



## Enhancement of catalytic activity of a programmed gold nanoparticle superstructure modulated by supramolecular protein assembly

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### ABSTRACT

Improving the efficiency of the oxygen reduction reaction (ORR) for use in commercial fuel cells has been the subject of diverse synthetic research activities. However, due to their inferior catalytic performance and dispersibility, there are still limitations to achieving breakthroughs regarding ORR catalytic activity using carbon nanomaterials, despite their high electron-transfer and mass-transport properties. In this study, we mimicked nature by using a biominingalization approach for controlling the growth of inorganic materials and demonstrated improved ORR values. The designed peptide, Hexcoil-Ala, is able to supramolecular assembly on single-walled carbon nanotubes (SWNTs), leading to SWNTs that are well dispersed in aqueous solution. In order to direct gold nanoparticle (AuNP) nucleation sites, we substitute two residues in Hexcoil-Ala with cysteine to provide the mutated peptide, HexCoil-Ala-2Cys. This peptide affords a sophisticated, size-controlled, and well-dispersed arrangement of AuNPs. High-resolution transmission electron microscopy studies confirmed the homogeneously well-aligned distribution of nanosized AuNPs on the HexCoil-Ala-2Cys structure, along the direction of SWNT axis. The (AuNPs/P-SWNT) composite in water provides dispersed and stable metallic nanoparticles of electrostatically modified Au through synergistic effects involving the peptide. Consequently, this catalyst exhibits improved ORR performance compared to bulk gold and even, in case of number of electrons ( $n$ ) transferred, higher than the number of Pt/C. X-ray photoelectron and Raman spectroscopies reveal the details of the electronic interactions among the components of the AuNP/P-SWNT composite, and how they facilitate the four-electron reaction pathway. This study provides valuable information for the optimization of catalyst synthesis and precise particle-size control, leading to stable, water-dispersive composites, with improved electronic properties for enhanced ORR performance in fuel cells.

### 1. Introduction

Although Pt has been recognized as a most suitable noble metal for the catalyst, research to replace Pt with other precious metals has been attracting attention for a long time [1–4] due to their many limitations [5–8]. Gold has also been extensively studied as a substitute for Pt, but it has many drawbacks for catalyst because they have a filled d-band confirmed by density functional theory (DFT) calculations [7]. The modification of size, shape, composition and the interface/surface engineering of catalytic components is considered key to improving the

catalytic activity. In particular, control of nanoparticle size is a powerful driving factor that can increase the catalyst surface area and improve the ORR properties. This is especially important in the case of gold, since bulk gold is mostly inert [9–12], whereas nano-sized gold particles smaller than 5 nm show high electrocatalytic activity [13]. Therefore, many researchers have adopted the following approaches for achieving the required size: 1) reduction to the nano-size using nanoporous structures and 2) dispersal of nanoparticles on either high- or low-aspect-ratio supports in order to achieve elaborate arrangements [8]. However, extremely small-sized particles aggregate readily, due to

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their high surface potentials and are also difficult to synthesize [14]. Moreover, existing approaches are limited because they require additional external growth factors such as surfactants, heat, and pH control, resulting in reduced catalytic activity and the loss of ORR catalytic sites [15,16]. Therefore, in order to improve this catalytic reaction, a new synthetic protocol that uses homogeneous, nano-sized, and well-dispersed particles, is required.

A current, emerging approach involves biomineralization, a method for growing inorganic materials on biomolecular templates; this approach is attracting attention as an alternative method for the synthesis of size-controlled nanoparticles [17,18]. Biologically assembled architectures offer nucleation sites for growing well-aligned inorganic particles along their surfaces. These biomineralized nanoparticles impart good physical and chemical properties that translate into catalytic ORR activity. For example, Rosi's group designed peptide-conjugate molecules for the direct synthesis and assembly of CoPt nanoparticles into hollow spherical magnetic superstructures that can serve as catalysts for the oxidation of methanol [19]. Belcher and coworkers reported that the introduction of a surfactant from a genetically modified M13 template greatly enhanced the surface structure of as-synthesized nanowires, resulting in Au nanowires with controlled diameters [20]. Clearly, the catalytic activity of a nanoparticle depends on its size; however, the support material has also been suggested to improve catalytic activity [21–25]. Allotropes of carbon such as graphene and single-walled carbon nanotubes (SWNTs) that offer high surface areas and good electrolyte permeability and electron-transfer pathways have been considered as templates for biomineralization [26–30]. This approach has made significant contributions to maintaining uniform size control and well-dispersed states; however, little research into creating precisely defined structures using composites with support materials having high surface areas has been reported. Furthermore, there have been few studies utilizing catalysts prepared through this method, and detailed explanations of their catalytic activities are rare.

Previously, we presented a new virus-like protein superstructure assembled on single-walled carbon nanotubes (P-SWNTs) via computational design [31]. The designed peptide assembly on the SWNT has a highly ordered, textured structure that fully covers the chemically inert carbon nanotube surface. This structure is a high-surface-area material that provides tunable chemical functionality through modification of the amino acid sequence. In these P-SWNTs, we successfully demonstrated the formation of helical hexamer arrays along the SWNT axis, with long-scale order for the direct assembly of metal nanoparticles. In this work, we demonstrate the electrocatalytic reactions of direct Au-assembled superstructures using this P-SWNT. The protein, which affords programmable self-assembled structures, is a useful scaffold for ensuring sophisticated size control by maintaining a well-dispersed state. In addition, it allows for the control of particle arrangement through modification of the amino acid sequence, since the catalyst nucleation sites can be predicted theoretically from the protein structure. It is possible to measure these delicate nanoparticle arrangements and to create composites containing CNTs having high surface areas, in order to explore the effect of structure on ORR activity. In fact, despite gold being regarded as a poor catalyst because its filled *d*-band, we confirmed improved onset potentials and electron-transfer numbers for ORR when gold is grown on P-SWNT using the above approach.

