Integrated Experimental and Theoretical Study of Shape-Controlled Catalytic Oxidative Coupling of Aromatic Amines over CuO Nanostructures

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Supporting Information

ABSTRACT: We have synthesized CuO nanostructures with flake, dandelion-microsphere, and short-ribbon shapes using solution-phase methods and have evaluated their structure–performance relationship in the heterogeneous catalysis of liquid-phase oxidative coupling reactions. The formation of nanostructures and the morphological evolution were confirmed by transmission electron microscopy, scanning electron microscopy, X-ray diffraction analysis, X-ray photoelectron spectroscopy, Raman spectroscopy, energy-dispersive X-ray spectroscopy, elemental mapping analysis, and Fourier transform infrared spectroscopy. CuO nanostructures with different morphologies were tested for the catalytic oxidative coupling of aromatic amines to imines under solvent-free conditions. We found that the flake-shaped CuO nanostructures exhibited superior catalytic efficiency compared to that of the dandelion- and short-ribbon-shaped CuO nanostructures. We also performed extensive density functional theory (DFT) calculations to gain atomic-level insight into the intriguing reactivity trends observed for the different CuO nanostructures. Our DFT calculations provided for the first time a detailed and comprehensive view of the oxidative coupling reaction of benzylamine over CuO, which yields N-benzylidene-1-phenylmethanamine as the major product. CuO(111) is identified as the reactive surface; the specific arrangement of coordinatively unsaturated Cu and O sites on the most stable CuO(111) surface allows N−H and C−H bond-activation reactions to proceed with low-energy barriers. The high catalytic activity of the flake-shaped CuO nanostructure can be attributed to the greatest exposure of the active CuO(111) facets. Our finding sheds light on the prospective utility of inexpensive CuO nanostructured catalysts with different morphologies in performing solvent-free oxidative coupling of aromatic amines to obtain biologically and pharmaceutically important imine derivatives with high selectivity.

1. INTRODUCTION

Incredible change in electronic structure arises when nanostructured metal oxides are formed, as a result of alteration in bond percolation networks, coordination modes, electron–lattice coupling, and atomic arrangement on surfaces, giving rise to chemical and physical properties distinctly different from their bulk properties. Various nanostructured materials even on atomic or molecular scales have been designed and developed for a variety of catalytic applications to deliver fine organic chemicals with high atomic efficiency and diminished formation of unwanted by-products.1−3 In recent years, morphology-dependent nanocatalysis has attracted increasing attention in the areas of surface science and catalysis, because the chemical reactivity and selectivity of a catalytic reaction can be controlled effectively by changing the shape and interface of solid nanostructured catalysts.4−6 According to Xia et al.,6 shape control of nanocatalysts helps to optimize the catalytic applicability and reduce the cost of materials. Examples include the morphology-dependent catalytic activity of spinel LiMn1.3Ni0.7O4 for the oxygen evolution reaction (OER)
investigated by Manthiram et al., who showed that the OER activity increased in the order truncated octahedral < cubic < spherical < octahedral. Different morphologies of CuO nanocrystals also exhibited different catalytic activities in the oxidative decomposition of formaldehyde, which decreased in the order nanobelts > nanoplates > nanosheets. Outstanding electrochemical performance with high lithium storage capacity was found by Wang and co-workers for single crystalline CuO having a nanoplatelet morphology, and a superior catalytic performance of octahedral \( \varepsilon \)-CuO compared to that of cubic \( \varepsilon \)-CuO was also observed in CO oxidation.

There are two possible reasons underlying the different catalytic activities of different morphologies. First, different morphologies could expose different reactive crystal facets (with high density of atomic steps, edges, kinks, and dangling bonds), resulting in different modes and strengths of interactions between organic molecules and crystal surfaces. For example, Pt cubic nanoparticles that mainly exposed the (100) facet showed better catalytic performance in catalytic hydrogenation of benzene compared to that of Pt cuboctahedral nanoparticles that expose the (100) and (111) facets. The catalytic activity of different crystal planes of \( \text{Cu}_2\text{O} \) nanocrystals changed significantly and decreased in the order \([112] \gg [011] \gg [001]\) in methane combustion. Hua et al. showed that different morphologies of \( \text{Cu}_2\text{O} \) gave very different selectivity in propylene oxidation because of differently exposed active facets. In that study, the octahedral morphology of \( \text{Cu}_2\text{O} \) exposing (111) facets was the most selective in the formation of acrolein, \( \text{Cu}_2\text{O} \) cubes with exposed (100) facets were the most active for complete oxidation to \( \text{CO}_2 \), and \( \text{Cu}_2\text{O} \) rhombic dodecahedra with exposed (110) facets gave the highest selectivity for propylene oxide instead. Similarly, Vilé et al. showed that \( \text{Cu}_2\text{O} \) nanocubes with exposed (100) facets and conventional polyhedral \( \text{Ce}_2\text{O}_3 \) with (111) crystal surfaces were active in CO oxidation and \( \text{C}_2\text{H}_2 \) hydrogenation, respectively.

Varghese et al. theoretically evaluated the catalytic activity of the experimentally observed \( \text{CuO}(111), \text{CuO}(110), \text{CuO}(011), \text{CuO}(001) \), and \( \text{CuO}(010) \) facets in activating the C–H bond of methane, revealing that the energy barriers for C–H activation on these facets differ significantly and that the synergistic effect of adjacent unsaturated Cu and O atoms on the surface constitutes a main reason for the significantly reduced activation barrier. Quasicubic \( \text{Fe}_2\text{O}_3 \) nanoparticles exhibited enhanced catalytic CO oxidation activity compared to that of flower-like nanoparticles featuring exclusive exposure of the (110) crystalline planes, and strong facet-dependence of propane hydrogenation activity over ceria catalysts was also reported.

The second factor that contributes to the different activities of different morphologies is the extent to which an active facet is exposed, and this is important especially when the active facet is known. The catalytic activity decreased in the order nanobelts > nanoplates > nanosheets in the formaldehyde oxidative decomposition on different morphologies of \( \text{Cu}_2\text{O} \) nanocrystals, and this trend was explained in terms of different specific surface areas and different abundance of active surface-situated oxygen in these morphologies. The same trend was observed in an integrated experimental and theoretical study conducted by Amaniampong et al., who showed that the regenerative nanoleave-shaped \( \text{CuO} \) catalyst with dominant (111) facets activated the formyl C–H bond in glucose effectively by use of the surface lattice oxygen, to give gluconic acid in high yield (~87%), whereas \( \text{CuO} \) nanocubes were much less active (~50%) because of much less exposure of the active \( \text{CuO}(111) \) surface. Stereoselectivity in deoxygenation of aromatic epoxides was significantly affected by the morphology (wires, plates, or cubes) of \( \text{Cu} \) catalysts with different degrees of exposed \( \text{Cu}(100) \) facets. The highest specific surface area also resulted in maximum activity of the star-shaped structure of \( \text{CuO} \) in the catalytic reduction of 4-nitrophenol; the activity was higher than that of the rod-, sphere-, and flower-shaped \( \text{CuO} \) morphologies. As was demonstrated in these reports, nanostructured metal oxides act as effective catalysts when appropriate crystalline facets are exposed and used.

