Global-Local CNTs Conductive Network Couple with Co-Based Polyhedral Promotes the Electrocatalytic Reduction of Oxygen

Jinhua Sun, Yuanhui Zuo, Hanyun Wang, Huancong Shi, and Shijian Lu

Abstract: The three-dimensional (3D) nanoreactor of global-local CNTs conductive network coupled with bimetallic MOFs-derived Co@N-C nanopolyhedra (denoted as gl-CNTs/Co@N-C) promotes the electrocatalytic reduction of oxygen owing to the improved mass transfer ability and stability. Here, the 1D/3D gl-CNTs/Co@N-C nanostructures with enhanced electrocatalytic properties were synthesized in one step by the direct thermolysis of Zn/Co-ZIF/MWCNTs precursor. Based on systematical optimization of the composition and structure, gl-CNTs/Co@N-C carbonaceous porous hybrids containing uniform Co nanoparticles (NPs) can not only effectively enable the conductivity but also expose more active sites. Consequently, the optimal gl-CNTs/Co@N-C nanostucture showed a significantly enhanced catalytic activity for the reduction of oxygen, the half-wave potential ($E_{1/2}$) and diffusion-limited current density are 0.86 V (vs. RHE) and 5.34 mA cm$^{-2}$, respectively. Moreover, this catalyst also showed long-term durability and methanol tolerance property, further highlighting the structure superiority of a precisely controllable nanoreactor.

Keywords: global-local CNTs; conductive network; carbon-based catalysts; oxygen reduction reaction; methanol tolerance

1. Introduction

The dramatic depletion of fossil fuels has led to the environmental issue of global warming and climate changes which stimulates extensive research interest on highly efficient alternative energy conversion and storage systems [1,2]. Electrochemical oxygen reduction reaction (ORR) is a crucial process for the emerging renewable energy technologies, such as fuel cells and metal-air batteries [3–6]. However, the sluggish cathode ORR significantly limits the electrocatalytic performance. In the recent years, carbon-based catalysts are promising alternatives to replace precious metal electrocatalysts for the ORR owing to the economic cost, high conductivity, controllable porosity, and regulatable active sites [7,8]. Among them, transition metals encapsulated in nitrogen-doped carbon (M/N-C) materials as promising heterogeneous catalysts have attracted great attention due to the catalytically active centers [9,10]. For heterogeneous catalysts, the performance is determined not only by their intrinsic activity but also the number of accessible active sites [11–13]. Therefore, it is desirable to develop M/N-C catalysts with hierarchical pore and/or hollow structures to enhance the accessibility of active sites. Metal-organic frameworks (MOFs), with controllable pore structure and tunable composition, have provided a good platform for fabricating various functional nanomaterials [14–17]. In particular, N-rich zeolitoid imidazolate frameworks (ZIFs) have been demonstrated to be ideal precursors to design M/N-C catalysts through a facile pyrolysis process at high temperatures. The Zn-based ZIF-8 has been well demonstrated to afford a high-surface-area carbon matrix with high N content through annealing, whereas it cannot provide critical valid active sites and good graphitized
carbon [18]. To target the problem, Co-based ZIF-67, isostructural to ZIF-8, was employed as a template for graphitic carbon with high crystallinity and conductivity, attributing to the catalytic graphitization of amorphous carbon by cobalt in the pristine ZIF-67, but can only offer carbon with low surface area and porosity [19–21]. All things considered, bimetallic MOFs (Zn/Co-MOF) can not only combine the merits of both high-surface-area carbons and graphitic carbons but also serve as excellent precursors/templates for the synthesis of functional nanomaterials with controlled sizes, compositions, and microstructures [22–24]. In addition, carbon nanotubes (CNTs), a typical class of one-dimensional (1D) material with the advantages of large surface area, high conductivity, toughness, and light weight, are widely applied in energy conversion applications [25]. Substantial research has been focused on the addition of CNTs to optimize the overall property [26]. In a nutshell, developing a simple and low-cost method to synthesize CNTs-based material and achieve effective conductive and catalytic property modulation is meaningful.

