View Article Online View Journal

NJC Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: J. Zhang, F. Zhang, S. Guo and J. Zhang, *New J. Chem.*, 2018, DOI: 10.1039/C8NJ01533C.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/njc

NJC

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Three-dimensional Composite of Co₃O₄ Nanoparticles and Nitrogen Doped Reduced Graphene Oxide for Lignin Model Compounds Oxidation

Jiali Zhang, ^{§a} Fangwei Zhang, ^{§a} Shouwu Guo*^a and Jingyan Zhang*^b

Three dimensional composite of Co_3O_4 nanoparticles and nitrogen doped reduced graphene oxide (3D Co_3O_4/N -rGO) with unique 3D porous structure is prepared and its catalytic activity in lignin model compounds oxidation is explored. The 3D Co_3O_4/N -rGO composite exhibits better catalytic performance than Co_3O_4 nanoparticles or 3D N-rGO in the oxidation of lignin model compounds. The higher catalytic activity of the 3D Co_3O_4/N -rGO composite attributes to the combination of their porous structural feature, large surface area that provided by 3D N-rGO matrix, and active Co_3O_4 nanoparticles doped on the N-rGO surface. The structural feature of the 3D Co_3O_4/N -rGO is beneficial to the reactant and product diffusion and transportation, and also is helpful in preventing aggregation of Co_3O_4 nanoparticles. In addition, the introduction of N atoms in GO also is favorable to the formation of active oxygen species for the oxidation of model compounds. Given the high activity and the easy recovery from the reaction system, the 3D Co_3O_4/N -rGO composite should be applicable nonnoble metal catalytic system for lignin model compounds.

Introduction

The decomposition of lignin can produce value-added chemicals and fuel,^{1, 2} but, owing to the complicacy, the decomposing processes and also the underneath chemical mechanisms are studied usually using lignin model compounds.^{3, 4} Lignin model compounds, such as veratryl alcohol (VA) can be selectively oxidized to veratraldehyde in the presence of catalysts, including enzymes,⁵ ⁶ metal complexes, ⁷⁻¹¹ and many others. However, the poor stability and recyclability of these homogeneous catalysts limit deadly their practical applications. Accordingly, owing to their inherent advantages in recovery, recycling and amenability for continuous processing as compared to the homogeneous counterparts, heterogenous catalysts for lignin decomposition become more attractive. Heterogeneous catalysts for lignin transformation were designed using metals or metal oxide as active components, metal oxide, metal organic framework (MOF), or mineral as matrices. For instances, Ru/Al₂O₃,¹² Ru/PG,¹³ Pd/PG,¹³ Pd/SiO₂,¹⁴ Au/Al₂O₃,¹⁵ Au/CeO₂,¹⁶ Co₃O₄,^{17, 18} MnO_x,^{19, 20} RGO-MnCoO,²¹ Co-ZIF-9,²² and Ru@ZIF-8+CuO²³ systems have been developed. Among these

catalytic systems, cobalt-based catalysts have been relatively popular.²⁴ However, oxidation reactions with cobalt-based catalysts usually require the use of organic solvents, high oxygen pressure, high temperature or long reaction time.

Recently, three dimensional (3D) graphene-based materials, including graphene foams and aerogels, are found to be robust matrices for accommodating metals, metal oxides, and metal complexes for various applications.²⁵⁻³⁵ We have demonstrated that nitroarene compound can be reduced efficiently using graphene quantum dots (GQDs) anchored on 3D reduced graphene oxide (3D rGO) as catalyst.³⁶ The porous motif of 3D rGO offers a large surface area and mass transfer pathways for reactant and product, thus 3D GQDs/rGO exhibits better performance in substrate adsorption as well as product diffusion. However, the activity of 3D GQDs/rGO composite is relatively low, originated from the limited surface/edge defects of GQDs which are hard to control through the synthesis. Recently, it was found that the nitrogen-doped graphene exhibits excellent catalytic performance possibly due to the incorporation of N heteroatoms into the backbone lattice of graphene nanosheets as pyridinic, pyrrolic, and quaternary N complexes.^{37, 38} More detailed researches showed that the introduction of nitrogen species could enhance the electron donor property of the carbon matrix, resulting in an improvement of the interaction between carbon and substrate molecules.^{30, 39} In this work, the composite of Co₃O₄ nanoparticles and porous 3D N-rGO was prepared, and its catalytic property in the decomposition of lignin model compounds was explored.



^{a.} Department of Electronic Engineering, School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P.R. China. E-mail: swquo@situ.edu.cn

^{b.} State Key Laboratory of Bioreactor Engineering, Shanghai Key Laboratory of New Drug Design, School of Pharmacy, East China University of Science and Technology, Shanghai 200237, P. R. China. E-mail: jyzhang@ecust.edu.cn

[§] Authors contributed equally.

