Catalysis
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View Article Online
DOI: 10.1039/C8CY00618K

Journal Name

ARTICLE

Photocatalytic Sonogashira Reaction over Silicon Carbide Supported Pd-Cu Alloy Nanoparticles under Visible Light Irradiation

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Sonogashira reaction is an important reaction for forming carbon-carbon bond in organic synthesis, which is typically carried out under harsh reaction conditions. We herein report that PdCu alloy nanoparticles supported on SiC can efficiently catalyze the Sonogashira reaction by visible light irradiation under ligand-free and mild condition. The addition of Cu enhanced the activity of PdCu alloy nanoparticles. Pd_3Cu_1/SiC catalyst exhibited the highest catalytic performance for the Sonogashira reaction of iodobenzene with phenylacetylene, and the conversion of iodobenzene and selectivity of diphenylacetylene were 99.7% and 98.7%, respectively. The Sonogashira reaction catalyzed over SiC supported PdCu alloy is a light-driven process, and the reaction rate was greatly influenced by light intensity and wavelength. A possible reaction mechanism for the photocatalytic Sonogashira reaction over Pd_3Cu_1/SiC was proposed.

1. Introduction

Bimetallic nanoparticles usually show superior catalytic properties over their monometallic counterparts, which have attracted intensive attentions.[1-2] Among bimetallic nanomaterials, PdCu alloy catalysts exhibit high activity and selectivity in many reactions, such as formic acid oxidation,[3] photocatalytic nitrate reduction,[4] hydrogenation of CO_2,[5] electrocatalytic oxidation of methanol [6] and so on. Wang et al synthesized Pd-Cu nanoalloy catalysts supported on Vulcan XC-72 carbon by a facile one-pot polyol reduction process for formic acid oxidation (FAO),[7] and found the Pd_1Cu_1/C catalyst exhibited the best electrocatalytic performance toward FAO among the alloy catalysts. The enhanced electrocatalysis performance was due to the alloying of Pd with Cu. Generally, the addition of Cu can lower the d-band center of Pd to weaken the adsorption of reaction intermediates and increase the thermal stability of PdCu alloy nanoparticles.[8-9] Thus, PdCu alloy catalysts are very potential in catalytic areas. Sonogashira cross-coupling reaction is an important method for constructing C(sp^2)-C(sp) bonds.[10] Traditionally, palladium phosphine complexes with CuI (cuprous iodide) as co-catalyst were employed for the Sonogashira cross-coupling reaction, which always required usage of organic ligands and high amount of copper. [11] Recently, many studies are focused on developing PdCu bimetallic catalysts for Sonogashira reaction.[12-14] For example, Diyarbakir et al used PdCu alloy nanoparticles supported on reduced graphene oxide as efficient catalysts for the Sonogashira reaction,[13] which showed good activity and applicability.

Photocatalysis uses solar energy to effectively trigger chemical reactions under mild conditions, which has been widely studied in water splitting, cancer therapy, CO_2 reduction and so on.[15] Cubic silicon carbide (SiC) with a band gap of 2.4 eV can effectively absorb and harvest visible light.[16] In our previous work, SiC supported Pd and Au nanoparticles showed outstanding photocatalytic activity towards Suzuki-Miyaura coupling reaction[17] and hydrogenation of cinnamaldehyde,[18] respectively. From our previous work, Pd/SiC catalyst showed photocatalytic activity towards the Sonogashira cross-coupling reaction under copper-, and ligand-free conditions.[19] Under the visible light irradiation, the photo-generated electrons on SiC were transferred to Pd nanoparticles through the Mott-Schottky contact. Electron-rich Pd nanoparticles can facilitate the cleavage of carbon-halogen bonds in aryl halides. Then, the final products were achieved by the substitution reaction and reductive elimination processes. However, the photocatalytic Sonogashira process catalyzed by Pd/SiC still needed high reaction temperature (120 ˚C). Considering the synergetic effect in PdCu alloy nanoparticles, we prepared SiC supported PdCu alloy catalysts through liquid-reduction method for photocatalytic Sonogashira cross-coupling reaction. According to TEM, SEM-EDS and XPS analysis, PdCu alloy nanoparticles are successfully prepared and homogeneously dispersed on SiC support. SiC-supported PdCu alloy nanoparticles can efficiently drive the

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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DOI: 10.1039/C8CY00618K

Sonogashira reaction between aryl halides and phenylacetylene under visible light irradiation and mild reaction condition.

