.*, the inlet gas of the reactor). The nanocatalysts were added into 50 mL phenol aqueous solutions. The pH values were initially adjusted to the same value (pH = 4.8) by adding 0.1 M hydrochloric acid or sodium hydroxide solutions, which was not buffered to avoid the effect of buffer salts on the catalysts' properties. The solution was then mixed for 30 min and introduced into the reactor. Throughout the experiments, samples (2 mL) were withdrawn from the reactor at regular intervals, quenched in 0.05 M thiosulfate to consume remaining ozone species, centrifugalized to remove the catalysts, and diluted with water for further analysis. Experiments were performed in triplicate under the same condition. The data reported are the average of the triplicates. All experiments were performed at an ambient temperature that averaged 23±2 °C. Notably, in computing the residual phenol concentration, the influence of oxidative coupling products should be taken into consideration and the absorbance resulting from oxidative coupling products were subtracted from the total absorbance at 271 nm according to the following Eq. (1):

$$A_{271}^{PhOH} = A_{271} - A_{290}^{x} - 19\left(A_{290}^{x} - A_{300}^{x}\right) / 10 \tag{1}$$

in which A_{nm}^{x} was the absorbance resulting from oxidative coupling at the indicated wavelength. It is then reasonable to assign the residual absorbance at 271 nm to phenol.

3. Results and discussion

3.1 Structure, morphological and spectral characterization

The integrate investigations of the formation of Co_3O_4 nanocrystals on the graphene nanosheets were carried out. Preliminarily, the crystal phase composition of nanocomposites was examined by wide-angle powder XRD patterns as shown in Fig. 1A. The crystalline phases of Co_3O_4/G and Co_3O_4/NG showed a series of peaks at 21.4°, 31.2°, 36.6°, 44.7°, 59.1° and 65.2°, which were assigned to the (111), (220),

(311), (400), (511) and (440) crystallographic planes of the face centered cubic (fcc) Co_3O_4 (*Fd3m*; JCPDS No. 42−1467), respectively. The lower and broader peak shape of Co_3O_4/G and Co_3O_4/NG nanocomposites revealed their smaller nanoscale crystallite size. No CoN_x or CoO_x phase was identified. The featured (002) diffraction peak of graphene nanosheets located at 23.5° was estimated with interlayer space (*d*-spacing) of 11.75 nm, larger than that of pristine graphite (0.34 nm) indicating the complete exfoliation from the long-term ordered graphitic structure into single- or few-layered structure. In addition, the restacking of the graphene had been successfully prevented by the incorporating of Co_3O_4 as spacers between nanosheets.

The typical morphology and microstructure of the nanocomposite samples was investigated by HR TEM analysis, as displayed in Fig. 1 B-G. The immobilization of Co_3O_4 without significant aggregation on the flat surface of graphene nanosheets was clearly observed. The Co_3O_4 particles were monodispersed along with a fairly even distribution. It also revealed smaller particles and narrower size distribution in Co_3O_4/NG than Co_3O_4/G, attributed to NH_3 coordination with cobalt cations after thermolysis of urea in reducing Co_3O_4 particle size and enhanced particle nucleation on NG nanosheets. The HR TEM image in Fig. 1F shows an ultrafine cubic Co_3O_4 nanocrystal with sizes about 100 nm dispersed over the basal plane of NG nanosheet. Its corresponding high-energy SAED image (inset) shows well resolved diffraction rhombic spots array, providing strong evidence to support the single crystallinity of these formed Co_3O_4 nanoparticles. The BET specific surface area for G, NG, Co_3O_4/G and Co_3O_4/NG are 97.13, 113.44, 93.25 and 97.42 m^2/g, respectively. This result suggests that the nitrogen doped graphene and its Co_3O_4 composites possess larger surface area, which is beneficial to improve the catalytic performance in the catalytic ozonation reaction.

