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Atomically Dispersed Semi-Metallic Selenium on Porous Carbon Membrane as Excellent Electrode for Hydrazine Fuel Cell

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Dedicated to 100th Anniversary of Nankai University

Abstract: Electrochemically functional porous membranes of low cost are appealing in various electrochemical devices used in modern environmental and energy technologies. Here we describe a scalable strategy to construct electrochemically active, hierarchically porous carbon membranes containing atomically dispersed semi-metallic Se, denoted SeNCM. The isolated Se atoms were stabilized by carbon atoms in the form of a hexatomic ring structure, in which the Se atoms were located at the edges of graphitic domains in SeNCM. This unique atomic configuration is utterly different from that of previously reported transition/noble metal single atom catalysts. The positively charged Se, enlarged graphitic layers, robust electrochemical nature of SeNCM endow them with excellent catalytic activity that is even superior to state-of-the art commercial Pt/C catalyst, and long-term operational stability towards hydrazine oxidation reaction in practical hydrazine fuel cell. This finding will shed light on and initiate the development and understanding of a family of single semi-metallic atom heterogenous catalyst for practical applications.

Introduction

Electrocatalytic hydrazine oxidation reaction (HzOR)¹ has attracted much attention recently because it is not only important for health and environmental monitoring, but also critical for hydrazine fuel cells (HzFCs)^{2,3}. Particularly, the latest advance in alkaline membrane technologies has stimulated intensive studies on HzOR to be used in practical HzFCs⁴. In this context, enormous efforts have been devoted towards developing efficient, low-cost anode electrocatalysts for HzOR to replace the costly state-of-the-art platinum (Pt) based nanomaterials⁵⁻⁷, along with optimizing the electrode fabrication craft⁸⁻⁹.

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Recently, single-atom catalysts, especially atomically dispersed metals anchored on conductive nitrogen (N)-doped carbons (AMCs), have been intensively studied for multifarious applications¹⁰⁻¹⁵ because of their maximized atom utilization, unusual electronic structure and intriguing properties that differ from their nanoparticle (NPs) counterpart in terms of *i.e.* improved activity and/or selectivity^{16,17}.

Although there have been progresses in the design of AMCs by pyrolysis of carefully engineered metal/carbon precursors (i.e. metal-organic-frameworks)¹⁸, in which metal atoms were coordinated with N atoms and in the form of typical MNn atomic configuration (n represents coordination numbers), controlling the aggregation of single atoms in carbons during synthesis and in the later utilization remains challenging, because the high surface energy makes them easily aggregate into NPs at high pyrolysis temperature and in complex catalytic reactions, which decrease their activity¹⁹. Though a very low concentration of the metal content in precursor could logically mitigate aggregation of single atoms during pyrolysis, the low content of single atoms in AMC adversely meet the requirement of practical applications (>1wt% metal content18); Therefore, from a viewpoint of real-life application, challenges remain in the quest to explore scalable, efficient synthetic routes to AMC of high single atom content. In term of a scientific perspective, to correlate the intrinsically electronic structures of active sites and performance is a formidable task, since an uncontrollable pyrolysis process makes it extremely difficult to fabricate MNn with exactly the same atomic configuration throughout carbons.

Additionally, intensive studies on single atom catalysts hitherto have been focused on transition/noble metals¹⁷. In this regard, a very important family of semi-metal elements, *i.e.* selenium (Se), has rarely been discussed. It is well-known that Se as redox center in Se-dependent enzymes is vital to maintain human health²⁰. A structural merit of incorporating semi-metallic atoms is that they can be easily stabilized by numerous C atoms in form of covalent bonds rather than a spot of N atoms in N-doped carbons, creating a well-defined atomic configuration in favor of precisely correlating their electronic structure and performance.

Herein, we report the first scalable fabrication of semi-metallic single-atom heterogeneous membrane catalyst that consists of atomically dispersed Se atoms, which are stabilized by C atoms, analogous to selenabenzene structure, and anchored on a hierarchical porous carbon membrane. The membrane is demonstrated to function as binder-free, high performance electrocatalyst for HzOR in practical OHzFCs.