Herein, we report that the catalytic activity of \( \text{CuO} \) nanostructures depends on the morphology (flake, dandelion, or short ribbon) and that they can catalyze the oxidative coupling of aromatic amines to deliver imines. This organic transformation plays an indispensable role in constructing highly valuable building blocks for a variety of molecules of pharmaceutical significance. However, conventional methods have problems such as the low selectivity in the condensation of primary aliphatic aldehydes and amines, the low reaction efficiency, and the need for harsh reaction conditions, which have hampered versatile applications of these procedures. The oxidative coupling of amines to produce imines, which uses benign and readily available molecular \( \text{O}_2 \) or air as an oxidant, has drawn widespread attention. There are strong incentives to use heterogeneous catalysts in producing imines, because their high stability, high activity, reusability, and ease of product separation potentially reduce the cost of the process. Among the various catalysts studied so far, \( \text{Cu} \)-based ones appear promising because of the high abundance and low price of copper. However, although many \( \text{Cu} \)-based homogeneous catalysts have been developed, the number of \( \text{Cu} \)-based heterogeneous catalysts is still limited. \( \text{Cu}(0) \) has been considered for use in this reaction under aerobic conditions, but despite the high activity attained, leakage of copper to the reaction media was detected, and the structure of the catalyst changed drastically after the reaction. There are also reports that \( \text{Cu} \) could be easily converted to the copper oxide phase in \( \text{O}_2 \) atmosphere. \( \text{CuO} \) catalysts have also been tested for oxidative coupling of amines to imines; however, their activities have not been optimized to a satisfactory level.

In addition, our mechanistic understanding of the formation of imines over these heterogeneous catalysts is insufficient, which impedes efficient development of better catalysts. It is important to note that the surfaces of metal oxides are much more complex than pure metal surfaces, because they have many different active sites (saturated coordination and undercoordination sites), making detailed mechanistic studies of the reaction on \( \text{CuO} \) challenging but warranted. These apparent problems motivated us to examine the potential of \( \text{CuO} \) as the catalyst and optimize the reaction conditions, particularly for the oxidative coupling of aromatic amines. Our findings demonstrate the prospective utility of \( \text{CuO} \) nanostructured catalysts with different morphologies for the catalysis of solvent-free oxidative coupling of aromatic amines to deliver imines with high activity and high selectivity. We found that the catalytic activity of the flake-shaped \( \text{CuO} \) nanostructure is higher than that of the dandelion- and short-ribbon-shaped \( \text{CuO} \) nanostructures. To the best of our knowledge, this is the first example of nanocatalysis that utilizes different morphologies of \( \text{CuO} \) for shape-controlled oxidative coupling of aromatic amines. Furthermore, by performing extensive density functional theory (DFT)
calculations, we were able to delineate a detailed mechanism of the oxidative coupling reaction on the CuO surface for the first time. DFT calculations also helped us understand the different catalytic activities of different CuO morphologies in terms of how significantly the active facets are exposed. Thus, the research outcomes in this study provide a compelling rationale for the structure–performance relationship of CuO nanostructures.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of CuO Nanostructures. Uniform flake (Cu-1), dandelion-microsphere (Cu-2), and short-ribbon (Cu-3)-shaped CuO nanostructures were synthesized by following conventional solution-phase methods (Scheme S1, Supporting Information (SI)). To synthesize the CuO nanostructure with a flake shape (Cu-1), a facile template-free solution-phase method was adopted that involves precipitation of copper acetate with an aqueous sodium hydroxide solution to generate a copper hydroxide acetate precursor, followed by thermal decomposition of the metal hydroxide salt. A hierarchical dandelion-like CuO nanostructure (Cu-2) was prepared by a facile hydrothermal method in the presence of ethanol and ethylene glycol. Here, ethylene glycol played a crucial role as a structure-directing agent to initiate the self-assembly through nucleation and aggregation processes, which eventually led to the formation of microspheres. The CuO nanostructure with short-ribbon morphology (Cu-3) was prepared with co-precipitation of a Cu(OH)₂ precursor, followed by thermal decomposition of Cu(OH)₂ at a lower temperature and then calcination at a higher temperature. The copper content in each of these CuO nanostructured materials was determined by using atomic absorption spectroscopy (AAS), which predicted that the Cu-1, Cu-2, and Cu-3 materials include 23.0 wt % (0.362 mol %), 22.8 wt % (0.358 mol %), and 21.5 wt % (0.338 mol %) of copper, respectively. Morphological evolution in the three CuO nanostructures was investigated by performing transmission electron microscopy (TEM) and scanning electron microscopy (SEM) studies (Figures 1 and 2).

Figure 1. Field emission SEM (FE-SEM) images of flake-shaped CuO (Cu-1) (A–C), dandelion-shaped CuO (Cu-2) (D–F), and short-ribbon-shaped CuO (Cu-3) (G–I).
Figure 2. TEM images of flake-shaped CuO (Cu-1) (A–C). HR-TEM image of Cu-1 (D); selected-area electron diffraction (SAED) pattern of Cu-1 (E). TEM images of dandelion-microsphere-shaped CuO (Cu-2) (F–H). HR-TEM image of Cu-2 (I); SAED pattern of Cu-2 (J). TEM images of short-ribbon-shaped CuO (Cu-3) (K–M). HR-TEM image of Cu-3 (N); SAED pattern of Cu-3 (O). FFT patterns of Cu-1, Cu-2, and Cu-3 are shown in the insets of D, I, and N, respectively.
thickness in the range of \(\sim 307-384\) nm. Close inspection of the regions marked by blue arrows in Figure 1B shows that each nanosheet consists of two to three well-defined nanoflakes that make the composite very bulky. The SEM image in Figure 1D shows that the dandelion-type CuO microspheres (Cu-2), which have varying sizes (5.2–6.4 \(\mu\)m), are homogeneously distributed throughout the sample. Figure 1E,F demonstrates that nanoneedles with sizes of 3–5 nm are self-assembled to develop each dandelion microsphere of CuO.\(^{34}\) The short-ribbon-like morphology of Cu-3 with a mean particle length of \(\sim 225\) nm can be seen in Figure 1G–H.\(^{35}\)

TEM images of Cu-1 (Figure 2A–C) demonstrate that the black-colored small nanograins are fused together to give flake-shaped morphology. Black-colored nanograins are clearly visible in Figure 2C; they are self-assembled to give flake-like morphology to the Cu-1 material. TEM images of Cu-2 (Figure 2F–H) show distinct microspheres, congruent with the SEM results. The diameter was calculated as \(\sim 172\) nm for the microsphere in Figure 2F. Short-ribbon-like morphology of Cu-3 is also seen in Figure 2K–M. Figure 2L is a magnified image of the marked portion (red) of Figure 2K, in which short ribbons with a length of around 203–221 nm are clearly visible. In the high-resolution TEM (HR-TEM) image of the Cu-1 material (Figure 2D), the crystalline lattice fringes zone is marked with a red frame. Fast Fourier transform (FFT) analysis of this marked area (inset of Figure 2D) showed that it contained (111) and (110) crystal planes.\(^{36}\) The similar crystalline lattice fringes in HR-TEM images were captured and marked with red frames for the Cu-2 and Cu-3 materials (Figure 2I,N), and FFT was also carried out at these specified regions, which yielded (111) and (110) crystal planes for the dandelion CuO (inset of Figure 2I) and (111), (110), and (021) reflections for the short-ribbon CuO material (inset of Figure 2N). SAED patterns of all CuO nanostructures (Figure 2E,J,O) imply a polycrystalline nature, and diffraction rings can be indexed to the monoclinic CuO phases.