As shown in Fig. 2, FT-IR spectra of G and NG revealed that most oxygenated groups have been removed during the solvothermal treatment and drying process since no related absorption peak has been detected. As for the FT-IR spectra of Co_3O_4/G and Co_3O_4/NG composites, their peak positions and shape was similar and displayed nearly identical structural confirmation. Obviously, two distinctive strong

bands in the fingerprint region (500−1000 cm^{-1}) confirmed the spinel structure of Co$_3$O$_4$ nanoparticles. The former characteristic band at 582 cm^{-1} was assigned to the stretching vibration mode of Co−O [CoO$_6$] in which Co was Co+3 and octahedrally coordinated. The latter at 667 cm^{-1} was attributed to Co−O [CoO$_4$] vibration of Co+2 in the tetrahedral sites of Co$_3$O$_4$ lattice. Another strong absorption band at 1583 cm^{-1} was assigned to the stretching vibrations of C−O, illustrating Co$_3$O$_4$ was firmly bonded/fixed on graphene's surface via Co−O−C coordinative chemical bonds. No corresponding skeletal vibrations of the aromatic C=C in the unoxidised graphitic domains was observed due to the high coverage of Co$_3$O$_4$ over G and NG or most of the characteristic absorption bands of graphene were overlapped by Co$_3$O$_4$. The absorption peaks at 3418 and 1631 cm^{-1} corresponded to O−H stretching and bending vibration of surface hydroxide functional groups (Co−OH). The large amount of hydroxyl groups present on Co$_3$O$_4$ surface act as available Lewis acid catalytic sites, responsible for initializing ozone decomposition.

For further elucidating the elemental composition and nitrogen bonding configurations, XPS survey has been employed as shown in Fig. 3. The quantitative information on elemental (C, O, N and Co) contents on the surface of such composites materials after deconvolution of the XPS spectra was obtained and listed in Table 1. Comparing the G and NG results from Fig. 3A, nitrogen signals have been clearly identified, confirming that the N atoms have replaced the original O atoms within pristine GO frameworks. Accordingly, the O content decreased by 8.93%, while the N content accordingly increased by 9.68% after N doping process. The reduction degree also differed between G and NG, as indicated by the C/O ratio. NG was highly reduced (C/O = 7.36), whereas G was mildly reduced (C/O = 4.07) with a small fraction of oxygen-containing functional groups retained. It was attributed to the continuous release of ammonia ions during the thermolysis of urea, which induces substitution of the epoxy, carbonyl, carboxyl, and hydroxyl groups of pristine GO. The change of nitrogen and oxygen contents before and after nitrogen doping indicates the reduction of GO induced by the doping with nitrogen. Nitrogen doping and deoxidation has been achieved simultaneously.

The high resolution C 1s core-level XPS spectrum of Co_3O_4/G (Fig. 3C) was deconvoluted into four types of carbon bands: (a) graphitic sp^2 C at 284.6 eV (C−C/C=C), (b) hydroxyl C at 286.0 eV (C−OH), (c) carbonyl C at 286.7 eV (C=O), and (d) carboxyl C at 288.5 eV (O−C=O). The relative peak area of carboxyl C has been decreased from 12.02% (Co_3O_4/G) to 9.72% (Co_3O_4/NG) calculated based on their occupied area. This indicated the formation of $CO-NH_2$ bonds after the solvothermal process. The C 1s signal in Co_3O_4/NG consisted of an extra peak with binding energies of (e) 285.3 eV, associated with C−N/C=N bond formation due to the fact that nitrogen atoms were covalently incorporated into the graphene skeleton.(Yamada et al., 2014) The relative ratio of C−N/C=N bond was calculated to be 13.31%. Accordingly, NG showed the characteristic N 1s peak at 399.3 eV (Fig. 3D). The peak deconvolution revealed the N atoms in the NG sample were in three different valence states (Fig. 3E). That was: (a) pyridic-N at 400.0 eV, referred to the N atom contributing two 2p-electrons to the π-conjugated system; (b) amide or amine-N at 399.3 eV, derived from the formation of amidated graphene by the reaction between oxygen-containing functional groups of graphene and ammonia below ∼300 °C; and (c) pyrrolic-N at 398.6 eV, contributed one 2p-electron to the π-conjugated system. The relative atomic percentage of the pyridinic-N, amide/amine-N and pyrrolic-N were 31.9%, 8.2%, and 59.9%, respectively. The pyridine- and pyrrole-N dominated the N-configurations without subsequent thermal annealing treatment (∼600 °C). These N-containing surface groups (pyridinic and pyrrolic groups) in graphene contributed to the basic character of the surface.