Results and Discussion

RESEARCH ARTICLE



Figure 1. a-e) Schematic illustration of the preparation process for the SeNCM-x and structural models of the intermediates. f-h) A digital photograph, a crosssection SEM image and the HRTEM image of SeNCM-1000, respectively. i-l) STEM image and the corresponding elemental mapping.

The electrocatalyst construction was implemented via a bottom-up method. Figure 1a-e show the synthetic procedure and structural models of the intermediates and SeNCM. Firstly, a homogeneous mixture solution of two polymerized ionic liquids, also termed poly(ionic liquid)s (PILs) in DMF was cast onto a glass plate, dried at 80 °C and finally immersed in an aqueous NH₃ solution to build up the porous PIL membrane (Figure 1b-c. Detail synthesis and characterizations of the PILs and membrane fabrication procedure were provided in supporting information, Figure S1-9. Afterwards, in situ pyrolysis²¹ of the as-prepared PIL membrane at different temperatures under vacuum leads to the targeted SeNCM-x, where x indicates the pyrolysis temperature (Figure 1d, e). It is worth mentioning the carbon membrane produced in our laboratory are already several square centimeters in size (Figure 1f, Figure S10). The fabrication method is straightforward and readily scaled up to the membrane in size and quantity.

Figure 1g shows a cross-section scanning electron microscopy (SEM) image of SeNCM-1000, in which the three-dimensionally interconnected porous systems can be clearly observed. High resolution transmission electron microscopy (HRTEM) image revealed a well-defined lattice spacing of 0.38 nm for (002) plane of a graphitic carbon (**Figure 1h**). This value was larger than that of common graphite (0.34 nm) because the introduction of large sized Se bends individual graphitic planes and inevitably enlarges the interlayer spacing. The sharp X-ray diffraction peaks of SeNCM-x at 23.3°, 43.8°, and 80.2° are attributed to the (002), (100), and (110) reflections of a graphitic carbon, respectively (**Figure S11**). Such a graphitic structure of SeNCM-x endows them with high conductivity. The conductivity of SeNCM-800/900/1000 is measured to be 254, 298 and 356 S cm⁻¹ at 298

K as determined by two probe method, which favors fast charge transport, a mandatory requirement for an efficient electrocatalyst. Energy-filtered transmission electron microscopy mappings indicate that C, N, and Se (**Figure 1i-I**) are uniformly distributed throughout SeNCM-1000, which is typical for molecular doping of carbon membrane.

The atomic structures of SeNCM-x were directly visualized by atomic-resolution scanning transmission electron microscopy (STEM) performed in a high-angle annular dark field (HAADF) mode. The STEM image (Figure 2a) shows a high density of homogeneously distributed large Se atoms (1.22Å in size) exclusively in a single-atom state, as represented by bright dots highlighted with red circles, throughout the SeNCM-1000 matrix. Moreover, these Se atoms are identified in the thick area of SeNCM-1000, which revealed that most of them are located at the edge of graphitic domains. The atomic thickness of graphitic layer provides an ideal imaging platform for visualizing structural details at the atomic scale. As shown in Figure 2b, the highresolution STEM image obtained in the ultrathin area of SeNCM-1000 shows four representative Se atoms sitting at the step sites as the defect sites. The defective nature of SeNCM-x was further supported by Raman spectrum analysis. The intensity ratio of D band to G band (I_D/I_G) reflects the degree of structural irregularity in the carbons^{22}. As shown in Figure S12, the $I_{\text{D}}/I_{\text{G}}$ value increased from 1.09 for SeNCM-800 to 1.16 for SeNCM-1000, reflecting enhanced structural disorder²³ in SeNCM-1000. This means that SeNCM-1000 may have higher electrocatalytic activity.