⁺ Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/C8NJ01533C

ARTICLE

Experimental

Materials

Cobalt (II) acetate tetrahydrate (Co(CH₃COO)₂·4H₂O, AR), benzyl alcohol and ethanol absolute (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Veratryl alcohol (VA, 98%), 4-methoxyl benzyl alcohol (99%) and 3,4,5trimethoxyl benzyl alcohol (98%) were bought from Saen Chemical Technology, Co., Ltd, Shanghai, China. Vanillyl alcohol (99%) was bought from Molbase Biotechnology Co, Ltd, Shanghai, China. 4-Methyl benzyl alcohol (98%) was obtained from Aladdin Industrial Co., Ltd, Shanghai, China. Ammonium Hydroxide (NH₃·OH, 25-28%, AR) was obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China. All chemicals were used as received without further purification. Graphene oxide (GO) was prepared following the procedures described in our previous work.⁴⁰

Synthesis of 3D N-rGO

Typically, 15 ml of aqueous dispersion of GO (2 mg/ml) was added to an autoclave (40 ml size), ammonia solution (1 ml) was added and stirred for 5 min. The autoclave was then transferred to an oven at 180 °C for 6 h. The product with cylinder-like bulk morphology was collected and was immersed into deionized water to remove the residual $NH_3 \cdot H_2O$ (as shown in Scheme 1). The cylinder-like 3D N-rGO bulk product was ground into powder for analysis.

For comparison, 3D rGO was prepared by hydrothermal reaction of the GO under similar condition without using $NH_3 \cdot H_2O$.

Synthesis of 3D Co₃O₄/N-rGO Composite

Sixty mg of Co(CH₃COO)₂·4H₂O was added into 1.24 ml of H₂O, 6.26 ml of ethanol and stirred for 5 min, followed by the addition of 0.5 ml of NH₃·H₂O and stirred for 5 min. Subsequently, the mixture was transferred to a 40 ml size autoclave. The as-prepared cylinder 3D N-rGO (30 mg) was immersed into the above solution at RT for 2 h. The autoclave was solvothermally treated at 150 °C for 3 h. After cooling down to room temperature, the product was obtained by centrifugation and washed 3 times with deionized water, dried for 24 h by lyophilization. The product is named as 3D Co₃O₄/N-rGO. Except for SEM measurement, the cylinder 3D Co₃O₄/N-rGO composite was ground into powder for testing and analyses.

Control sample Co_3O_4 NPs were also prepared through the same method as 3D $Co_3O_4/N\mbox{-}rGO$ without adding 3D N-rGO.

Catalytic Oxidation of Lignin Model Compounds using 3D $\rm Co_3O_4/N-rGO$

Oxidation of the lignin model compounds was studied using VA as an example, other lignin model compounds were oxidized under the same conditions. Generally, the oxidation reaction of VA was carried out in a 10 ml quartz reactor containing 2 mg of 3D Co_3O_4/N -rGO composite and 100 µl of VA (0.1 M) in 2.5 ml of H₂O, then filled with 0.5 MPa O_2 and closed with septum. The reaction solution was stirred at 140 °C for 4 h. After cooling to room temperature, the catalyst was separated by centrifugation. The supernatant was directly analyzed by 1220 HPLC (Agilent

Technologies, USA) with 60% acetic acid buffer (A) and 40% methanol (B) as mobile phase at a column temperature of 30 °C with flow rate of 1 ml/min. The products and substrates were detected using the UV detector at λ_{max} = 235 nm. Product identification was achieved by comparison of retention times to those of standard solutions of pure compounds. Conversions of lignin model compounds and yields of product were determined by HPLC using external standard method.

The catalyst turnover frequency (TOF), the milligrams of VA consumed 1 mg of catalyst (active metal/metal oxide loading) per hour was calculated under the same reaction condition.

Reusability of Catalyst

After catalytic reaction, the 3D Co_3O_4/N -rGO composite was separated from the reaction system centrifugation (8000 rpm, 10 min). Then, it was washed three times with ethanol, dried at $60^{\circ}C$ for 12h in a vacuum oven to reuse.