2. Experimental section

2.1 Catalyst preparation

SiC support was prepared by a sol-gel and carbonthermal reduction process.[20] SiC-supported PdCu alloy catalysts with different molar ratios of Pd to Cu were prepared by impregnation-reduction method. The Pd content of all SiC-supported PdCu alloy catalysts was fixed at around 3 wt%. Taking Pd_3Cu_1/SiC for example, 200 mg SiC was added into the mixture of 5.64 mL $Pd(NO_3)_2$ aqueous solution (0.01 M) and 1.88 mL $Cu(NO_3)_2$ aqueous solution (0.01 M). After stirring for 30min, 20 mL lysine aqueous solution (0.53 M) was added dropwise into the above mixture. Subsequently the mixture was stirred for another 30 min. Then 20 mL of $NaBH_4$ solution (0.35 M) was added drop by drop. After 24 h of stirring, the mixture was washed, filtered with deionized water and ethanol, and then dried in a vacuum-drying chamber at 60 °C. The dried mixture was reduced in a mixture of H_2 (5 vol %) and Ar at 400 °C for 0.5 h. The obtained powder was Pd_3Cu_1/SiC catalyst. Pd_2Cu_1/SiC, PdCu/SiC, Pd/SiC and Cu/SiC catalysts were prepared by the similar method.

2.2 Catalyst characterization

X-ray diffraction (XRD) spectra were collected on a Rigaku D-Max/RB X-ray diffractometer using Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was recorded on a AXIS ULTRA DLD spectrometer using Al Kα radiation, and binding energies were calibrated by the position of C 1s peak at 284.8 eV. The loading of metals was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). High resolution transmission electron microscopy (HRTEM) pictures and line profile analysis by an energy dispersion X-ray (EDX) spectrum were observed on JEOL-2100 transmission electron microscope at accelerating voltage of 200 kV. The elemental mapping was examined by field emission scanning electron microscopy (FESEM) on JSM-7100F coupled with energy dispersion spectroscopy (EDS). The ultraviolet-visible (UV-vis) absorption spectra were measured by a UV-3600 spectrophotometer with Al_2O_3 as a reference. The photoluminescence (PL) spectra were detected by the fluorescence spectrophotometer (F-700 FL) under the 320 nm excitation wavelength.

2.3 Sonogashira cross-coupling reaction.

Sonogashira reaction was carried out in a 150 mL glass reaction vessel under Ar atmosphere. 1 mmol of iodobenzene or one of its derivatives, 1.2 mmol of phenylacetylene, 2 mmol of Cs_2CO_3, 10 mL of N,N-Dimethylformamide (DMF), and 50 mg of SiC-supported PdCu alloy catalyst were put into the glass reactor, and the reaction temperature was kept at 60 °C by oil bath. The reactant was irradiated under a 300 W Xe lamp for 8 h with light intensity of 0.7 W/cm^2. After the reaction, the mixture was collected and centrifuged to get supernatant liquid which was analyzed by BRUKER SCION SQ 456 GC-MS. The influence of light wavelength on catalytic performance was investigated by employing various low pass optical filters to block light below specific cut-off wavelengths while keeping the light intensity unchanged.