X-ray photoelectron spectroscopy (XPS) revealed that Se content are 5.90 wt%, 5.06 wt%, and 3.23 wt% in SeNCM-800/900/1000, respectively, being consistent with inductively

RESEARCH ARTICLE

coupled plasma-atomic emission results. The characteristic Se 3d signals of SeNCM-x at 56.1 eV is ascribed to the formation the Se-C bond²⁴ (Figure S13-14). To clearly determine the coordination environment and chemical state of Se atoms in carbon membrane, X-ray absorption fine structure spectroscopy (XAFS) measurement was performed. As shown in Figure 2c, the Fourier-transformed (FT) k³-weighted extended X-ray absorption fine structure (EXAFS) spectrum shows one main peak at the low R value of 1.45 Å, in well agreement with the Se-C peak of the 3,4-propylenedioxyselenophene (ProDOS) reference (the structure of ProDOS was provided in Figure S15), and no Se-Se coordination peak at high R value of 2.2 Å was detected. These results demonstrated that Se is bonded by C and atomically dispersed throughout the SeNCM-1000. To further clarify the Se atomic configuration in SeNCM-1000, the EXAFS spectrum was fitted in the R and k space by the IFEFFIT software (Figure S16-17). The experimental FT-EXAFS curve of the SeNCM-1000 has been perfectly reproduced (Figure 2d). The fitting result gives the coordination number of 2, the distance of 1.90 Å, and the disorder of 0.0058 Å² (Table S1). These results suggest that Se atoms should be located at the edge of SeNCM-1000 in a hexatomic ring structure (inset in Figure 2d). X-ray absorption near-edge structure (XANES) shows that the absorption edge position of SeNCM-1000 is located between that of Se foil and SeO₂, suggesting Se atom carries a positive charge and the valence state of which is between 0 and +4 (Figure 2e).



Figure 2. a, b) STEM images of the SeNCM-1000. c) Se K-edge Fourier transformed EXAFS spectra in the R space of the SeNCM-1000 compared with the other two references. d) Fourier transformed EXAFS spectrum of SeNCM-1000 and the corresponding simulation curve, inset is a model structure of SeNCM-1000. e) Se K-edge XANES of the SeNCM-1000, Se foil and SeO₂ as the references. f) N₂ absorption-desorption isotherms of SeNCM-x.

The specific surface area is critical for optimizing the activity of heterogeneous catalysts. The Brunauer-Emmett-Teller (BET) surface area of the SeNCM-800/900/1000 is measured to be 258,

330, and 450 m² g⁻¹ and their total pore volumes are 0.13, 0.15, and 0.17 cm³ g⁻¹, respectively (**Figure 2f**). The observed sharp uptake of nitrogen at low pressures (P/P₀ < 0.05) provides clear evidence for the preservation of micropores (below 2 nm), in accordance with the pore size distribution curves derived from the N₂ adsorption branch (**Figure S18**). BET results, taken in conjunction with SEM imaging, clearly confirm that SeNCM-x is composed of hierarchical architectures with pores traversing the micro- to macropore range, which facilitates the charge transfer and mass diffusion efficiency.

To demonstrate the practical applications of the newly designed materials, we directly utilized SeNCM-x as electrodes without the need for a binder for HzOR. Hydrazine is a very promising liquid fuel candidate for fuel cells due to its high theoretical electromotive force (1.56 V), high power density, and environmentally benign byproducts²⁵ (Figure 3a). The cyclic voltammetry (CV) curves of SeNCM-x exhibited obvious oxidation peaks in 1M KOH solution with 100 mM N₂H₄, but no peaks in the pure KOH solution (Figure 3b). This reveals that the following reaction: N_2H_4 + 4OH⁻ $\rightarrow N_2$ +4H₂O+4e⁻ occured over SeNCM-x in 1M KOH with 100 mM N₂H₄. The onset potentials and peak current densities of SeNCM-800/900/1000 were 0.43/0.40/0.34 V (vs. RHE) and 15.6/22.3/30.8 mA cm⁻², respectively. Notably, SeNCM-1000 has the lowest onset potential and largest peak current density, demonstrating its highest reactivity towards HzOR. It is noted that SeNCM-1000 in fact is, to our knowledge, one of the best electrocatalysts reported so far for HzOR. (Table S2). The operating stability of HzOR catalysts is essential to their application. We examined the electrochemical stability of SeNCM-1000 by both chronoamperometry and cvclic voltammetry (CV) cycling in 100 mM hydrazine, as shown in Figure S19-21, no appreciable decrease in current is observed in this time interval.