Instrumental

Atomic Force Microscopic (AFM) image of graphene oxide was taken on a MultiMode Nanoscope V scanning probe microscopy (SPM) system (Veeco, USA), and AN-NSC 10AFM cantilever tips (SHNIT Co., Russia) with a force constant of ~ 37 N/m and resonance vibration frequency of ~ 330 kHz were used. Sample for AFM was prepared by dropping aqueous suspension (~ 0.02 mg/mL) of GO on freshly cleaved mica surface and dried in air, respectively. The SEM and TEM images were acquired using Ultra 55 field emission scanning electron microscope (Zeiss, Germany) with the working voltage of 10.0 kV, and JEOL JEM-2100F transmission electron microscope (JEOL, Japan) with the operation voltage of 200 kV, and the high-resolution TEM (HRTEM) image was measured on the same instrument. The TEM specimen was prepared by placing the ethanol suspensions on the lacey support films and drying under ambient condition. The FT-IR spectra were acquired on a EQUINOX 55 FT-IR spectrometer (Bruker, Germany). The specimens for FT-IR measurement were prepared by grinding the dried powder of GO or 3D Co₃O₄/N-rGO with KBr together, and then compressing them into thin pellets. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance PC diffractometer (Bruker, Germany) using Cu/K α radiation ($\lambda = 1.55406$ Å), with the 2 θ range of 10 to 80° and the scan rate of 0.2° s⁻¹. The surface area was determined using the Brunauer-Emmett-Teller (BET) method by ASAP 2020 M (Micromeritics, USA). X-ray photoelectron spectra (XPS) was recorded on Krotos AXIS-Ultra DLD (SHIMADZU, Japan). The mass ratio of Co₃O₄ in the hybrid was determined iCAP 7600 ICP-OES (Thermo Fisher Scientific, USA). 10 mg specimen for ICP-OES measurement was dissolved in 6 ml mixture of HNO₃ and HClO₄ with volume ratio of 3:1, then the mixture was heated at 120-150 °C to remove C and N in composite. After cooling, the solid was dissolved in 1 ml mixture of HCl and HNO₃ with volume ratio of 3:1, then the mixture solution was diluted by H₂O to the constant volume of 100 ml. The reaction by-products of lignin model compounds oxidation were analyzed by ACQUITY UPLC & Q-TOF MS Premier (Waters) with water (A) and acetonitrile (B) as mobile phase under gradient elution conditions.

Published on 24 May 2018. Downloaded by Hacettepe Universitesi on 30/05/2018 02:38:26



Scheme I. Illustration of the preparation process of the 3D $Co_3O_4/N\mbox{-}rGO$ composite.

Results and discussion

Preparation and Characterization of 3D Co₃O₄/N-rGO Composite

3D Co₃O₄/N-rGO composite is synthesized through a threestep procedure as schematically shown in Scheme 1. Single-layer GO sheets (AFM image in Figure S1) are first reduced and selfassembled to 3D N-rGO through a hydrothermal treatment in the presence of $NH_3 \cdot H_2O$ at 180 °C. Subsequent hydrothermal reaction at 150 °C in the presence of cobalt salt leads to the growth and crystallization of Co₃O₄ nanoparticles on the surface of 3D N-rGO, forming 3D Co₃O₄/N-rGO composite. As shown in Figure 1a and b, the as-prepared composite consists of the 3D interconnected porous N-rGO nanosheets and Co₃O₄ nanoparticles. The size of Co_3O_4 nanoparticles is in the range of 5-10 nm (Figure 1c). The HRTEM image showed that the lattice constant of the Co₃O₄ nanoparticles was ca. 0.234 nm, closing to (311) facet of Co₃O₄, confirming the good crystallinity of Co_3O_4 in the composite.⁴¹ The formation of Co_3O_4 nanoparticles was further verified by X-ray powder diffraction data. As depicted in Figure S2a, the diffraction peaks at 20 of 19.1, 31.5, 37.0, 45.0, 59.4 and 65.3[°] in are contributed to (111), (220), (311), (400), (511) and (440) diffractions of Co_3O_4 with spinel crystalline phase (JCPDS Card No.42-1467).^{39,41} The FT-IR spectrum of the as-prepared composite shows that the vibration bands of -OH, -C=O, -C-O groups from the starting GO



Figure 1. SEM (a, b), TEM (c) and HRTEM (d) images of 3D $\rm Co_3O_4/N\mbox{-}rGO.$



DOI: 10.1039/C8NJ01533C

ARTICLE

Figure 2. (a) The survey XPS spectra of the 3D Co_3O_4/N -rGO. (b-d) C 1s, N 1s, and Co 2p XPS spectra of the composite.