Wide-angle powder X-ray diffraction (XRD) patterns of the CuO nanostructures with different morphologies presented in Figure 3A inform us about the crystalline nature of the as-synthesized CuO samples. The XRD patterns can be readily indexed to the matched crystalline planes, corresponding to the monoclinic arrangement of CuO with the JCPDS card No. (80-1917). In fact, some shifts in the XRD peak positions were observed in the higher \(2\theta\) region in the wide-angle powder XRD patterns of the CuO materials presented in Figure 3A. This shifting could be explained in terms of thermal expansion or change of the structure. Peak widths can vary as a result of changing the crystallite size and microstrain. There may be redistribution of peak intensities arising from change in crystalline preferred orientation, texture, or increasingly poor grain statistics upon grain growth, which could cause shifting of XRD peaks.\(^{37}\) No other impurity peaks can be observed, which indicates entire conversion of the as-synthesized Cu precursors into crystalline CuO.\(^{38}\) Cu 2p XPS spectra of all CuO nanostructured materials are provided in Figure 3B. The binding energy peak of Cu 2p\(_{3/2}\) in the CuO nanostructure centered at 933.7 eV and the characteristic satellite peak at 942.2 eV can be attributed to the presence of Cu in the +2 oxidation state.\(^{39}\) A higher binding energy peak of the Cu 2p\(_{1/2}\) core level of the CuO materials appeared at 953.6 eV along with a shakeup satellite at 961.9 eV. The Cu 2p\(_{3/2}\) binding energy peak for metallic copper, Cu(0), and Cu\(_2\)O, Cu(I), should be observed at 932.5 eV, which is about 1.3 eV lower than the peak for the main Cu 2p\(_{3/2}\) core level transition.

Figure 3. Wide-angle powder XRD patterns (A), XPS spectra of Cu 2p region (B), O 1s region for Cu-1 (C), Cu-2 (D), and Cu-3 (E), and Raman spectra (F) of all CuO materials.
of Cu(II)O. Therefore, from the Cu 2p X-ray photoelectron spectroscopy (XPS) data, we can conclude that neither Cu(0) nor Cu(I) was produced in this case. In addition, the prominent satellite peaks mentioned above are hardly noticeable for Cu(I) in XPS. O 1s XPS spectra are shown in Figure 3C–E, and deconvolution of these spectra shows that the binding energy peaks are situated at 296.6 eV (attributable to the presence of lattice oxygen) and 531.6 eV (attributable to the presence of surface oxygen). The presence of another peak around 529.6 eV (attributable to the presence of lattice oxygen) and 531.6 eV (attributable to the presence of surface oxygen) was confirmed by deconvolution of these spectra. A noticeable difference in the binding energy between Cu(I) and Cu(II) was observed in this study. The presence of another peak around 282.8 eV could be assigned to other O–Cu bonds. Figure 3C displays the Raman spectra of the CuO nanostructures. Three main stretching vibration one-photon modes are found at 282, 337, and 613 cm$^{-1}$, which can be assigned to the $A_g$ and two $B_g$ modes, respectively, arising from the vibrational motions of Cu–O bonds. Energy-dispersive X-ray (EDX) spectroscopy and elemental mapping data for all CuO nanostructures (Figure S4) reveal the presence of Cu and O elements with no other impurities. Fourier transform infrared (FT-IR) spectra of all CuO-based materials (Figure S5) suggest the presence of characteristic Cu–O stretching vibrations.

### 2.2. Catalytic Activity of CuO Nanostructures for Oxidative Coupling of Aromatic Amines

Catalytic performance of the CuO nanostructured materials was evaluated by carrying out oxidative coupling of aromatic amines under solvent-free conditions at 100 °C (oil bath) with an O$_2$ balloon; benzylamine (0.2 mL, 1.8 mmol) was used as a model substrate. We observed remarkable differences in catalytic performance when the three CuO catalysts with different shapes were used for the reaction. Initially, low catalytic conversion (only 5% at 4 h) could be observed when Cu-1 (flake shape) was used as the catalyst for this oxidative coupling reaction (Table 1, entry 1). Only 23% conversion was achieved after 10 h of the reaction using the Cu-1 material (Table 1, entry 3). Surprisingly, however, the catalytic conversion with Cu-1 could be improved to 98%, and the reaction was completed within 12 h (Table 1, entry 4). In contrast, by using Cu-2 (dandelion microsphere) and Cu-3 (short ribbon) catalysts under identical reaction conditions, 55 and 72% product conversions, respectively, were reached after 12 h (Table 1, entries 5 and 6). Notably, catalytic reactions using Cu-2 (dandelion microsphere) and Cu-3 (short ribbon) catalysts both led to 98% conversions (Table 1, entries 7 and 8) after 17 and 15 h, respectively. A comparison study was performed using bulk CuO (Table 1, entry 9) and commercial CuO catalysts (Table 1, entry 10); neither of them was as active as Cu-1, and the commercial CuO catalyst exhibited lower selectivity (91%). Our methodology using the Cu-1 nanocatalyst is also effective for a large-scale reaction (2 mL, 18.3 mmol), with consistent product conversion of 98% observed (Table 1, entry 11).

The effect of atmosphere on this catalytic oxidative coupling reaction was investigated by performing this reaction in O$_2$ (1 atm), air, N$_2$, and Ar atmospheres using benzylamine as the model substrate for the CuO nanostructures of different shapes (Figure 4A). The catalytic performance of all CuO nanostructured materials with different shapes was enhanced in an O$_2$ atmosphere compared to that for the reaction in air. Noticeable differences in catalytic activity of the three CuO nanostructures with different shapes were observed under both O$_2$ and air conditions. To investigate the intrinsic activity of the catalyst, the turnover frequency (TOF) values were calculated using the expression “biphenyl converted per gram of catalyst per hour”. This is a convenient choice for comparing the activities of different morphologies of the same catalyst, and it was also applied in other studies. As catalysis is a surface phenomenon, we have investigated the morphology-dependence of TOF assuming that all of the exposed surface atoms are accessible and act as catalytically active sites for these nanostructured catalysts. CuO with the flake shape (Cu-1) exhibited superior catalytic performance (with TOF values of 2.06 and 1.79 h$^{-1}$) compared to that of Cu-2 (with TOF values of 1.15 and 1.01 h$^{-1}$) and Cu-3 (with TOF values of 1.51 and 1.2 h$^{-1}$) under O$_2$ and aerobic conditions, respectively. Substantial decreases in the TOF (h$^{-1}$) values were observed upon introduction of N$_2$ and Ar atmospheres, indicating that oxygen is essential for this oxidative coupling reaction of amine. Changes over time in catalytic performance of all three CuO nanostructured catalysts with different shapes were examined for solvent-free oxidative coupling of benzylamine under optimized reaction conditions at 100 °C (Figure 4B), by monitoring samples in GC at 1 h intervals. Initially, the rates of the catalytic reactions for all three CuO nanocatalysts were very low, indicating that there is an initiation period before the catalysts acquire full activity. After 10 h of the reaction, conversion was only 25%; however, within 2 h after that, the Cu-1, Cu-2, and Cu-3 catalysts provided 98, 55, and 72% conversions of benzylamine, respectively. Thus, some induction period is necessary for this catalytic process, which may be attributed to poor surface–substrate interactions in the initial stage, activation of the nanocatalyst during the reaction time by heating the solvent from room temperature to the optimum higher temperature, catalyst wetting processes, or the presence of excess amine that causes poisoning of the catalyst.

