# Bioinspired synthesis of well faceted CuI nanostructures and evaluation of their catalytic performance for coupling reactions†

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Well faceted CuI, truncated tetrahedral nanocrystals, were fabricated by an ascorbic acid-assisted green strategy at room temperature in a short period of time. A possible growth mechanism of such highly faceted nanostructures based on typical biomolecule-crystal interactions in aqueous solution is tentatively proposed. The large surface area and rich exposed active sites are expected to endow such truncated tetrahedral nanostructures with excellent performances in catalysis, as demonstrated here for the remarkable catalytic activity with respect to the coupling reaction between benzylamine and iodobenzene. This interesting result highlights the advantage of such a CuI nanostructure over the bulk counterpart, *i.e.* the high density of active sites and large specific surface area, which places a solid foundation for the feasible and promising application of such highly faceted nanomaterials in catalysis. It is the first report on the nanometre-sized faceted CuI acting as a catalyst for a coupling reaction and simultaneously a good example for the combination of green chemistry and functional materials.

## 1. Introduction

Generally, the catalytic performance of nanocrystals can be finely tuned either by their composition, which mediates the electronic structure,[1,2] or by their shape, which determines the surface atomic arrangement and coordination.[3,4,5] Several groups have intensively investigated the effect of shape of the nanocrystals on their catalytic activity and stability[6,7,8,9] and found that (i) some specific facets are believed to be the most catalytically active and (ii) when nanocrystals with different shapes are applied to the electron transfer reaction, the average rate constant of the reaction increases exponentially as the percentage of surface atoms at the corners and edges increases. From these studies, we know that the well-defined shapes of nanocrystals not only retain the catalytic properties of the bulk materials, but also greatly enhance the catalytic performance especially in the presence of more active sites (*e.g.* corners, edges, and steps). Cuprous iodide (CuI) as a catalyst for coupling reactions has been well-documented because it is safe, cheap and has high theoretical capacity, environmental benignity, *etc.*[10,11,12] One of the uncertainties is the lower efficiency. How to improve catalytic performance has become more and more urgent and ranks as one of the hot topics in the chemistry and materials field. So, why not synthesize nanometre-sized CuI with specific active facets to improve the catalytic activity? However, it is a great pity that, to the best of our knowledge, neither nanometre-sized CuI as a catalyst for coupling reactions nor the effect of shape on their catalytic activity has been reported.

A fundamental goal of materials science is the design and synthesis of materials with controllable shape and size and tailored functionality. Hence, in this paper, a facile one-step green synthetic route is described to construct truncated tetrahedral CuI nanostructures assisted by ascorbic acid (AA) at room temperature in a short reaction time. In comparison with reported protocols, our method is green, environment-friendly, facile, time-saving, and mild. Furthermore, these particles have sharp edges and corners, especially predominant {111} facets, which are expected to be chemically and dynamically active and therefore catalytically active, as demonstrated here for the excellent catalytic activity with respect to the coupling reaction between benzylamine and iodobenzene. To the best of our knowledge, it is the first report on nanometre-sized facted CuI nanostructures acting as a catalyst for a coupling reaction and simultaneously as a good example for the combination of green chemistry and functional materials.

## 2. Experimental section

### 2.1. Preparation of truncated tetrahedral CuI nanoparticles

All chemical reagents were of analytical grade and used without further purification. All water used in this investigation was deionized by a Nanopure filtration system to a resistivity of 18 MΩ·cm. The preparation of AA-assisted truncated tetrahedral CuI nanoparticles is quite straightforward. 5 mL of 0.15 M $CuSO_4$ aqueous solution, 15 mL of 0.005 M AA aqueous solution and 5 mL of 0.15 M KI aqueous solution were added under constant stirring, respectively, to 15 mL of ultrapure water. The mixture was stirred for 2 h in a 50 mL round-bottom flask at room temperature to prepare the sample. When the reaction was

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completed, a large quantity of white precipitate and a colorless supernatant were obtained. The resulting precipitate was filtered and washed with distilled water and finally dried in air naturally.

### 2.2. Sample characterization

The product was characterized by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) techniques to obtain detailed information on the morphology, component, and crystalline structure. The FESEM images were obtained on an XL30 ESEM FEG scanning electron microscopy operating at 20 kV. TEM and HRTEM were taken with a JEOL JEM-2010 transmission electron microscope. The XRD pattern was recorded in the $2\theta$ range of 20~80° on a Rigaku-D/Max 2500 V/PC X-ray diffractometer using Cu-K$\alpha$1 radiation ($\lambda$ = 1.54056 Å) at 40 kV and 200 mA. XPS was collected on an ESCALab MKII X-ray photoelectron spectrometer, using nonmonochromatized Mg-K$\alpha$ X-ray as excitation source.

