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Bimetal MOF derived mesocrystal $ZnCo_2O_4$ on rGO with High performance in visible-light photocatalytic NO oxidization

Shuning Xiao[a,c], Donglai Pan[b], Rui Liang[b], Wenrui Dai[c,e], Qitao Zhang[a], Guoqiang Zhang[a,c], Chenliang Su[a,*], Hexing Li[b,*], Wei Chen[c,d,e,**]

[a] SZU-NUS Collaborative Innovation Center for Optoelectronic Science & Technology, International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China
[b] International Joint Laboratory of Resource Chemistry SHNU-NUS-PU, Department of Chemistry, Shanghai Normal University, Shanghai 200234, China
[c] Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543, Singapore
[d] Department of Physics, National University of Singapore, 2 Science Drive 3, 117542, Singapore
[e] National University of Singapore (Suzhou) Research Institute, 377 Lin Quan Street, Suzhou Industrial Park, Jiangsu 215123, China

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ABSTRACT

A mesocrystal $ZnCo_2O_4$ on reduced graphene oxide (rGO) nano-composite was successfully synthesized by a low-temperature annealing of bimetal organic frameworks on rGO. In this nano-composite, rGO nanosheets worked as the two-dimensional support to significantly improve the dispersity and conductivity of nano-composites. The mesoporous $ZnCo_2O_4$ crystal derived from ZnCo-ZIF worked as the main active sites with the optimized Zn/Co ratio to ensure an ideal valence band structure as well as enhanced visible-light harvesting properties. The as-prepared rGO@$ZnCo_2O_4$ nano-composites showed a remarkable activity in visible-light photocatalytic NO oxidation with the conversion of 83.8% under visible light and 92.6% under simulated solar light. It also exhibited a higher stability than that of N-doped TiO_2, thereby making this nano-composite as a promising and stable photocatalyst for environmental remediation.

1. Introduction

The concentrations of nitrogen oxide (NO_x) in the atmosphere are continuously increasing due to the springing growth of the industrial development and automobile exhausting. It can even cause severer secondary pollutions, such as photochemical smog, acid rain, $PM_{2.5}$ and other serious environmental problems to the human health [1]. Among the NO_x, nitric oxide (NO) accounts for about 95% of the total emission. After entering into the air, NO can react with O_2 to produce a series of NO_x due to the highly reactive chemical properties. Therefore, the effective removal of NO before its conversion is particularly important for the health security and sustainable economic development of modern society [2]. During the past few decades, different routes, such as selective catalytic reduction (SCR) [3–9], selective non-catalytic reduction (SNCR) [10–12], and photocatalytic technologies have been explored for removing NO. Among them, the photocatalytic route [13–16] have attracted substantial attentions due to its preferred advantages, including simple operation, mild reaction condition, low cost, high efficiency, and good durability [17].

TiO_2 is the most commonly used semiconductor photocatalysts for NO oxidation since its highly positive valence band position that makes it possible for photo-excited holes to oxide NO directly [18–22]. However, the rapid recombination rate of photo-excited electron-hole pairs as well as the merely UV-response restricts its more extensive application in the practical low-concentration NO removal. Numerous catalysts-design strategies have been developed to solve these issues, such as co-catalyst with noble-metals [23–25], ions doping [26–28], composited with carbon materials [29–31] and other semiconductors [32–34]. On the other hand, novel visible-light driven photocatalysts are gradually developed for this reaction, like g-C_3N_4 [35,36], Bi-based semiconductors [37–40] and so on. Recently, metal organic frameworks (MOF) and their derivatives have become one of the most attractive series of functional materials that can be widely utilized in energy storage [41–43], gas storage and absorption [44–46], electro-catalysis [47–49] as well as photocatalysis [50–52] due to their large surface area, controllable functional groups and uniform pore size. For mild photocatalytic gas-phase reaction, MOF-based materials can retain their pore structures under the reaction environment, and of utmost significance, such special structure shows excellent adsorption ability with great potential for gas-phase catalysis. However, to the best of our

* Corresponding authors.
** Corresponding author at: Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543, Singapore.
E-mail addresses: chmsuc@szu.edu.cn (C. Su), hexing-li@shnu.edu.cn (H. Li), phycw@nus.edu.sg (W. Chen).