3. Results and Discussion

3.1 Catalyst activity

The common constitutions of PdCu alloy are Pd_3Cu, Pd_2Cu, PdCu, $PdCu_2$ and $PdCu_3$. For the Sonogashira cross-coupling reaction, Pd is always used as main active components. Thus, we fixed Pd content at 3 wt% and prepared Pd_3Cu_1/SiC, Pd_2Cu/SiC and PdCu/SiC catalysts by adjusting the content of Cu. For comparison, we also prepared Pd/SiC and Cu/SiC catalysts, which had the same metal content as their counterpart in Pd_3Cu_1/SiC catalyst, respectively. The Sonogashira reactions of iodobenzene with phenylacetylene over SiC-supported PdCu alloy catalysts under visible light irradiation were performed and the results are summarized in Table 1. SiC support alone had no catalytic activity (entry 1). The iodobenzene conversion of Pd/SiC catalyst was only 28.6% without Cu. The addition of Cu can evidently enhance the photocatalytic activity of Pd/SiC for Sonogashira reaction (entries 3-5). Pd_3Cu_1/SiC catalyst showed highest iodobenzene conversion among SiC-supported PdCu alloy catalysts, and increasing Cu content caused the decrease in conversion (entries 4-5). The decrease in catalytic activity may be due to the fact that the presence of excess Cu could occupy the active sites and shelter the interaction between Pd and reactants. Cu/SiC catalyst showed no catalytic activity towards Sonogashira reaction (entry 6). It can be noted that the conversion of iodobenzene of Pd_3Cu_1/SiC was only 2% in the dark (entry 7), and it means that Sonogashira cross-coupling reaction over SiC-supported PdCu alloy catalysts is a light-driven process.

Table 1 Photocatalytic Sonogashira reaction of iodobenzene with phenylacetylene over SiC-supported PdCu alloy catalysts.[a]

Entry	Catalyst	Conv. of Iodobenzene/%	Select. of Diphenylacetylene [c]/%
1	SiC	-	-
2	Pd/SiC	28.6	96.6
3	Pd_3Cu_1/SiC	99.7	98.7
4	Pd_2Cu_1/SiC	74.6	99.2
5	PdCu/SiC	33.5	97.8
6	Cu/SiC	-	-
7	Pd_3Cu_1/SiC [b]	2	92.6

[a] Reaction conditions: 1 mmol iodobenzene, 1.2 mmol phenylacetylene, 2 mmol Cs_2CO_3, 50 mg of catalyst in 10 mL of DMF. The reactions were conducted in an argon atmosphere at 60 °C under Xe-lamp irradiation (400-800 nm) with light intensity of 0.7 W/cm^2. The reaction time was 8 h. [b] Without visible light irradiation. [C] Among the generated compounds, diphenyls were the main byproduct.

DOI: 10.1039/C8CY00618K

3.2 Catalyst characterization

To better understand the synergistic effect of PdCu alloy nanoparticles, Pd_3Cu_1/SiC catalyst was characterized in detail. High resolution transmission electron microscopy (HRTEM) is used to verify the surface morphology and structure of Pd_3Cu_1 alloy. As shown in Figure 1 A and B, the Pd_3Cu_1 alloy nanoparticles are homogeneously dispersed on the SiC support and an interplanar spacing of 0.22 nm corresponds to the (111) crystal face of Pd_3Cu_1 alloy nanoparticles in the inset of HRTEM image.[8] Line profile analysis of Pd_3Cu_1/SiC catalyst by energy dispersion X-ray spectroscopy indicates that Pd and Cu exist as alloy nanoparticles in Figure 1 C.[21-22] The elemental mapping of Pd and Cu by field emission scanning electron microscopy (FESEM) also confirms that Pd and Cu are homogeneously dispersed on the SiC (Figure 1 D, E and F). In addition, the atomic ratio of Pd and Cu in the Pd_3Cu_1/SiC catalyst is 2.89:1 calculated by ICP analysis, which is close to the theoretical value of 3:1. The X-ray diffraction (XRD) patterns of Pd_3Cu_1/SiC are shown in Figure 1 G. All strong diffraction peaks can be indexed to SiC crystal and no diffraction peaks corresponding to Pd_3Cu_1 alloy nanoparticles are detected. This phenomenon may be due to the low loading of metals and high homodisperse.