### 2.3. Catalytic tests

The coupling reaction between benzylamine and iodobenzene, using the as-prepared CuI sample as the catalyst, ethylene glycol as ligand and unpurified 2-propanol as the solvent, was performed without protection from air or moisture. CuI (10 mg, 0.05 mmol) and potassium phosphate (425 mg, 2.00 mmol) were put into a Teflon septum screw-capped test tube followed by the addition of 2-propanol (1.0 mL), ethylene glycol (111 µL, 2.00 mmol), benzylamine (131 µL, 1.20 mmol), and iodobenzene (112 µL, 1.00 mmol) by microsyringe at room temperature. The tube was capped and the reaction mixture was heated at 80 °C for the specified time and then allowed to cool to room temperature followed by adding diethyl ether (2 mL) and water (2 mL). The organic layer was analyzed by GC.[11] The solid remainder entered the next reaction to test the recyclability of the catalyst.

## 3. Results and discussion

### 3.1. Structural analysis

The powder XRD pattern of the as-prepared sample (Fig. 1) reveals the formation of a single cubic phase CuI with a Marshite, *syn* structure (JCPDS 06-0246). No other diffraction peaks arising from metallic Cu or Cu oxides are present in the XRD pattern and indicate the high phase purity of the as-prepared sample. The outstanding aspects are the extremely strong reflection peaks of (222) plane and the seriously suppressed reflection peak of (200) and (400) planes, demonstrating that the sample is highly oriented along the [111] crystal axis. To obtain chemical states of the elements within the samples, we performed detailed analysis of the XPS spectra. The binding energies were corrected for specimen charging by calibrating the C1s peak to 284.6 eV. Fig. 2A and Fig. 2B show XPS spectra of Cu 2p1/2, 2p3/2 and I 3d5 core level acquired from the as-prepared sample. The positions of the peaks of Cu 2p1/2 and 2p3/2 of the sample CuI are 952.2 and 932.2 eV with very weak shake-up, which implies a feature of Cu$^+$.[13] The peak positions of I3d5, 619.5 and 631.0 eV, are consistent with the ones in the database of I 3d5.