Herein, the additionally introduced CNTs coupled with the in situ generated short N-doped CNTs which possesses unenclosed construction and global-local CNTs conductive network positively contribute to the electrocatalytic oxygen reduction reaction. Concurrently, embedding tiny multicore Co particles in the carbonaceous nanopolyhedra as much as possible can protect the small particles from serious aggregation during the preparation and reaction processes [27,28]. The rational unobstructed structure and large specific surface area of the gl-CNTs/Co@N-C electrocatalysts act as a key role in the sufficient exposure of active sites and accessible mass transport of the reactant species in the electrolyte, for the purpose of the efficient ORR procedure at three-phase interfaces.

2. Results and Discussion

The fabrication process of the target hierarchically porous gl-CNTs/Co@N-C (i.e., C-Z8/67/M mentioned later) catalyst is schematically shown in Scheme 1. The process started with the formation of ZIF-8/67/MWCNTs composite by one-step mixing and stirring. After then, the gl-CNTs/Co@N-C electrocatalyst was obtained by directly pyrolysis of ZIF-8/67/MWCNTs at 900 °C under inert N2 atmosphere. The gl-CNTs/Co@N-C well preserved the approximate outline of ZIF-8/67/MWCNTs precursor after high temperature carbonization. Consequently, the successfully prepared gl-CNTs/Co@N-C was further explored as a highly effective electrocatalyst for oxygen reduction reaction. In the constructed global-local crosslink model of gl-CNTs/Co@N-C, the connection of the introduced one-dimensional CNTs could be improved by the Co/N-C polyhedra cross-link nodes, thus playing a role in stabilizing the conductive network [29]. The purposeful design of unobstructed 1D/3D structure for the catalyst gl-CNTs/Co@N-C effectively enhances the stability and activity.

To figure out the morphology and composition of C-Z8/M, C-Z67/M, C-Z8/67, and C-Z8/67/M (i.e., target sample gl-CNTs/Co@N-C), some complementary characterization techniques such as SEM, TEM, XRD, BET, Raman, XPS were adopted. The SEM results of C-Z8/M, C-Z67/M, C-Z8/67, and gl-CNTs/Co@N-C are shown in Figure 1a–d. The MWCNTs can be clearly observed, as well as the hollow carbon particles (Figure 1a) carbonized from ZIF-8 suffered from structural disintegration owing to the totally Zn evaporation at high pyrolysis temperature, marked with orange and green arrows, respectively. In Figure 1b, the C-Z67/M nanostructures with uneven size indicate that the morphology and structure of precursor ZIF-67 were destroyed during pyrolysis process. Comparing Figure 1c,d, it can be seen that the C-Z8/67 is fluffy and irregular, by contrast, the gl-CNTs/Co@N-C shows a uniform small size and regular morphology. It is worth pointing out that the specially designed gl-CNTs/Co@N-C exhibits good steric hindrance effects of size growth and the best structural stability which is due to the synergies of introduced MWCNTs, ZIF-8, and ZIF-67 during the growth process.
Scheme 1. Schematic illustration for the synthesis and property measurements of gl-CNTs/Co@N-C nanostructures.

Figure 1. (a–d) SEM of C-Z8/M, C-Z67/M, C-Z8/67 and gl-CNTs/Co@N-C (orange arrows mark MWCNT and green arrows mark hollow carbon particles); (e–g) XRD, Raman patterns, and N2 adsorption–desorption isotherm of C-Z8/M, C-Z67/M, C-Z8/67, gl-CNTs/Co@N-C, and MWCNTs.

