The most active Cu facet for low-temperature water gas shift reaction

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Identification of the active site is important in developing rational design strategies for solid catalysts but is seriously blocked by their structural complexity. Here, we use uniform Cu nanocrystals synthesized by a morphology-preserved reduction of corresponding uniform Cu\textsubscript{2}O nanocrystals in order to identify the most active Cu facet for low-temperature water gas shift (WGS) reaction. Cu cubes enclosed with \{100\} facets are very active in catalyzing the WGS reaction up to 548 K while Cu octahedra enclosed with \{111\} facets are inactive. The Cu–Cu suboxide (Cu\textsubscript{x}O, \(x \geq 10\)) interface of Cu(100) surface is the active site on which all elementary surface reactions within the catalytic cycle proceed smoothly. However, the formate intermediate was found stable at the Cu–Cu\textsubscript{x}O interface of Cu(111) surface with consequent accumulation and poisoning of the surface at low temperatures. Thereafter, Cu cubes-supported ZnO catalysts are successfully developed with extremely high activity in low-temperature WGS reaction.
Catalyst nanoparticles (NPs) generally expose a variety of surface sites (e.g., facets, steps, and corners), each with their distinct reactivity. Such structural complexity seriously impairs efforts to identify their active site for developing rational design strategies in heterogeneous catalysis. The complexity of catalyst NPs has been traditionally simplified by the use of single crystals with well-defined surface structures as model catalysts. Recently uniform catalyst nanocrystals (NCs) with tunable structures have demonstrated great potential in heterogeneous catalysis either as a novel type of model catalysts that can be studied under the same conditions as powder catalysts or as excellent candidates as efficient catalysts. However, capping ligands on catalyst NCs inherited from the wet chemistry synthesis strongly affect their applications in heterogeneous catalysis, particularly in gas-solid heterogeneous catalytic reactions.

The water gas shift (WGS) reaction is commonly used in the chemical industry for the production of clean H₂. It is mildly exothermic and thermodynamically favors low reaction temperatures. Cu-based catalysts are currently used industrially for low-temperature WGS reaction. Thus it is of great importance to fundamentally understand the structure-activity relation of Cu-based catalysts for optimizing the catalyst structure. The WGS reaction were studied over Cu (100), (110), and (111) single-crystal surfaces, and the results demonstrated its structure-sensitivity.

**Fig. 1** Structural characterizations. The scale bars of a–c and (g1–i1) correspond to 1000 nm, that of (g2–i2) correspond to 500 nm, and that of (g3–h3) correspond to 2 nm. Representative SEM images of a Cu₂O cubes, b Cu₂O octahedral, and c Cu₂O rhombic dodecahedra. d XRD patterns, e Cu LMM AES spectra measured without exposure to air, and f in situ DRIFTS spectra of CO adsorption at 123 K of Cu₂O cubes (a1), octahedra (b1), rhombic dodecahedra (c1) and Cu cubes (a2), octahedra (b2) and rhombic dodecahedra (c2). Representative SEM, TEM and HRTEM images of (g1–g3) Cu cubes, (h1–h3) Cu octahedra and (i1–i3) Cu rhombic dodecahedra. The insets in the HRTEM images show the ED patterns of corresponding Cu nanocrystals. The lattice fringes of 1.80 and 2.08 Å, respectively, correspond to the spacing of Cu(200) and (111) crystal planes (JCPDS card NO. 89-2838).
Here, we report the identification of the most active Cu facet for low-temperature WGS reaction up to 548 K employing uniform capping ligands-free Cu NCs synthesized by a morphology-preserved reduction of corresponding uniform Cu$_2$O NCs. Cubic Cu NCs enclosed with [100] facets are more catalytically active than dodecahedral Cu NCs enclosed with [110] facets while octahedral Cu NCs enclosed with [111] facets are inactive. The Cu–Cu suboxide (Cu$_x$O, $x \geq 10$) interface of Cu (100) surface is the active site on which all elementary surface reactions within the catalytic cycle proceed smoothly, but the Cu–Cu$_2$O interface of Cu(111) surface is poisoned by an accumulation of formate intermediate stable at low reaction temperatures. Thereafter, we successfully developed Cu cubes-supported ZnO catalysts with extremely high activity in low-temperature WGS reaction.

