

Single Co-Atoms as Electrocatalysts for Efficient Hydrazine Oxidation Reaction

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Single-atom catalysts (SACs) have aroused great attention due to their high atom efficiency and unprecedented catalytic properties. A remaining challenge is to anchor the single atoms individually on support materials via strong interactions. Herein, single atom Co sites have been developed on functionalized graphene by taking advantage of the strong interaction between Co²⁺ ions and the nitrile group of cyanographene. The potential of the material, which is named G(CN)-Co, as a SAC is demonstrated using the electrocatalytic hydrazine oxidation reaction (HzOR). The material exhibits excellent catalytic activity for HzOR, driving the reaction with low overpotential and high current density while remaining stable during long reaction times. Thus, this material can be a promising alternative to conventional noble metal-based catalysts that are currently widely used in HzOR-based fuel cells. Density functional theory calculations of the reaction mechanism over the material reveal that the Co(II) sites on G(CN)-Co can efficiently interact with hydrazine molecules and promote the N-H bond-dissociation steps involved in the HzOR.

1. Introduction

The rapidly growing global energy demand has led to the consumption of increased amounts of non-renewable fossil fuel resources, including coal, petroleum, and natural gas. However, the extensive use of fossil fuels not only causes severe environmental issues but also compromises efforts to attain a sustainable energy future.^[1,2] This has made researchers to investigate cost-effective and non-polluting alternatives to produce energy in a greener manner, through such systems as photovoltaic cells, electrolyzers, and fuel cells. Among them, fuel cells have attracted great attention over the past few years.^[1] These devices can convert the chemical energy in fuels such as hydrogen, alcohols, organic acids, and hydrazine into electricity, with high efficiency and minimal greenhouse gas emissions. Among the fuels used in fuel cells, hydrazine is of particular interest for the following three reasons: 1) It produces only N₂ and H₂O and it does not release the greenhouse gas CO₂ or other harmful byproducts as fossil fuels do; 2) Hydrazine is relatively easy to store and transport

with existing infrastructures, as it is liquid at room temperature; and 3) Direct hydrazine fuel cells (DHFCs) have a large theoretical cell voltage (+1.61 V) and higher energy/power density than many other fuel cells (e.g., compared with H_2/O_2 fuel cell, which is considered one of the best fuel cells).^[1] However,

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Scheme 1. Synthesis of G(CN)-Co catalyst. In the structural model, C, F, N, and Co atoms are represented by grey, cyan, blue, and green balls.

in order to enable DHFCs to work effectively and find largescale practical applications, the rational design and synthesis of advanced, efficient, and sustainable electrocatalysts that can replace noble metal-based electrocatalysts (such as Pt, Pd, Ir, Au, and their alloys), which are currently widely used in them, is required.^[3]

In recent years, single-atom catalysts (SACs) have attracted increased research attention in heterogeneous catalysis since they offer an ultimate atom economy and allow for the full exposure of active sites, resulting in greater catalytic activity in comparison to nanocatalysts.^[4-9] Some SACs have also been reported to catalyze various electrochemical reactions with excellent efficiency. However, there are also challenges when applying SACs in practical systems, due to the tendency of single atoms to cluster and leach during the reactions. One effective strategy to address these challenges entails the use of 2D materials as substrates to anchor the single atoms.^[8,10-20] Graphene, a 2D material, which has large surface area, high electrical conductivity, and good stability, has received significant interest as a support material for making SACs. Graphene is of interest also because of its ability to tune the electronic properties of the guest atoms. Surface-functionalized graphene derivatives, in particular, can render strong interactions with the single atoms, and thereby stabilize SACs and prevent their aggregation and transformation into nanoparticles during catalytic reactions.^[17,19–27]