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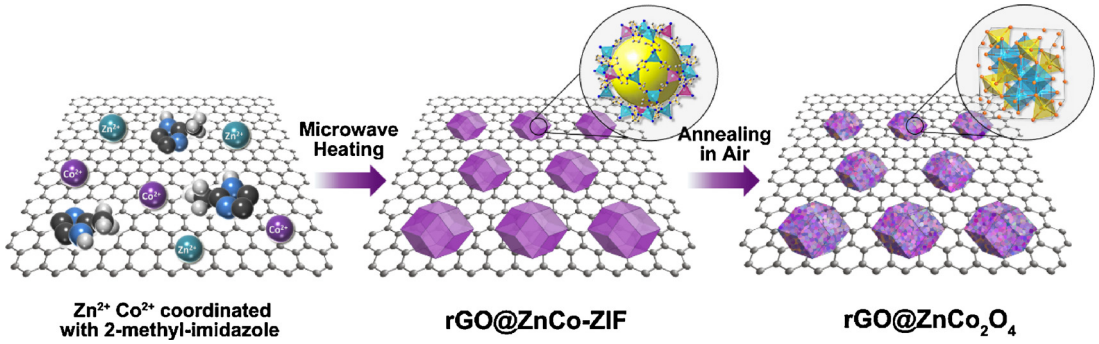

Scheme 1. Schematic illustration the formation of the rGO@$ZnCo_2O_4$ hybrid with hierarchical structure.

knowledge, only Ag doped MIL-125-like MOF was used as catalyst for NO oxidation with limited stability [53], possibly due to the limited electron conductivity and the less utilized inner surface in microporous structures for MOF-based materials. Therefore, to be used for the gas-phase NO oxidation reaction, it is highly desirable to improve the porous structure, conductivity and the stability for the MOF and their derivative materials

Herein, we reported a novel MOF-derived nano-composite for visible-light driven NO oxidation reaction, comprising the reduced graphene oxide (rGO) nanosheets as the two-dimensional (2D) support with the loaded mesoporous $ZnCo_2O_4$ crystal as semiconductor photocatalyst. Scheme 1 showed the formation of the rGO@$ZnCo_2O_4$ hybrids with hierarchical structure. As illustrated, after ultrasonication in methanol, the abundant hydroxyl and carbonyl functional groups on the surface of the well dispersed GO could strongly bind with metal ions (Zn^{2+} and Co^{2+}). Meanwhile, the 2-methyl-imidazole ligands could also be attracted by the benzene rings from GO via noncovalent π-π interactions. After that, upon irradiated by the microwave, the GO with strong electromagnetic-to-heat conversion ability could be induced to form a super-hot surfaces. It resulted in the rapid nucleation and gradual growth of ZnCo-ZIF dodecahedron crystals on GO. In addition, with the thermal reduction property of the solvent, the GO could be reduced to rGO. Finally, by annealing the as-prepared rGO@ZnCo-ZIF in air at 300 °C, the ZnCo-ZIF crystals were oxidized to form $ZnCo_2O_4$ with the morphology changing to the mesoporous with retained frameworks in the shape of rhombic dodecahedron. Such unique nano-architecture of rGO@$ZnCo_2O_4$ hybrid could benefit from the synergistic effects of each component to meet the critical requirements for high-performance photocatalytic air purification, including (1) the $ZnCo_2O_4$ mesocrystals could effectively favor the gas pollutant absorption; (2) the in-situ growth leads to an intimate contact between the $ZnCo_2O_4$ mesocrystals and the rGO nanosheets to improve the hybrids conductivity and to further create an interconnected electron transport percolation network for the photo-excited carriers; (3) the optimized Zn/Co ratio in the crystal can result in a suitable valence band structure with enhanced visible-light harvesting properties, further improving the photocatalytic activities. As a result, the as-prepared rGO@$ZnCo_2O_4$ nano-composite represents a promising visible-light driven photocatalyst with an improved gas pollutant removal efficiency and long-term stability.