decreased dramatically, suggesting that GO was reduced to rGO (Figure S2b).⁴⁰ Meanwhile, the new absorption bands at around 1390 $\rm cm^{\text{-1}}$ and 1574 $\rm cm^{\text{-1}}$ are attributed to C-N stretching and C=N stretching, respectively.⁴² Moreover, the distinct absorption bands at 661 cm⁻¹ and 571 cm⁻¹ are ascribed to the symmetric and asymmetric stretching vibrations of Co-O group comparing with bare Co₃O₄ nanoparticles, which suggests the existence of cobalt oxide in the composite.43 The chemical composition of the 3D Co₃O₄/N-rGO composite is determined further by X-ray photoelectron spectroscopy (XPS) as shown in Figure 2a. The peaks at 284.7 eV, 285.8 eV, 286.4eV, 287.1 eV, 287.6 eV and 289.5 eV can be assigned, respectively, to C 1s XPS of C=C/C-C, C=N, C-O, C-N, C=O, O=C-O groups (Figure 2b).³⁹ The N1s XPS spectrum, Figure 2c, reveals the presence of pyridinic N, pyrrolic N, graphitic N and pyridinic N-oxide within the N-rGO structure.⁴⁴ For Co 2p XPS spectrum (Figure 2d), two major peaks with binding energies at 779.7 and 794.9 eV are fitted, respectively, to $2p^{3/2}$ and $2p^{1/2}$ of Co bonded with O, indicating the presence of Co₃O₄ in the composite.^{18,} ⁴¹ The Co content, \sim 10 wt% (\sim 15 wt% of Co₃O₄), in the composite is quantitatively determined further by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis. The nitrogen adsorption-desorption isotherms of the composite clearly indicate that it assumes porous structure (Figure S3). Consequently, these results undoubtedly confirm the formation of 3D porous Co₃O₄/NrGO composite.

Catalytic Activity of 3D $\text{Co}_3\text{O}_4/\text{N-rGO}$ Composite for Oxidation of Lignin Model Compound VA

The catalytic performance of the 3D Co_3O_4/N -rGO composite in oxidation of lignin model compounds, using VA as an example, with O_2 as oxidant agent is evaluated in aqueous solution, and the results are summarized in Table 1. The conversion of VA is generally increased with the increase of the amount of catalyst, and can reach 91.2% when the catalyst loading is 27.0%. Higher catalyst

Table 1. Effect of the 3D Co_3O_4/N -rGO composite loading on VA oxidation reaction.

	СП ₂ ОП О ₂	OCH ₃ CHO OCH ₃ OCH ₃ OCH ₃ OCH ₃		
Entry	Catalyst (Co ₃ O ₄	Conv. (%) 1a	Selectivity (%)	
	content/ing //		1b	1c
1	none	1	>99	-
2	0.5 mg (4.5%)	63.2	94.1	4.6
3	1.0 mg (9.0%)	66.8	89.8	6.0
4	2.0 mg (18.0%)	90.0	81.4	8.7
5	3.0 mg (27.0%)	91.2	80.4	10.2

Reaction condition: VA (0.01 mM), H_2O (2.5 ml), oxygen (0.5 MPa), temperature (140 °C), time (4 h). Conversion and selectivity were determined by HPLC.

loading facilitates the oxidation of veratraldehyde further to veratric acid, though major product is veratraldehyde. The oxidation of VA is probably accomplished in two steps, namely, VA was converted to veratraldehyde first, then the veratraldehyde is continuously oxidized to veratric acid as proposed in literature.¹⁷ The effects of the reaction time and temperature on the VA oxidation with 3D Co_3O_4/N -rGO as catalyst, mainly conversion and selectivity, were also examined. As shown in Figure 3a, the conversion of VA increased from 38.2 to 93.5% with an increase of reaction time from 1 to 5 h, while the selectivity to veratraldehyde slightly decreased from 81.4 to 78.8%, and the yield of veratric acid



Figure 3. The effects of reaction time (a), temperature (b), and oxygen pressure (c) on the conversion and product distribution of VA oxidation using 3D Co_3O_4/N -rGO as catalyst. Reaction condition: VA (0.01 mM), catalyst (2 mg, Co_3O_4 loading 18%), H₂O (2.5 ml), oxygen (0.5-3.0 MPa), temperature (100-140 °C), time (1-5 h). Conversions and selectivity were determined by HPLC.

increased from 5.5 to 11.6%. The effect of temperature on the conversion of VA and selectivity to veratraldehyde at the range of 100-150 °C was more obvious to the reaction time, Figure 3b. The conversion of VA increased from 29.7 to 97.4%, while the selectivity to veratraldehyde dropped from 86.5% to 78.1% when the reaction temperature was raised from 100 to 150 °C. This is expected, since at a higher temperature the reaction was accelerated, and more veratraldehyde was further oxidized to veratric acid.