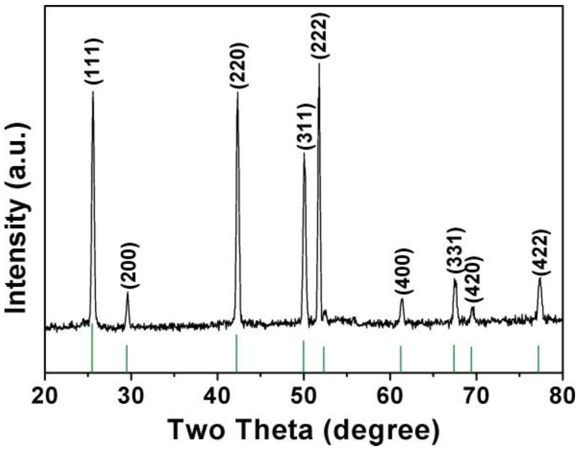


**Fig. 1** Typical XRD pattern of the sample, compared with the normal pattern of Marshite CuI (JCPDS card no. 06-0246).

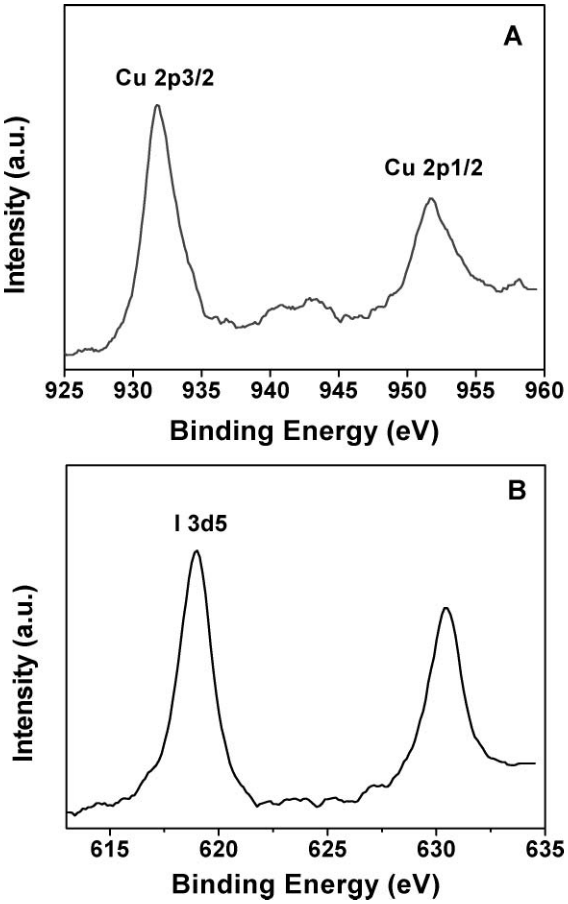


**Fig. 2** High-resolution XPS spectra taken for the Cu and I region of the sample: (A) Cu 2p and (B) I 3d5.

In order to obtain the detailed information about the microstructure and morphology of the as-synthesized sample, FESEM observations are carried out and shown in Fig. 3. The low magnified image in Fig. 3A indicates that the panoramic morphology of the as-prepared sample is mainly composed of uniform faceted polyhedral nanoparticles with diameter of *ca.* 150 nm. The high-magnification image in Fig. 3B clearly shows

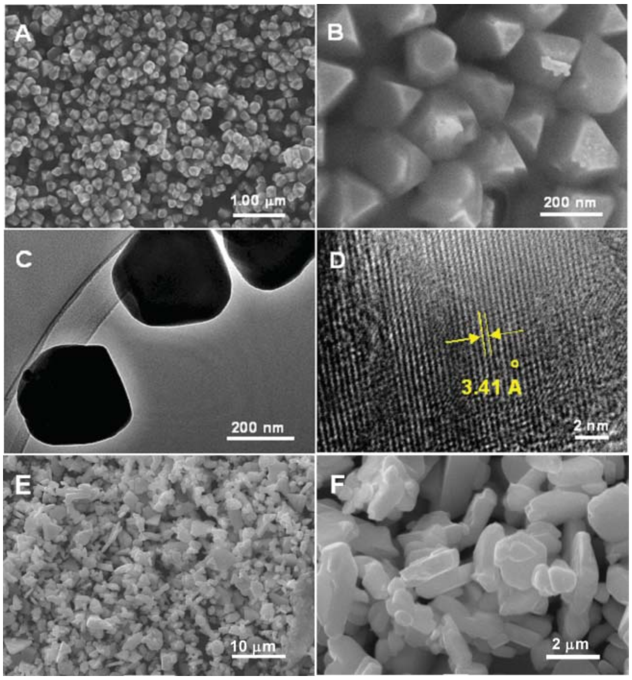


**Fig. 3** A typical FESEM image (A), high-magnification image (B), TEM image (C), and HRTEM (D) of the product; (E) and (F) FESEM images of CuI prepared without AA.

the triangular and hexagonal facets with diameters ranging from 50 to 100 nm. For one polyhedron, there are four triangular and hexagonal facets, separately. This configuration is consistent with that of a truncated tetrahedron, and therefore, our sample is termed as truncated tetrahedral CuI nanostructures. The microstructure of the as-grown sample is further analyzed using TEM and HRTEM. The TEM image of a single nanocrystal (Fig. 3C) clearly reveals the polyhedral morphology. The length of the side is around 180 nm. The HRTEM image in Fig. 3D can give further insight into the details of the structure. The lattice fringes can be clearly distinguished, which indicates its single-crystalline nature and the *d* spacing of 3.41 Å corresponds to the {111} plane. This result is consistent with the XRD pattern.