The XRD patterns among MWCNTs, C-Z8/M, C-Z67/M, C-Z8/67, and gl-CNTs/Co@N-C are presented in Figure 1e. The diffraction peaks of c-Z67/M, c-Z8/67, and gl-CNTs/Co@N-C are all at around 44.2°, 51.5°, and 75.9°, corresponding to the (111), (200), and (220) planes of metal Co⁰ (JCPDS, NO.15-0806), respectively. The metal Co⁰ particles
are generated due to the pyrolysis of ZIF-67 at high temperature. The diffraction peak at around 26° corresponding to the (002) plane of graphitic carbon belongs to introduced MWCNTs and/or carbon converted from amorphous carbon catalyzed by Co species in ZIF-67. The carbon matrix was further investigated by the Raman spectra shown in Figure 1f. All the samples showed two strong peaks at 1347 cm\(^{-1}\) and 1580 cm\(^{-1}\) corresponding to the D-bands and G-bands of graphitic carbon, respectively. In addition, the pore structures of the C-Z8/M, C-Z67/M, C-Z8/67, and gl-CNTs/Co@N-C were further verified through the analysis of nitrogen adsorption/desorption. The adsorption and desorption isotherms of C-Z8/M, C-Z67/M, C-Z8/67, and gl-CNTs/Co@N-C are shown in Figure 1g. All the pore property of different catalysts are further given in Table 1. The specific surface area (SSA) for C-Z8/M, C-Z67/M, C-Z8/67, and gl-CNTs/Co@N-C were calculated to be 212.90 m\(^2\)/g, 203.31 m\(^2\)/g, 280.72 m\(^2\)/g, and 275.09 m\(^2\)/g, respectively. Compared with C-Z8/M and C-Z67/M, the porosity of gl-CNTs/Co@N-C increased considerably due to the introduced porous ZIF-8/67 MOF precursor and the designed mesoporous global-local CNTs framework. The SSA of C-Z8/67 and gl-CNTs/Co@N-C are not much different indicating that the main factor affecting the SSA is not the introduced MWCNTs but the bimetallic MOF structure. As can be seen from Table 1, gl-CNTs/Co@N-C has the largest pore volume (0.39 cm\(^3\)/g) and average the pore size (5.22 nm) which can contribute more active sites and abundant mass/charge transfer channels, thus improving the electrocatalytic activity. The presence of mesopores mainly facilitates efficient transfer of reactants and products to and from the catalytic sites. The porous structures of gl-CNTs/Co@N-C are conducive to the advancement of oxygen electrocatalysis. The in situ generated nitrogen-doped CNT-based frameworks and the uniformly distributed Co-based species of gl-CNTs/Co@N-C provide ample accessible active sites which are conducive to the provision of electrocatalytic performance of the gl-CNTs/Co@N-C nanoreactor. The permeable carbon matrix enables facile mass transportation for the reactive species and protects the catalytically active sites against leaching even under harsh reaction conditions, leading to enhanced activity and stability.

**Table 1.** Specific surface area and pore parameters of different samples.

| Element       | S\(_{\text{BET}}\) (m\(^2\)/g) | Pore Volume (cm\(^3\)/g) | Average Pore Size (nm) |
|---------------|-------------------------------|--------------------------|------------------------|
| C-Z8/M        | 212.90                        | 0.28                     | 4.60                   |
| C-Z67/M       | 203.31                        | 0.21                     | 4.01                   |
| C-Z8/67       | 280.72                        | 0.30                     | 4.08                   |
| C-Z8/67/M     | 275.09                        | 0.39                     | 5.22                   |

The detailed morphology and internal structure of the as-prepared gl-CNTs/Co@N-C were further characterized by high-magnification SEM along with TEM. As shown in Figure 2a,b, the exquisite microstructures composed of externally mesoporous graphitized carbon polyhedral and global-local CNTs as well as cobalt-based particles dispersed internally can be clearly observed; in addition, the mean size of polyhedra is ~200 nm. The overall Zn evaporation under high pyrolysis temperature accelerates the growth of in-site CNTs under the catalysis of Co nanoparticles produced from ZIF-67 precursor [24]. The high-resolution TEM image (Figure 2c) displays two distinct fringes with lattice spacing of 0.21 nm and 0.33 nm, respectively, corresponding to the (111) plane of metallic cobalt and graphitic carbon. The elemental distribution, as well as composition of gl-CNTs/Co@N-C were analyzed by EDS. Element mapping (Figure 2d) shows that multiple elements (Co, N, C) co-exist throughout the gl-CNTs/Co@N-C structure. The homogeneity of multiple elements distribution is ascribed to the in situ pyrolysis of precursor mixed atomically.
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Figure 2. (a) SEM image (orange arrows mark global CNTs and green arrows mark local CNTs), (b) TEM image, (c) High-resolution TEM image with the index crystal plane of nanoparticles, and (d) Element mappings of C, Co, N elements of gl-CNTs/Co@N-C.