Table 2. Comparison of the oxidation of VA with different catalysts.							
$OCH_3 OCH_3 OCH_$							
Entry	Catalyst	metal/metal oxide content (wt%)	Conv. (%) ^h	Selectiv	ity ^h (%)	TOF ⁱ (h⁻¹)	Ref.
1	Co ₃ O ₄ NPs ^a	120.0	1a 29.7	91.9	2.4	0.062	this work
2	3D rGO ^a	—	46.2	93.5	1.3	_	this work
3	3D N-rGO ^a	—	61.2	90.0	1.1	_	this work
4	N-rGO ^a	_	43.7	90.6	4.1	_	this work
5	Co ₃ O ₄ NPs+3D N-rGO ^a	59.2	56.8	91.7	4.0	0.24	this work
6	3D Co ₃ O ₄ /N-rGO ^a	18.0	90.0	81.4	8.7	1.26	this work
7	Nano spinel Co ₃ O ₄ ^b	40.0	85.0	96.0	4.0	0.30	15, 16
8	MnO _x ^c	20.0	90.0	98.0	_	2.20	17
9	Co-ZIF-9 ^d	7.4	47.0	98.0	_	1.60	20
10	RGO-MnCoO ^e	18.3	74.0	84.0	6.0	2.04	19
11	Ru/Al ₂ O ₃ ^f	5.0	93.0	72.0	—	3.72	10
12	Au/CeO ₂ ^g	0.6	73.0	83.0	_	17.8	14

Journal Name

^a Reaction condition: VA (0.01 mM), catalyst (2 mg), H₂O (2.5 ml), oxygen (0.5 MPa), temperature (140 °C), time (4 h). Conversion and selectivity were determined by HPLC. ^b Reaction condition: substrate (0.5 g), water (70 ml), catalyst loading (0.2 g), temperature (140 °C), oxygen (4 MPa), time (7 h). ^c Reaction condition: VA (0.5 g), catalyst (0.1 g), temperature (120 °C), acetonitrile (60 ml), air (2.1 MPa), time (1.5 h). ^d Reaction condition: toluene (5.0 g), Co-ZIF-9 (0.05 g), NaOH (0.04 g), VA (0.68 g), oxygen (0.5 MPa), temperature (150 °C). ^e Reaction condition: aromatic alcohol (3.24 mmol), RGO-MnCOO catalyst (0.1 g), temperature (140 °C), acetonitrile (70 ml), air (2.1 MPa), time (2 h). ^f Reaction condition: VA (100 mg), catalyst (100 mg, 5 wt % metal), water (10 ml), temperature (160 °C), air (0.5 MPa), time (5 h). ^g Reaction condition: Substrate (4.85 mmol), Au/CeO₂ (0.5 mol%), temperature (80 °C), oxygen (0.1 MPa) (flow rate: 25 ml min⁻¹), time (7h).^h Some conversion and selectivity were estimated or calculated from data provided in the original articles.

In order to find optimal oxygen pressure, the VA oxidation was carried out with the identical amount of catalyst, but different conversion of VA slightly increased from 90.0 to 94.7% with an increase of partial pressure of oxygen from 0.5 to 3.0 MPa, while selectivity to veratraldehyde almost unchanged. The reaction rate remains the same with the increase of oxygen pressure. The minor oxygen pressures of 0.5-3.0 MPa at 140 $^{\circ}$ C. As shown in Figure 3c, the influence of oxygen pressure to the reaction rate and selectivity suggests that oxygen pressure of 0.5 MPa seems high enough for VA oxidation. Therefore, the conditions for VA oxidation used in the following experiments are as following: catalyst loading is 18%, reaction time is 4 h, temperature is 140 $^{\circ}$ C, and oxygen pressure is 0.5 MPa.

In order to understand further the catalytic property of the 3D Co_3O_4/N -rGO composite, VA oxidations were also performed with Co₃O₄, 3D rGO, 3D N-rGO, N-rGO and the physical mixture of Co₃O₄ and 3D N-rGO (named as Co₃O₄ + 3D N-rGO) as catalysts, and the results are summarized in Table 2. Overall, the 3D Co₃O₄/N-rGO composite exhibits higher activity than the others under the same condition. 3D N-rGO alone can catalyze the oxidation of VA with a relatively low activity, but more active than 3D rGO. The catalytic activity of 3D N-rGO may be partially contributed by the nitrogen species as pyridinic, pyrrolic, and graphitic N complexes into skeleton lattice of rGO (Figure 2c). $^{30, 39}$ Nitrogen-doped chemically reduced GO (N-rGO) show lower activity than 3D N-rGO (table 2, entry 4), indicating that 3D porous morphology of 3D N-rGO might also contribute to their activity. The assumption is supported by the large specific surface area of 3D N-rGO (~255 m²/g) vs N-rGO (~220 m²/g) determined by nitrogen adsorption/desorption isotherm curves vs (Table 3). The porous structure and the large surface area

Table 3. Textua	I parameters of different catalysts.
-----------------	--------------------------------------

Catalysts	S _{BET} (m²/g)	S _{Ext} (m²/g)	V _{Total} (cm ³ /g) ^a	V _{micro} (cm ³ /g) ^b	V _{meso} (cm ³ /g) ^c
Co ₃ O ₄ NPs	74.09	70.06	0.15	0	0.15
3D N-rGO	255.32	233.54	0.32	0.01	0.31
N-rGO	220.57	177.91	0.30	0.02	0.28
3D Co ₃ O ₄ / N-rGO	196.89	144.44	0.22	0.03	0.19

 S_{BET} : BET surface area, S_{Ext} : External surface area, V_{Total} : Total pore volume, V_{meso} : Mesopore volume. V_{mirro} : Micropore volume.

