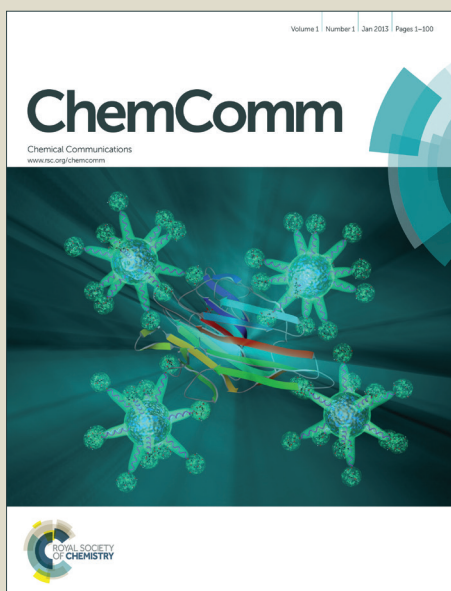


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COMMUNICATION

P-Modified and Carbon-Shell Coated Co Nanoparticles for Efficient Alkaline Oxygen Reduction Catalysis

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Described herein is elucidation of a novel Co-based oxygen electrode catalyst coupled with unique carbon structures. The present carbon shell coated Co nanoparticles of which surface composites are modified with phosphorus incorporation exhibit efficient oxygen reduction activities as well as oxygen evolving properties.

Electrochemical reduction of oxygen in alkaline media plays key roles in many renewable-energy technologies including fuel cells and metal-air batteries. Furthermore, the replacement of hydrogen-evolving cathode with an air cathode in chlor-alkali electrolyzers is expected to save considerable amount of energy by lowering the cathode-operating overpotential.¹ Since cathode oxygen electrocatalyst has been one of the major limiting factors for energy conversion efficiency, cost, and stability of these devices, the development of more efficient electrocatalysts is crucial to future advances.² Despite tremendous efforts, developing effective catalysts from earth-abundant elements to substitute high cost Pt based catalysts remains a great challenge for accomplishing large-scale implementation of these technologies.³

Among non-precious metals, cobalt has drawn remarkable attention for oxygen reduction reaction (ORR). Progress has been initiated through the utilization of macrocyclic molecular compounds particularly those containing Co-N₄ moieties, or high-temperature synthetic materials possessing separately or collectively transition metal-nitrogen-carbon (MNC) composites.⁴ Meanwhile, recent studies revealed that cobalt oxides coupled with versatile carbon based functional materials such as N-doped graphene and carbon nanotubes (CNTs), can enhance efficiency of ORR and even oxygen evolution reaction (OER) through their synergetic chemical effects.⁵ Similarly, a well-known in-situ electrodeposition technique originally for preparing OER-active cobalt-oxide-phosphate (Co-Pi) complex has been newly applied to generate Co-Pi hybrid coupled with reduced graphene oxide nanosheets, thus realizing a novel alkaline ORR catalytic system.⁶ Likewise, combination of Co-based nanostructures with carbon materials have been actively pursued to get high ORR activities.

Inspired by above-mentioned works, we envisioned to develop a novel Co-based oxygen electrode catalyst effectively coupled with carbon materials. Described herein is a new type of carbon-shell coated cobalt nanoparticles of which surface composites are modified with phosphorus incorporation, thereby exhibiting efficient oxygen electrode catalytic activities. Cobalt in the present system was revealed to have significant roles in electrocatalysis.

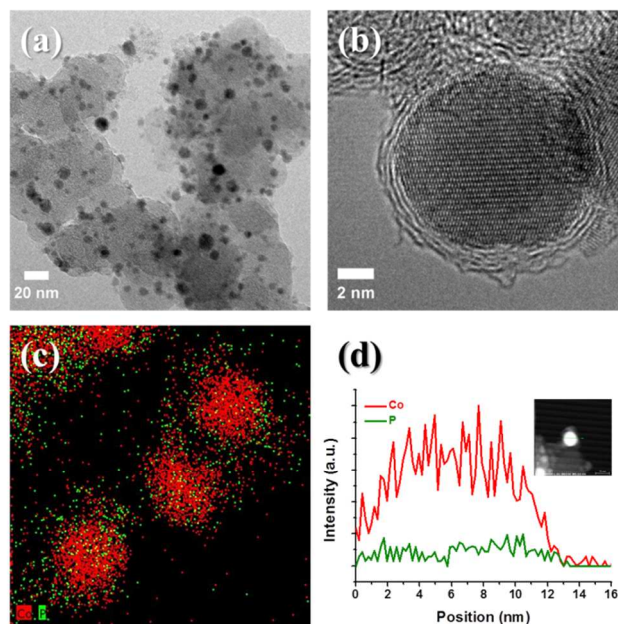


Fig 1. (a,b) TEM images of C@Co-P/C. (c) EDS mapping images and (d) line profile spectra of C@Co-P/C.