Figure 3 shows the XPS results of the gl-CNTs/Co@N-C. In Figure 3a, the XPS survey indicates the coexistence of Co, C, and N elements. The atomic percentages for Co, C, and N are 1.09at%, 94.47at%, and 4.44at%, respectively. The conclusion is consistent with the EDS results mentioned above. In the high-resolution XPS spectra of Co 2p (Figure 3b), the peaks at about 780.4 eV from Co 2p$_{3/2}$ and 796.3 eV from Co 2p$_{1/2}$ are attributed to Co$^{2+}$. The peaks at 777.9 eV from Co 2p$_{3/2}$ and 793.4 eV from Co 2p$_{1/2}$ are due to metallic Co$^0$ [30,31]. In addition, two relatively obvious peaks located at around 786.0 eV and 802.5 eV belong to satellite peaks. The N1s spectra (Figure 3c) could be deconvoluted to five characteristic peaks, scilicet pyridinic-N (398.2 eV), Co-N$_x$ (399.2 eV), N-C-O (399.9 eV), graphitic-N (400.5 eV), and O-N (404.8 eV). Pyridinic-N and Co-N$_x$ are the most dominating active sites in ORR activities [32–34]. Pyridinic-N can enhance the spin density and π state density of C atoms near the Fermi level and lower the energy barrier of O$_2$ adsorption upon the adjacent C atom [35]. Graphitic-N can accelerate structural stability and limit the current density of the carbonaceous material [36]. Meanwhile, oxygen adsorption on the carbon skeleton is promoted by attracting an electron from the adjacent C atom [37]. Figure 3d shows the high-resolution XPS spectra of C1s and four peaks at about 284.4, 285.2, 286.4, and 288.4 eV belong to C-C, C=N, C-N and O-C=O, respectively [38]. The high peak intensity of C-C sp$^2$ means the high-degree graphitization of gl-CNTs/Co@N-C that corresponds to Raman analyses. The existence of O-C=O and C-N demonstrates that O and N elements are mixed into the carbon matrix successfully.
The ORR polarization (LSV) analysis was implemented to explore the electrocatalytic activity of all catalysts (Figure 4a). In contrast, remarkable cathodic peaks can be seen in O2-saturated electrolytes, no prominent redox peaks were discovered for all prepared catalysts (Figure 4a). The different catalytic properties of all samples were further evaluated by RDE measurements. The ORR polarization (LSV) analysis was implemented to explore the electrocatalytic activity of all catalysts within 0.1 M KOH solution saturated with O2 under a rotating rate of 1600 rpm and the scan rate of 10 mV s\(^{-1}\). The LSV results are shown in Figure 4b. The half-wave potentials (\(E_{1/2}\)) of C-Z8/M, C-Z67/M, C-Z8/67, gl-CNTs/Co@N-C, and Pt/C are 0.69 V, 0.80 V, 0.84 V, 0.86 V, and 0.86 V versus RHE. Furthermore, gl-CNTs/Co@N-C presents the highest diffusion-limited current density (≈5.34 mA cm\(^{-2}\) at 0.4 V). Compared to other catalysts, the ORR activity of modified gl-CNTs/Co@N-C is markedly improved, indicating that the particular in-site cross-linked structure of the 1D/3D N-rich porous carbon matrix is of importance in electrocatalytic activity enhancement. Mesoporous structure is beneficial to enhance the mass transfer performance and increase the specific surface area, which has been demonstrated concretely by the higher ORR diffusion-limited current of gl-CNTs/Co@N-C compared with those of other reference catalysts C-Z8/M, C-Z67/M and C-Z8/67. Figure 4c shows the Tafel plots of gl-CNTs/Co@N-C and other reference samples. gl-CNTs/Co@N-C has a lower Tafel slope (59 mV decade\(^{-1}\)) than that of C-Z8/M (97 mV decade\(^{-1}\)), C-Z67/M (60 mV decade\(^{-1}\)), C-Z8/67 (78 mV decade\(^{-1}\)), and Pt/C (62 mV decade\(^{-1}\)), which indicates the good kinetic process toward ORR. Moreover, rotat-
ing ring-disk electrode (RRDE) measurements were carried out to monitor ORR pathways and evaluate ORR kinetics (Figure 4d). The loop current generated by peroxide oxidation of gl-CNTs/Co@N-C and Pt/C is much lower than the disk current generated by peroxide oxidation (H$_2$O$_2$). The yield of H$_2$O$_2$ calculated from RRDE data was less than 7% on gl-CNTs/Co@N-C within the potential range of 0.3 to 0.8 V. The gl-CNTs/Co@N-C possesses an obvious four-electron reduction, which is close to the value of commercial Pt/C, demonstrating that gl-CNTs/Co@N-C has been a kind of potential non-noble metal catalyst.

