

Cu₂O Nanocrystals-Catalyzed Photoredox Sonogashira Coupling of Terminal Alkynes and Arylhalides Enhanced by CO₂

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Herein the first visible-light-activated Sonogashira C-C coupling reaction at room temperature catalyzed by single-metal heterogeneous Cu₂O truncated nanocubes (Cu₂O TNCs) was developed. A wide variety of aryl halides and terminal alkynes worked well in this recyclable heterogeneous photochemical process to form the corresponding Sonogashira C-C coupling products in good yields. Mechanistic control studies indicated that CO₂ enhances the formation of light-absorbing heterogeneous surface-bound Cu^I-phenylacetylide ($\lambda_{max} = 472 \text{ nm}$), which further undergoes single-electron transfer with aryl iodides/bromides to enable Sonogashira C_{sp2}-C_{sp} bond formation. In contrast to literature-reported bimetallic TiO₂-containing nanoparticles as photocatalyst, this work avoided the need of cocatalysis by TiO₂. Single-metal Cu¹ in Cu₂O TNCs was solely responsible for the observed C_{sp^2} - C_{sp} coupling reactions under CO₂ atmosphere.

shira cross-couplings are the predominant inexpensive protocols for constructing conjugated alkynes,^[3d,4,5] However, the usage of excess ligands and the harsh thermal reaction conditions diminish their merits.

To address the above challenges, we previously reported visible-light-triggered CuCl-catalyzed Sonogashira crosscoupling between aryl halides and terminal alkynes at room temperature.^[6] We envisioned that the C–C coupling reactions can be initiated by photoexcited copper(I)-phenylacetylide that undergoes a single-electron transfer (SET) process with ground-state aryl halides via inner-coordination sphere to initiate the C-C coupling reaction upon visible-light irradiation. We questioned whether it is possible to replace the molecular CuCl catalyst with recyclable solid copper-containing nanoparticles (NPs) for the Sonogashira $C_{sp^2}-C_{sp}$ cross-coupling reactions between aryl halides and terminal alkynes under visible-

Ar−X + = R b)

The Sonogashira coupling reaction is one of the most powerful and straightforward methods for construction of aryl alkynes/conjugated alkynes through C_{sp²}-C_{sp} cross-coupling of aryl/alkenyl halides and terminal alkynes, which are the most substantial intermediates in the synthesis of natural products as well as pharmaceutical, polymeric, and organic materials.^[1] In such transformations, conventional methodologies involve the use of palladium phosphine complexes along with copper as a cocatalyst in the presence of excess organic amine bases (Scheme 1 a).^[2] However, these methods often require expensive Pd catalysts and Cu salts as cocatalyst with excessive ligands/ amines or harsh thermal conditions. Recently, a number of reports have demonstrated different modifications in a catalytic fashion,^[3] such as a) Cufree Pd-catalytic systems, [3a-d] b) Pd-free Fe-, Ni-, or

Cu-complexes,^[3e,f] and c) Cu-catalysts with ligands under harsh conditions.[3g] Among them, Pd-free copper-catalyzed Sonoga-

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IEE active [Pd]/[Ci Pyrazine TICT aeneral Sonoaashira coupling ^{~60°}°C d) Ar−X + = _P Ar-X + - R C) Present work: visible-light-initiated single-metal heterogeneous Sonogashira C-C Coupling

Previous work: bimetallic heterogeneous Sonogashira coupling supported by photocatalysts



In situ-generated Cu₂O-Cu(I)-phenylacetylide as photocatalyst OCO2 enhances reaction Support-free, Cu₂O-catalyzed Sonogashira reaction Recyclable solid catalyst

Scheme 1. Various methods for Sonogashira coupling.

light irradiation at room temperature. Such recyclable heterogeneous photocatalysts are highly desirable for Sonogashira coupling reactions and remain unexplored in the literature.