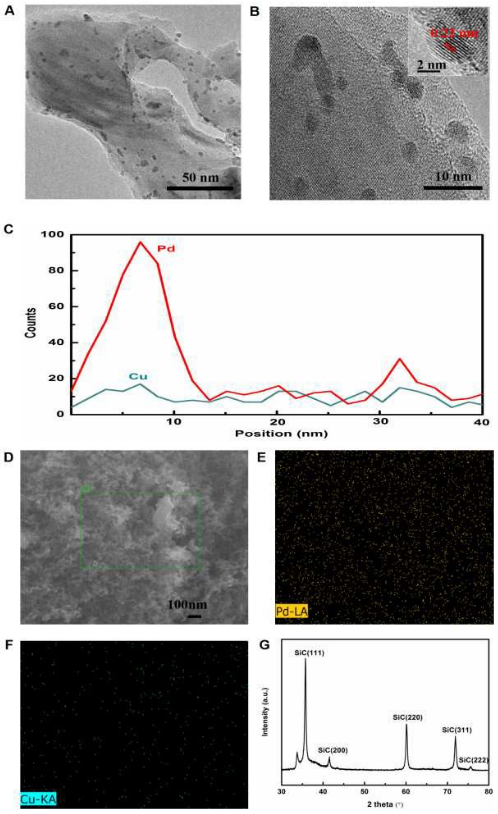

Fig.1 (A, B) TEM images of Pd_3Cu_1/SiC, (C) Line profile analysis of Pd_3Cu_1 alloy nanoparticles, (D) SEM image of Pd_3Cu_1/SiC for element mapping, (E) Palladium mapping, (F) Copper mapping, and (G) XRD pattern of Pd_3Cu_1/SiC. The inset in (B) is a HRTEM of Pd_3Cu_1 alloy nanoparticles.

Figure 2 shows the X-ray photoelectron spectroscopy (XPS) analysis of Pd/SiC, Cu/SiC and Pd_3Cu_1/SiC catalysts. The binding energy (BE) values of metallic Pd are 334.8 eV for Pd $3d_{5/2}$ and 340.2 eV for Pd $3d_{3/2}$.[23] Due to the electron transfer from SiC to Pd,[17] the BE values of Pd in Pd/SiC shift to lower values (334.6 eV and 340 eV) in Figure 2 A. The BE values of Pd in Pd_3Cu_1/SiC are 334.3 eV and 339.8 eV (Figure 2 C). Lower binding energies of Pd in Pd_3Cu_1/SiC than those in Pd/SiC mean more electrons are transferred to Pd. For Cu/SiC, there are two peaks at 934 eV and 953.8 eV,[24] which correspond to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of CuO, respectively (Figure 2 B). It suggests that metallic Cu is unstable in air and easily oxidized to CuO. The binding energies of Cu in Pd_3Cu_1/SiC are at 952 eV for Cu $2p_{1/2}$ and 932.6 eV for Cu $2p_{3/2}$, respectively (Figure 2 D). According to the literature, the binding energies of Cu^0 state are around at 951.9 eV for Cu $2p_{1/2}$ and 932.4 eV for Cu $2p_{3/2}$.[25] Similarly, binding energies of Cu^{+1} are at 952.4 eV and 932.7 eV.[24] Due to the fact that the Cu^0 and Cu^{+1} cannot be distinguished by the XPS spectra, we use Auger electron spectrum to confirm the valance state of Cu in Pd_3Cu_1 catalyst. The inset of Figure 2 D shows the Cu LMM Auger electron spectrum, and the binding energy of the Auger peak is around at 568 eV which corresponds to metallic Cu.[26] The Cu in Pd_3Cu_1/SiC is slightly positively charged due to electron transfer from Cu to Pd, which is in accord with the negative shift of BE values of Pd in Pd_3Cu_1/SiC as mentioned above. Based on these analyses, we can conclude that PdCu bimetallic nanoparticles are homogeneously dispersed over SiC in a form of alloying.