3.2 Catalytic ozonation performance

The catalytic ozonation has been compared and characterized using phenol as a model contaminant in a high bubble dispersion reactor in order to increase the transfer rates of ozone from the gas bubbles to the liquid as shown in Fig. 4A. In order to confirm the high degradation ability of catalytic ozonation over nanocatalysts, a high phenol concentration solution, almost saturated one at room temperature, has been chosen. UV−vis spectroscopy was used to monitor its degradation progress. In Fig. 4B, the characteristic peak observed in the UV−vis spectrum of phenol was a signal at 271

nm, which ascribes to the $\pi \rightarrow \pi^*$ transitions of the aromatic C–C bonds due to p-π conjugate of hydroxyl groups. In less than 30 min, the total conversion of phenol has been achieved at the presence of Co_3O_4/NG nanocatalysts, suggesting a fast conversion rate. This was quite important for practical applications since the room temperature (20 ^oC) half-life time of dissolved molecular ozone was falling in a range from 16.7 min to 278 hr at low pH (< 4) (Bin, 2013; Gardoni et al., 2012).

The averaged degradation rate of phenol ($\overline{v}$) under pure ozone was 1.04 mg min^{-1} at 15 min reaction time at inlet ozone concentration of 4 mg/L at 0.5 L/min. In contrast, the calculated degradation rate has been improved to a certain degree at the presence of the four nanocatalystes, as displayed in Fig.5. Taken the minimal (50 mg/L) catalyst dosage as an example, the averaged degradation rate has been increased by 35.58%, 54.81%, 60.58%, 51.92% at the presence of G, NG, Co_3O_4/G and Co_3O_4/NG, respectively, evidencing graphene acted as ozonation catalysts and either Co_3O_4 or nitrogen modification further promoted its catalytic ability. Interestingly, the less dosage applied, the faster the degradation rate exhibited in regards of G and NG, suggesting indirectly adsorption didn't dominate the degradation process since the two materials showed high adsorption ability towards phenol. The reason might contribute to the reactivity of G and NG with ozone. In this sense, it was of importance from an economic perspective since this could reduce the dosage of catalysts. However, Co_3O_4/G and Co_3O_4/NG did not suffer from such problems, which illustrates Co_3O_4 modification could improve the whole resistance towards ozone and thus increase the stability of the catalysts. Moreover, the oxidation ability of Co_3O_4/G at the end stage of reaction decreased whereas Co_3O_4/NG always maintained high reaction ability during the whole progress. Thus, Co_3O_4/NG displayed the highest catalytic ability and stability taking advantage of Co_3O_4 and nitrogen modification.

Ozone concentration was proven to be a crucial factor affecting the degradation efficiency for heterogeneous catalytic ozonation in aqueous solutions since the low solubility of ozone in water, which barely reaches 570 mg L^{-1} at 20 ^oC for pure ozone

in the gas phase.(Zhang et al., 2013) This solubility dramatically drops down at lower ozone concentrations in the gas phase according to Henry's law. Taking Co_3O_4/NG as an example, increasing the ozone inlet concentration from 4 mg/L to 8 mg/L and even 9.999 mg/L significantly raised the initial rate of phenol conversion as shown in Fig. 6A. The other three nanocatalyts shared the similar applied ozone effect: higher applied ozone doses speeded up phenol removal kinetics. However, another issue arose: once the higher dosage of ozone applied, the ozone consumption per volume of phenol solution also increased, further increasing the operating cost inevitably. In particular, at the end stage of reaction, there showed almost no significant difference as for the averaged degradation rate whereby merely increasing the feeding ozone supply could not benefit the degradation degree but indeed exerted a positive effect on improving the initial reaction rate. Solution pH has been found another crucial operation parameter strongly affecting ozone stability, catalyst surface property and ozone decomposition mechanism.(Lage, 2010; Xing et al., 2014; Zhai et al., 2010) It was also a variable during the catalytic ozonation process. Fig. 6B showed the pH variation of the solution during the reaction period. The initial pH value was fixed at 4.8, which was quite close to the calculated value (4.9) based on pK_a = 9.89 at 25 °C due to the acidity of phenol. The pH value decreased gradually to 2.6 with prolonging the treatment time, indicating the success cleavage of the aromatic ring of phenol into small chain fatty acids with stronger acidity (e.g., malonic acid (pK_{a1} = 2.83), oxalic acid (pK_{a1} = 1.25), acetic acid (pK_a = 4.76), and formic acid (pK_a = 3.77)). (Hoigné and Bader, 1983)