### 3.2. Growth mechanism

What growth mechanism is operating here for the formation of such truncated tetrahedral nanostructures? In order to explain this issue, we collected samples over various periods of time. Fig. 4 shows the FESEM images of the samples obtained at different stages of the reaction. It can be seen that during the reaction process from 10 min to 50 min, the morphology evolved from irregular particles to gradually faceted particles. According to the Gibbs-Curie-Wulff theorem, the shape of a crystal is determined by the relative surface free energy of individual crystallographic faces. The final crystal shape results from minimizing the total free energy of the system.[14] For a face-centred-cubic (fcc) single crystal, surface energies associated with different crystallographic planes are usually different, and a general sequence may hold, $\gamma$ (111) < $\gamma$ (100) < $\gamma$ (110). Generally, the selective adsorption of surfactants, ions, ligands, or polymers on a given crystal plane can inhibit the crystalline growth along one specific direction, leading to a preferential growth along another direction.[15,16,17] Therefore, the introduction of an additive with a selective adsorption function is widely used for the synthesis of anisotropic nanocrystals in a solution phase. Based on these, a possible mechanism is proposed (Scheme 1). It is believed that the growth of truncated tetrahedron should be completed by two steps, *i.e.* nucleation and growth, respectively. In our synthesis route, AA plays a crucial role in controlling the shape of the nanocrystals. There is a functional hydroxy group OH on the AA molecules, which is a hydrophilic group and can provide coordination sites, namely nucleation sites. When $Cu^{2+}$ ions enter into aqueous solution, there is electrostatic attraction between the positively charged $Cu^{2+}$-water complex and the negatively charged hydroxy groups of AA, thus forming complex $Cu^{2+}$–AA. Upon the introduction of $I^-$, the rapid redox reaction between $Cu^{2+}$–AA and $I^-$ results in the formation of spherical CuI crystal seeds. It has been revealed that a slow reaction is favorable for the formation of anisotropic nanocrystals.[18] Here, the existence of $Cu^{2+}$–AA complex will reduce the reduction rate of $Cu^{2+}$ ions. Under the slow reaction, AA molecules seem to be preferentially adsorbed on the {100} planes of the nuclei during the reaction, and consequently the area ratio of {111} to {100} increased, which facilitates the formation of truncated tetrahedral CuI nanocrystals based on the idea that an increase in the area ratio of {111} to {100} results in the evolution of particle shapes to a truncated tetrahedron.[19] No external reductant was needed for $Cu^{2+}$ reduction in the present method, further suggesting that AA itself is responsible for this reduction reaction. As is well known, a redox reaction occurs immediately when $Cu^{2+}$ and $I^-$ are mixed in water solution at room temperature to form irregular CuI microparticles (Fig. 3E and F). Besides, the failure of producing truncated tetrahedron CuI when substituting sodium citrate and L-tryptophan for AA also further confirms the special role of AA

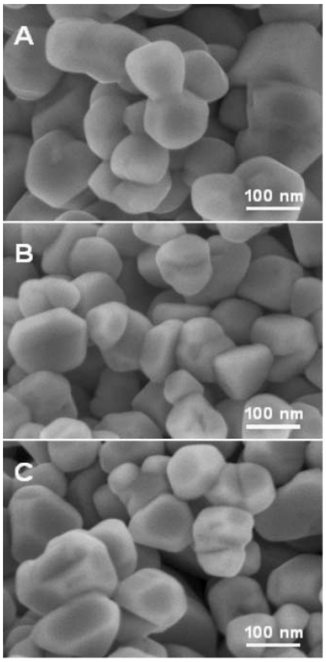
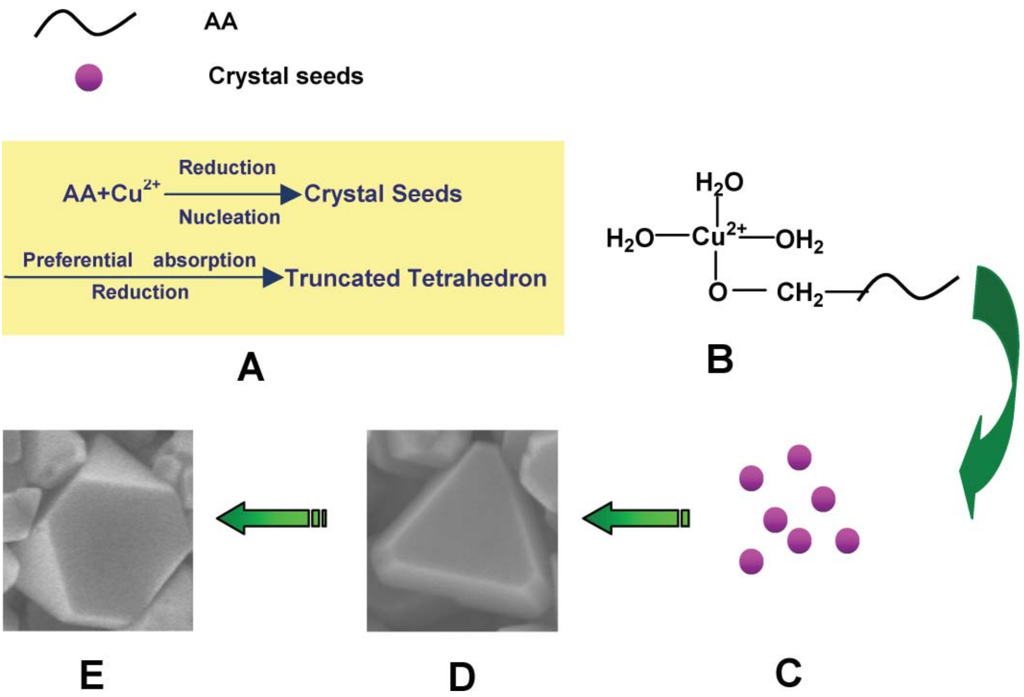