To this end, herein we present a novel approach to anchor single Co(II) ions on cyanographene (G-CN) sheets to obtain Co-based single atom catalysts (G(CN)-Co SACs). The synthetic process is schematically described in Scheme 1. The amounts of Co(II) ions on G-CN could easily be varied by changing the relative amount of Co(II) ions mixed with G-CN. The materials showed efficient electrocatalytic activity toward the hydrazine oxidation reaction (HzOR). Complementary experiments and density functional theory (DFT) calculations corroborated the anchoring of atomically isolated cobalt sites on G-CN. The successful binding of Co(II) ions to G-CN was verified with inductively coupled plasma mass spectrometry, high-resolution transmission electron microscopy (TEM), extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure spectra (XANES). The resulting materials exhibited among the highest electrocatalytic activities for HzOR as well as better activities than many noble metal-based catalytic systems reported in the literature. The stability of the materials was also investigated, and the results suggested that both G-CN and the strong bond between its CN groups and Co(II) ions were crucial in preventing single Co sites from leaching during the electrocatalytic reaction.

2. Results and Discussion

2.1. Synthesis and Structural Characterization of G(CN)-Co Catalyst

The procedure applied to synthesize G(CN)-Co is illustrated in Scheme 1 (see Supporting Information for more details). It follows similar steps as those used to produce various functionalized graphene.^[28] Powder X-ray diffraction pattern (Figure 1a; Figure S1, Supporting Information) confirmed the absence of distinctive peaks associated with Co or Co-based inorganic particles. This indirectly suggests the dispersion of Co in isolated forms on the structures of the material. The representative TEM image revealed the presence of G–CN sheets (Figure 1b) without any heavy element-associated inorganic particles. Furthermore, high-angle annular dark-field scanning TEM (HAADF-STEM) (Figure 1c) showed that individual Co atoms are uniformly dispersed on the G-CN sheets. The Co atoms are the bright spots marked with yellow circles in the magnified HAADF-STEM images shown in Figure 1d. In the literature, advance detectors had been used for HAADF-STEM images to probe Co SACs on N-doped carbon.^[25,29,30]

Elemental mapping performed with HAADF-STEM image (Figure 1e–j) confirmed a homogenous dispersion of Co single atoms on the G–CN sheets, besides O, N, and C atoms. However, as precise identification of the lighter elements with HAADF-STEM is challenging,^[31,32] we had to resort to XANES and EXAFS to indirectly determine them (see below).

X-ray photoelectron spectroscopy (XPS) was applied to investigate the chemical composition of G(CN)-Co. The survey spectra (Figure 2a) confirmed the presence of C (85.7%), N (8.8%), O (4.8%), and Co (0.7%). The deconvolution of the C 1s spectrum (Figure S2a, Supporting Information) displayed distinct peaks with binding energies (BEs) of 284.82 and 286.01 eV that can be assigned to sp² C and sp³ C atoms bound to -CN groups.^[9,33] Deconvolution of the N 1s spectrum (Figure S2b, Supporting Information) gave three peaks at 398.77, 400.00, and 401.31 eV corresponding to different nitrogen functional groups, respectively (see further details in the Supporting Information). The peak at BE of 781.87 eV (Figure 2b), with the corresponding satellite peaks at 785.19 and 788.77 eV, was assigned to Co²⁺ 2p species.^[34] The charge transfer and the interaction between Co(II) cations and N-atoms in G-CN was analyzed by high-resolution (HR)-XPS of N 1s envelope (Figure S3, Supporting Information).

The oxidation state and coordination environment of cobalt species in G(CN)–Co were further determined by XANES and EXAFS. The pre-edge XANES peak can be used to identify the oxidation state of the catalyst (Figure 2c).^[35] The pre-edge energy of G(CN)–Co SACs (7708.1 eV) was very similar to that







Figure 1. Characterization of G(CN)—Co (3.4 wt%): a) Powder X-ray diffraction (XRD) patterns of G—CN and G(CN)—Co; b) TEM image; c) representative high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image; d) magnified HAADF-STEM image showing the presence of single Co atoms (highlighted by yellow circles); and e) another HAADF image of G(CN)—Co along with the corresponding elemental mapping images of f) Co, g) O, h) N, i) Co and N, and j) Co, N, and C.

of CoO (7708.3 eV) and single site Co(II) on SiO₂. The result we obtained for the latter is similar to one reported before.^[36] The k^2 -weighted magnitude of the first shell peak of EXAFS spectrum for G(CN)—Co (black) and CoO (blue) are very similar to each other (Figure 2d). CoO has 6 Co—O bonds at 2.06 Å (about 1.7 Å phase uncorrected distance in Figure 2d), as can be seen from the fitting results given in Table S1, Supporting Information. In the case of CoO, there is a large second shell peak due to the scattering by Co—(O)—Co at about 2.8 Å. This higher shell peak is characteristic of Co-oxide nanoparticles.