Results

Synthesis and structures of Cu NCs. A morphology-preserved reduction strategy was firstly developed to synthesize uniform Cu NCs from corresponding Cu$_2$O NCs. Uniform capping ligands-free Cu$_2$O cubes (denoted as c-Cu$_2$O), octahedra (denoted as o-Cu$_2$O) and rhombic dodecahedra (denoted as d-Cu$_2$O) respectively were enclosed with [100], [111] and [110] facets were synthesized following our previously established procedures$^{12}$. Their structures were confirmed by both microscopic and spectroscopic characterizations (Fig. 1a–f, Supplementary Figs. 1 and 2). The size distribution of c-Cu$_2$O, o-Cu$_2$O, and d-Cu$_2$O is 1000 ± 150, 1056 ± 207, and 595 ± 113 nm, respectively (Supplementary Fig. 3). Accordingly, the CO-temperature programmed reduction (CO-TPR) spectra (Supplementary Fig. 4), a reduction process in 5% CO/Ar at 548 K for 2 h was chosen to reduce Cu$_2$O NCs. After CO reduction, the XRD patterns change from those of starting Cu$_2$O (JCPDS card NO. 78-2076) completely into those of metallic Cu (JCPDS card NO. 89-2838) (Fig. 1d) while the scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM) images (Fig. 1g–i) show a well preservation of the morphologies of starting Cu$_2$O NCs. The electron diffraction (ED) patterns confirm that all acquired Cu NCs are single crystals. Thus, uniform Cu$_2$O cubes, octahedra, and rhombic dodecahedra can be reduced respectively into uniform Cu cubes (denoted as c-Cu), octahedra (denoted as o-Cu), and rhombic dodecahedra (denoted as d-Cu). Such a morphology-preserved reduction of Cu$_2$O NCs into Cu NCs can be attributed to the cubic phase structures of both Cu$_2$O and Cu, the not too large difference between the lattice constants of Cu$_2$O ($a = 426.7$ pm) and Cu ($a = 361.5$ pm), the large sizes of Cu$_2$O NCs, and the low reduction temperature. However, the acquired Cu NCs exhibit rough surfaces likely resulting from the lattice mismatch between Cu$_2$O and Cu. The acquired Cu NCs are finer than the corresponding Cu$_2$O NCs, and the size distribution of c-Cu, o-Cu, and d-Cu is 877 ± 157, 937 ± 216, and 497 ± 137 nm, respectively (Supplementary Fig. 3). Consequently, c-Cu, o-Cu, and d-Cu exhibit larger specific BET surface areas, respectively, of 1.17, 2.35, and 3.33 m$^2$ g$^{-1}$ than the corresponding c-Cu$_2$O, o-Cu$_2$O, and d-Cu$_2$O, respectively, of 0.67, 1.58, and 1.98 m$^2$ g$^{-1}$. Although with a larger average edge length, the o-Cu$_2$O and o-Cu NCs exhibit larger specific BET surface areas, respectively, than the c-Cu$_2$O and c-Cu NCs due to the morphology and facet effects. The surface area-to-volume ratio of an octahedron and a cube can be geometrically calculated, respectively, as $3\sqrt{3}/L$ and $6/L$ ($L$ being the edge length); meanwhile, the surface atom density of the [100] facets exposed on octahedral NCs is higher than that of the [100] facets exposed on cubic NCs for Cu$_2$O and Cu with cubic phases.