Heterogeneous catalysts are important owing to their recyclability and easy separation/recovery, especially in industrial applications. Recently, a few reports demonstrated the feasibility of photoinduced heterogeneous catalysis for Sonogashira cross-coupling at room temperature, such as: a) using a supramolecular ensemble of a twisted intramolecular charge-transfer states aggregation-induced emission enhancement (TICT-AIEE) active pyrazine and CuO nanoparticles (Scheme 1 b),^[7] b) a sili-



con carbide-supported Pd-Cu alloy (Pd₃Cu₁/SiC) or TiO₂supported palladium NPs (Pd@TiO₂) (Scheme 1 c);^[8,9] and c) TiO₂-supported CuO bimetallic photocatalysts (Scheme 1 d), for which cocatalysis of Ti to Cu ions is required for the coupling reactions to occur.^[10] Despite increased attention, most heterogeneous NP-based catalysts still have some limitations. They require cocatalysis from a metal-oxide support (e.g., TiO₂, ZnO, Fe₂O₃, Nb₂O₅, CdS, BiTaO₄), usually have poor photocatalytic activities owing to weak light absorption and an inefficient charge separation,^[11,12] and have limited substrate scope and poor recyclability. Thus, a single-metal-based heterogeneous catalyst would be more attractive for Sonogashira C-C coupling. CO₂ is known to be a major contributor to global warming and can promote or trigger some chemical reactions, which has received significant attention in organic synthesis.^[13] It was reported in the literature that CO₂ (a Lewis acid) can physically/chemically absorb on various kinds of metal oxides (Lewis bases), leading to formation of carbonates or undergoing electrochemical reductive conversion to methanol on the Cu₂O electrode surface.^[14a-d] Theoretical calculations also showed that chemical adsorption of CO2 on the Cu2O solid surface will release -56 to -233 kJ mol⁻¹ adsorption energy, depending on the mode of adsorption.^[14e,f] In other words, adsorption of CO₂ on the Cu₂O surface is exothermic and will occur spontaneously. Herein we report (Scheme 1e) singlemetal-based heterogeneous catalysis that avoids the requirement of cocatalysis by metal-oxide support (such as TiO₂) and achieves visible-light-activated Sonogashira C-C coupling between aryl halides and terminal alkynes at room temperature catalyzed by heterogeneous Cu₂O truncated nanocubes (TNCs). The notable key features of current method are as follows: (i) Cu₂O TNCs are solely responsible for the generation of the surface-bound light-absorbing Cu¹ TNCs-phenylacetylide complex; (ii) CO₂ was shown to enhance the C-C crosscoupling product yields; (iii) moderate-to-good yields were achieved with no significant loss in catalytic efficiency even after five cycles; (iv) good recyclability of the catalyst was achieved, in which the heterogeneous Cu₂O TNCs photocatalyst can be recycled by simple centrifugation-filtration.

We synthesized the highly stable Cu₂O TNCs through a hydrothermal route,^[15] further analyzed their morphologies by SEM and TEM, and investigated their photophysical properties by methods such as UV/Vis/near-IR (NIR), and XRD (for details of synthesis and structural characterization, see Figure S1 in the Supporting Information). Inspired our previous work,^[6] we intended to develop a single-metal heterogeneous Cu catalyst for photoinduced C-C cross-coupling reactions. We began our investigations by using phenylacetylene (1 a) and iodobenzene (2a) as substrates under blue-light irradiation with different NP-based catalysts, solvents, and bases. We were delighted to find that the combination of Cu₂O TNCs and K₂CO₃ in CH₃CN/ CH₃OH (1:1 v/v) as a cosolvent provided **3a** in 68% yield along with 22% of Glaser homocoupling product under visible-light irradiation in N₂ atmosphere at room temperature (Table 1, entry 1). Further optimization of the reaction conditions showed that the presence of CO₂ could further boost the yield of 3a to 89% accompanied by a trace amount of homocou-