We also examined the influence of the reaction temperature on the shape-dependent catalytic performance of the CuO catalysts in solvent-free oxidative coupling of benzylamine at different temperatures (Figure 4C). All of the reactions were carried out at a particular temperature for 12 h. The catalytic

| Table 1. Oxidative Coupling of Benzylamine Promoted by Various CuO Nanostructures$^a$

| entry | catalyst | temperature (°C) | time (h) | conv (%) |
|-------|----------|-----------------|----------|----------|
| 1     | Cu-1 flake | 100             | 4        | 5        |
| 2     | Cu-1 flake | 100             | 6        | 8        |
| 3     | Cu-1 flake | 100             | 10       | 23       |
| 4     | Cu-1 flake | 100             | 12       | 98       |
| 5     | Cu-2 dandelion | 100     | 12       | 55       |
| 6     | Cu-3 short ribbon | 100 | 12       | 72       |
| 7     | Cu-2 dandelion | 100     | 17       | 98       |
| 8     | Cu-3 short ribbon | 100 | 15       | 98       |
| 9     | CuO bulk    | 100             | 12       | 3        |
| 10    | Com-CuO     | 100             | 12       | 14       |
| 11$^a$Cu-1 flake | 100     | 12       | 98       |

$^a$Reaction conditions: benzylamine (0.2 mL, 1.83 mmol), CuO nanostructures (0.3619 mol % of Cu), O$_2$ balloon (1 atm pressure), determined by gas chromatography (GC) using diphenyl as the internal standard and confirmed by GC-(mass spectrometry) MS.

$^b$Reaction was performed with benzylamine (2 mL, 18.3 mmol).
Figure 4. (A) Effect of atmosphere on shape-controlled catalytic oxidative coupling of benzylamine over CuO nanostructures. Activity expressed in terms of TOF (h⁻¹). (B) Conversion of benzylamine over the flake (Cu-1)-, dandelion (Cu-2)-, and short-ribbon (Cu-3)-shaped CuO nanostructures against time. Reaction condition: benzylamine (0.2 mL, 1.83 mmol), CuO nanocatalyst (0.3619 mol % of Cu), O₂ balloon (1 atm pressure), temperature 100 °C. (C) Influence of the reaction temperature on shape-controlled catalytic oxidative coupling of benzylamine over flake (Cu-1)-, dandelion (Cu-2)-, and short-ribbon (Cu-3)-shaped CuO nanostructures (0.3619 mol % of Cu); time 12 h. Each reaction was carried out for 12 h. (D) Comparison of the desired product selectivity in the oxidative coupling reaction of benzylamine over CuO nanostructures of different shapes in different atmospheres. (E) Effect of the CuO catalyst dose on oxidative coupling of benzylamine. Reaction condition: benzylamine (0.2 mL, 1.83 mmol), CuO nanocatalyst, O₂ balloon (1 atm pressure), temperature 100 °C, time 12 h. (F) TOF h⁻¹ of the CuO nanostructures against the catalyst surface area.
activity expressed in terms of TOF (h\(^{-1}\)) at different temperatures clearly signifies that temperature plays a crucial role in this reaction. When the temperature was increased gradually from 40 to 100 °C, significant enhancement in TOF was observed for all of the CuO nanocatalysts, whereas the desired imine was obtained as a sole product with good selectivity. This may be because the catalyst is activated effectively at higher reaction temperatures. The products selectivity obtained under various reaction conditions and with different CuO nanostructures are compared in Figure 4D. N-Benzylidene-1-phenylmethanamine is obtained as a major product, along with a small amount of benzonitrile (ca. 5−10% selectivity), in the oxidative coupling of benzylamine under O\(_2\) and aerobic conditions. The same trend was not noticed when the reaction was conducted under an inert atmosphere. The formation of benzonitrile and N-benzylidene-1-phenylmethan-

| Entry | Substrate | Product | Time (hr) | Conv (%) | Selectivity (%) |
|-------|-----------|---------|-----------|----------|-----------------|
| 1     |           |         | 12        | 95       | 98              |
| 2     |           |         | 12        | 94       | 98              |
| 3     |           |         | 12        | 96       | 98              |
| 4     |           |         | 12        | 93       | 99              |
| 5     |           |         | 12        | 98       | 100             |
| 6     |           |         | 12        | 97       | 96              |
| 7     |           |         | 10        | 98       | 100             |
| 8     |           |         | 12        | 98       | 86              |
| 9     |           |         | 13        | 100      | 100             |
| 10    |           |         | 13        | 95       | 97              |
| 11    |           |         | 12        | 51       | —               |
| 12    |           |         | 14        | 100      | 100             |
| 13    |           |         | 12        | 85       | —               |
| 14    |           |         | 14        | 100      | 99              |
| 15    |           |         | 16        | 100      | 99              |
| 16    |           |         | 20        | 65       | —               |

“Reaction conditions: amine (1.83 mmol), Cu-1 nanocatalyst (0.3619 mol % of Cu), O\(_2\) balloon (1 atm pressure), 100 °C temperature, conversion was determined by GC using diphenyl as the internal standard and confirmed by GC-MS.
amine as the minor and major products, respectively, can be attributed to the successive oxidative dehydrogenation of an in-situ-generated imine derivative and a self-coupling reaction between the unreacted benzylamine and the in-situ-formed benzylimine. The effect of the catalyst dose (mol % of Cu) was investigated for the oxidative coupling of benzylamine under optimized reaction conditions using all CuO nanocatalysts (Figure 4E). Obvious improvement in catalytic performance was observed with increasing mol % of Cu in the catalyst, but the selectivity for the desired imine product was not diminished (∼98% selectivity). This result suggests that the selectivity is independent of catalyst loading. In addition, saturation in the catalytic performance (∼60–99% conversion) was observed when the catalyst dose was increased from 0.072 to 0.108 mmol. This observation indicates that the catalytic performance is independent of the mol % of Cu loading after reaching a certain amount. Our efforts to establish structure–activity relationships for the nanostructured catalysts led us to find a correlation between the activity and the surface area. TOF ($h^{-1}$) is plotted as a function of the surface area in Figure 4F; the data in the figure imply that the catalytic performance gradually decreases with the decreasing external active surface area or the decreasing number of catalytically active sites of the CuO nanostructures. A similar linear correlation between the activity and the Cu surface area has been observed by Natesakawai et al.46

With the optimized conditions in hand, we then examined the substrate scope using the Cu-1 nanocatalyst and amines bearing a variety of functional groups (Table 2). In general, our newly developed methodology works fine for substrates having either an electron-donating or an electron-withdrawing functional group on the aromatic ring; in either case, good conversion and high selectivity could be achieved (Table 2, entries 1–4). Ortho-substituted benzylamines underwent the oxidative coupling reaction very smoothly despite possible steric hindrance effects. Similarly, 2-aminobenzyl amine and 2-chlorobenzyl amine could be transformed into the corresponding imines with excellent conversion efficiency (Table 2, entries 9 and 10). The reaction of 4-tert-butyl benzylamine also proceeded efficiently (Table 2, entry 6), with 97% conversion and 96% selectivity after 12 h. The position of substitution on the aromatic ring did not have much effect on the reaction.