Given good catalysts could not bring in an accelerated oxidation rate but also a higher mineralization of organic matters, COD_{Cr} and TOC parameters were also investigated throughout the phenol conversion process. As observed from Fig. 7, when G, NG, Co_3O_4/G or Co_3O_4/NG was present, both COD and TOC removal performance was all enhanced with respect to the non-catalytic progress. Furthermore, NG and Co_3O_4/NG gave higher TOC and BOD removal degree than their undoped counterparts. The maximum (26.6%) TOC removal value among the four

nanocomposites after 1 h treatment was observed in the case of NG. Co_3O_4/NG produced the best COD removal performance, achieving 65.4% after 1 h treatment.

The oxidation degree of the nanocatalysts was indexed by average oxidation state of carbon (AOSC), which was defined by the following expression(Contreras et al., 2003):

$$AOSC = \frac{4(TOC - COD)}{TOC} \qquad (2)$$

where TOC and COD were expressed in moles of C/L and moles of O_2/L, respectively. AOSC took values between +4 for CO_2, the most oxidized state of carbon, and –4 for CH_4, the most reduced state of carbon. Fig. 8 clearly showed that Co_3O_4/NG gave rise to the highest oxidation state and pristine G yields the lowest one at both 30 min and 1 h reaction time, respectively. The value obtained was in a range between the oxidation state of formic acid (+2) and oxalic acid (+3). It revealed that the byproducts formed during phenol ozonation were already highly oxidized and the major oxidation products were some low-molecular weight fatty acids. The increase of AOSC has been slowed down and there was only slight enhancement for the four nanocatalysts after 30 min. This result could be correlated to the decrement of solution pH and the yields of small chain fatty acids during catalytic ozonation. The 1 h AOSC results followed the order: Co_3O_4/NG (2.18) >NG (2.03) > Co_3O_4/G (1.78) > G (1.47) > O_3 (1.18), implying both Co_3O_4 and nitrogen modification contributed to enhance the oxidation activity of graphene.

The influence of catalysts dosage on the oxidation degree performance has been also investigated systematically in the range from 50 mg/L to 400 mg/L, respectively, as shown in Fig. 9. Generally, G, NG and Co_3O_4/G shared the same pertinence: more catalysts applied, higher oxidation degree exhibited. Notably, as for Co_3O_4/NG, the oxidation degree was not proportional to the dosage of catalysts within the studied range, evidencing the excellent catalytic behavior of Co_3O_4/NG from an economic perspective. Only a small dosage could achieve a highest catalytic ozonation performance and no further enhancement was observed at extended catalysts dosage.

Molecular ozone was an electrophilic oxidant (2.07 V *vs.* NHE in acidic solution) that can oxidize water impurities via direct reactions or via a chain reaction mechanism resulting in the production of free hydroxyl radicals. Generally, the main ozonation reaction at acidic pH and the ozonation of phenol catalyzed by Co_3O_4 were both supposed to support the direct molecular ozonation reaction pathway.(Nawrocki and Kasprzyk-Hordern, 2010) Although these ozonation reactions precede via heterogeneous processes, since they involved, at least, a surface reaction between a gas (ozone) and a liquid media containing the organic pollutants, it is still could not attribute the reaction to pure homogenous catalytic ozonation abusively. This's because we could not exclude the possibility of homogeneous direct ozonation with dissolved phenol pollutants in the bulk solution yet. Meanwhile, both direct ozone reaction and catalytic reaction can be involved simultaneously during the reaction process. The scheme presented in Fig. 10 only illustrated the tentative mechanism discussion regarding the enhancement in oxidation reaction focusing on the heterogeneous catalytic ozonation reaction part. Firstly, adsorption between phenol and the catalyst occurred, hence a solid–liquid interface might be formed. Both ozone molecule and phenol immigrated and concentrated in the vicinity of nanocatalysts' surface, leading to an enhanced interaction between phenol and ozone present at this solid–liquid interface. Then the electrophilic attack of ozone on the ortho and para positions of the aromatic ring of phenol took place.(Liotta et al., 2009) Phenol further underwent ring opening due to Criegee cycloaddition reaction of ozone to afford fumaric and maleic acid, along with fumaric, glyoxylic, oxalic and formic acids. Such derivatives usually exhibit weak reactivity toward oxidizing species due to the decrease of the electron density of the targeted molecules.(Sun et al., 2012) This explained why at the final stage of reaction both the reaction rate and oxidation degree decreased.