The acquired Cu NCs were characterized by x-ray photoelectron spectroscopy (XPS) without exposure to air. The Cu LMM Auger electron spectra (AES) (Fig. 1e) and Cu 2p XPS spectra (Supplementary Fig. 5) demonstrate dominance of metallic Cu on surfaces of all acquired Cu NCs; however, the Cu(I) feature is still visible. In the corresponding O 1 s and C 1 s XPS spectra (Supplementary Fig. 5), all Cu NCs exhibit three O 1 s components at 529.5, 530.3, and 531.8 eV and three C 1 s components at 284.8, 289.0, and 287.7 eV while o-Cu NCs exhibit an additional minor C 1 s component at 286.6 eV. The O 1 s components at 529.5 and 531.8 eV could be respectively assigned to oxygen adatoms and hydroxyl groups/oxygenates species while the O 1 s component at 530.3 eV was observed to vary simultaneously with the Cu(I) feature for all acquired Cu NCs and, thus, could be assigned to Cu suboxide (Cu$_x$O, $x \geq 10$)$^{13,14}$. The C 1 s components at 284.8, 289.0, 287.7, and 286.6 eV could be assigned respectively to adventitious carbon, carbonate, carboxylate and formate species$^{15}$. In situ diffuse reflectance infrared Fourier transformed spectra (DRIFTS) of the reduction processes of Cu$_2$O NCs into Cu NCs (Supplementary Fig. 6) show significant attenuations of Cu$_2$O vibrational features ($652, 794, and 1123$ cm$^{-1}$)$^{16}$ and formations of carboxylate ($1277$ cm$^{-1}$) and carbonate ($1235, 1455$ and $1506$ cm$^{-1}$) species on all Cu NCs and
formate species (1588 cm\(^{-1}\))\(^{17, 18}\) exclusively on o-Cu NCs, in consistence with the above XPS results. All these observed surface species on acquired Cu NCs are common on metal powder catalysts.

Figure 1f compares in situ DRIFTS spectra of CO adsorption on Cu \(2O\) and Cu NCs at 123 K. Agreeing with previous reports\(^{12, 19–21}\), a vibrational band at \(\sim 2108\) cm\(^{-1}\) was observed on o-Cu\(_{2}O\) and d-Cu\(_{2}O\) and assigned to CO-adsorbed at the Cu(I) sites exposed on \{111\} and \{110\} facets while no feature was observed on c-Cu\(_{2}O\) enclosed with O-terminated Cu\(_{2}O\) (100) facets. Additional vibrational bands at \(\sim 2193\) and 2225 cm\(^{-1}\) were observed on o-Cu\(_{2}O\) and assigned to CO \(2\) adsorbed at the coordination-unsaturated Cu(I) sites of \{111\} facets formed by the reaction of CO with adsorbed oxygen species\(^{12, 19}\). Vibrational bands of CO adsorbed on Cu NCs are diffuse and weak, and depend on their morphologies. It is located at 2080 cm\(^{-1}\) on c-Cu, 2073 cm\(^{-1}\) on o-Cu, and 2093 cm\(^{-1}\) on d-Cu that respectively correspond well to that of CO adsorbed on Cu (100), (111), and (110) single-crystal surfaces\(^{22–25}\). No feature of CO adsorbed at the Cu(I) site could be observed for all Cu NCs, indicating that CuxO on Cu NCs is O-terminated. Absence of vibrational features above 2100 cm\(^{-1}\) corresponding to CO adsorbed at stepped sites and defects on Cu surfaces\(^{26}\) suggests low densities of stepped sites and defects on the surfaces of all acquired Cu NCs. These CO adsorption results demonstrate that although with rough surfaces, uniform c-Cu, o-Cu, and d-Cu NCs dominantly expose \{100\}, \{111\}, and \{110\} terrace Cu sites on the surfaces, respectively. Therefore, the above comprehensive characterization results demonstrate a successful synthesis of uniform c-Cu, o-Cu, and d-Cu NCs respectively with well-defined \{100\}, \{111\}, and \{110\} surfaces via a morphology-preserved reduction of corresponding c-Cu\(_{2}O\), o-Cu\(_{2}O\), and d-Cu\(_{2}O\) NCs.

