

Cite this: *Chem. Commun.*, 2012, **48**, 8484–8486

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ZnO–CuO core–branch nanocatalysts for ultrasound-assisted azide–alkyne cycloaddition reactions†

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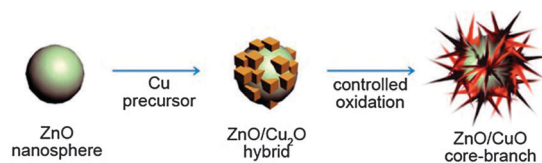
Received 6th March 2012, Accepted 17th April 2012

DOI: 10.1039/c2cc31654d

ZnO–CuO core–branch hybrid nanoparticles, synthesized by copper oxide growth and controlled oxidation on ZnO nanospheres, exhibited remarkable enhancement of catalytic activity and stability for ultrasound-assisted [3 + 2] azide–alkyne cycloaddition reactions, due to their high surface area and active facets of the CuO branches.

Hybrid nanostructures offer multi-functionality with synergistic effects between independent domains.^{1,2} From the viewpoint of heterogeneous catalysis, these hybrid nanostructures could supply optimal architectures for bifunctional catalytic systems.³ Simply put, one of the components serves as an active surface for the reaction, and the other behaves as a support to stabilize the entire structure. The inorganic interface between the two components can either tailor the chemical nature of the active component, or generate new species to enhance catalytic activities. Although these well-defined hybrid nanostructures are ideal for heterogeneous catalysts, their use in real catalytic reactions has been rarely reported.⁴ Xia *et al.* published a pioneering report on Pd–Pt dendritic heterostructures, which exhibited high activity and stability in oxygen reduction reactions.⁵

In the present study, we combined the concepts of bifunctional catalysts and branched morphology into a colloidal metal oxide system. The ZnO–Cu₂O hybrid nanoparticles were synthesized by the reduction of the copper precursor onto polycrystalline ZnO spheres. Controlled oxidation of the particles led to the formation of CuO branches, which were strongly anchored on the ZnO surface. The resulting hybrid structure, so-called ZnO–CuO core–branch nanoparticles, has active facets and defects as well as a large surface area, showing good promise for catalytic applications. For instance, the particles exhibited the highest catalytic activity among conventional heterogeneous catalysts in ultrasound-assisted [3 + 2] azide–alkyne cycloaddition reactions.



Scheme 1 Synthetic scheme of ZnO–CuO core–branch hybrid nanoparticles.

The ZnO–CuO core–branch nanoparticles were synthesized *via* two steps from ZnO nanospheres (Scheme 1). ZnO nanospheres were prepared by hydrolysis and condensation of a zinc precursor in an alcoholic medium.⁶ A copper precursor was subsequently injected *in situ* to yield ZnO–Cu₂O core–shell type aggregates. Briefly, zinc(II) acetylacetonate hydrate (Zn(acac)₂·H₂O) and poly(vinyl pyrrolidone) (PVP) were dissolved in 1,5-pentanediol (PD). The mixture was slowly heated to 230 °C for 12 min, and aged for additional 3 min. A PD solution of copper(II) acetylacetonate (Cu(acac)₂) was then injected into the hot ZnO–PVP mixture, and stirred for 10 min at 230 °C. Prior to injection of the copper precursor, uniform ZnO nanospheres with an average diameter of 101 ± 4 nm were obtained as aggregates of small particle domains (Fig. S1, ESI†). X-ray diffraction (XRD) data show a hexagonal wurtzite phase of ZnO (Fig. S1d, ESI†; JCPDS No. 36-1451). After the reaction, Cu₂O nanocubes were uniformly generated on the surface of the ZnO spheres. The resulting ZnO–Cu₂O particulates were very stable in solution even after prolonged sonication. The transmission electron microscopy (TEM) image in Fig. 1a shows that the Cu₂O nanocubes with an average edge size of 27 ± 4 nm were attached on the ZnO surface. The energy dispersive X-ray spectra (EDX) at different positions show that square projections on the surface were mainly composed of copper and oxygen, whereas the core part contains copper and zinc together with oxygen (Fig. S2, ESI†). The XRD pattern is a combination of wurtzite ZnO and primitive cubic Cu₂O reflections (Fig. 1d, JCPDS No. 77-0199). The distance between neighbouring lattice fringes in the HRTEM image is 0.21 nm, in good agreement with the distance between {200} crystallographic planes of the Cu₂O phase (Fig. S3, ESI†). These results indicate that the Cu₂O nanocubes are strongly anchored on the ZnO spheres to yield ZnO–Cu₂O core–shell type aggregates, where the structural stability is rooted from the small lattice mismatch of 0.7% between Cu₂O(111) and ZnO(101) planes.