In control experiments, it is demonstrated that commercial nanostructured Se powder (SEM and XRD characterizations were provided in **Figure S22**) has no electroactivity for HzOR; N-doped porous carbon membrane without Se doping (NCM-1000, structural characterizations were provided in **Figure S23-24**) has negligible HzOR activity, which reflected by a very high onset peak potential (0.6 V *vs* RHE) and low peak current intensity (5.6 mA cm⁻²). The electrochemical active surface area (ECSA) of SeNCM-1000 was determined to be 1175 cm² by double layer capacitance method²⁵ (**Figure S25**), which is two orders of magnitudes higher than that of NCM-1000 (57.5 cm²). This investigation suggests that the existence of atomically dispersed Se could dramatically enhance the ECSA of SeNCM-1000 thereby exhibiting outstanding catalytic activity toward HzOR.

To deeply understand the HzOR process on SeNCM-1000, the effects of scan rate (v) and hydrazine concentration on the voltammetric waves were systemically investigated (**Figure 3c**). The peak current density (j_P) varies linearly with v^{1/2}, revealing that the HzOR on SeNCM-1000 is a diffusion-controlled electrochemical process (**Figure 3d**). Furthermore, the linear dependence of peak current density on hydrazine concentration (**Figure 3e, f**) and only an oxidation peak is observed during the CV curves, suggesting that the hydrazine oxidation is irreversible. To evaluate the possible structural changes of catalyst, we performed XPS analysis on the SeNCM-1000 before and after 1000 cycles of electrolysis in 100 mM hydrazine. As shown in

RESEARCH ARTICLE

Figure S26-27, the quantity and valence state of N and Se species of them are quite similar, which is indicative of its excellent electrochemical stability.



Figure 3. a) Schematic illustration of the SeNCM-x structure and applied for HzOR. b) CV curves of SeNCM-x, Se powder and NCM-1000 for HzOR (100 mM NzH4, 1 M KOH, scan rate 5 mV/s). c) CV curves of SeNCM-1000 in 1 M KOH with 100 mM NzH4 at different scan rates (5, 10, 15, 20, 40, 100 mV s⁻¹). d) Plot of peak current density in relation to the square root of scan rate. e) CV curves of SeNCM-1000 in different concentrations of hydrazine (10, 20, 40, 60, 80, 100 mM) in 1M KOH at a scan rate of 100 mV s⁻¹. f) Plot of peak current density with respect to the concentration of hydrazine.

To probe the catalytic kinetics of the HzOR on SeNCM-1000, electrochemical impedance spectroscopy measurement was conducted under different overpotentials. The series resistance (R_s), pore resistance (R_p), and charge-transfer resistance (R_{ct}) of the HzOR on SeNCM-1000 were fitted by Nyquist plots. As shown in **Figure S28**, the overpotential-independent behavior of R_p (ca. 1.55 Ω cm⁻²) for the HzOR indicates the robust nature of the hierarchical pore structure of the SeNCM-1000, and these structures also serve as efficient channels for mass transport to access the exposed active sites.

Chemically, the outermost orbitals of Se are apparently overlapped with C atoms, which could introduce the positively charge characteristics on the Se atoms, being consistent with our XAFS result. Previous works have demonstrated positively charged species in heteroatom doped carbons are active centers²⁶⁻²⁷, in this case, Se atoms. Additionally, the incorporation of larger atomic radius of Se atom could enlarge graphitic interlayer spacing and lead to structural strains and defects at the graphitic edges^{28, 29}, which is in favor of promoting the mass transportation efficiency in the graphitic layers and exposing numerous active sites for the HzOR. Based these analyses, the superior catalytic activity of SeNCM-1000 could mainly be attributed to the positively charged Se sites and the enlarged graphitic layer spacing, and the HzOR process may involve four consecutive dehydro-generation steps on Se atom sites³⁰: $N_2H_4 \rightarrow N_2H_3 \rightarrow N_2H_2 \rightarrow N_2H \rightarrow N_2$ (Figure 4). Further experiments are needed to unveil the detailed mechanism of the HzOR by SeNCM-x.