Effect of Cu facet on activity. Various types of Cu NCs exhibit morphology-dependent catalytic activity in the WGS reaction. CO conversion over the c-Cu and d-Cu NCs was observed, respectively, at 473 and 498 K but not for the o-Cu NCs up to 548 K (Supplementary Fig. 7). Catalytic activity of commercial Cu/ZnO/Al\(_2\)O\(_3\) catalyst in the WGS reaction was also evaluated (Supplementary Fig. 8). On the basis of surface Cu atoms derived from the specific surface areas of c-Cu and d-Cu NCs and the Cu atom densities of Cu (100) and (110) surfaces, the calculated surface Cu atom-specific reaction rates of c-Cu NCs are much higher than those of d-Cu NCs (Fig. 2a). The c-Cu and d-Cu NCs are also catalytically stable at 548 K (Fig. 2b and Supplementary Fig. 7). SEM images (Supplementary Fig. 9) demonstrate that the Cu NCs preserve their morphologies after the activity evaluation.
that Cu₂O NCs undergo an in situ morphology-preserved in situ restructuring of Cu₂O NCs into Cu NCs to 673 K. We found that, when directly used as catalysts for WGS reaction, various types of Cu₂O NCs exhibited the steady-state catalytic activity and calculated apparent activation energy almost identical to those of corresponding Cu NCs (Supplementary Fig. 11). Structural characterization results (Supplementary Figs. 12–14) demonstrate that Cu₂O NCs undergo an in situ morphology-preserved reduction into corresponding Cu NCs with the presence of both Cu(0) and Cu(I) on their surfaces during WGS reaction up to 548 K. These results demonstrate that Cu NCs with co-existing Cu(0) and Cu(I) species on the surfaces are active in catalyzing low-temperature WGS reaction and further support that the Cu{100} facet is the most active facet.

**Reaction mechanism.** Figure 3a presents temperature-programmed reaction spectra of WGS reaction over Cu NCs. The CO₂ production was observed to occur prior to the H₂ production, suggesting the H₂ production as the rate-limiting step in the Cu-catalyzed WGS reaction. Both CO₂ and H₂ productions proceed most facilely over c-Cu, in consistence with its highest catalytic activity. o-Cu exhibits a higher initial CO₂ production than d-Cu, but a much more difficult H₂ production. With the WGS reaction proceeding at 548 K, c-Cu and d-Cu capable of catalyzing both CO₂ and H₂ productions exhibit stable activity, respectively, while o-Cu capable of catalyzing the CO₂ production but few H₂ production gets gradually poisoned. These observations suggest that the inactivity of o-Cu in WGS reaction up to 548 K should result from self-poisoning due to the formation and accumulation of stable hydrogen-containing intermediates on the surface.

Various used Cu NCs catalysts after WGS reaction at 548 K were characterized by XPS without exposure to air. As shown in the C 1s XPS spectra (Supplementary Fig. 10), the C 1s component of adventitious carbon (284.8 eV), carboxylate (287.7 eV), and carbonate (289.0 eV), the C 1s component of formate species (286.6 eV) absent on the fresh c-Cu and d-Cu catalysts appears on the used c-Cu and d-Cu catalysts after the WGS reaction and its intensity greatly increases on the used o-Cu catalyst as compared to that on the fresh o-Cu catalyst. In the corresponding Cu LMM AES spectra, Cu 2p, and O 1s XPS spectra (Supplementary Fig. 15), no Cu(II) XPS feature appears on all used Cu catalysts and the Cu LMM AES spectra and O 1s XPS spectra of the used o-Cu catalyst change very slightly, but the metallic Cu LMM AES component increases at the expense of the Cu(I) LMM AES component on the used c-Cu and d-Cu catalysts, and accordingly, the O 1s components of oxygen adatoms (529.5 eV) and hydroxyl groups/oxygenates species (531.8 eV) increase at the expense of the O 1s component of the Cu₂O species (530.3 eV). Thus, during the WGS reaction up to 548 K, the copper speciation does not vary much on the inactive o-Cu catalyst surface but an accumulation of formate species obviously occurs, and the transformation of Cu₂O species

**Fig. 4** Water activation. a Cu LMM AES and b O 1s XPS spectra of various Cu NCs (black lines), Cu NCs exposed to H₂O at 423 K (red lines), Cu NCs exposed to H₂O at 523 K (blue lines) and Cu NCs exposed to H₂O at 523 K and then to CO at 473 K (brown lines). All spectra were measured without exposure to air.
into the Cu(0) and oxygen adatoms, together with the formation of hydroxyl groups and oxygenates species (including the formate species), occurs on the active c-Cu and d-Cu surfaces.