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† Electronic supplementary information (ESI) available: Details of experimental procedures, TEM and SEM images, and EDX and XRD spectra of hybrid nanostructures. See DOI: 10.1039/c2cc31654d

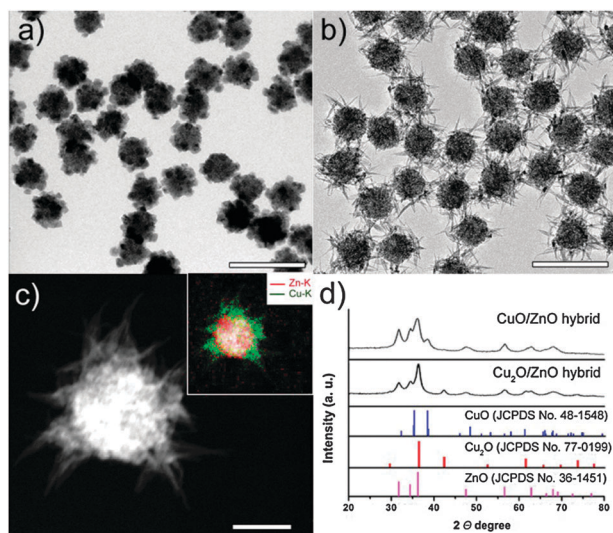


Fig. 1 TEM images of (a) ZnO–Cu₂O core–shell hybrid nanoparticles and (b) ZnO–CuO core–branch nanoparticles. (c) HAADF-STEM image and (inset) elemental mapping of Zn (red) and Cu (green) for a single ZnO–CuO core–branch nanoparticle. (d) XRD spectra of ZnO–Cu₂O and ZnO–CuO hybrid nanoparticles. The bars represent (a,b) 200 nm and (c,d) 50 nm.

By controlled oxidation with base, the Cu₂O cubes were transformed into thin CuO branches. The addition of NaOH aqueous solution into the ZnO–Cu₂O particle dispersion in ethanol at room temperature in air yielded ZnO–CuO core–branch nanoparticles. The TEM image shows needle-like CuO branches with an average length of 49 ± 4 nm and a thickness of 8 nm (Fig. 1b). The density and structure of the branches are uniform over all ZnO–CuO nanoparticles (Fig. S4, ESI[†]). The XRD pattern is a sum of wurtzite ZnO and monoclinic CuO diffraction peaks (Fig. 1d, JCPDS No. 48-1548). The high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image and elemental mapping of zinc (red) and copper (green) clearly exhibit anisotropic distribution of each component (Fig. 1c). Zn is detected at the original spherical core region, and Cu is mainly found at the surrounding branches, confirming the ZnO–CuO core–branch structure. The EDX spectra at the different regions also reveal CuO at the branches and ZnO at the cores, respectively (Fig. S5, ESI[†]).

The HRTEM analysis provides detailed surface structures of the CuO branches (Fig. 2). The ZnO core is polycrystalline composed of single-crystalline domains (Fig. 2b). Interestingly, the CuO branches have many defect sites with high surface index facets. Fig. 2c clearly shows the distinct lattice fringe images with the distances of 0.25 nm of the neighboring (11–1) planes and 0.23 nm of the (200) planes, respectively, and the defect sites between the fringes. The Fourier-transform (FT) pattern includes the intense spots assignable to (11–1) and (200) (Fig. 2c inset). The surface facets are mostly {311}, which are exceptional against low energy surfaces such as {100} and {111} facets. Most of the branches analyzed by HRTEM have clear defects with distinct lattice fringe image regions, and many of them particularly have {311} facets, as well as low index facets on their surface (Fig. S6, ESI[†]). Although many defects are