**Fig. 4** FESEM images of samples obtained after a reaction time of (A) 10 min, (B) 30 min, and (C) 50 min.

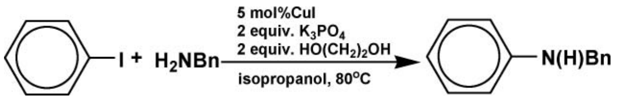


**Scheme 1** Schematic illustration of the proposed formation mechanism for the as-obtained truncated tetrahedral nanotructures. (A) Simple representation of the formation of truncated tetrahedron; (B) the electrostatic attraction between the positively charged $Cu^{2+}$-water complex and the hydroxy groups of the negatively charged AA; (C) rapid seed generation and formation of secondary spherical particles; (D) preferential adsorbion on the {100} planes of the nuclei, forming a faceted angle; (E) shape and size focusing.

in the formation of such unique truncated tetrahedral CuI (see Electronic Supplementary Information, Fig. S1†).

### 3.3. Catalytic activity

The formed truncated tetrahedral CuI nanoparticles are highly faceted, abundant in {111} planes and corners and edges, which are expected to be chemically and dynamically active and therefore catalytically active to accommodate reactant molecules to react on their active sites. Transition metal catalyzed C–N bond-forming processes are extensively utilized in the medicinal chemistry and material sciences. Although it has been proved that Pd is an efficient catalyst, significant defects, such as the high cost and relative sensitivity to exogenous oxygen and moisture, limit its attractiveness. Thus, less costly alternatives and operationally simple procedures are desirable. Kwong *et al.*[11] reported a mild, practical Cu-catalyzed amination of functionalized aryl iodides using commercial CuI as the catalyst. Based on the literature,[10,11,12] the catalytic properties of the as-prepared truncated tetrahedral CuI nanoparticles were tested for the first time for the coupling reaction between benzylamine and iodobenzene (Scheme 2) under conditions as described in the Experimental Section. The catalytic data are summarized in Table 1 and Fig. 5, which clearly demonstrate that the truncated tetrahedral CuI nanoparticles show much higher catalytic activity than that of commercial CuI and can be recycled at least three times without appreciable loss of the catalytic activity



**Scheme 2** The coupling reaction between benzylamine and iodobenzene catalyzed by the as-prepared highly faceted CuI with truncated octahedral nanostructures.

**Table 1** Test of catalytic activity of truncated tetrahedral CuI nanostructures for coupling reaction

| Entry | Catalyst | Reaction Time/h | Yield [%][a] |
|---|---|---|---|
| 1 | CuI | 9 | 96.4 |
| 2 | Recovered from entry 1 | 9 | 93.4 |
| 3 | Recovered from entry 2 | 9 | 89.8 |
| 4 | Commercial CuI | 18 | 89 |

[a] Yield of *N*-(phenyl) benzylamine.

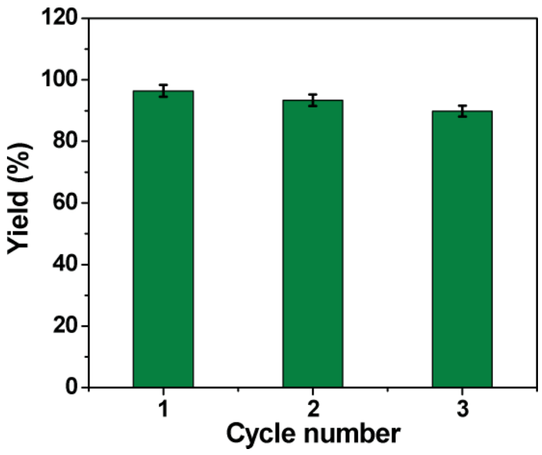
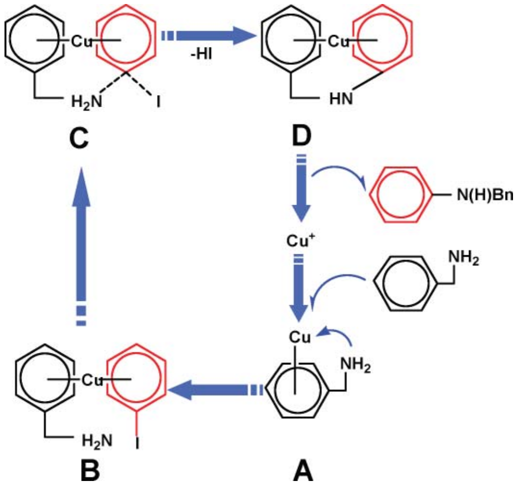