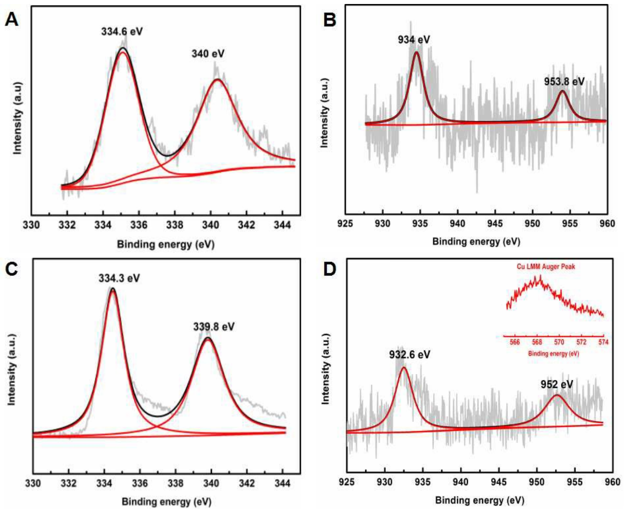

Fig. 2 XPS of (A) Pd in Pd/SiC, (B) Cu in Cu/SiC, (C) Pd in Pd_3Cu_1/SiC and (D) Cu in Pd_3Cu_1/SiC. The inset in (D) is Auger electron spectrum of Cu in Pd_3Cu_1/SiC.

The ultraviolet-visible (UV-vis) absorption spectra and photoluminescence (PL) spectra are used to measure the optical properties of the catalyst. The UV-vis absorption

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DOI: 10.1039/C8CY00618K

spectra and PL spectra of SiC, Pd/SiC, Cu/SiC and Pd_3Cu_1/SiC catalysts are shown in Figure 3 A and B. The pure SiC and Cu/SiC have similar absorption curve. Pd/SiC exhibits a stronger UV and visible absorption than pure SiC, which means a better utilization of light energy. For Cu/SiC, the localized surface plasmon resonance (LSPR) absorption of Cu at 560 nm is not detected since metallic Cu is easily oxidized to CuO in the air. Pd_3Cu_1/SiC shows the strongest light absorption, and it is the consequence of the absorption of alloy nanoparticles in the visible light region. All metal-supported catalysts have obvious decrement of PL intensity compared with SiC. Especially, the Pd_3Cu_1/SiC has the lowest PL intensity suggesting that the recombination of photogenerated electrons and holes has been effectively suppressed.

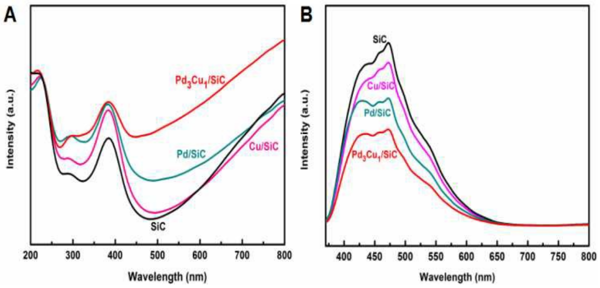


Fig. 3 (A) UV-vis absorption spectra and (B) PL spectra of SiC, Pd/SiC, Cu/SiC and Pd_3Cu_1/SiC.

3.3 Photocatalytic performance

For the photocatalysis, the light intensity and wavelength have critical influence on the catalytic activity. The dependence of the photocatalytic performance over Pd_3Cu_1/SiC on the light intensity and wavelength was investigated and shown in Figure 4 A and B. The iodobenzene conversion had an almost linear growth with the increase of light intensity (Figure 4 A). Higher light intensity can generate more energetic electrons and lead to higher reaction rate and increment of iodobenzene conversion. A series of optical pass filters were employed to block light below a specific cut-off wavelength and the results were shown in Figure 4 B. Without any filter (400-800 nm), the conversion of iodobenzene reached to 99%. Under the light with wavelengths in 450-800, 500-800 and 600-800 nm, the conversion of iodobenzene was 75%, 52% and 18%, respectively. After subtracting the contribution of thermal effect (2%), the conversion of iodobenzene within each wavelength range was 24% for 400-450 nm, 23% for 450-500 nm, 34% for 500-600 nm and 16% for 600-800 nm. The light in the range of 400-600 nm made a great contribution to the conversion of iodobenzene.