Based on our new synthetic method using trioctylphosphine (TOP) as a possible P source as well as a kind of surfactant,^{7a,7b} we were able to prepare P-containing and carbon-shell coated cobalt nanoparticles anchored on carbon black support (~20 wt% Co) (Figure

1 and Figure S1). The present Co nanoparticles-carbon hybrid material, which is hereafter denoted as C@Co-P/C, was synthesized in one pot through thermal decomposition of cobalt complexes in solution containing Vulcan XC-72 (see supporting information for details). After reaction finished, washing process as well as heat treatment (360 °C, 1 hr) under argon atmosphere was conducted in order to remove chemical residues. From our preliminary experimental results (Figure S2),⁸ we initially expected that ligand variations in precursive cobalt complex would affect its thermal stability against decomposition reaction. Accordingly, a pre-heated mixture of Co(acac)₃, oleylamine, and TOP, which presumably contains mixed-ligated cobalt complexes,⁹ rather than Co-TOP complexes,⁷ was added fast to carbon suspension at 120 °C and heat up to 300 °C. Throughout the process, the concentration of Co monomer, probably from decomposition of the modified Co complexes, was believed to increase enough to generate Co nuclei, eventually yielding Co nanoparticles first instead of CoP nanoparticles.^{7c,9}

Along with the crystalline lattice ($d_{101} = 0.19$ nm) of as-resultant spherical cobalt nanoparticles (~10 nm) which is clearly observable in high-resolution transmission electron microscopy (TEM) (Figure 1 and S1), X-ray diffraction (XRD) peaks matched with ϵ -cobalt confirm the majority bulk phase of metallic Co composite in C@Co-P/C (Figure S3). Of note, we have ascertained that cobalt nanoparticles are surrounded by three or four layers of onion-like carbon shell ($d = \sim 0.34$ nm, Figure 1b and S1). In fact, cobalt and other transition metals have been known for mediating formation of ordered carbon structures.¹⁰ Since the coating layers are observed in as-prepared state of C@Co-P/C before heat treatment (Figure S4), it is likely that the shell structures presumably derived from the long-carbon chain containing surfactants during the solution-phase synthesis. Considering that acid treatment (0.5 M H₂SO₄) of C@Co-P/C dissolved the core metal severely without compromising the shell structures (Figure S5), the present carbon shells in C@Co-P/C are considered as penetrable, providing accessibility of electrolyte to contact inside cobalt. Detectable redox responses of cobalt with electrolyte also indicate the penetrability of electrolyte across the carbon shells (Figure S7). In this sense, participation of cobalt species in electrocatalysis can be expectable as well.

Meanwhile, phosphorus diffusion to surface of Co nanoparticles probably before complete formation of outer carbon shells was revealed to be facilitated, depending on the amount of employed TOP. In fact, inward-diffusion of phosphorus into cobalt phase at around 300 °C is a known process to form outer Co-P composites around ϵ -Co core.^{7b} Phosphorus species was readily detected on energy dispersive x-ray spectroscopy (EDX) around Co nanoparticles of C@Co-P/C, which was synthesized with 10 mL of TOP (Figure S8). Location of phosphorus at edge side of Co nanoparticles was ascertained by EDX line profiling and mapping techniques (Figure 1c and 1d). Meanwhile, absence of cobalt phosphide peaks in the XRD spectrum of CoP@Co/C indicates that Co-P composite may remain as a few monolayers or adopt an amorphous order at the surface.^{7b} Otherwise, some phosphorus species might exist as oxidized forms due to its high oxophilicity and air sensitivity. On the contrary, negligible phosphorus incorporation (3% in EDX) was accompanied with spherical ϵ -Co nanoparticles (C@Co/C) when reduced amount TOP (4 mL) was used in synthesis under otherwise identical condition (Figure S8 and S9). Other features of C@Co/C including carbon shell structures, particle size, and cobalt weight percent (~20 wt%) are similar to those of C@Co-P/C.