**Fig. 5** Catalytic activity cycle. Each point represents the mean ±2 standard error.

for the coupling reaction. Therefore, catalytic performance for coupling reactions can be greatly improved using the as-prepared truncated tetrahedral CuI nanoparticles. The catalysis process is shown in Scheme 3 and outlined as follows: first, cuprous ion reacts with a benzylamine to form the chelate 3A, which coordinates with a suitable iodobenzene to provide the complex 3B. Next, intramolecular nucleophilic substitution occurs at the aromatic ring to give the transition state 3C. This step might be the rate-determining step, and the intramolecular attack would lower the activation energy of this step. Finally, HI was removed from 3C with the assistance of potassium phosphate to deliver another complex 3D, which could decompose to produce the coupling product and regenerate the cuprous ion.[20]



**Scheme 3** Possible reaction mechanism for the coupling reaction between benzylamine and iodobenzene catalyzed by the as-prepared truncated tetrahedral CuI nanostructures.

In our case, the improvement of the catalytic performance may be attributed to the following factors: (1) the large surface area of the nanoparticles and (2) the increased density of catalytically active sites. On the one hand, as known to us, nanometre-sized materials can exhibit very different catalytic properties from those of the corresponding bulk materials due to their higher surface area.[21] The external surface of particles is used as a contact surface in catalytic reactions. The larger the external surface area of a catalyst, the higher the chance of contact between the reagent and particles. On the other hand, the activity and selectivity of the catalytic reactions are sensitive to the crystallographic planes and typically the catalytic activity can be enhanced on high-index facets that are rich in stepped and dangling atoms.[22,23] For instance, El-Sayed and co-workers have investigated that (1) catalysis on transition metal crystal surfaces depends on the crystal face used, (2) different nanoparticles with different shapes have different facets and different ratios of the number of atoms on corners and edges to those on the facets, and (3) the average rate constant of the reaction increases exponentially as the percentage of surface atoms at the corners and edges increases.[6,7,8,24] In our case, the illustrations about the unit cell of the Marshite CuI and the Cu atoms on the different crystallographic planes of CuI are displayed (see Electronic Supplementary Information, Scheme S1†). More information has been provided in the Electronic Supplementary Information. Additionally, when truncated tetrahedral CuI nanostructures form, more sharp edges and corners are exposed, where it is expected that $Cu^+$ become much more catalytically active and accounts for the improved catalytic activity than in the case of the bulk material. This interesting result highlights the advantage of such CuI nanostructures over the bulk counterpart, *i.e.* the high density of active sites and large specific surface area, which places a solid foundation for the feasible and promising application of such highly faceted nanomaterials in catalysis.

## 4. Conclusion

In summary, we have developed a bioinspired and environmentally friendly procedure for rapid room temperature synthesis of highly faceted CuI with truncated tetrahedral nanostructures circumventing the extra controls and additives.

Control experiments clearly verify the dual-functionality of the AA molecule, a reducing and structure-directing agent. In comparison with the reported protocols, our method is green, environment-friendly, facile, time-saving, and mild. Compared with the bulk materials, such truncated tetrahedral nanostructures feature extremely strong reflection peaks of the {111} plane and possess abundant sharp edges and corners, which endow them with excellent catalytic performance, as demonstrated here for the remarkable catalytic activity with respect to the coupling reaction between benzylamine and iodobenzene. This interesting result highlights the advantage of such CuI nanostructures over the bulk counterpart and places a solid foundation for the feasible and promising application of such highly faceted nanomaterials in catalysis. To the best of our knowledge, it is the first report on nanometre-sized CuI acting as a catalyst for a coupling reaction and simultaneously is a good example for the combination of green chemistry and functional materials.

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