2. Experimental

2.1. Synthesis of rGO@ZnCo-ZIF composites

In a typical synthesis, 50 mg of graphene oxides (GO, 0.2 ~ 10 μm in average dimeters, Shanghai Ashine Technology Development Co., Ltd.) were dispersed in 20 mL of methanol under ultrasonication for 30 min. Then 8 mmol of 2-methylimidazole (H-Mim) was slowly added into the GO dispersion with continuous magnetic stirring to form solution A. To form solution B, 4 g of polyvinylpyrrolidone (PVP, Mw ~55,000) and a certain ratio of $Zn(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ with total molar of 2 mmol were added into 20 mL of methanol by ultrasonication for 30 min. After that, with continuous stirring, solution B was added dropwise into solution A. The mixture was then transferred into a 60 mL of double-walled Teflon-lined microwave reaction vessel in high-pressure microwave synthesis system (Ethos ONE, Milestone). It was then heated at a heating rate of 10 °C min^{-1} to 140 °C and was kept at this temperature for 30 min. After being cooled down to room temperature, as-synthesized samples were washed thoroughly with methanol and ethanol for 3 times and dried at 0 °C in a low-temperature vacuum drier. By adjusting the amount of $Zn(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$, we got different samples with the Zn/Co molar ratios in the order of 2.0, 1.5, 1.0, 0.75 and 0.50, respectively. For convenience, the Gr-ZnCo-ZIF-1.0 sample was abbreviated as Gr-ZnCo-ZIF. In addition, Gr-ZIF67 and Gr-ZIF8 were synthesized with only adding one metal (Co and Zn, respectively) into the precursors. Sample ZnCo-ZIF was obtained by similar approach without the addition of GO in solution A.

2.2. Synthesis of rGO@$ZnCo_2O_4$ composites

The rGO@$ZnCo_2O_4$ composites were synthesized from the Gr-ZnCo-ZIF. In a typical synthesis, 200 mg of the as-prepared sample Gr-ZnCo-ZIF was placed on the bottom of a quartz boat. Then, it was heated to 300 °C in a tube furnace with 10 °C min^{-1} heating rate under 200 sccm airflow. After holding at a certain temperature for 3 h, the rGO@$ZnCo_2O_4$ sample was obtained. With adjusting annealing temperature for Gr-ZnCo-ZIF of 100, 200, 300, 400 and 500 °C, as-synthesized samples were labeled as GZC-100, GZC-200, GZC-300, GZC-400 and GZC-500. For comparison, GC-300, GZ-300 and ZC-300 were synthesized by the similar annealing approach of samples Gr-ZIF67, Gr-ZIF8 and ZnCo-ZIF, respectively. GZC-300-MX was the mechanical mixture of rGO and ZC-300.

2.3. Characterization

The crystal phase was determined by X-ray diffraction (XRD, Rigaku Ultima IV Cu-Kα). Materials morphologies were characterized on a transmission electron microscopy (TEM, JEOL, 2010 F) and a field scanning electron microscopy (FESEM, HITACHI, S-4800). The high-angle annular dark-field scanning transmission electron microscopy HAADF-STEM was recorded by using FEI Tecnai G2 F20 TEM, 200 kV. The energy-dispersive X-ray spectroscopy (EDX) element mapping signals was recorded and analyzed by Oxford X-Max^N 100TLE SDD detector installed at FEI Tecnai TEM instrument. Materials surface electronic states were collected by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, ESCALAB 250Xi, Al-Kα). All the binding energy values were calibrated by using C1 s = 284.6 eV as a reference. The specific surface area (S_{BET}), pore volume (V_P) were tested by nitrogen adsorption and desorption isotherm and calculated by applying Brunauer–Emmett–Teller (BET) models on desorption branches (Micromeritics, TriStar II 3020).