^a Total pore volume at $P/P_0= 0.95$.

^b t-plot.

^c V_{meso}=V_{Total}-V_{micro}.

of the 3D N-rGO is apparently more favorable to mass transfer of the substrate and products. $^{\rm 45}$

The better catalytic performance of the 3D Co₃O₄/N-rGO composite over Co₃O₄ nanoparticles might be assigned to the 3D porous structure of N-rGO matrix. This assumption is confirmed by their nitrogen adsorption-desorption isotherm (Figure S3). The N₂ physisorption measurements show that Co₃O₄ nanoparticles and 3D Co₃O₄/N-rGO both exhibit the hysteresis phenomenon that belong to the type IV isotherms with H₂ loops and H₃ loops, respectively, suggesting that 3D Co_3O_4/N -rGO has mesoporous structural feature. However, BET specific surface area of the 3D Co₃O₄/N-rGO is up to \sim 197 m²/g with a pore size of 2.5 nm and 4 nm, while it is only \sim 74 m^2/g for the bare Co₃O₄ nanoparticles (Table 3). The porous structure and the large surface area of the 3D Co₃O₄/N-rGO composite are apparently more favorable to substrate adsorption and product diffusion in VA oxidation. Besides, the catalytic activity of 3D Co₃O₄/N-rGO composite is remarkably higher than physical mixture of Co₃O₄ and 3D N-rGO (Co₃O₄ NPs+3D N-rGO), implying that the catalytic activity of the composite should be from the combination of the unique 3D structure of N-rGO and the Co₃O₄ nanoparticles anchored on it. Taken together, 3D N-rGO might not only plays a metal-free catalyst, but also the excellent support for Co_3O_4 nanoparticles in the catalytic reaction.

The better catalytic performance of the 3D Co₃O₄/N-rGO is also reflected by their higher turnover frequency (TOF) comparing to bare Co₃O₄ nanoparticles under the same reaction condition (Table 2). However, TOF of the 3D Co₃O₄/N-rGO composite is still lower than those noble metal catalysts, such as Au/CeO₂, a very efficient catalyst for VA oxidation in the absence of solvent.^{12, 16, 19-22} However, most of the oxidation reactions with those catalysts (listed in Table 2) were accomplished in organic solvents, except for Ru/Al₂O₃ (TOF, 3.72),¹² and Au/CeO₂ (TOF, 17.8).¹⁶

Catalytic Activities of 3D Co_3O_4/N -rGO in the Oxidations of Other Lignin Model Compounds

To evaluate further the catalytic performance of 3D Co_3O_4/N -rGO in the oxidations of other lignin model compounds, benzyl alcohol and its derivatives were investigated under the same reaction condition, and the results are summarized in Table 4. In general, 3D Co_3O_4/N -rGO can catalyze the oxidization of all these lignin model compounds, but shows different conversion rates. Comparably, the benzyl alcohols with more substitution groups can be oxidized quickly. The reason might be that certain electron-donating group enhances the oxidation process. For instances, the conversion rate of vanillyl alcohol is much higher than that of VA, and selectivity is much lower (entry 1 *vs* 6), and 4-methoxybenzyl alcohol can be oxidized a little easier than 4-methylbenzyl alcohol

lignin model compounds. соон 02 1h Entry R Conv. (%) Selectivity (%) 1a 1b 1c 1 3,4-dimethoxyl 90.0 81.4 8.7 17.7 2 4-methoxyl 55.0 82.3 3 3.4.5-trimethoxyl 66.9 75.6 18.2 4 4-methyl 46.5 77.6 21.7 5 Н 33.0 82.4 15.8 6 > 99.0 20.7 4.2 4-hydroxyl-3methoxyl

Table 4. Catalytic activity of 3D Co₃O₄/N-rGO in oxidation of

Reaction condition: aromatic alcohol (0.01 mM), catalyst (2 mg, Co_3O_4 loading 18%), H₂O (2.5 ml), oxygen (0.5 MPa), temperature (140 °C), time (4 h). Conversions and selectivity were determined by HPLC.