Figure 5. (A) Effect of benzylamine concentration on the selectivity toward benzonitrile and activity expressed in terms of TOF ($h^{-1}$). (B) Hot-filtration experiments in which the Cu-1 catalyst was removed after 10 or 14 h, followed by addition of 0.2 mL of benzylamine in the filtrate, and the reaction was continued for another 24 h. (C) Recyclability of all CuO nanocatalysts for oxidative coupling of benzylamine. Reaction conditions: benzylamine (0.2 mL, 1.83 mmol), CuO nanocatalyst (20 mg), O2 balloon (1 atm pressure), temperature 100 °C. (D) TOF during the recyclability test of oxidative coupling of benzylamine catalyzed by CuO nanostructures.
Scheme 1. Possible Mechanisms for the Oxidative Coupling of Amine on the CuO Catalyst

We have investigated the influence of the concentration of benzylamine (Figure 5A) on the nitrile selectivity and the catalytic activity expressed in terms of TOF (h⁻¹). We observed that with decreasing concentration of benzylamine, selectivity for the nitrile product (doubly dehydrogenated product) increased despite the decrease in the TOF value. This result can be rationalized by considering the coupling reaction between an in-situ-generated imine intermediate and benzylamine, which is favored in the presence of additional amine substrates over a second dehydrogenation process leading to the formation of a benzonitrile derivative. The trend observed for our reactions is consistent with the activity trend experimentally observed by Hermans et al.⁵¹ To assess whether our CuO nanocatalyst is indeed heterogeneous in nature, we carried out hot filtration tests by performing oxidative coupling of benzylamine under optimized reaction conditions for 10 or 14 h using the Cu-1 nanocatalyst (Figure 5B). In one test, after 10 h of the catalytic reaction, the catalyst was separated by centrifugation, and the reaction was continued; however, conversion did not go beyond 25%. This experimental result clearly signifies that no leaching of catalytically active species took place in the reaction mixture. In the other test, after 14 h of the reaction, we found that a trace amount of Cu leached into the reaction mixture (light blue solution), which was confirmed by the AAS analytical technique. After completion of the reaction, we removed the catalyst, and excess benzylamine was added into the filtrate with the leached homogenous Cu species, and the reaction was continued for another 24 h. However, only 2–3% product conversion was obtained after 24 h, which proved that leached copper species contributed to the oxidative coupling of amine but did not catalyze this reaction up to full conversion. The Cu content in the Cu-1 nanocatalyst after 14 h of the catalytic run was found to be 3.523 mmol g⁻¹, as determined by the AAS analysis, which is still analogous to that of the fresh one (3.619 mmol g⁻¹). The efficacy of all of the CuO nanocatalysts was evaluated in terms of the recyclability and reusability by carrying out catalytic oxidative coupling of benzylamine using the nanostructured catalysts under optimized reaction conditions. The catalysts were recovered from the reaction mixture by the centrifugation technique and washed with ethanol and acetone to remove organic substrates adsorbed on the surface, followed by drying at 80 °C before its use in the next catalytic run. No special technique like addition of acid or base or calcination at a higher
temperature was applied for the reactivation of our catalyst. To examine the durability of the nanocatalysts, the catalytic reactions were continued for 5 successive catalytic runs (12 h); the conversion and TOF values dropped gradually but were maintained relatively well during this period (Figure 5C,D). We also performed the FE-SEM analysis for the three catalysts after the catalytic cycles (Figure S12), which indicates that their morphologies are still retained.

2.3. Mechanistic Study of the Oxidative Coupling of Amine on the CuO(111) Surface. Because the CuO(111) surface is the most stable surface of CuO,30,32 it will be the dominant exposed facet of the CuO nanocatalysts. Indeed, the CuO(111) surface was observed in other morphologies of CuO such as nanoleaves,21 nanocubes,21 nanowires,32,52 and nano thin-films,53,54 and the predominance of this surface was also evidenced from XRD and HR-TEM images for all CuO morphologies examined in this study. Therefore, the mechanism of oxidative coupling of amine was evaluated computationally using the CuO(111) surface. There are two different types of Cu sites, Cu3 and Cu4, and also two types of oxygen sites, O3 and O4; these are named after the coordination numbers of Cu or O18,21,30,32 (Figure S6). Previous computational studies showed that unsaturated Cu3 and O3 sites act as active sites in C–H bond activation of the formyl group of glucose21 and methane.18 It is widely accepted that the essential role of the catalyst in producing the desired secondary imine is to facilitate the generation of the key benzylimine intermediate from benzylamine27,28,50,55. A complete mechanism based on this assumption is shown in Scheme 1, which consists of two competing pathways that could be responsible for this oxidative coupling of amine for the formation of desired product N-benzylidene-1-phenylmethanamine. The first pathway involves three stages. Stage 1 is associated with the dehydrogenation of amine to form imine, and stage 2 is for subsequent coupling between amine and imine. In stage 3, an ammonia molecule dissociates to yield the secondary imine product.31,56 In addition, further dehydrogenation of the imine intermediate to the benzonitrile by-product is also possible (Scheme 1). To determine the most plausible reaction pathway, we performed the GC-MS analysis while quenching the reaction mixture at different time intervals (Figure S13). However, no signal of the hydrolyzed benzaldehyde product was detected in the GC-MS spectra, although a small amount of the benzonitrile by-product was
observed. These results show that the hydrolysis pathway is unfavorable and thus can be ruled out. We also note that this conclusion is in full agreement with the recent work of Gao and co-workers on oxidative coupling of amines to imines over mesoporous carbon.48 Therefore, we examined the three-stage pathway that proceeds through coupling between amine and imine in our simulation studies. It should be noted that, although this kind of mechanism is sometimes proposed, the detailed mechanism has not been probed in the literature, especially for the CuO-catalyzed reactions. Lack of precise mechanistic understanding makes it difficult to design and engineer more efficient catalysts. Therefore, here we addressed this issue by performing DFT calculations. The DFT-calculated energy profile and the structures of transition states are shown in Figure 6.