Table 1. Effects of reaction parameters.			
	Ph H + Ph-I Cu ₂ O TNCs (5 mg) K ₂ CO ₃ (1.05 equiv.) 1a 2a CH ₃ CN/CH ₃ OH, RT, blue LEDs, 8 h, CO ₂ (1 atm)	PhPh 3a	
Entry	Variation from standard conditions	Yield ^[a] [%]	
1	under N_2	68 ^(b) 89 ^(c)	
3	Au NCs	n.r.	
4 5	Pd NPs no light, 80°C	n.r. 10	
6	no base	n.r.	
7	no Cu ₂ O INCs CuO nanospheres	n.r. n.r.	
9 10	Cu ₂ O octahedral NCs Cu ₂ O NCs	82 80	
[a] Yield of the isolated product. [b] 22% homocoupling product, 1,4 diyne, was observed. [c] Trace amount of homocoupling products. n.r.=			

no reaction.

pling byproduct (entry 2). The increase in the 3a yield under CO₂ atmosphere is probably owing to two factors. First, removal of molecular O₂ can suppress the homocoupling products because an O₂ atmosphere is known to promote formation of Glaser homocoupling products. Second, coordination of CO₂ onto the surface of Cu₂O TNCs probably enhances the formation of surface-bound Cul-phenylacetylide and prolongs its excited-state lifetime, leading to more efficient SET to aryl halides (see below). We also found that CuO NPs were not able to catalyze the formation of 3a (entry 8) under the standard conditions, whereas Cu₂O NCs with different morphologies all could catalyze formation of 3a with good yields (entries 9, 10, see Figure S3-S5 in the Supporting Information). These results unambiguously indicate that only Cu^I- but not Cu^{II}-containing NPs can catalyze the Sonogashira C-C coupling reactions between aryl halides and terminal alkynes.

Under the optimized conditions (Table 1, entry 2), we then investigated the scope of the aryl iodides (2) with 1 a. Various aryl iodides containing neutral, electron-rich, halogen-substituted, or electron-poor moieties all reacted well with 1 a to afford C–C coupling products 3a-i in good yields (70–89%, see Table 2). To our disappointment, we observed very low yields of products 3f and 3k in the case of aryl bromide substrates.

Further, we explored the scope of alkyl/aryl terminal alkynes with 4-iodoanisole (**2 f**) under the optimized conditions (Table 3). A wide range of aliphatic terminal alkynes reacted well with **2 f** to form the corresponding C–C cross-coupling products **4a–f** in 81–89% yield. In addition, the system worked very well for aryl terminal alkynes substituted with neutral, halogen, and electron-withdrawing groups (*t*Bu, Cl, CN, acyl) and heterocyclic alkynes (e.g., carbazole), producing C–C coupling products **4g–p** in good yields.

To gain mechanistic insights into the Cu₂O TNCs-catalyzed Sonogashira C–C coupling reaction, several experiments were performed (Scheme 2). Addition of Cu₂O TNCs to a phenylace-tylene/CH₃CN/CH₃OH solution (with or without CO₂) resulted in

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[a] Yield of the isolated product. [b] Under 0.5 atm N_2 +0.5 atm CO_2 . [c] Under 1.5 atm CO_2 . [d] Instead of aryl iodide, aryl bromide substrates were used for 18 h. [e] Reaction for 10 h.



the formation of a yellow Cu₂O TNCs-phenylacetylide complex suspension, of which the Fourier-transform (FT)IR spectrum (Figure 1 a) shows the characteristic C=C peak at 2200 cm⁻¹

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Scheme 2. Mechanistic control studies of the Cu_2O TNCs Cu^l -phenylacetylide complex.

and a peak at 1930 cm⁻¹, a characteristic feature for the presence of C=C-Cu^{1,[16,17]} Then, UV/Vis/NIR spectra of Cu₂O TNCs, the yellow suspension, and starting materials were measured, respectively (Figure 1 b). The maximum UV/Vis absorbance at 472 nm was observed for the yellow suspension, indicative of formation of a Cu₂O TNC-Cu¹-phenylacetylide complex, which serves as a light-absorbing photocatalyst. Notably, this result closely resembles our previous free molecular Cu¹-phenylacetylide complex.^[6] Furthermore, sequential addition of different amounts of **2 f** to a solution containing the Cu₂O-TNCs(I)phenylacetylide complex resulted in a progressive photoluminescence quenching of the Cu₂O TNCs-Cu¹-phenylacetylide.