For further understandings of electronic and structural features of cobalt in the present materials, X-ray studies were conducted. First, analysis of X-ray photon spectroscopy (XPS) results ensured that

surface oxidation occurred spontaneously to deliver oxygen-bound Co and P species to C@Co-P/C (Figure 2). The P_{2p} region of C@Co-P/C solely exhibited a typical signal (~133 eV) of phosphate species (Figure S10) rather than that of phosphides.^{11,12a,12b} Higher P/Co ratio measured in XPS (47%) compared to EDX analysis (28%) additionally implies surface location of phosphates. In contrast, C@Co/C did not show any P_{2p} signal in this region, again verifying its lack of phosphorus incorporation (Figure S10). Along with phosphate species at the surface, C@Co-P/C was revealed to have enhanced population of oxidized Co than C@Co/C does. Co 2p_{3/2} fitting results (Figure 2 and Table S1) show that the portion of metallic cobalt (0) (~779 eV) was decreased (40% for C@Co/C, 10% for C@Co-P/C) as P contents increased. The Co peaks at ~782 eV, commonly assigned to C@Co-P/C and C@Co/C, are related to Co^{II} species in accordance with previously reported data of cobalt species bound to oxygen and cobalt phosphate.¹² Besides, enhanced white line intensity in the Co K-edge X-ray absorption near edge spectroscopy (XANES) spectrum of C@Co-P/C compared to C@Co/C (Figure 2c) reveals larger population of oxidized cobalt in C@Co-P/C. In accordance with XPS, Co^{II} species are assigned by its edge position in XANES (~7725 eV). Also, smaller magnitude (~50%) of extended X-ray absorption fine structure (EXAFS) oscillation than that observed for C@Co/C (Figure S11) shows non-metallic contribution, thus indicating composite changes at the surface of cobalt nanoparticles in C@Co-P/C.^{11b}

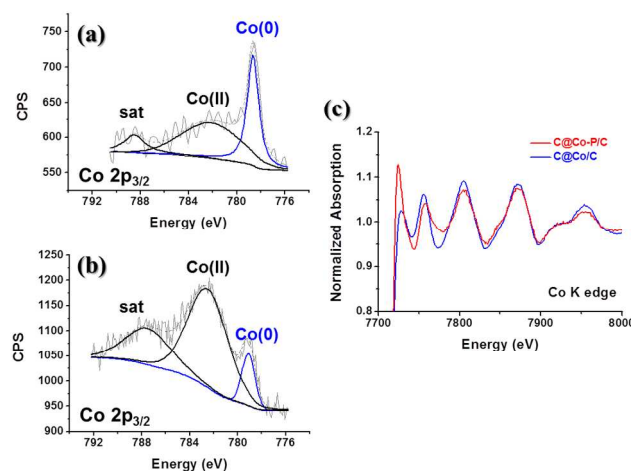


Fig 2. (a,b) Co 2p_{3/2} XPS spectra of C@Co-P/C and C@Co/C. (c) Co K edge XAS profiles of C@Co-P/C and C@Co/C.

Based on the aforementioned analysis, the surface of cobalt in C@Co-P/C can be tentatively described as a combination of cobalt phosphate with cobalt oxide species, mostly in the Co^{II} state. Although exact mechanistic details on the formation of such oxidized cobalt species couldn't be elucidated, we suggest that phosphorus incorporation to form Co-P composite at the surface of Co may enhance the susceptibility toward oxidation, eventually engendering Co^{II}-rich surface. Since the present carbon shells are shown to be penetrable to electrolyte, surface oxidation might proceed through air contact. The possibility of surficial Co-P composite to become oxidized was simply examined by our preliminary theoretical calculation which mainly deals with d-band center and oxygen binding energy of cobalt in cobalt phosphide. Along with the phosphorus involvement, up-shift of d-band center and enhanced oxygen binding energy of cobalt were obtained (Table S2 and Figure S13), implying its preference for being oxidized. This result is well-consistent with previous reports which revealed that metal phosphides of higher P content have larger sensitivity to air,

eventually bearing more oxidized surface which includes metal oxides and phosphates.¹³

Next, electrocatalytic activities of present materials were evaluated in an alkaline electrolyte (0.1 M KOH solution). Figure 3a includes ORR polarization curves of several carbon black containing hybrid materials deposited onto a glassy carbon working electrode, measured on a rotating disk electrode (RDE). Pleasingly, the performance of C@Co-P/C (~0.80 V of half-wave potential in 0.1 M KOH) is comparable to that of even Pt/C catalyst (20 wt%, Premetek) and other best reported cobalt-based materials (CoO/N-CNT and Co₃O₄/N-graphene)^{5c} which exhibited ~0.85 V of half-wave potential in 1 M KOH. Compared to commercial Co/C (20 wt%, Premetek) which contains carbon-shell free ε-Co nanoparticles on carbon black, both C@Co-P/C and C@Co/C exhibited higher ORR efficiency. Of note, C@Co-P/C outperformed C@Co/C in terms of ORR onset and half-wave potentials. Tafel slope of C@Co-P/C is also much smaller than that of C@Co/C, implying more favorable ORR kinetics of C@Co-P/C (Figure 3b). Additionally, catalytic pathway mediated by C@Co-P/C was revealed to follow almost perfect four-electron transfer mechanism according to rotating ring-disk electrode (RRDE) measurement (Figure S14). Based on the ring and disk current values, it was estimated that less than 5% peroxide species was formed over the potential range, 0.25–0.85 V (Figure 3c). Furthermore, C@Co-P/C catalyst displayed outstanding stability. According to our durability test (Figure S15), deterioration in half-wave potential was negligible even after 5000 cycles swept between 0.45 and 0.95 V under O₂ saturation.