## 2. Materials and methods

### 2.1. Preparation of the peptide

We have described the synthesis of HexCoil-Ala-2Cys in a previous paper [31]. Engineered peptides were synthesized by Fmoc chemistry on a LibertyBlue automatic microwave synthesizer system (0.1 mmol scale) using the H-Rink Amide ChemMatrix<sup>®</sup> resin (PCAS 0.47 mmol/g loading). For removing the Fmoc protecting groups, a mixture of piperidine/dimethylformamide (DMF) (20:80 v/v) was used. In each

coupling step, the reactants were used in a 5:4.9:10:1 molar ratio of amino acid:*N,N'*-diisopropylcarbodiimide (DIC):ethyl 2-cyano-2-(hydroxyimino)acetate (Oxyma):resin. The products were cleaved from the resin using a mixture of trifluoroacetic acid (TFA), triisopropylsilane (TIS) and deionized water (DI water) (95:2.5:2.5 v/v) for 2 h in room temperature. After the resin was removed by filtration, the solvent was evaporated under a stream of pure N<sub>2</sub> gas, and cold anhydrous diethyl ether (Alfa Aesar) was added to the residue. The white precipitate was collected and fully dried using a lyophilizer (Labconco<sup>®</sup> FreeZone<sup>®</sup> 6 Plus). The crude peptide was purified by reverse phase high performance liquid chromatography (HPLC, Waters Quaternary Gradient Module 2545) using a C4 column (Waters XBridge<sup>™</sup> BEH300 Preparative C5 5 μm) with a linear gradient of buffer A (99.9% H<sub>2</sub>O and 0.1% TFA) and buffer B (90% acetonitrile, 9.9% H<sub>2</sub>O and 0.1% TFA). Molecular masses of all engineered peptides were confirmed by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry (Bruker Ultraflex III, Flex control 1.3).

### 2.2. Preparation of the peptide/SWNT (P-SWNT) superstructure

SWNT (20 mg) (Sigma-Aldrich) was dispersed in 20 ml of a 1 wt% glycerol solution (Sigma Aldrich). The mixture was tip-sonicated (QSonica, Q125, 1/8 inch tip) for approximately 20 min to homogeneously disperse the SWNT. For each experiment, a 500 μl sample of the well-dispersed SWNT solution was collected and centrifuged (Eppendorf Centrifuge 5430R) at 5000 rpm for 5 min and the supernatant removed. This process was repeated two more times; each time 500 μl of DI water was added to the SWNT pellet, followed by sonication, as described above. The SWNT pellet (about 0.1 mg/ml in the mixture solution) was added to 1 ml of a 1 mg/ml solution of peptide in 20 mM sodium phosphate, 100 mM NaCl, at pH 7.5. The solution was tip-sonicated in an ice bath for 30 min. Cooling was maintained to prevent destabilization of the protein structure through excessive heating by the tip sonicator. The sample, P-SWNT suspension, was warmed to room temperature and centrifuged at 5000 rpm for 10 min.

### 2.3. Peptide-sequence mutation for nanoparticle arrangement

To bind gold nanoparticles onto the target surface, the peptide sequence was partially permuted by the introduction of cysteine residues because of their high selectivity toward metals. The sequence substitution was implemented without the destruction of the optimal helix–helix and helix–SWNT interactions in the hexamer. We first identified six outward-facing binding sites, E8, Q12, E15, L19, Q22, and Q26, from the 30 amino acid sequence and arbitrarily selected E8 and Q22 for modification. We also considered the size of the Au nanoparticles to be grown on the peptide because size greatly affects the activity of the electrocatalytic oxygen reduction process. When the gold nanoparticles are larger than 2.5 nm, they begin to coalesce, the interparticle distances become less than 0.1 nm, and catalytic activity drops sharply. Therefore, we selected 2.5 nm as the desired size for the gold nanoparticles in this work.

### 2.4. Preparation of the AuNPs/P-SWNT superstructures

The goal was to grow the nucleus in order to make small-sized gold nanoparticles on the cysteine residues in HexCoil-Ala-2Cys. The P-SWNT suspension, prepared as detailed above, was treated with 1 mM tris(2-carboxyethyl)phosphine hydrochloride (TCEP, Sigma-Aldrich) in order to reduce the sulfhydryl group of the Cys residues. This is to prevent the formation of disulfide bond between the Cys groups of the HexCoil-Ala-2Cys peptides. Next, the TCEP-treated P-SWNT suspension was purified by centrifugal filtration (Amicon<sup>®</sup> Ultra-4 centrifugal Filters, Ultracel<sup>®</sup>-10K) and reconstituted into 100 μl buffer solution (20 mM sodium phosphate, 150 mM NaCl, pH 7.4). We synthesized AuNPs on the template by adding precursor solution of 1.5 mM of

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