Furthermore, we also explored the coupling reactions between electron-donating/-withdrawing aryl iodides with linear aliphatic/electron-donating/-withdrawing aryl terminal alkynes to obtain the desired C–C cross-coupling products **4k–4n** in moderate-to-good yields (79–87%). The addition of 2 mm **2 f** reduced the excited-state lifetime of Cu¹-phenylacetylide complex from 13.20 to 6.15 μ s. This result also suggested that a SET process is operative from surface-bound photoexcited Cu¹phenylacetylide complex to **2 f** (see lifetime measurements in Figure S6 in the Supporting Information).

Next, we performed a coupling reaction between **2 f** and **1 a** in the presence of a radical scavenger (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) or butylated hydroxytoluene (BHT). The presence of radical scavengers dramatically inhibited the product formation, indicating the presence of a radical intermediate during the reaction. Next, we measured electron paramagnetic resonance (EPR) spectra under the standard reaction conditions by using a spin-trapping agent, (3,3,5,5-tetramethyl-1-pyrroline-*N*-oxide) to trap the proposed aryl radical. Figure 1d depicts the EPR signal of the aryl radical adduct, of which the *g* value and splitting pattern match well with those reported in the literature.^[17]

To look for more experimental evidence to rationalize how CO_2 enhances the C–C coupling product yields, we performed (a) steady-state phosphorescence measurements, (b) phosphorescence-lifetime measurements of the surface-bound Cu_2O-Cu^1 -phenylacetylide under a CO_2 atmosphere, and (c) EPR measurements of phenyl radical trapping by TEMPO in the presence/ absence of CO_2 . In the presence of CO_2 , the steady-state phosphorescence intensity of surface-bound Cu_2O-Cu^1 -phenylacetylide increases slightly (see Figure S7 a in the Supporting Information), indicating that CO_2 can promote formation of surface-



Figure 1. Mechanistic studies. (a) FTIR-spectra of in situ-generated Cu₂O-Cu¹-phenylacetylide. (b) UV/Vis/NIR spectra of in situ-generated Cu₂O-Cu¹-phenylacetylide in CH₃CN; PhAC = phenylacetylene. (c) Photoluminescence quenching of photoexcited Cu₂O-Cu¹-phenylacetylide by addition of **2 f**. (d) EPR spectrum of the adduct of aryl radical with a spin-trapping agent (3,3,5,5-tetramethyl-1-pyrroline-*N*-oxide) in dark and under photoirradiation. The *g* value is 2.0053 with a coupling constant $a_{\rm H}$ = 15.90 G.

bound Cu₂O-Cu¹-phenylacetylide because the steady-state luminescent intensity is in general proportional to the amount of luminescent compound present in the solution. The phosphorescence lifetime of the surface-bound Cu₂O-Cu¹-phenylacetylide changes from 13.9 μ s in the absence of CO₂ to 15.3 μ s under a CO₂ atmosphere (see Figure S7 b in the Supporting Information). A longer excited-state lifetime is more favorable to a bimolecular electron transfer from surface-bound photoexcited Cu₂O-Cu¹-phenylacetylide to aryl halide in the solution, which should lead to higher amounts of aryl radical as well as a higher yield of C-C coupling product. Indeed, we observed a slightly stronger aryl radical EPR signal under a CO₂ atmosphere than under normal air conditions (see Figure S7c in the Supporting Information). Overall, the presence of CO₂ enhances the Sonogashira C-C coupling product yield through enhanced formation of the surface-bound Cu₂O-Cu¹-phenylacetylide intermediate and slightly prolonged excited-state lifetime.