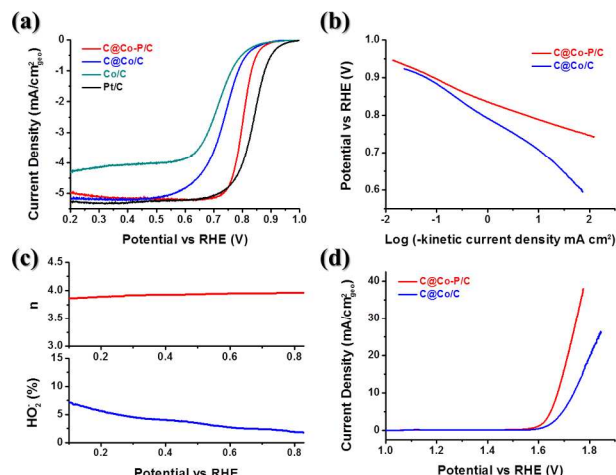


Fig 3. (a) ORR polarization curves measured in 0.1M KOH with a scan rate of 5 mV/s (catalyst loadings: ~0.4 mg_{total}/cm² for Co-based materials and ~40 μg_{total}/cm² for Pt/C). (b) Tafel plots of C@Co-P/C and C@Co/C extracted from (a). (c) Electron transfer number and peroxide yield of C@Co-P/C. (d) OER polarization curves of C@Co-P/C and C@Co/C measured in 0.1M KOH with a scan rate of 5 mV/s. All polarization curves are iR-compensated (R=30 ohm).

There are several examples of (nitrogen doped) carbon-encapsulated metal nanoparticle catalysts for ORR,^{10,14} however, active sites for these catalysts are still elusive. The dependency of ORR activities to cobalt environments for present materials (C@Co-P/C vs C@Co/C) indicates that cobalt in our system has significant roles in the electrocatalysis. Along with the well-penetrable carbon shell structures and oxidized cobalt species mostly as Co^{II} state, C@Co-P/C is believed to have ORR-effective environments. Surficial phosphates might have positive effects on the ORR activity

as well.⁶ In fact, oxidation state of cobalt has been described as a critical factor reflecting the ORR efficiency.^{5c,5f} Particularly, Co^{II} sites are often suggested as ORR active in several reports.^{5c,5f} Considering that C@Co-P/C exhibited higher ORR efficiency than C@Co/C and Co^{II}-rich CoO/C which also has similar particle size and metal weight percent to those of C@Co-P/C (Figure S16 and S17), a kind of synergetic effect between surficial Co^{II} species and the carbon shell structures can be expected. Not only carbon shell structures are known to enhance the conductivity and corrosion-resistance,¹⁵ but also even its direct involvement in ORR catalysis was scrutinized in the previous report.^{14a}

It is highly challenging but desirable to develop efficient bifunctional catalysts for both ORR and OER, particularly for unitized regenerative fuel cells (URFCs) and rechargeable metal-air batteries.¹⁶ To our delight, the present C@Co-P/C catalyst also displayed desirable OER efficiency, suggesting its promising bifunctionality. A current density of 10 mA/cm², which is a frequently used standard metric in OER literatures and solar fuel synthesis,¹⁷ was achievable at an overpotential of ~0.45 V with C@Co-P/C in 0.1M KOH, comparable to the performance of best reported Co-based hybrid catalyst (Co₃O₄/N-graphene, overpotential of ~0.40 V at 1M KOH)^{5a} Also, C@Co-P/C exhibited superior OER activities to C@Co/C, with higher current and earlier onset of catalytic current (Figure 3d). The oxygen evolving nature of the present materials manifests participation of Co species in the electrocatalysis, consistent with our demonstration made for ORR catalysis.

In summary, we have described a novel Co-based oxygen electrode catalyst coupled with spontaneously formed unique carbon architectures. The present carbon-shell coated cobalt nanoparticles of which surface composites are modified with phosphorus incorporation exhibit efficient and durable alkaline ORR activities. Furthermore, satisfactory OER activity was obtainable with the catalyst, thereby displaying its promising bifunctionality. Overall, we provide a new protocol for inexpensive, earth-abundant, and easily constructed catalysts, which are in high demand for energy conversion technologies.

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† Electronic Supplementary Information (ESI) available: [details of synthesis and characterization method of present materials as well as additional electrochemical data are available]. See DOI: 10.1039/c000000x/

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