The EXAFS of G(CN)–Co shows only the first shell Co-X scattering, also with 6 Co–N (or O), at 2.07 Å with no scattering from Co atoms at longer distance, which is consistent with single Co^{2+} ions. In EXAFS, the scattering is proportional to the number of electrons; thus, it is not easy to distinguish the type of scattering from C, O, and N atoms. The first shell coordination number of Co/SiO₂ is 4 Co–O at 1.98 Å, which is similar to the result previously reported for this material.^[36] The absence of a higher shell Co–O–Co (in Co/SiO₂) is similar to that of G(CN)–Co, which is a SAC containing Co(II)







Figure 2. a) Survey X-ray photoelectron spectra of G(CN)–Co. b) High-resolution X-ray photoelectron spectra of G(CN)–Co showing the Co 2p region. X-ray absorption spectra of G(CN)–Co (black curve), CoO reference (blue curve), and Co(II)/SiO₂ (another reference material, which we prepared for comparative study (red curve). c) Co K-edge XANES and d) k^2 weighted magnitude of Fourier transformation of EXAFS (inset: the proposed model for G(CN)–Co.

sites with 6 Co–N (or Co–O) bonds, each with a bond distance of 2.07 Å.

2.2. Electrocatalytic Performance of G(CN)-Co for HzOR

The electrocatalytic performances of the as-prepared materials containing different amounts of Co (i.e., G(CN)-Co (1.2 wt%), G(CN)-Co (1.5 wt%), and G(CN)-Co (3.4 wt%)) for HzOR were studied. First, cyclic voltammetry (CV) curves for the catalysts in the presence of 50 mmol L⁻¹ hydrazine solution in phosphate buffered saline (PBS) (pH 7.4) at a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$ from -0.5 to 0.3 V (vs SCE) were recorded (Figure 3a). The anodic peaks, which were observed in the CV curves of all three catalysts, could be attributed to the oxidation of hydrazine, demonstrating that all samples had catalytic activity toward HzOR. Among the catalysts, G(CN)-Co (3.4 wt%) displayed the best electrocatalytic activity for the reaction, with a relatively large negative onset potential (which means a low overpotential), with a value of \approx -0.28 V (vs SCE). The corresponding values for G(CN)-Co (1.2 wt%) and G(CN)-Co (1.5 wt%) were -0.25 and -0.26 V, respectively. G(CN)-Co (3.4 wt%) also gave a large negative peak potential of -0.1 V (vs SCE) while the corresponding values for G(CN)-Co (1.2 wt%) and G(CN)-Co (1.5 wt%) were -0.07 and -0.09 V, respectively. Additionally, the peak current density during the HzOR over G(CN)-Co (3.4 wt%) was \approx 3.5 mA cm⁻², which was higher than those of

G(CN)-Co (1.2 wt%) and G(CN)-Co (1.5 wt%), with values of 2.7 and 3.0 mA cm^{-2} , respectively. These results showed that G(CN)-Co (3.4 wt%) required a lower overpotential to catalyze HzOR compared with G(CN)-Co (1.2 wt%) and G(CN)-Co (1.5 wt%), indicating that the electrocatalytic activity of these materials increases with the amount of Co. The result also indicated that G(CN)-Co's electrocatalytic activity for HzOR was related to the Co(II) single sites. In addition, the support material, G-CN, showed negligible activity toward HzOR, indirectly corroborating that the anchored Co(II) cations were the active sites. It is also worth adding that the catalytic performance of G(CN)-Co (3.4 wt%) for HzOR was higher than that of many other transition and noble-metal based nanocatalysts that were recently reported (see Table S2, Supporting Information). The mass activities of the three materials for HzOR were compared by normalizing the current densities to the mass of Co atoms in the materials. The results indicated that G(CN)-Co (1.2 wt%) gave the highest catalytic activity for HzOR per mass of Co (Figure 3b). This means, although higher loading of Co could enhance the overall HzOR activity in terms of current density, their relationship was not linear. Therefore, the loading of metals could be optimized to further lower the cost of such catalysts while achieving optimal electrocatalytic activity or current density.