In stage 1, benzylamine is adsorbed on the CuO(111) surface by coordination of the −NH₂ group to a Cu₃ site; the computed adsorption energy for this process is −23.5 kcal/mol (Figure 6B). Other adsorbed configurations are much less stable and detailed in Figure S7. Adsorbed amine is initially activated by N−H dissociation, which has a barrier of 15.8 kcal/mol (Figure 6C). If C−H activation occurs instead in the first step, the barrier is significantly higher (24.9 kcal/mol, Figure 7C); therefore, this alternative scenario is less likely than the mechanism that starts with N−H activation. Interestingly, if the first step is N−H activation, the subsequent C−H dissociation in step 2 is well feasible because the activation barrier (19.9 kcal/mol, Figure 6D) is lower than the above-mentioned C−H activation barrier for another pathway (Figure 7B−D) and the barrier for second N−H dissociation (23.2 kcal/mol, Figure S8) in a pathway involving sequential N−H activation steps. Importantly, both the initial N−H activation in step 1 and the subsequent C−H activation in step 2 are facilitated by the O₃ site on the surface (Figure 6C,D), demonstrating its critical role in activating both of these bonds. Another possible pathway, in which N−H and C−H bonds are activated by a Cu₃ site, has much higher barriers of 62.7 and 47.2 kcal/mol, respectively (Figure 7A,B). This observation is consistent with the previous findings on the role of the O₃ site of C−H bond dissociation of other substrates on the CuO(111) surface.18,21 The essential role of surface chemisorbed oxygen on Cu-based catalysts in facilitating the generation of imine has also been demonstrated in other experimental studies.27,28

The generated imine intermediate subsequently couples with the reactant amine to form an intermediate in stage 2 (Scheme 1). However, the uncatalyzed pathway has a very high barrier of 46.1 kcal/mol (Figure S9), demonstrating the essential role of the CuO catalyst not only in forming the key imine intermediate but also in the coupling reaction. Instead, the barrier for the coupling between amine and imine is much lower, that is, 15.9 kcal/mol, when the reaction proceeds on the CuO(111) surface (Figure 6E). The coupling between amine and imine follows a concerted pathway, in which C=N coupling occurs concomitantly with H-transfer from the NH₂ group of amine to the NH group of imine. Finally, intramolecular deammoniation in stage 3 may form a secondary amine product (Scheme 1). However, as in the case of stage 2, the uncatalyzed concerted reaction in stage 3 has a very high barrier (49.8 kcal/mol, Figure S9) and is therefore unlikely to proceed without the catalyst. Instead, the deammoniation on the surface of the heterogeneous CuO catalyst should proceed through a two-step pathway: the first step is N−H activation by the lattice O₃ site on the surface, which has a barrier of 13.6 kcal/mol (Figure 6F), and the second step is C−N dissociation to form adsorbed NH₂ and the final product, which has a barrier of 12.1 kcal/mol (Figure 6G). In the latter reaction, C−N scission could also take place through a direct deamination assisted by a surface hydrogen, but this process has a much higher barrier of 40.0 kcal/mol and is therefore much less likely to occur (Figure S10).

2.4. Roles of Surface Cu₃ and O₃ Sites in N−H Activation. It is of utmost importance to identify the active facet of nanocatalysts. In this study, we investigated the characteristics of different facets in detail to better understand the origin of different catalytic activities observed for different CuO morphologies. The above DFT calculations confirmed that the CuO(111) surface is a very active facet and that all of the N−H and C−H bonds of aromatic amines can be activated on the surface, specifically at the O₃ site, while maintaining the coordination bond of the amine moiety with the Cu₃ site (Figure 6C,D,F). This implies that, to activate X−H (X = C, N) bonds efficiently, both of the adjacentley situated Cu₃ and O₃ sites on the CuO(111) surface must be used. Varghese et al.18 reported that there is a synergistic effect between the Cu₃ and O₃ sites on the CuO(111) surface when activating the C−H bond of methane through a “four-center mechanism”, by which the activation barrier is lowered significantly. To gain clearer insights, we studied other N−H and C−H bond activation pathways on different sites of the CuO(111) surface as well as...
on two other facets: CuO(111) and CuO(110)\textsubscript{O} (where “CuO(110)\textsubscript{O}” stands for the CuO(110) surface terminated by oxygen atoms). CuO(111) is the second most stable surface after CuO(111).\textsuperscript{30,32} In addition, the signal of the CuO(111) surface also appeared strongly in the XRD patterns of CuO nanoleaves,\textsuperscript{21} nanowires,\textsuperscript{32} nano thin-films,\textsuperscript{33} and all as-synthesized CuO morphologies examined in this study (Figure 3A). In addition, there is some similarity in how Cu\textsubscript{3} and O\textsubscript{3} sites are arranged on the CuO(111) and CuO(111) surfaces.\textsuperscript{18,32} The CuO(110) surface has a much higher surface energy and is therefore much less stable.\textsuperscript{18,30,32} However, the O\textsubscript{2} atmosphere can stabilize the CuO(110) surface by terminating it by oxygen atoms (denoted as CuO(110)\textsubscript{O}),\textsuperscript{30,32} and this facet could be detected in HR-TEM images for all as-synthesized CuO morphologies (Figure 2), although the XRD patterns show that the ratio of this surface is much smaller than the ratios of the CuO(111) and CuO(111) surfaces (Figure 3A). There are only O\textsubscript{3} sites, and no Cu\textsubscript{3} sites, on the CuO(110) surface; thus, evaluation of CuO(110)\textsubscript{O} will validate our hypothesis regarding the necessity of both Cu\textsubscript{3} and O\textsubscript{3} sites in activating X atoms.

There are no Cu\textsubscript{3} sites on the CuO(110)\textsubscript{O} surface; thus, the activation barrier for N–H dissociation by an adjacent O\textsubscript{3} site is much higher (37.4 kcal/mol, Figure 8D). The Cu\textsubscript{4} site is a saturated site that resembles the Cu site in the bulk CuO,\textsuperscript{18,21} and therefore its affinity to the reactant is much lower than that to the Cu\textsubscript{3} site. This also affects the extent of transition-state stabilization. More specifically, the adsorption energy of benzylamine on the Cu\textsubscript{4} site of the CuO(111) surface is only −7.1 kcal/mol (Figure 8A), which is much smaller in magnitude than the adsorption energy for the Cu\textsubscript{3} site (−23.5 kcal/mol, Figure 6B). It is clear from these analyses that both Cu\textsubscript{3} and O\textsubscript{3} sites are needed to reduce the barrier for N–H activation, in which the O\textsubscript{3} site abstracts the hydrogen atom, whereas the Cu\textsubscript{3} site binds strongly to the nitrogen to stabilize the transition state. This argument also holds for the reaction on the CuO(111) surface; the transition state of this reaction is shown in Figure 8E. Because the arrangement of Cu\textsubscript{3} and O\textsubscript{3} sites on the CuO(111) surface is somewhat similar to that on the CuO(111) surface, the barrier for N–H activation is not too high (20.1 kcal/mol). Nevertheless, the adsorption is weaker (ΔE\textsubscript{ads} = −19.9 kcal/mol) than in the case of the CuO(111) surface (ΔE\textsubscript{ads} = −23.5 kcal/mol); hence, the barrier for the reaction on the CuO(111) surface is higher. There are no Cu\textsubscript{3} sites on the CuO(110)\textsubscript{O} surface; thus, the adsorption energy of benzylamine on a Cu\textsubscript{4} site is only −9.8 kcal/mol (Figure 8C), which results in a very high barrier for N–H activation (32.5 kcal/mol, Figure 8F). The barrier is high not only for the N–H activation, but also for the initial C–H bond activation on CuO(110)\textsubscript{O} (33.9 kcal/mol, Figure S11), showing that the CuO(110)\textsubscript{O} surface is not an active facet. For the four different cases examined, we can see a good correlation between the adsorption energy and the N–H activation barrier (Figure 8G). We also found that the same argument regarding the necessity of both Cu\textsubscript{3} and O\textsubscript{3} sites holds true for the initial C–H bond activation. The barrier for C–H activation by only a Cu\textsubscript{4} site is 47.2 kcal/mol (Figure 7B) and is significantly higher than the barrier for the C–H bond activation by an O\textsubscript{3} site (24.9 kcal/mol, Figure 7D), demonstrating that O\textsubscript{3} is the catalytically relevant site for C–H activation. It is important to note that the transition state shown in Figure 7D is stabilized by a coordination bond between the amine and a Cu\textsubscript{4} site. If the transition state is not stabilized by the Cu\textsubscript{4} site, the activation barrier is still very high (46.3 kcal/mol, Figure 7C), even though the C–H bond is activated by an O\textsubscript{3} site. This observation demonstrates that the arrangement of adjacent Cu\textsubscript{3} and O\textsubscript{3} sites is a key catalytic factor for C–H bond activation, as in the case of N–H activation.

