



# Electrocatalytic activities of alkyne-functionalized copper nanoparticles in oxygen reduction in alkaline media



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## HIGHLIGHTS

- Copper nanoparticles stabilized by self-assembly of alkynes onto the Cu surface.
- Formation of Cu–C≡ interfacial bonds as manifested by FTIR and PL measurements.
- Formation of metal oxides within the Cu nanoparticles revealed in XPS studies.
- Electrocatalytic activity in oxygen reduction by the Cu nanoparticles in 0.1 M NaOH.
- Best performance observed with nanoparticles with the least amount of metal oxides.

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## ABSTRACT

Stable alkyne-capped copper nanoparticles were prepared by chemical reduction of copper acetate with sodium borohydride in the presence of alkyne ligands. Transmission electron microscopic measurements showed that nanoparticles were well dispersed with a diameter in the range of 4–6 nm. FTIR and photoluminescence spectroscopic measurements confirmed the successful attachment of the alkyne ligands onto the nanoparticle surface most likely forming Cu–C≡ interfacial bonds. XPS measurements indicated the formation of a small amount of CuO in the nanoparticles with a satellite peak where the binding energy red-shifted with increasing Cu(II) concentration. Cu<sub>2</sub>O was also detected in the nanoparticles. Similar results were observed with commercial CuO nanoparticles. Electrochemical studies showed that the as-prepared alkyne-capped copper nanoparticles exhibited apparent electrocatalytic activity in oxygen reduction in alkaline media, a performance that was markedly better than those reported earlier with poly- or single-crystalline copper electrodes; and the fraction of peroxides in the final products decreased with decreasing concentration of oxide components in the nanoparticles.

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## 1. Introduction

Proton exchange membrane fuel cells are clean and environmental-friendly power sources [1,2]. For hydrogen fuel cells, with a large Gibbs free energy of  $-273.13 \text{ kJ mol}^{-1}$ , the reaction of hydrogen and oxygen is thermodynamically favorable and expected to exhibit a high theoretical efficiency on energy conversion. However, as oxygen reduction reactions (ORR) on the cathode are kinetically sluggish, the reactions can proceed only at significantly large overpotentials and consequently compromise the overall efficiency [3]. Platinum-based nanoparticles have been used extensively as the catalysts of choice for ORR [4–7]; and a variety of strategies have been reported in the literature to further

improve the ORR activities, such as rational design and preparation of Pt-based alloys [8] and surface engineering of Pt nanoparticles by selected organic ligands [9–11]. This is motivated by a deliberate balance between surface accessibility of active sites and control of electronic structures of the metal cores which may manipulate the adsorption and reduction of oxygen. Meanwhile, owing to the high price and scarcity of platinum, extensive efforts have also been focused on Pt-free catalysts such as transition metal oxides and chalcogenides [12,13], pyrolyzed metal macrocycles [14,15], N-doped carbon nanostructures [16], etc. Among these, studies of copper-based electrocatalysts for ORR have been relatively scarce. In fact, copper has been largely used as a supporting substrate or non-active component in the electrocatalytic reduction of oxygen [17–21]. Yet, using a polycrystalline copper electrode, Schiffrin and coworkers [22,23] have shown that the electrode exhibited apparent electrocatalytic activity in oxygen reduction in a borax buffer solution, though at a large overpotential, and proposed that

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surface redox couples like  $\text{Cu}_2\text{O}/\text{CuO}$  played an important role in the reduction sequence with a CE mechanism whereas direct electron transfer to oxygen might occur from the oxide-free electrode surface. Brisard et al. [24,25] also observed electrocatalytic activity of Cu(100) and Cu(111) single-crystal electrodes in oxygen reduction in sulfuric acid where the reaction kinetics was impacted by the adsorption of (bi)sulfate ions on the electrode surface. In a more recent study [26], it was reported that cuprous oxide nanoparticles might serve as efficient catalyst for oxygen reduction; however, no detailed mechanism was included. Nevertheless, these earlier studies suggest that partial oxidation of copper surfaces might be a key step in enhancing the adsorption and eventual electroreduction of oxygen on copper. This is the primary motivation of the present study.

Herein we prepared alkyne-capped copper nanoparticles by reducing copper acetate with sodium borohydride in the presence of alkyne ligands at two temperatures, 0 °C and room temperature. 1-Decyne was chosen as the illustrating example, primarily because (i) the acetylene moiety can self-assemble onto copper surfaces forming relatively strong metal-ligand interfacial bonds, and (ii) the chainlength of the ligands is long enough to stabilize the nanoparticles and yet not too long to inhibit electron transfer in ORR studies. Transmission electron microscopic (TEM) studies showed that as-prepared copper nanoparticles were well separated, suggesting effective protection of the nanoparticles by the alkyne ligands; and the nanoparticle diameters were found to be in the range of 4–6 nm. FTIR and photoluminescence spectroscopic measurements confirmed the bonding attachment of the alkyne ligands onto the nanoparticle surface most likely forming  $\text{Cu}-\text{C}\equiv$  interfacial bonds. XPS measurements revealed the formation of a small amount of CuO in the nanoparticles with the concentration higher in the samples prepared at ambient temperature than that at 0 °C.  $\text{Cu}_2\text{O}$  was also identified in the nanoparticles, as well as in commercial CuO nanoparticles. Electrochemical studies indicated that the 0 °C samples exhibited the best electrocatalytic activity in oxygen reduction among the three in 0.1 M NaOH. This was accounted for by the low oxide concentration within the nanoparticles and the ready formation of  $\text{Cu}_2\text{O}$  that likely facilitated the further reduction of peroxide into hydroxide.