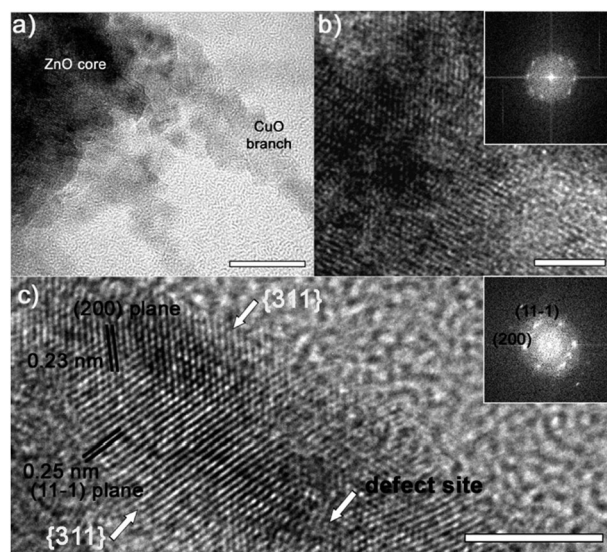


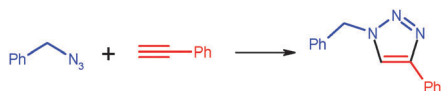
Fig. 2 (a) TEM image of a ZnO–CuO core–branch nanoparticle. HRTEM images of (b) the ZnO core and (c) the single CuO branch along the [011] zone axis and corresponding FT patterns (insets). The bars represent (a) 10 nm, (b) 3 nm, and (c) 5 nm.

observed, the branches are straight and continuously connected between distinct fringe regions.

For the evaluation of potential catalytic uses, the BET (Brunauer–Emmett–Teller) surface areas of the ZnO nanoparticles and the ZnO–CuO core–branch nanoparticles are measured to be 90 and $117 \text{ m}^2 \text{ g}^{-1}$, respectively, by nitrogen sorption experiments. By considering the copper loading content of 34 wt% in the ZnO–CuO particles, the surface area of the pure CuO branches is estimated to be $169 \text{ m}^2 \text{ g}^{-1}$. Pure CuO hollow spheres with short branches were also prepared by controlled oxidation of Cu₂O nanocubes with ammonia for comparison (Fig. S7, ESI[†]).⁷ The average diameter of the CuO hollows is 110 nm, and the surface area is measured to be $113 \text{ m}^2 \text{ g}^{-1}$, which is comparable to the value of the ZnO–CuO core–branch nanoparticles, but quite smaller than the surface area of the pure CuO branches.

Heterogeneous systems such as copper nanoparticles, Cu(I)-modified zeolites, or copper hydroxides on solid supports have been used for Huisgen alkyne–azide [3 + 2] cycloaddition reactions with high efficiency.^{8–10} To demonstrate the promineny of the ZnO–CuO core–branch nanoparticles as an organic reaction catalyst, the particles were employed as a heterogeneous catalyst for cycloaddition reactions of benzyl azide and phenylacetylene to yield 1,4-disubstituted 1,2,3-triazoles. The catalytic reactions were carried out in a mixed solvent of H₂O and *t*-BuOH (2 : 1) at room temperature in the presence of corresponding catalysts. The ZnO–CuO nanocatalysts exhibited 47% conversion yield, under vigorous stirring for 3 h with the usage of 3 mol% catalysts.

Notably, the catalytic performance was largely enhanced by applying ultrasound (Table 1). Ultrasound irradiation has been widely used in synthetic chemistry to contribute mechanical effects on heterogeneous reactions.^{8,11} In the present reaction conditions with the ZnO–CuO nanocatalysts under ultrasound irradiation, the reaction yield increased to complete conversion

Table 1 [3 + 2] Azide–alkyne cycloaddition reactions catalyzed by the ZnO–CuO hybrid nanocatalysts under ultrasonic irradiation^a

Entry	Cat (mol%)	Time/min	Temp.	Conv. ^b (%)
1	ZnO–CuO (3 mol%)	5	R.T.	80
2	ZnO–CuO (3 mol%)	10	R.T.	100
3	ZnO–CuO (1 mol%)	10	R.T.	21
4	ZnO nanoparticles (3 mol%)	10	R.T.	N.R.
5	CuO hollows (3 mol%)	10	R.T.	14
6 ^c	Commercial CuO (3 mol%)	10	R.T.	<1
7	ZnO–Cu ₂ O (3 mol%)	10	R.T.	31
8	Recovered from #2	10	R.T.	100
9	Recovered from #8	10	R.T.	100
10	Recovered from #9	10	R.T.	100
11	Recovered from #10	10	R.T.	82
12	Recovered from #11	10	R.T.	76

^a Reaction conditions: benzyl azide (0.6 mmol) and phenylacetylene (0.9 mmol) in H₂O–*t*-BuOH (2 : 1). ^b Determined by ¹H-NMR spectra.