![Figure 4](image-url)

**Figure 4.** CV (a), LSV (b), and Tafel (c) curves for MWCNTs, C-Z8/M, C-Z67/M, C-Z8/67, gl-CNTs/Co@N-C, and Pt/C; (d) Peroxide yields (H$_2$O$_2$ %) and electron transfer numbers (n) of gl-CNTs/Co@N-C and Pt/C. All electrolytes involved have been 0.1 M KOH solution.

Meanwhile, the contrast measurements were implemented to evaluate the performance difference between as-synthesized gl-CNTs/Co@N-C and commercial Pt/C catalyst, including the tiresome methanol crossover and the long-term electrochemical durability. In order to investigate the methanol tolerance, the CV measurements within O$_2$-saturated 0.1 M KOH solution with or without methanol (0.5 M) were performed. In Figure 5a, the oxygen reduction peak of gl-CNTs/Co@N-C is almost unchanged, indicating that gl-CNTs/Co@N-C possesses good tolerance for methanol crossover. Conversely, according to CV curve of Pt/C (Figure 5b), there is a significant methanol oxidation peak, which further indicated the poor methanol tolerance of Pt/C. Furthermore, methanol tolerance of commercial Pt/C and gl-CNTs/Co@N-C (Figure 5c) was evaluated and compared using the i-t technique. The ORR current density of the gl-CNTs/Co@N-C did not change significantly after injection of methanol for 900 s, indicating that gl-CNTs/Co@N-C had good resistance to methanol cross-effects. In contrast, the ORR current density of commercial Pt/C catalysts was significantly reduced due to the inherent vulnerability of Pt electrocatalysts to methanol.
Furthermore, the stability of the catalyst gl-CNTs/Co@N-C was investigated and the results are given in Figure 6. The CV measurement (Figure 6a) was performed between 0.15 and 1.1 V at 50 mV s\(^{-1}\) within 0.1 M KOH solution saturated with O\(_2\). As shown in Figure 6b, after 5000 cycles of experiments, the \(E_{1/2}\) value of gl-CNTs/Co@N-C presents only a negligible negative displacement, showing high durability. The \(E_{1/2}\) value of Pt/C shown in Figure 6c changes significantly. The current-time (i-t) curves of gl-CNTs/Co@N-C and commercial Pt/C were measured within O\(_2\)-saturated 0.1 M KOH solution with the rotation rate of 1600 rpm. Figure 6d shows that gl-CNTs/Co@N-C still reserves 97% of its initial current density, in obvious contrast to the commercial Pt/C with 60000 s of testing, which further demonstrated the prominent electrochemical stability durability of gl-CNTs/Co@N-C toward ORR. This could be related to the steady porous frame structure, which provided plenty of paths for a large amount of transport while avoiding the possible structure collapse.
Figure 6. (a,b) CV and LSV curves of gl-CNTs/Co@N-C before and after 5000 cycles; (c) LSV curves of Pt/C before and after 5000 cycles; (d) Chronoamperometric responses within gl-CNTs/Co@N-C and Pt/C catalysts.

3. Conclusions

In conclusion, gl-CNTs/Co@N-C hybrids were successfully prepared as high-performance electrocatalysts for ORR through pyrolyzing the ZIF-8/67/MWCNTs precursors in a one-step process. The obtained gl-CNTs/Co@N-C led to a high specific surface area, good electrical conductivity, and mesoporous architecture, which are beneficial for highly exposed active sites and fast transfer for electrons as well as O$_2$. Hence, the as-prepared gl-CNTs/Co@N-C has manifested an excellent ORR performance with a half-wave potential of 0.86 V in 0.1 M KOH, which even exceeded many analogous catalysts derived from Co-based MOF (Table 2). Moreover, it also owns rapid ORR kinetics, a high electron transfer number, and superior methanol-tolerance ability.