### 2.5. Origin of the Different Catalytic Activities and the Role of the O\textsubscript{2} Atmosphere.

As pointed out above, judiciously arranged Cu\textsubscript{3} and O\textsubscript{3} atoms play synergistic roles in activating N–H and C–H bonds of the substrate. The CuO(111) surface has such Cu\textsubscript{3} and O\textsubscript{3} atoms and is the most stable of all the CuO surfaces.\textsuperscript{18,30,32} The CuO(111) surface is also the dominant exposed surface for all three as-synthesized CuO morphologies. Therefore, it is likely that each of the CuO morphologies uses this surface for the catalysis. Nevertheless, this surface will be exposed to varying extents in different morphologies, and this difference could render their catalytic activity different. Indeed, Amaniampong et al.\textsuperscript{21} showed that CuO nanoleaves (Brunauer–Emmett–Teller (BET) area, 23 m\textsuperscript{2}/g) was more active than nanocubes (BET area, 4.07 m\textsuperscript{2}/g) in the glucose oxidation. The BET surface areas for all of the CuO morphologies examined in this study are measured and...
example, the flake-shaped CuO catalyst has the largest surface area; thus, the CuO(111) facet will be exposed most significantly, thereby leading to the highest activity. By contrast, the dandelion-microsphere-shaped CuO catalyst has the smallest surface area, and therefore its activity is the lowest.

Experiments show that the conversion in an O2 atmosphere is much more efficient than that in an inert atmosphere (N2, Ar) (Figure 4A). We also sought to identify the origin of this discrepancy. During the X−H activation (X = C, N), all of the produced hydrogen atoms are bound to lattice O3 sites (Figure 7C,D,F), which could lead to reduction of the CuO state to Cu. In fact, it was previously shown that CuO was reduced to Cu in a hydrogen atmosphere29,30 and by other reductants such as glucose,57 but Cu could be recovered to CuO in an O2 atmosphere.21 To confirm the validity of this notion, we examined the structures of the flake-shaped CuO catalyst (Cu-1) before and after the reaction in an O2 atmosphere and in a N2 atmosphere. The XRD pattern data clearly show that CuO retains the same structure after the reaction, when the reaction is carried out in an O2 atmosphere (Figure 9A). By contrast, in a N2 atmosphere (in the absence of O2), the structure of CuO was reduced to Cu (Figure 9B). The intact CuO structure in an O2 atmosphere could be due to the chemical looping effect, in which O2 compensates the consumed lattice oxygen during the reaction.45,58−60 Finally, we evaluated the activity of the Cu(111) surface. Amine is adsorbed weakly on the Cu(111) surface with a computed adsorption energy of −11.3 kcal/mol (Figure 9C). As expected from the lack of active O3 sites, the N−H activation barrier is very high (46.7 kcal/mol) (Figure 9D). This computational result substantiates the important role of O2 atmosphere in restoring the CuO catalyst. It is our hope that the mechanistic principles established in this study facilitate the design of nanostructured materials with different shapes for performing various chemical reactions.61−63

3. CONCLUSIONS

In this work, we have demonstrated for the first time the shape-controlled catalytic activity of CuO nanostructures for oxidative coupling of aromatic amines to deliver biologically and pharmaceutically important imine derivatives under solvent-free conditions with high selectivity for desired products. Morphological evolution of all CuO nanostructures was investigated by performing FE-SEM and TEM analyses. An improved catalytic performance of the flake-shaped CuO nanostructure in the oxidative coupling of aromatic amine was observed compared to that of the dandelion- and short-ribbon-shaped CuO nanostructures. DFT calculations provided detailed insights into the reaction mechanism and identified the reason why three different CuO morphologies show different catalytic trends. The specific arrangement of Cu3 and O3 sites on the CuO(111) surface is the most suitable for activating N−H and C−H bonds, and this surface is always the dominant one regardless of the morphology, although this facet is exposed to different extents in different morphologies. Thus, the observed high catalytic activity of the flake-shaped CuO nanostructure is attributable to its greatest exposure of active CuO(111) facets, which can be used to drive N−H and C−H bond activations. The O2 molecules in the atmosphere play an indispensable role in compensating for the loss of the consumed lattice oxygen and thereby keeping the CuO structure intact during the reaction.

summarized in Table 3. As can be seen in the table, the larger the surface area, the more reactive the morphology. For example, the flake-shaped CuO catalyst has the largest surface area; thus, the CuO(111) facet will be exposed most significantly, thereby leading to the highest activity. By contrast, the dandelion-microsphere-shaped CuO catalyst has the smallest surface area, and therefore its activity is the lowest.

Table 3. Comparison of BET Surface Area for Different CuO Morphologies

| sample name | morphology     | BET surface area (m²/g) |
|-------------|----------------|-------------------------|
| Cu-1        | flake          | 42.0                    |
| Cu-2        | dandelion microsphere | 10.6                   |
| Cu-3        | short ribbon   | 26.0                    |

Figure 9. (A) XRD pattern of a Cu-1 sample after reaction in an O2 atmosphere. (B) XRD patterns of a Cu-1 sample before and after the reaction in a N2 atmosphere; a comparison of the patterns shows that CuO has been reduced to Cu after the reaction. (C) Adsorption and (D) N−H activation of benzylamine on the Cu(111) surface. Adsorption energy (∆E_ads) and activation barriers (E_a) are given in kcal/mol.

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reaction. Theoretical insights obtained in this study not only shed light on the microscopic aspects of the complex coupling reaction and the observed shape-dependence activity, but also pave the way for the design and engineering of more efficient catalysts for other reactions.

4. EXPERIMENTAL AND COMPUTATIONAL METHODS

4.1. Synthesis of CuO Nanocatalysts with Different Morphologies. 4.1.1. Synthesis of the Cu-1 Material with a Flake Shape. A copper hydroxide acetate precursor was synthesized by adding an aqueous solution of NaOH (0.25 M, 25 mL) to an aqueous solution of copper acetate (0.2 M, 25 mL) at room temperature under continuous stirring for 10 min. A pale-green-colored product was isolated by centrifugation and washed with water and then with ethanol and then dried at room temperature. The CuO nanocoated material (Cu-1) was prepared by annealing the pale-green solid at 300 °C for 3 h in a furnace.