The surface species on various used Cu NCs catalysts after WGS reaction at 548 K were further probed by temperature-programmed desorption spectra (TDS) in Ar and in situ DRIFTS spectra. In the TDS spectra in Ar (Fig. 3c), the used c-Cu and d-Cu catalysts exhibit a weak and broad CO2 desorption peak at 560 K and a strong H2O desorption peak at 610 K while the used o-Cu catalyst exhibits strong CO2 and H2O desorption peaks simultaneously at 540 K and H2, and H2O desorption peaks simultaneously at 640 K. In the corresponding in situ DRIFTS spectra (Fig. 3d), the used c-Cu and d-Cu catalysts exhibit weak attenuation of vibrational peaks of carboxylate (1272–1291 cm−1), carbonate (1255 and 1402–1429 cm−1), formate (1363, 1588, 2856, and 2922 cm−1), and hydroxyl (1708 and 3400 cm−1) species17, 18 while the used o-Cu catalyst exhibits strong loss of vibrational peaks of formate and hydroxyl species and weak attenuation of vibrational peaks of carbonate and carboxylate species. Therefore, upon heating, the reactions of carboxylate/carbonate and formate species on the used c-Cu and d-Cu catalysts produce minor CO2 at 560 K and the hydrogen groups react each other to predominantly produce water at 610 K while the reaction between co-adsorbed formate species and hydroxyl group on the used o-Cu catalyst produce much CO2 and H2O at 540 K29 and the hydroxyl groups react each other to simultaneously produce H2 and H2O desorption peaks at 640 K.

The above comprehensive characterization results demonstrate accumulations of formate and hydroxyl intermediates during the WGS reaction up to 548 K on the o-Cu surface but not on the c-Cu and d-Cu surfaces that should lead to the self-poisoning and subsequent inactivity of o-Cu NCs. It is noteworthy that the surface reaction between co-adsorbed formate and hydroxyl to produce CO2 and H2O at 540 K observed on the used o-Cu catalyst should be thermodynamically quenched during WGS reaction with H2O as a reactant. Meanwhile, the accumulation of formate and hydroxyl intermediates on the o-Cu surface could be alleviated at higher reaction temperatures, as the o-Cu NCs are active in catalyzing the WGS reaction at 623 K and above.

Activation of H2O on various Cu NCs, a key step in WGS reaction, was studied by XPS without exposure to air (Fig. 4, Supplementary Figs. 16, 17, and Supplementary Table 1). H2O dissociation was observed to occur on the c-Cu and d-Cu surfaces at 423 K but barely on the o-Cu surface, resulting in the growth of both hydroxyl group and oxygen adatoms at the expense of CuO. This suggests the Cu–CuO interface as the active site for the H2O dissociation into the hydroxyl group accompanied by the decomposition of CuO into oxygen adatoms. In the corresponding Cu LMM AES spectra, the decomposition of CuO on the c-Cu and d-Cu surfaces at 423 K is also evidenced by the growth of Cu(0) at the expense of Cu(I), and this process is more extensive on the c-Cu surface than on the d-Cu surface. H2O dissociates on all Cu NCs at 523 K, leading to the growth of oxygen adatoms and CuO at the expense of hydroxyl group, indicating the decomposition of hydroxyl group into oxygen adatom that can further transform into CuO.

The Cu NCs subjected to H2O dissociation at 523 K were then exposed to CO at 473 K. Both Cu LMM AES spectra and O 1s XPS spectra (Fig. 4, Supplementary Fig. 17 and Supplementary Table 1) demonstrate a reaction of CuO with CO on the c-Cu surface, but not on the d-Cu and o-Cu surfaces. Thus CuO on the Cu surface is an active oxygen species for the CO2 production during WGS reaction while the co-existing oxygen adatoms serve as an oxygen reservoir for the formation and decomposition of CuO. Since CO adsorbs on the metallic Cu surface instead of the CuO surface (Fig. 1f), the reaction of CuO with CO on the c-Cu surface should proceed at the CuO–CuO interface. The reactivity of CuO at the CuO–CuO interface toward CO is higher on the c-Cu surface than on the d-Cu and o-Cu surfaces.

Therefore, the Cu–CuO interface on the Cu surface capable of both dissociating water and reacting with CO should be the active site to catalyze the WGS reaction. The Cu–CuO interface on the c-Cu surface is more active in both water dissociation and CO2 production than that on the d-Cu and o-Cu surfaces, consequently, the c-Cu NCs is more catalytic active in the WGS reaction than the d-Cu and o-Cu Cu NCs.