Figure 4. Proposed mechanism of the HzOR on SeNCM-x in 1 M KOH aqueous solution.

Considering SeNCM-1000 has the highest activity toward HzOR among all the samples studied in this work, we employed SeNCM-1000 as anode for fabricating OHzFCs (Figure 5a). For comparison. 20% Pt/C was also integrated as anode in OHzFCs. Note that 20% Pt/C was employed as cathode in all studied OHzFCs in this work using standard procedure in this field for oxygen reduction reaction and the electrolyte is KOH-doped polybenzimidazole membrane, unless stated. The performance testing showed that the open-circuit potential, maximum current density and power density of SeNCM-1000-OHzFC were 0.91 V. 605.3 mA cm⁻² and 182.2 mW cm⁻², respectively (Figure 5b). These performance metrics are comparable or even superior to that of Pt/C-OHzFC (0.92 V, 605.4 mA cm⁻² and 170.9 mW cm⁻²), and among the best performances reported so far for OHzFC (Table S3). Additionally, stability testing showed almost no decay of SeNCM-1000/HzFC after continuous operations for 6 h (Figure 5c), confirming that SeNCM-1000-OHzFC is stable under operating conditions. These results suggest promising usability of SeNCM-1000 for OHzFC.



Figure 5. a) Schematic diagram of OHzFC. b) Polarization and power density plots for SeNCM-1000-OHzFCs and Pt/C-OHzFCs at 80 °C. Testing conditions:

RESEARCH ARTICLE

the anolyte is 6.0 M KOH + 0.5 M hydrazine hydrate with a flow rate of 1 mL min⁻¹; the catholyte is oxygen with a flow rate of 0.2 slpm. c) Long-term stability of the SeNCM-1000-OHzFC.

It is notable that much higher power densities at the high current areas of SeNCM-1000-OHzFC were observed in comparison to that of Pt/C-OHzFC, which can be attributed to the rapid mass transfer throughout the hierarchical pore system as well as the intrinsic bubble-repelling nanostructure surface³¹ of the SeNCM-1000 (Figure S29). Traditionally, the powdery nanocatalysts have to be engineered into predefined shapes by mixing and pressing with electronically insulating polymer binder (i.e. PVDF, Nafion) to make them useful as practical electrode, which is a time/labourconsuming process. Moreover, the insulating binder deteriorates the electrode conductivity, blocks the pores, and also leads to undesirable side-reactions in electrochemical devices³². In contrast, utilizing integrated SeNCM-1000 as binder-free electrode for fabricating OHzFC (Figure S30-31) is extremely appealing in terms of multiple merits, i.e. simplified electrode fabrication craft and improved device performance and long-term operational stability.

Conclusion

In conclusion, we developed a facile way to fabricate large scale, freestanding hierarchical porous carbon membrane with atomically dispersed semi-metallic Se. The unique atomic configuration of Se in membrane was for the first time determined by integrated analytic methods. The membrane is proven to be binder-free, high performance anode for HzOR in practical OHzFC. This finding may aid the development of efficient single semi-metallic atom catalyst for catalytic applications. We believe that the membrane design platform described here will be applicable to produce a broad range of functional porous carbon membranes for practical applications, particularly those in energy conversion devices that require heterogeneous membrane catalysts.

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Keywords: hydrazine oxidation • poly(ionic liquid) • atomically dispersed selenium • porous carbon membrane

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RESEARCH ARTICLE

A scalable strategy to hierarchically structured porous carbon membrane containing atomically dispersed semimetallic selenium atoms has been developed. The membrane is demonstrated to function as binderfree, high performance anode for hydrazine oxidation reaction in practical hydrazine fuel cell.



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Page No. – Page No.

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