Table 2. Comparisons between gl-CNTs/Co@N-C and other catalysts over ORR.

| Catalyst          | $E_{1/2}$ (V) | $J_d$ (mA cm$^{-2}$) | Medium    | Ref.          |
|-------------------|---------------|----------------------|-----------|--------------|
| gl-CNTs/Co@N-C    | 0.86          | 5.34                 | 0.1 M KOH | this work    |
| Co$_3$N-C/T0CNF   | 0.74          | 4.5                  | 0.1 M KOH | [4]          |
| CoNC-CNFs         | 0.8           | 5.9                  | 0.1 M KOH | [5]          |
| Mn$_2$O$_4$/NCNTs | 0.76          | 6.06                 | 0.1 M KOH | [7]          |
| CNCo-20           | 0.81          | 6.0                  | 0.1 M KOH | [8]          |
| NC@GC             | 0.89          | -                    | 0.1 M KOH | [20]         |
| Co/N-CNTFs        | 0.83          | 6                    | 0.1 M KOH | [22]         |
| CoNHPC            | 0.87          | 5.41                 | 0.1 M KOH | [31]         |
| Co-N/S-C-3.5      | 0.75          | 3.7                  | 0.1 M KOH | [39]         |
| Co@NPC/C-MWCNTs   | 0.79          | 4.32                 | 0.1 M KOH | [40]         |
4. Experimental Section

4.1. Chemicals and Materials

All reagents, Zn(NO$_3$)$_2$·6H$_2$O(99%), Co(NO$_3$)$_2$·6H$_2$O(99%), Methanol(>99.9%), 2-Methylimidazole(98%), and MWCNTs(>95%) were obtained from commercial suppliers (Aladdin Biological Technology Co., Ltd., Shanghai, China), and used without further purification unless otherwise stated. Deionized water has been applied in all experiments.

4.2. Synthesis of gl-CNTs/Co@N-C

Zn(NO$_3$)$_2$·6H$_2$O and/or Co(NO$_3$)$_2$·6H$_2$O were dissolved in 50 mL methanol successively. Later, MWCNTs were added and stirred violently at room temperature for half an hour. Then, 50 mL methanol with 2-methylimidazole was rapidly injected into the above mixed system and persistently stirred for 12 h. Finally, hybrids ZIF-8/MWCNTs, ZIF-67/MWCNTs, ZIF-8/67 and ZIF-8/67/MWCNTs were gained. The as-synthesized ZIF-8/MWCNTs, ZIF-67/MWCNTs, ZIF-8/67 and ZIF-8/67/MWCNTs were later annealed at 900 °C under N$_2$ with a slow heating rate of 5 °C min$^{-1}$ for three hours. All the carbonized samples were denoted as C-Z8/M, C-Z67/M, C-Z8/67 and gl-CNTs/Co@N-C. The optimal catalyst gl-CNTs/Co@N-C was identified as gl-CNTs/Co@N-C according to the composition and structure.

4.3. Electrochemical Measurements

The electrochemical measurements were performed by means of the CHI 760E electrochemical workstation (CH Instruments Inc., Shanghai, China). The rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) were developed in a custom three-electrode system consisting of the saturated calomel electrode, the modified glassy carbon working electrode, and the graphite carbon electrode. The ORR catalytic activity of the catalyst within 0.1 M KOH electrolyte saturated with O$_2$ was studied by RDE and RRDE systems.

A total of 5.0 mg of gl-CNTs/Co@N-C powder was dispersed in a mixture (1000 µL isopropanol + 1000 µL deionized water + 50 µL 5 wt% Nafion), and the slurry was obtained uniformly by ultrasound; 20 µL of slurry was dropwise coated on the surface of the working electrode, dried to form a film at room temperature. The catalyst loading was 0.255 mg cm$^{-2}$.

The commercial Pt/C (46%, TKK) catalyst powder was dispersed in deionized water to obtain a catalyst slurry concentration of 0.25 mg Pt mL$^{-1}$, and 20 µL was applied dropwise to the surface of the glassy carbon electrode. The catalyst loading was 0.025 mg Pt cm$^{-2}$.

4.4. Characterizations

The investigation on the morphology and composition of the as-prepared samples were implemented by scanning electron microscope (SEM, Hitachi S4800, 3 kV) equipped with energy-dispersive spectrometer (EDS), X-ray diffraction (XRD, D/max2550VB3+/PC), transmission electron microscopy (TEM, at 200 kV, JEM-2011-HR), X-ray photoelectron spectroscopy (XPS, ESCALAB, PerkinElmer) with 250 X-ray photoelectron spectrometer has been tested. Raman spectra of the nanocomplexes were tested by Renishaw in Via Reflex (UK). The Brunauer–Emmett–Teller (BET) specific surface of the catalyst was analyzed by a nitrogen isothermal adsorption instrument (Micromeritics ASAP 2020). The Barrett–Joyner–Harlanda (BJH) method is used to analyze and calculate the distribution of the bore diameter.

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