The mechanisms of morphology-dependent catalytic performance of Cu NCs in WGS reaction were further explored by DFT calculations employing Cu(100) and Cu(111) surfaces with Cu2O islands to respectively model the c-Cu and o-Cu surfaces with CuO (Fig. 5a, b). According to previous results30–33, ring-like structures were adopted for Cu2O islands on both Cu(100) and Cu(111) surfaces. This gives a zig-zag chain structure of Cu2O at the Cu–Cu2O interface that was used during simulations of reactions at the Cu–Cu2O interface. In consistence with previous reports34, 35, the dissociation of water on Cu(100) and Cu(111) into OH group and H adatom needs to overcome barriers respectively of 1.68 and 1.70 eV (Fig. 5c, Supplementary Figs. 18, 19 and Supplementary Table 2); however, the dissociation of water at the Cu–Cu2O interface on Cu(100) and Cu(111) into a OH group on Cu surface (OHCu) and a H adatom at the O of Cu2O (O(O2Cu2H)) proceeds facilely with barriers respectively of 0.40 and 0.58 eV, and the H of O(O2Cu2H) can migrate to the neighboring Cu atom to form a H adatom on the Cu surface (O(O2Cu2H → O(O2Cu2 + HCu)) with activation energies of 1.09 and 0.98 eV at the Cu–Cu2O interface respectively on Cu(100) and Cu(111) surfaces. Thus the water activation is much more facile at the Cu2O–Cu surface than at the Cu surface, and the water dissociation at the Cu–Cu2O interface into OHCu and O(O2Cu2H) should proceed more facilely.
Fig. 6 Calculated energy diagram of WGS reaction. a The reaction for CO at the Cu site (COCu) and O of CuO at CuO–Cu(111) (black line) and CuO–Cu(100) (red line) interfaces. Ov represents an oxygen vacancy in CuO. b The reaction for COCu and OOH at the CuO–Cu(111) (black line) and CuO–Cu(100) (red line) interfaces; the subsequent elementary reactions following the formation of CO2(g) + Ov + OHCu + HCu are identical to those in a. d The elementary reaction between CO2,ad and HCu to form HCOO,ad at the Cu2O–Cu(111) and Cu2O–Cu(100) interfaces.

The c-Cu catalyst is active in catalyzing the low-temperature WGS reaction up to 548 K while the o-Cu catalyst is inactive and with accumulated formate species on the surface (Figs. 2 and 3).

Therefore, our comprehensive experimental and theoretical calculation results clearly demonstrate a facet-dependent catalytic performance of Cu catalysts in low-temperature WGS reaction in which Cu{100} is the most active facet with the Cu–Cu suboxide interface as the active site. Interestingly, such a facet-dependent catalytic performance results mainly from a facet-dependent surface poisoning of the active site instead of from a facet-dependent intrinsic activity. All elementary surface reactions within the catalytic cycle can proceed smoothly at the Cu–CuO interface of active Cu{100} facets during low-temperature WGS reaction; however, the Cu–CuO interface of Cu{111} facets initially is also active, but will be soon self-poisoned by the accumulation of stable formate intermediate. These results nicely demonstrate a key feature of an active site of solid catalysts that an active site must be able to recycle during catalytic reactions.

Design and realization of highly efficient ZnO/c-Cu catalyst. The WGS reaction is mildly exothermic and thermodynamically favors low reaction temperatures. The above fundamental understandings of facet-dependent catalytic performance of Cu catalysts reveal a strategy of designing efficient copper-based catalysts for low-temperature WGS reaction using c-Cu NCS. Cu–ZnO-based catalysts are commercial catalysts for WGS reaction. A c-Cu2O NCS-supported ZnO catalyst with a ZnO weight ratio of 1% (1%wt-ZnO/c-Cu2O) was thus synthesized and then reduced to acquire a c-Cu NCs-supported ZnO catalyst with a ZnO weight ratio of 1.67% (1.67%wt-ZnO/c-Cu2O) (Fig. 7a–d and Supplementary Fig. 24). Similarly, an o-Cu2O NCS-supported ZnO catalyst (1%wt-ZnO/o-Cu2O) was also synthesized and then reduced to acquire an o-Cu NCS-supported ZnO catalyst.
1.67% wt-ZnO/c-Cu catalyst in the WGS reaction as a function of reaction temperature and corresponds to the spacing of Cu{200} (JCPDS card NO. 89-2838) and hexagonal ZnO{101} (JCPDS card NO. 89-1397) crystal planes. The data of c-Cu NCs are included for comparisons. The data of c-Cu NCs are included for comparisons. The lattice fringes of 1.80 and 2.50 Å, respectively, was evaluated between 573 and 673 K, for which the Cu{111} surface might restructure. Meanwhile, no Cu(0) or Cu(I) exist on the surface of Cu NCs catalysts. The ZnO/c-Cu catalyst exhibits a similar apparent activation energy to the commercial Cu/ZnO/Al2O3 catalyst but much lower than that of ZnO/c-Cu catalyst. Therefore, the ZnO/c-Cu catalyst is stable (Supplementary Fig. 26).