## 2. Experimental section

### 2.1. Chemicals

Copper acetate ( $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ , 99.9%, Alfa Aesar), 1-decyne (HC10, TCI America), sodium borohydride ( $\text{NaBH}_4$ ,  $\geq 98\%$ , ACROS), and copper oxide nanopowders (CuO, 99%, dia.  $\sim 40$  nm, SkySpring Nanomaterials) were all used as received without any further purification. Solvents were purchased at the highest purity available from typical commercial sources and also used as received. Water was deionized with a Barnstead Nanopure water system (18.3 M $\Omega$  cm).

### 2.2. Synthesis of copper nanoparticles

In a typical synthesis, 0.1 mmol of copper acetate was dissolved in 2 mL of water, into which was added a 10-fold molar excess of 1-decyne dissolved in 10 mL of ethanol and 50 mL of dichloromethane. This solution was kept either in an ice-water bath or at ambient temperature, into which was added dropwise 1 mmol of  $\text{NaBH}_4$  (37.8 mg) dissolved in 2 mL of water under vigorous stirring and  $\text{N}_2$  protection. In both syntheses, the originally blue solutions were found to turn green, light yellow, brown and finally black during the course of  $\text{NaBH}_4$  addition. After three hours of magnetic stirring, the solutions were dried under rotary evaporation and the

solids were washed with methanol five times to remove excessive ligands and reaction byproducts, affording purified 1-decyne-protected copper nanoparticles that were denoted as CuHC10-IB and CuHC10-RT, respectively. The nanoparticles were found to be readily dispersible in apolar solvents such as  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , THF, toluene, etc, but insoluble in polar solvents like alcohols, acetone, and acetonitrile.

### 2.3. Characterizations

The morphology and sizes of the nanoparticles were characterized by transmission electron microscopic studies (TEM, Philips CM300 at 300 kV). UV–vis spectroscopic studies were performed with an ATI Unicam UV4 spectrometer using a 1 cm quartz cuvette at a resolution of 2 nm. Photoluminescence characteristics were examined with a PTI fluorospectrometer. FTIR measurements were carried out with a Perkin–Elmer FTIR spectrometer (Spectrum One, spectral resolution 4  $\text{cm}^{-1}$ ), where the samples were prepared by casting the particle solutions onto a ZnSe disk. The crystalline properties of the nanoparticle catalysts were evaluated by powder X-ray diffraction (XRD) measurements with a Rigaku Mini-flex Powder Diffractometer using  $\text{Cu}-\text{K}\alpha$  radiation with a Ni filter ( $\lambda = 0.154059$  nm at 30 kV and 15 mA). X-ray photoelectron spectra (XPS) were recorded with a PHI 5400/XPS instrument equipped with an Al  $\text{K}\alpha$  source operated at 350 W and  $10^{-9}$  Torr. Silicon wafers were sputtered by argon ions to remove carbon from the background and used as substrates.

### 2.4. Electrochemistry

Electrochemical tests were carried out in a standard three-electrode cell connected to a CHI 710C electrochemical work station, with a Pt foil counter electrode and a saturated calomel electrode (SCE) reference electrode. The working electrode is a rotating platinum ring-glassy carbon disk electrode (RRDE, disk diameter 5.61 mm, from Pine Instrument). To prepare catalyst solutions for oxygen reduction tests, dilute solutions of Cu nanoparticles in toluene were mixed with XC-72 carbon black and a Nafion 117 solution (5 wt.%, Fluka) to form a well-dispersed catalyst “ink” (Pt:carbon black = 1:4 (w/w), Nafion: 0.05%) under ultrasound. A calculated amount of the catalyst ink was slowly dropcast onto the glassy carbon disk electrode of the RRDE, at a metal loading of 15  $\mu\text{g}$  for each nanoparticle catalyst. When the electrode was dried, a dilute Nafion solution (0.1 wt.%, 3  $\mu\text{L}$ ) was added onto the surface. The electrode was then dried in air and immersed into electrolyte solutions for electrochemical tests.

## 3. Results and discussion

Fig. 1 depicts a representative TEM micrograph of the (A) CuHC10-IB and (B) CuHC10-RT nanoparticles. It can be seen that both Cu nanoparticles are roughly spherical and well separated, suggesting successful attachment of the alkyne ligands on the Cu nanoparticle surface forming stable nanoparticles. Additionally, statistical analysis based on more than 100 nanoparticles showed that the average diameter of the nanoparticles synthesized at room temperature (CuHC10-RT) was  $4.28 \pm 0.46$  nm, whereas for the nanoparticles prepared at a lower temperature (CuHC10-IB), the size was somewhat larger at  $6.29 \pm 0.99$  nm, as manifested in the respective figure insets. Note that for organically capped metal nanoparticles, the size of the nanoparticles is largely determined by two competing processes, nucleation of metal atoms to form the nanoparticle cores and passivation of the metal cores by organic capping ligands that impedes the core growth [27]. For mercapto-stabilized gold nanoparticles, typically the lower the reaction

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