The CV curves of HzOR obtained over G(CN)—Co materials using different concentrations of hydrazine solution (ranging from 10 to 50 mmol L⁻¹) are shown in Figure S4a–c, Supporting







Figure 3. a) Cyclic voltammetry (CV) curves of HzOR obtained over G (CN)–Co (1.2 wt%), G–(CN)-Co (1.5 wt%), G(CN)–Co (3.4 wt%), and G(CN) using 50 mmol·L⁻¹ hydrazine in PBS (pH 7.4) at a scan rate of 10 mV·s⁻¹ and b) the corresponding current density normalized to the total mass of Co atoms.

Information. The current density in the CV curves was found to be proportional to the hydrazine concentration (see Figure S4d-f, Supporting Information). The shapes of the CV curves revealed only oxidation peaks and no cathodic peaks during the reverse scans, confirming that the oxidation (or HzOR) over G(CN)-Co was an irreversible process. On the other hand, kinetic studies revealed that increasing electrochemical scan rates resulted in a slight shift toward positive peak potential in the catalytic HzOR (Figure S5a-c, Supporting Information). This is related to the mass diffusion-controlled electrochemical processes involved in HzOR and the occupation of active sites by the reacting species, as reported in our previous works.^[36,39] The oxidation current density was found to be linearly proportional to the square root of scan rate (Figure S5d-f, Supporting Information), once again indicating that the HzOR over the materials was diffusion-controlled.^[1,37–41] The electron transfer number (n) involved in HzOR over the catalysts was determined based on the slope of the current density (I/A) versus square root of the scan rate $(\nu^{1/2})$ using equation:^[37–41]

$$I/A = 3.01 \times 10^{-5} n [(1-\alpha) n_{\alpha}]^{1/2} c D^{-1/2} v^{1/2}$$
(1)

where *I* is the current produced by the electrocatalytic reaction, *A* is the surface area of the working electrode ($A = 0.071 \text{ cm}^2$), *n* is the total number of electrons involved in the HzOR, α is the electron transfer coefficient, n_{α} is the number of electrons involved in the rate-determining step ($n_{\alpha} = 1$), *D* is the diffusion coefficient, *c* is the concentration of hydrazine ($c = 50 \text{ mmol L}^{-1}$), and *v* is the scan rate. The values of α and *D* are determined based on the linear relationship between the peak potential (E_p) and the natural logarithm of scan rate (log *v*) (Equation (2)) as well as on the linear correlation between the current density (*I*/*A*) and the inverse square root of time ($t^{-1/2}$) as expressed by the Cottrell equation (Equation (3)):

$$E_{\rm p} = k + \left[0.03 \,/\,\alpha n_{\alpha}\right] \log \nu \tag{2}$$

where *k* is a constant and $n_{\alpha} = 1$

$$I/A = nFCD^{1/2}\pi^{-1/2}t^{-1/2}$$
(3)

where *F* is Faraday constant ($F = 96496 \text{ C mol}^{-1}$).

By using Equations (1–3), the total number of electrons involved in the HzOR for the tested catalysts was calculated to be close to 4. This indicated that the reaction would proceed through a 4-electron process to complete the oxidation (Figure S5, Supporting Information), and the net reaction could be written as: $N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^-$.

The long-term stability of electrocatalysts is important for their practical application in DHFCs. Thus, the stability of the three materials during electrocatalysis was evaluated by monitoring the change in current density near their respective peak potentials in 50 mmol L⁻¹ hydrazine for 10 000 s (Figure S6, Supporting Information). The results showed that there was only a minimal change in the residual current density during the reaction, suggesting that the materials remained reasonably stable during the HzOR. All the above electrochemical results clearly demonstrated that G(CN)–Co materials could serve as efficient noble metal-free electrocatalysts for HzOR. This also means that these materials have a potential to serve as sustainable electrocatalysts at the anode side of DHFC, given their excellent activity as well as good atom economy and non-noble elemental composition.