The apparent activation energy of ZnO/c-Cu catalyst is smaller than that of commercial Cu/ZnO/Al2O3 catalyst, Cu/ZnO(0001) (52 kJ mol⁻¹)⁵, and ZnO/Cu (46 kJ mol⁻¹)⁶ model catalysts, and is similar to those acquired on CeOx/Cu(111) (30 kJ mol⁻¹)⁷ and Cu/CoO2(111) (37 kJ mol⁻¹)¹¹ model catalysts. It is noteworthy that the activity of CeOx/Cu(111) model catalyst was evaluated between 573 and 673 K, under which the Cu(111) surface might restructure. Meanwhile, no Cu–CeO2 and Cu–ZnO powder catalysts were reported to exhibit E_a in WGS reaction as low as the CeOx/Cu(111) and Cu/CoO2(111) model catalysts, suggesting the presence of so-called materials gap. The ZnO/o-Cu catalyst exhibits a similar apparent activation energy to the commercial Cu/ZnO/Al2O3 catalyst but much larger than that of ZnO/c-Cu catalyst. Therefore, the active structure of ZnO/c-Cu catalyst should be intrinsically more active than that of ZnO/o-Cu and commercial Cu/ZnO/Al2O3 catalysts. This demonstrates a key role of the Cu structure in the Cu–ZnO-based catalysts in determining the catalytic activity in WGS reaction, in which the ZnO/c-Cu catalyst with the Cu(100) structures is highly efficient. Meanwhile, it could also be inferred that the copper structure of commercial Cu/ZnO/Al2O3 catalyst should be dominated by the Cu{111} structures and its catalytic activity can be improved by engineering the Cu structure from the dominant Cu{111} structure into the Cu{100} structure. These findings demonstrate a successful experimental strategy of using catalyst NCs that realizes an all-chain investigation of heterogeneous catalysis from the fundamental understanding of active site and reaction mechanism to the structural design and realization of highly efficient catalysts.

**Methods**

**Materials.** All chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification. Commercial Cu/ZnO/Al2O3 WGS catalyst was purchased from Alfa Aesar Chemical Co. Ltd. 5% CO/Ar, 0.432% CO/Ar, 99.999%), CO (99.999%), CuCl2 (99.95%), CuCl (99.99%), and H2 (99.999%) were purchased from Nanjing Shangyuan Industrial Factory and used without further purification. Ultrapure water (>18.5 MΩ) was used.

**Synthesis.** Synthesis of cubic and octahedral Cu2O NCs followed the procedure reported by Zhang et al.³⁸. Typically, NaOH aqueous solution (2.0 mol L⁻¹; 10 mL) was added dropwise into CuCl2 aqueous solution (0.01 mol L⁻¹; 100 mL) at 328 K (c-Cu2O without polyvinylpyrrolidone (PVP), o-Cu2O containing 4.44 g PVP (Mw = 30 000)). After stirring for 0.5 h, ascorbic acid solution (0.6 mol L⁻¹; 10 mL) was added dropwise. The resulting solution was stirred at 328 K for 5 h and 3 h to synthesize cubic and octahedral Cu2O NCs, respectively. The resulting precipitate was collected by centrifugation, decanted by repeated washing with distilled water and absolute ethanol, and finally dried under vacuum at RT for 12 h. Synthesis of rhombohedral Cu2O NCs followed the procedure by Liang et al. Thirty, 4 mL oleic acid (OA) and 20 mL absolute ethanol were added successively into 40 mL CuSO4 aqueous solution (0.025 mol L⁻¹) under vigorous stirring. The solution was heated to 373 K and then 10 mL NaOH aqueous solution (0.8 mol L⁻¹) was added. After stirring for 5 min, 30 mL n-(-)+glucose aqueous solution (0.63 mol L⁻¹) was added. The resulting mixture was stirred at 373 K for additional 1 h and gradually turned into a brick-red color. The resulting precipitate was collected by centrifugation, decanted by repeated washing with distilled water and absolute ethanol, and finally dried in vacuum at room temperature (RT) for 12 h. The acquired cubic, octahedral, and rhombohedral Cu2O NCs were denoted as c-Cu2O, o-Cu2O-PVP, and d-Cu2O-OA, respectively.