Finally, we evaluated the recycling performance of the single-metal heterogeneous Cu_2O TNCs by using **1a** and **2h** under the optimal conditions and blue-LED irradiation (Figure 2). After completion of the reaction, the catalyst was collected by centrifugation and washed with water several times to remove K_2CO_3 . The recycled Cu_2O TNCs were further

examined for their ability to catalyze the Sonogashira coupling reaction, which showed that the catalytic activity decreased only slightly from 86% yield of **3a** in the first run to 80% in the fifth cycle. Notably, as shown in Figure 2 b, SEM images of the recycled catalyst displayed that the morphology and size of Cu₂O TNCs remain unchanged. The crystallinity of Cu₂O TNCs was stable even after five catalytic cycles (Figure 2 c). Besides Cu₂O TNCs, other Cu₂O NPs such as octahedral NPs and cubes can all catalyze the Sonogashira C–C coupling reaction, but they are less stable and tend to form aggregates and change morphologies after reactions (see Figures S4 and S5 in the Supporting Information).

The reaction mechanism for the photoinduced Sonogashira coupling reaction catalyzed by single-metal heterogeneous Cu₂O TNCs was proposed in Scheme 3. Based on the UV/Vis and FTIR spectroscopy and other supporting mechanistic evidence, Cu¹ on Cu₂O TNCs reacts with **1a** to form surface-bound Cu¹-phenylacetylide (**1a**') on Cu₂O TNCs. **1a**' has an absorption maximum at 472 nm, and its redox potential is probably close or similar to its molecular counterpart (E_{redox} = -2.048 V vs. saturated calomel electrode, SCE). Upon photoexcitation by blue LEDs, a long-lived triplet photoexcited copper(I)-phenylacetylide (**5**) was generated,^[18] followed by SET to





Figure 2. (a) Catalytic activities of Cu₂O TNCs versus number of cycles. (b) SEM image and (c) XRD pattern of recycled Cu₂O TNCs.



Scheme 3. Plausible reaction mechanism.

aryl iodide **2a** ($E_{redox} = -1.20$ V vs. SCE)^[19] to produce an aryl radical. The aryl radical can rapidly react with Cu^{II}-phenylacetylide (**6**) within the coordination sphere, regenerates the heterogeneous Cu₂O TNCs, and eventually leads to the formation of the C–C cross-coupling product **3a**. The presence of CO₂ can promote the formation of surface-bound Cu^I-phenylacetylide and prolong its excited-state lifetime, leading to more efficient bimolecular electron transfer to aryl halides and thus higher product yields.

In summary, we successfully demonstrated that single-metal heterogeneous Cu₂O TNCs are able to catalyze Sonogashira C– C cross-coupling reactions under visible-light irradiation at room temperature via formation of surface-bound Cu¹-phenylacetylide on Cu₂O TNCs. To the best of our knowledge, this is the first C–C cross-coupling catalyzed by single-metal heterogeneous Cu₂O nanoparticles under visible light. The heterogeneous-phase C–C coupling reaction was greatly enhanced upon coordination of CO₂ to the basic Cu₂O surface, leading to enhanced formation of surface-bound Cu₂O TNC-Cu¹-phenylacetylide and prolonged excited-state lifetime, which makes SET to aryl halides more efficient and results in higher product yields. The catalytic activity of this unique solid catalyst did not show noticeable degradation after five cycles. Moreover, our visible-light photocatalyst can be used to explore other Cu¹mediated reactions under photoredox conditions and is a good alternative for replacement of the existing expensive precious-metal catalysts in homogeneous and heterogeneous catalysis.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: $CO_2 \cdot Cu_2O$ truncated nanocubes \cdot heterogeneous catalysis \cdot photocatalysis \cdot Sonogashira reaction

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Surface-bound: A Cu₂O truncated nanocubes-catalyzed Sonogashira C–C coupling reaction between aryl halides and terminal alkynes is demonstrated at room temperature. The features of the reaction include in situ formation of a single-metal heterogeneous Cu¹-phenylacetylide ($\lambda_{max} = 472$ nm) photocatalyst, a C–C coupling product yield enhanced by CO₂, and good recyclability of the solid photoredox catalyst. M. Shanmugam, A. Sagadevan, V. P. Charpe, V. K. K. Pampana, K. C. Hwang*



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