2.3. Density Functional Theory Studies of the Reaction Mechanism of HzOR on the Catalysts

The mechanism of HzOR over the electrocatalyst was studied step-by-step by geometry optimizations of N2H4, N2, and all intermediates with and without G(CN)-Co catalyst using DFT in combination with the implicit solvation model^[42] to account for the aqueous environment. Theoretical models of the G(CN)-Co catalyst were derived from a trans-14f,14kdicyanoovalene molecule representing the G-CN substrate by anchoring either a single Co²⁺ cation (model A, Figure S7a, Supporting Information) or a Co²⁺ cation coordinated with five water molecules (model B, Figure S7b, Supporting Information) to one of the cyano groups. The positive binding affinity of Co²⁺ cations to G-CN was recently rationalized in terms of efficient charge transfer from the substrate to metal cations.^[43] The reaction mechanism consists of four deprotonation steps (in basic environment) and four electrochemical oxidation steps (Figure 4). In total, four electrons are released. The HzOR may





Figure 4. Reaction mechanism of hydrazine oxidation reaction (represented with yellow bubble) with and without the G(CN)—Co catalyst (in the center). The numbers marked in red and green correspond to reaction energies (in eV) obtained without and with the catalyst (model A), respectively.

proceed via two routes differing in steps 3-5 by dissociation of N-H bonds, which are however energetically comparable (see detailed mechanisms in Figures S8 and S9, Supporting Information). Without the catalyst, all reaction steps (except step 7) are energetically demanding (the values marked in red in Figure 4). The presence of G(CN)-Co catalyst significantly promotes the deprotonation steps 1, 3, 5, and 7 (the values marked in green in Figure 4) due to lowering of the N–H bond polarity (see Tables S3 and S4, Supporting Information). In addition, the negatively charged intermediates (i.e., the N-H bond dissociation products) are stabilized owing to charge transfer from N_2H_x (*x* = 1–4) to the catalyst (see q_{tot} values in Tables S3 and S4, Supporting Information), which further decreases the reaction energies of these steps. The electrochemical steps (i.e., electron releasing steps 2, 4, 6, and 8 in Figure 4) are energetically more demanding in the presence of the catalyst.

The coordination of Co²⁺ ion in G(CN)–Co with water molecules lowers the positive charge on Co²⁺ and thus decreases the binding affinity of hydrazine molecule to G(CN)-Co catalyst, from -1.3 to -0.6 eV (step 0 in Figures S8 and S10, Supporting Information). However, the reaction energies and ionization potentials do not substantially change compared to those attained by the simpler model, which does not explicitly take into account water molecules. For example, the reaction energies of steps 1 and 2 decrease from -0.4 to -0.3 eV and from 3.7 to 3.0 eV, respectively (Figures S8 and S10, Supporting Information). Interestingly, a deprotonation step involving coordinatively bound water molecules was also found feasible (path b in Figure S10, Supporting Information). Although, this process can face competition with one involving a direct attack of OH- on hydrazine, the deprotonation steps appear to be energetically more favorable in the presence of the catalyst.

3. Conclusions

In summary, we have successfully developed Co-based SAC, denoted G(CN)–Co, with well-defined Co(II) sites by a simple

synthetic method. The material showed efficient and selective electrocatalytic activity toward HzOR with low onset/peak potential, high current density, and good stability. The electrocatalytic performances of G(CN)—Co for HzOR were also found to be better than many metal-based catalysts reported in the literature. DFT calculations of the reaction mechanism indicated that single Co active sites would readily interact with the hydrazine molecules and significantly foster the N—H bond dissociation steps. The presented simple synthetic strategy used to produce G(CN)—Co SAC and their efficient catalytic properties can encourage further research into other SACs with improved catalytic activity for HzOR and other reactions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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electrocatalysis, hydrazine oxidation reaction, renewable energy, single atom catalyst, single Co atom catalyst

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