Graphene have also been used as ozonation catalysts and could achieve the local enrichment of dissolved ozone molecules at its surface. The enhancement of the catalytic activity could be associated with the unique characteristics of graphene, i.e., the large surface area and the high delocalized π electrons on the basal planes

rendered great affinity towards ozone. Theoretical studies have shown that the binding energy of ozone molecules on the graphene basal plane is 0.25 eV.(Lee et al., 2009) Meanwhile, the π electron-rich region could also form electron donor–acceptor complexes with H_2O molecules as shown in Eq. (3), yielding large amount of hydroxyl ions, and subsequently initiated the adsorbed ozone decompose into surface bound O−radicals, thereby catalyzing the ozonation reaction for pH = 2−6 solutions as proposed in Eqs. (4)−(6)(Kasprzyk-Hordern et al., 2003):

$$G_\pi + 2H_2O \rightleftharpoons G_\pi\text{−}H_3O^+ + OH^- \qquad (3)$$

$$O_3 + G \rightleftharpoons O_3\text{−}G \qquad (4)$$

$$O_3\text{−}G \rightleftharpoons O\text{−}G + O_2 \qquad (5)$$

$$O_3 + O\text{−}G \rightleftharpoons 2O_2 + G \qquad (6)$$

Nitridation could increase graphene's surface π electronic density by virtue of the strong electron donor feature of nitrogen and further enhanced the preponderance of adsorption capacity towards ozone molecules. Meanwhile, these basic active sites created by nitrogen-incorporation might also increase the π-electron coupling interaction between graphene and phenol as well as its intermediate products via acid-base interactions, which generally benefited the quicker and deeper ozonation reaction. It's because that the affinity of the catalyst surface toward ozone, water and (or) the organic substrate is expected to determine the kinetic-controlling step.

Moreover, some highly oxidative free radicals (e.g., superoxide anion, $O_2^{\bullet-}$) could be generated in the bulk solutions as a result of the presence of pyridinic-N and pyrrolic-N (Buffle and Von Gunten, 2006):

$$R_2NH + O_3 \rightarrow R_2NO^{\bullet} + H^+ + O_2^{\bullet-} \qquad (7)$$

Another possibility was that the synergetic catalytic effect of the transfer of electrons between the π orbitals of graphene and the d orbitals of Co atoms might enhance an obvious redox process occurred at water-catalyst interface during the catalytic decomposition of ozone, which might also account for the enhancement of the catalytic activity as reported elsewhere.

Conclusions

In summary, fine controlled cubic Co_3O_4 nanocrystals have in situ grown on the nitrogen doped graphene nanosheets by a facile solvothermal method. The results of the characterization demonstrate that Co_3O_4 nanocrystals were uniformly dispersed on the unique surface of NG nanosheets using urea as precipitator and nitrogen source. Comparative tests have shown that Co_3O_4/NG was the most effective nanocatalyst for the catalytic ozonation of high concentration phenol contaminants in aqueous solutions among the four nanocomposites (G, NG, Co_3O_4/G, and Co_3O_4/NG). This finding could not only be attributed to utilizing graphene as supporting materials but also the introduction of Lewis basic reactive centers (such as pyridinic-N and pyrrolic-N) by virtue of nitridation. Bifunctional property of NG acting as nanoparticles supports and co-catalysts has been confirmed. The superior reaction performance was also attributed to Co_3O_4 modification on nanocatalysts. Our results confirmed surface basicity and metal oxide modification benefits graphene for the enhanced catalytic ozonation of phenol with both improved organic degradation rate and oxidation degree. We therefore expect that our findings will lead to further development of a broad new class of metal oxide/carbon hybrids with enhanced properties for many advanced catalytic oxidation in water purification and environmental remediation applications.