Capping ligands on as-synthesized o-Cu2O-PVP and d-Cu2O-OA NCs were removed following a controlled oxidation procedure developed by Hua et al.¹².
Typically, Cu2O NCs (0.2 g) were placed in a U-shaped quartz microreactor and purged in the stream of C2H4 + O2 + N2 gas mixture (C2H4\textsubscript{2}O\textsubscript{2}N\textsubscript{2} = 2:1:2, flow rate: 50 mL min\textsuperscript{-1}) at room temperature for 0.5 h, and then heated to the desirable temperature (o-Cu2O-PVP: 473 K; d-Cu2O-OA: 488 K) at a rate of 5 K min\textsuperscript{-1} and kept for 0.5 h, then the stream was switched to pure Ar (flow rate: 30 mL min\textsuperscript{-1}) in which the sample was cooled down to room temperature. The acquired octahedral and rhombic dodecahedral Cu NCs without capping ligands were denoted as o-Cu2O and d-Cu2O, respectively.

Cu NCs with various morphologies were synthesized via a morphology-preserved reduction method. Cu2O NCs (0.1 g) were placed in a quartz microreactor and purged in the stream of 5% CO balanced with Ar (flow rate: 30 mL min\textsuperscript{-1}) at room temperature for 0.5 h, and then heated to 548 K at a rate of 1 K min\textsuperscript{-1} and kept for 2 h, then cooled down to room temperature. The acquired cubic, octahedral and rhombic dodecahedral Cu NCs were denoted as c-Cu, o-Cu, and d-Cu, respectively.

Cu2O NCs-supported ZnO catalysts (ZnO/Cu2O) were synthesized by incipient wetness impregnation method. Typically, Cu2O NCs (0.2 g) were adequately impregnated with 200 μL aqueous solution containing calculated amounts of zinc nitrate (Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O), and the resulting mixture was dried under vacuum at room temperature overnight and then heated at 623 K for 2 h in high-pure Ar with a flow of 30 mL min\textsuperscript{-1} to 423 K at a rate of 1 K min\textsuperscript{-1} and kept for 2 h to prepare corresponding ZnO/Cu catalysts that were stored in vacuum oven.

Details on structural characterizations, catalytic activity evaluation, and DFT calculations can be found in the Supplementary Methods.

Data availability. All data are available from the authors on reasonable request.

Received: 21 January 2017 Accepted: 13 July 2017
Published online: 08 September 2017

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Acknowledgements

This work was financially supported by National Basic Research Program of Ministry of Science and Technology of China (2013CB933104, 2013CB834603), National Natural Science Foundation of China (21525313, 21173204, U1332131, 91465202), Fundamental Research Funds for the Central Universities of Ministry of Education of China (WK2060030017), Hefei Science Center of Chinese Academy of Sciences.
Author contributions
W.H. designed and supervised the project. W.-X.L. supervised the DFT calculations. Z.Z. carried out all experiments. S.-S.W. carried out all DFT calculations. R.S., T.C., L.L., Y.G., X.C., and J.L. assisted with the experiments. W.H. and Z.Z. analyzed all the results. S.-S.W. and W.-X.L. analyzed the DFT calculation results. W.H., Z.Z., S.-S.W. and W.-X.L. prepared the manuscript and other authors commented on the manuscript.

Additional information
Supplementary Information accompanies this paper at doi:10.1038/s41467-017-00620-6.

Competing interests: The authors declare no competing financial interests.

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