(entry 2 vs 4). The residual selectivity for the oxidation of VA is ascribed to the formation of veratrole as a by-product,¹² which was confirmed by ultra-performance liquid chromatography quadrupole time-off-light mass spectrometer (UPLC-Q-TOF-MS) (Figure S4). The by-product of the oxidation of 3,4,5-trimethoxyl benzyl alcohol is 1,2,3-trimethoxybenzene. We believe the high conversion of vanillyl alcohol, but lower selectivity was also due to the formation of byproducts, like as 2-methoxy-1,4-benzoquinone and 2-methoxyphenol (Figure S5). Nevertheless, these results indicate that 3D Co₃O₄/N-rGO can catalyze lignin model compounds, and can be used in the oxidation of these compounds. The success of the oxidation of lignin model compounds also motivate us examine other substrate. The preliminary result shows that 3D Co_3O_4/N -rGO composite can catalyze the epoxidation of styrene. However, the optimization of catalytic performance of composite need to be explored further.

We also examined the reusability of the composite, one of the key properties that determine the practical applicability of a catalyst. Figure 3d showed that the conversion of VA decreased by 18% after 5 cycles, and no obvious aggregation of Co_3O_4 nanoparticles was observed (Figure S6a). However, the specific surface area of 3D Co_3O_4 /N-rGO (~98 m²/g) used 5 times determined by nitrogen adsorption/desorption isotherm curves is lower than that of as-prepared catalyst (~197 m²/g) (Figure S6b), which may lead to the decrease of catalyst activity. Moreover, the metal leaching test showed that cobalt content in the residual reaction solution is about 18.8 ppm, suggesting that the decent reusability of the composite as catalyst.

Conclusions

To pursue an applicable catalyst for lignin decomposition, 3D Co_3O_4/N -rGO composite was designed and prepared through a simple hydrothermal method. The as-prepared 3D Co_3O_4/N -rGO composite assumes a 3D porous structure that provides with diffusion and transportation space for reactant substrate and products. It was demonstrated that the 3D Co_3O_4/N -rGO composite has better catalytic performance than the individual Co_3O_4 nanoparticle or 3D N-rGO in the oxidation of lignin model compounds. The catalytic activity of the composite should be attributed to the unique 3D morphology of N-rGO, the as-doped N heteroatom, and the inherent catalytic activity of the 3D Co_3O_4/N -rGO, coupled with ease recovery and good stability, the 3D Co_3O_4/N -rGO composite should be potentially useful catalyst for the oxidation of lignin.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The work was financially supported by China Postdoctoral Science Foundation (Nos.2017M611567), the National "973 Program" of China (Nos. 2014CB260411 and 2015CB931801).

References

- X. Zhang, Q. Zhang, T. Wang, L. Ma, Y. Yu and L. Chen, Bioresource Technol., 2013, 134, 73-80.
- Y. Liu, L. Chen, T. Wang, Q. Zhang, C. Wang, J. Yan and L. Ma, ACS Sustain. Chem. Eng., 2015, 3, 1745-1755.
- H. Lange, S. Decina and C. Crestini, Eur. Polym. J., 2013, 49, 1151-1173.
- C. Li, X. Zhao, A. Wang, G. W. Huber and T. Zhang, *Chem. Rev.*, 2015, **115**, 11559-11624.
- M. A. Eisenstadt and K. G. Bogolitsyn, Russ. J. Bioorg. Chem., 2010, 36, 802-815.
- T. M. Larson, A. M. Anderson and J. O. Rich, *Biotechnol. Lett.*, 2013, 35, 225-231.
- 7. F. Cui and D. Dolphin, *Can. J. Chem.*, 1992, **70**, 2314-2318.
- 8. A. Haikarainen, J. Sipila", P. Pietika"inen and I. M. Mutikainen, *Bioorgan. Med. Chem.*, 2001, **9**, 1633-1638.
- K. Kervinen, P. Lahtinen, T. Repo, M. Svahn and M. Leskelä, Catal. Today, 2002, 75, 183-188.
- K. Kervinen, H. Korpi, M. Leskelä and T. Repo, J. Mol. Catal. A-Chem., 2003, 203, 9-19.
- V. O. Sippola and A. O. I. Krause, J. Mol. Catal. A-Chem., 2003, 194, 89-97.
- 12. M. Melián-Rodríguez, S. Saravanamurugan, S. Kegnæs and A. Riisager, *Top. Catal.*, 2015, **58**, 1036-1042.
- Z. Yang, X. Zhao, T. Li, W. Chen, Q. Kang, X. Xu, X. Liang, Y. Feng, H. Duan and Z. Lei, *Catal. Commun.*, 2015, 65, 34-40.
- 14. A. Kim, H. S. Bae, J. C. Park, H. Song and K. H. Park, *New J. Chem.*, 2015, **39**, 8153-8157.
- P. D. Giorgi, N. Elizarov and S. Antoniotti, *ChemCatChem*, 2017, 9, 1830-1836.
- 16. A. Abad, P. Concepción, A. Corma and H. García, *Angew. Chem.*, 2005, **117**, 4134-4137.
- 17. V. R. Mate, M. Shirai and C. V. Rode, *Catal. Comm.*, 2013, **33**, 66-69.