^c Commercial CuO purchased from Aldrich (cat. no. 544868).

within 10 min at room temperature (entry 2, Table 1). The reaction did not proceed without ultrasound. The CuO hollow spheres, one of the best catalysts among Cu-based heterogeneous systems,¹⁰ carried out the reaction in 14% yield, and commercially available μm-sized CuO particles proceeded the reaction in <1% yield under the same conditions (entries 5 and 6, Table 1). After the reaction, the ZnO–CuO nanocatalysts were readily recovered by centrifugation and were reused five times with slight loss of the catalytic activity (entries 8–12, Table 1). The catalyst structure with thin branches after recycling five times did not show significant damage from their original core–branch nanostructure (Fig. S8, ESI[†]). These remarkable activities along with the high stability of the ZnO–CuO core–branch nanocatalysts indicate that the CuO thin branches serve as highly active facets on the surface with the large surface area, and the ZnO cores tightly bind the CuO branches through an epitaxial interface to stabilize the active surface against aggregation.

The [3 + 2] alkyne–azide cycloaddition reactions are generally known to proceed *via* the Cu(I) intermediates.¹² Accordingly, the high activity of the ZnO–CuO catalysts under the present conditions is rather strange. To investigate the actual reaction mechanism, a few control experiments were carried out. By the addition of a well-known radical scavenger, TEMPO ((2,2,6,6-tetramethylpiperidine-1-yl)oxyl), under the conditions identical to those in entry 2, the reaction was carried out in negligible yields of 1–2%, indicating that radical intermediates formed during the reaction. The surface species of the catalysts were investigated by X-ray photoelectron spectroscopy (XPS) with the core-level of Cu 2p_{3/2} before and after the reaction (Fig. S9, ESI[†]). The peaks are deconvoluted into two peaks, where the peak at lower binding energy is attributed to Cu(I), and that at higher binding energy is attributed to the Cu(II) species. Before the reaction, the Cu(II) state mostly existed on the catalyst surface. However, after the reaction, the relative areal intensity ratio between Cu(I) and Cu(II) states remarkably increases up to more than 1 : 1 (Table S1, ESI[†]). Note that the Cu(II) state