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Figure Captions:

Figure 1 (A) XRD patterns of Co_3O_4/G and Co_3O_4/NG nanocomposites; HR TEM images of (B) G, (C) Co_3O_4/G and (E) Co_3O_4/NG nanocomposites; The inset plot shows the low-energy electron diffraction pattern of Co_3O_4/NG; The magnified view of (D) Co_3O_4 nanocrystals over G nanosheet and (F) Co_3O_4 nanocrystals over NG nanosheet; (G) HR TEM image of an individual Co_3O_4 nanocrystal supported over NG nanosheet with the inset plot showing the corresponding high-energy electron diffraction pattern

Figure 2 FT-IR spectra of the as-obtained G, NG, Co_3O_4/G and Co_3O_4/NG samples

Figure 3 (A) XPS full-scan survey of G, NG, Co_3O_4/G and Co_3O_4/NG; High-resolved (B) Co2p core-level peaks and (C) C1s core-level peaks of Co_3O_4/G and Co_3O_4/NG and (D) N1s core-level peaks of NG and Co_3O_4/NG; (E) Schematic illustration demonstrating the reactive centers in Co_3O_4/NG nanocomposites: hydroxyl groups in Co_3O_4 nanocrystals; pyridinic N, pyrrolic N and amino NH_2 groups in graphene structure

Figure 4 (A) The experimental setup used for the phenol degradation reaction in water solutions through the catalytic and non-catalytic ozonation processes; (B) UV-vis spectra monitoring the phenol degradation process in aqueous solutions during the catalytic ozonation reaction at the presence of 100 mg/L of Co_3O_4/NG. Operating conditions: phenol concentration: 941.1 mg/L, inlet O_3 gas concentration: 4 mg/L, flow rate: 0.5 L/min

Figure 5 Comparison of the averaged phenol degradation rate ($\bar{v}$) within 15, 20, 25 and 30 min intervals at the presence of (B) G, (C) NG, (D) Co_3O_4/G and (E) Co_3O_4/NG with various loading dosage (50, 100, 200 and 400 mg/L)

Figure 6 (A) Comparison of the averaged phenol degradation rate ($\bar{v}$) for 10-min and 20-min reaction during the catalytic ozonation process with increasing inlet O_3 gas concentrations (4000, 8000 and 9999 mg/L). Experimental conditions: PhOH

concentration, 941.1 mg/L; Co_3O_4/NG dosage, 100 mg/L and flow rate, 0.5 L/min; (B) Evolution of pH value for the phenol containing aqueous solutions during the catalytic ozonation process. Experimental conditions: PhOH concentration, 941.1 mg/L; Co_3O_4/NG dosage, 100 mg/L; inlet O_3 gas concentration, 4 mg/L and flow rate, 0.5 L/min

Figure 7 The variety of COD_{Cr} decrease and TOC removal of phenol containing aqueous solutions during the catalytic (the orange curves) and non-catalytic ozonation (the black cuves) processes with 100 mg/L of (A) G, (B) NG, (C) Co_3O_4/G and (D) Co_3O_4/NG nanocatalysts relative to non-catalytic ozonation treatment. Experimental conditions: PhOH concentration, 941.1 mg/L; inlet O_3 gas concentration, 4 mg/L and flow rate, 0.5 L/min

Figure 8 Comparison of average oxidation state of carbon (AOSC) of phenol containing aqueous solutions after 30 min and 60 min of ozonation with 100 mg/L of G, NG, Co_3O_4/G and Co_3O_4/NG nanocatalysts relative to non-catalytic ozonation treatment. Experimental conditions: PhOH concentration, 941.1 mg/L; inlet O_3 concentration, 4 mg/L and flow rate, 0.5 L/min

Figure 9 Average oxidation state of carbon (AOSC) of phenol containing aqueous solutions with increasing loading dosage of G, NG, Co_3O_4/G and Co_3O_4/NG nanocatalysts (50, 100, 200, and 400 mg/L) after 30 min and 60 min of catalytic ozonation process. Experimental conditions: PhOH concentration, 941.1 mg/L; inlet O_3 concentration, 4 mg/L and flow rate, 0.5 L/min

Figure 10 Scheme illustrating the possible mechanism for the catalytic ozonation of phenol at the presence of the Co_3O_4/NG nanocomposites