Journal Name

- V. R. Mate, A. Jha, U. D. Joshi, K. R. Patil, M. Shirai and C. V. Rode, *Applied Catalysis A: General*, 2014, 487, 130-138.
- A. Jha, T. Chandole, R. Pandya, H.-S. Roh and C. V. Rode, *RSC Adv.*, 2014, 4, 19450-19455.
- 20. A. Kamimura, H. Komatsu, T. Moriyama and Y. Nozaki, *Tetrahedron*, 2013, **69**, 5968-5972.
- A. Jha, D. Mhamane, A. Suryawanshi, S. M. Joshi, P. Shaikh, N. Biradar, S. Ogale and C. V. Rode, *Catal. Sci. Technol.*, 2014, 4, 1771-1778.
- J. Zakzeski, A. Dębczak, P. C. A. Bruijnincx and B. M. Weckhuysen, Appl. Catal. A-Gen., 2011, 394, 79-85.
- 23. H. Fan, Y. Yang, J. Song, G. Ding, C. Wu, G. Yang and B. Han, *Green Chem.*, 2014, **16**, 600-604.
- 24. R. Behling, S. Valange and G. Chatel, *Green Chem.*, 2016, **18**, 1839-1854.
- 25. M. Li, J. Hu and H. Lu, *Catal. Sci. Technol.*, 2016, **6**, 7186-7192.
- Z. Wang, Y. Pu, D. Wang, J. Shi, J. Wang and J.-F. Chen, AICHE J., 2017, 0, 1-9.
- 27. M. Dabiri, M. Kasmaei, P. Salari and S. K. Movahed, *RSC Adv.*, 2016, **6**, 57019-57023.
- 28. Z. Ma, Y. Qiu, Y. Huang, F. Gao and P. Hu, *RSC Adv.*, 2015, **5**, 79456-79462.
- 29. Z. Zhang, T. Sun, C. Chen, F. Xiao, Z. Gong and S. Wang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 21035-21040.
- M. Mahyari, M. S. Laeini and A. Shaabani, *Chem. Commun.*, 2014, **50**, 7855-7857.
- S. Zhang, X. Shen, Z. Zheng, Y. Ma and Y. Qu, J. Mater. Chem. A, 2015, 3, 10504-10511.
- P. Kumar Sahoo, B. Panigrahy, D. Thakur and D. Bahadur, New J. Chem., 2017, 41, 7861-7869.
- J. Liu, X. Yan, L. Wang, L. Kong and P. Jian, J. Colloid Interface Sci., 2017, 497, 102-107.
- X. Liu, X. Zhao, Y. Cao, T. Li, S. Qiu and Q. Shi, New J. Chem., 2017, 41, 865-872.
- 35. W. Zhong, X. Tian, C. Yang, Z. Zhou, X. Liu and Y. Li, *Int. J. Hydrogen Energ.*, 2016, **41**, 15225-15235.
- J. Zhang, F. Zhang, Y. Yang, S. Guo and J. Zhang, ACS Omega, 2017, 2, 7293-7298.
- J. Long, X. Xie, J. Xu, Q. Gu, L. Chen and X. Wang, ACS Catal., 2012, 2, 622-631.
- Y. Gao, G. Hu, J. Zhong, Z. Shi, Y. Zhu, D. S. Su, J. Wang, X. Bao and D. Ma, Angew. Chem. Int. Ed. Engl., 2013, 52, 2109-2113.
- R. Nie, J. Shi, W. Du, W. Ning, Z. Hou and F.-S. Xiao, J. Mater. Chem. A, 2013, 1, 9037-9045.
- 40. J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang and S. Guo, *Chem. Commun.*, 2010, **46**, 1112-1114.
- C. Wang, P. Shi, X. Cai, Q. Xu, X. Zhou, X. Zhou, D. Yang, J. Fan, Y. Min, H. Ge and W. Yao, *J. Phys. Chem. C*, 2015, **120**, 336-344.
- 42. S. Suresh Balaji, M. Karnan and M. Sathish, *Int. J. Hydrogen Energ.*, 2018, **43**, 4044-4057.
- R. K. Das and A. K. Golder, *Electrochim. Acta*, 2017, 251, 415-426.
- F. Yang, C. Chi, C. Wang, Y. Wang and Y. Li, *Green Chem.*, 2016, 18, 4254-4262.
- X. Fan, G. Zhang and F. Zhang, Chem. Soc. Rev., 2015, 44, 3023-3035.

New Journal of Chemistry Accepted Manuscript

Three-dimensional Composite of Co₃O₄ Nanoparticles and Nitrogen Doped Reduced Graphene Oxide for Lignin Model Compounds Oxidation

Table of contents



3D composite of Co_3O_4 nanoparticles and N-doped reduced graphene oxide can catalyze effectively oxidation of lignin model compounds.