4.1.2. Synthesis of the Cu-2 Material with a Dandelion-Microsphere Shape. Cu(OAc)2·H2O (0.5 g) was mixed in EtOH (20 mL) with ethylene glycol (6 mL). Subsequently, NH4·H2O (15 mL) and 5 mL aqueous NaOH (200 mg) were added to the previous reaction mixture. The resulting mixture was autoclaved at 130 °C for 16 h. The isolated black-colored material was washed with ethanol and acetone.

4.1.3. Synthesis of the Cu-3 Material with a Short-Ribbon Shape. CuCl2·2H2O (1 mmol) was dissolved in EtOH (5 mL) and H2O (10 mL). Solid NaOH (22.0 mmol) was added, followed by addition of H2O (25 mL) to the mixture. A blue precipitate appeared after 10 min. The blue precipitate was isolated and heated at 50 °C for 10 h, and the color turned black. The black-colored solid was calcined at 200 °C for 6 h to obtain the desired material.

4.1.4. Characterization. The as-synthesized CuO nanocatalysts were then carefully characterized by TEM, SEM, XRD, XPS, Raman spectroscopy, EDX, elemental mapping, and FT-IR analyses. XRD patterns were recorded on a Bruker D-8 Advance SWAX diffractometer operated at a 40 kV voltage and a 40 mA current. The instrument was calibrated with a standard silicon sample using Ni-filtered Cu Ka (α = 0.15406 nm) radiation. A JEOL JEM 6700F FE-SEM was used for determining the morphology of the samples. EDX and elemental mapping analyses were carried out with this JEOL JEM 6700F machine. HR-TEM images were recorded in a JEOL JEM 2100 machine using a tungsten electron microscope. Cu loading in the sample was estimated by using a Perkin-Elmer Optima 2100 DV Inductive Coupled Plasma Mass Spectroscopy. Raman spectra on a cleaned silicon substrate were measured with a Raman microscope (LabRAM HR, Horiba Yvon). The excitation wavelength of the irradiated light was 632.8 nm (He–Ne Laser, Melles Griot, laser excitation 0.1 mW), and signals were collected by using 50X objective lens. XPS analysis was carried out with a SPECs 15000 plus spectrometer using a Mg X-ray source. FT-IR spectra of the samples were recorded using a Nicolet MAGNA-FT-IR 750 Spectrometer Series II. Nitrogen adsorption/desorption isotherms were obtained using a Quantachrome Autosorb 1C at 77 K. The quadrupole ion trap mass spectrometer equipped with Thermo Accela LC and the Agilent 6890 GC system equipped with a flame ionization detector were used for the analysis of catalytic reactions.

4.2. Catalytic Testing. 4.2.1. Oxidative Coupling of Aromatic Amines Catalyzed by CuO Nanostructures under Solvent-Free Conditions. In a typical catalytic oxidative coupling reaction, a 10 mL Schlenk tube with a magnetic bar was charged with benzylamine (0.2 mL, 1.8 mmol) and the CuO nanostructured material (0.3619 mol %), which was vacuumed and equipped with an O2 balloon. Oxygen gas was continuously bubbled and thereby slowly introduced into the mixture. The reaction mixture was magnetically stirred at 600 rpm and heated at 100 °C for a desired period. After completion of the reaction, the catalyst was separated from the reaction mixture by centrifugation. The progress of the reaction was monitored periodically by analyzing the reaction mixture with GC-MS until full conversion of the substrate was attained. The products were characterized by using the GC-MS analysis technique. The conversion (%) of the product was determined by using biphenyl as the internal standard. We carried out catalytic measurements under kinetically limited conditions, avoiding transport limitations. In our reaction, the measurement was performed with vigorous magnetic stirring (600 rpm) under liquid-phase conditions. The mass transfer phenomenon could also be overcome under the vigorous magnetic stirring conditions, which can make the reaction mixture essentially quasihomogeneous. Therefore, we considered a diffusion limitation negligible for our catalyst. This assumption can only be applicable to cases with small particles and rapid stirring rates. Under these conditions, we can assume that all catalytic reactions in the liquid phase were conducted in a kinetically limited regime.

4.2.2. Hot-Filtration Test. In this test, a mixture of the Cu-1 nanocatalyst (20 mg) and benzylamine (0.2 mL, 1.83 mmol) in a 15 mL dry Schlenk tube was heated at 100 °C for 10 h with vigorous magnetic stirring. The Cu-1 nanocatalyst was separated from the hot reaction mixture after 10 h using the centrifugation technique. Only 25% conversion was achieved. The reaction was continued with the filtrate for another 24 h at the same reaction temperature. The reaction mixture turned blue and, a trace amount (below 2 ppm level) of copper was detected by the AAS analysis; however, no improvement in conversion was observed after 24 h, as confirmed by the GC analysis, which suggests that leached homogeneous copper species did not catalyze this reaction up to full conversion. This experiment clearly proved that our CuO-based nanocatalyst is truly heterogeneous in nature.

4.3. Computational Procedure. All DFT calculations were performed using Vienna ab-initio simulation program (VASP) software developed at the Fakulta fü für Physik of the Universität Wien. Spin-polarized periodic DFT calculations were performed with the Perdew–Burke–Enzerhof functional, the plane-wave basis set with a kinetic energy cutoff of 450 eV, and the projector-augmented wave method as implemented in VASP. To correctly describe the semi-conducting properties and optimize the bulk lattice constants for the CuO crystal structure while correcting the Coulomb interaction within CuO, Dularev’s GGA+U approach with the Hubbard term (U − J) = 7.0 eV was utilized. This correction predicted the bulk properties (band gap and magnetic momentum) of CuO accurately and was successfully applied to evaluate the activity of CuO in glucose oxidation and methane activation previously. To gain insight into the reaction mechanism and the different activities of different morphologies, we examined three different surfaces of CuO: CuO(111), CuO(110), and CuO(111). These surfaces were modeled as periodic three-layer (4 × 2) slabs, with each layer containing 16 Cu atoms and 16 O atoms. A vacuum region of 20 Å was included above the top layer,
which is large enough to avoid the interaction between repeated unit cells. The bottom layer was fixed at the optimized bulk lattice parameters, as was done in earlier studies.\(^1,18,21\) This constraint reduces the computational cost without compromising the accuracy of calculations critically.\(^3,70−74\) The structures of these surfaces are presented in Figure S6 in the SI. In addition, to assess the catalytic activity of a reduced catalyst that is formed in an inert atmosphere, a four-layer \(p(4 \times 4)\) \(\text{Cu}(111)\) slab, with an optimized lattice constant of 3.635 Å and a vacuum region of 20 Å above the top layer, was used. The Brillouin zone was sampled with a \(3 \times 3 \times 1\) Monkhorst-Pack grid for all calculations. Transition states were located using the nudged elastic band method, and subsequent frequency calculations confirmed the nature of transition states.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00331.

Synthetic schemes, FE-SEM images, EDX analysis and the corresponding elemental mapping of Cu and O, FT-IR spectra of all CuO materials with different morphologies, GC−MS data to rule out the mechanism involving a benzaldehyde intermediate, additional DFT simulation results, and comparison of the catalytic performance of various catalysts (PDF)

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### Notes

The authors declare no competing financial interest.

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