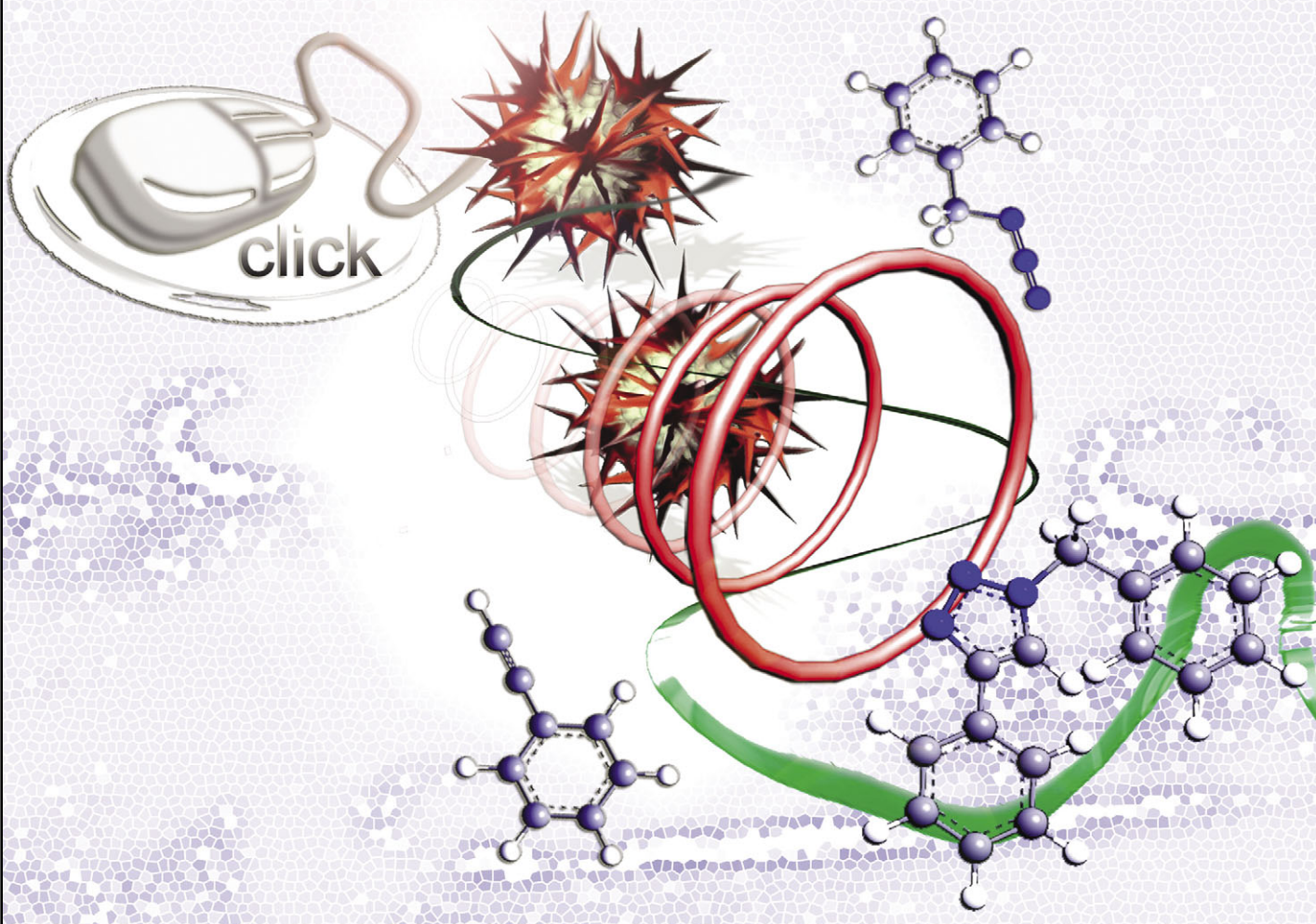
after the chemical reaction might be formed by air oxidation during the sample preparation of the XPS measurement. Consequently, it is believed that the present cycloaddition reactions were proceeded by the Cu(I) species formed *in situ* during the reaction. The excess amount of phenylacetylene could behave as a reductant to convert Cu(I) from the activated Cu(II) surface, *via* the formation of Cu(II)-acetylide.⁹ Ultrasonic irradiation played a critical role in activating the original Cu(II) surface and generating the Cu(I) species. The ZnO–Cu₂O particles were also active for the cycloaddition reaction, but the conversion yield was relatively low (31%, entry 7), due to the low surface area and low surface energy of {100} facets on the Cu₂O cubes.

In conclusion, we have synthesized ZnO–CuO core–branch hybrid nanoparticles and employed them as a highly active heterogeneous catalyst for [3 + 2] azide–alkyne cycloaddition reactions. Apparently, such a well-defined hybrid system with bifunctional components provides a new way to design high performance catalysts with high activity and reusability for gas- and solution-phase reactions. The choice of two distinct components with various metal and metal oxide elements widely expands the applicability to chemical, petroleum, environmental, and energy-related reactions.

This work was supported by the Core Research Program (2010-07592), Basic Science Research Program (2009-0070926, 2010-0002834), a National Research Foundation grant funded by the Korea Government (Ministry of Education, Science and Technology) (R11-2007-050-00000-0), and the grant-in-aid from the Korea Institute of Energy Research (Basic Project Program B2-2423).

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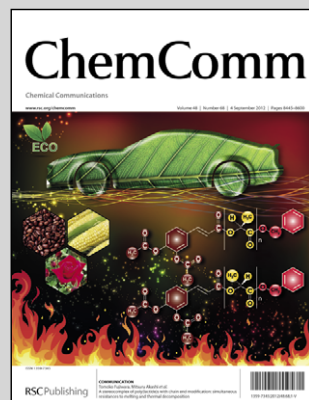


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ZnO–CuO core–branch nanocatalysts for ultrasound-assisted azide–alkyne cycloaddition reactions

A new type of nanocatalysts, ZnO/CuO core-branch hybrid nanostructure, has been demonstrated as an effective catalyst for ultrasound-assisted click reactions with remarkable activity and stability, due to their high surface area and active facets of the CuO branches.

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