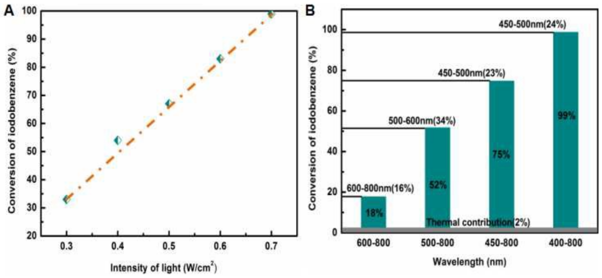
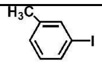
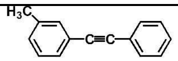
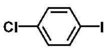
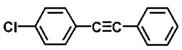
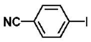
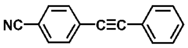
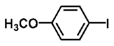
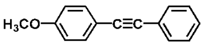
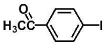
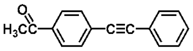
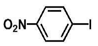
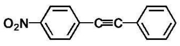
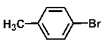
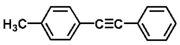
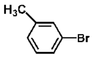
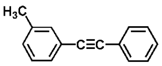
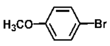
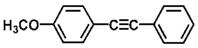
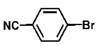
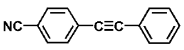
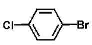
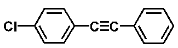


Fig. 4 Dependence of catalytic activity of Pd_3Cu_1/SiC for the Sonogashira on the intensity (A) and wavelength (B) of the irradiation.

A series of photocatalytic Sonogashira reactions between various aryl halides and phenylacetylene were performed to investigate the general applicability of the Pd_3Cu_1/SiC catalyst. Aryl iodides with electron-donating or electron-withdrawing substitutions had high conversion and selectivity towards the target products (entries 1-6, Table 2). Notably, Pd_3Cu_1/SiC catalyst also showed superior catalytic performance for aryl bromides, but a longer reaction time was required (entries 7-11, Table 2). It is due to the fact that activation of C-Br bonds is much more different than that of C-I bonds, which needs higher energy and more reaction time.

Table 2 Photocatalytic Sonogashira reaction of various aryl halides with phenylacetylene over Pd_3Cu_1/SiC catalyst. [a]

Enrty	Aryl halides	Product	Conv. /%	Select. /%
1			92	93
2			98	99
3			96	100
4			91	94
5			95	93
6			99	100
7			93	95
8			85	92
9			82	93
10			94	100
11			91	98

[a] Reaction conditions: 1 mmol aryl halides, 1.2 mmol phenylacetylene, 2 mmol Cs_2CO_3, 50 mg of Pd_3Cu_1/SiC catalyst in 10 mL of DMF. The reactions were conducted in an argon atmosphere at 60 °C under Xe-lamp irradiation

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(400-800 nm) with light intensity of 0.7 W/cm^2. The reaction time was 8 h. For aryl bromides, the reaction time was 12 h.

For practical applications, fivefold and tenfold scale-up experiments were performed for the photocatalytic Sonogashira reaction of iodobenzene with phenylacetylene over Pd_3Cu_1/SiC. The conversion of iodobenzene was 93.5% and 85.1% for fivefold and tenfold scale-up experiments, respectively. The selectivity of diphenylacetylene was almost not changed. It can be seen that with the increase of reaction scale the conversion has a slight decrease. This could be relative to the depth that the light irradiation can pass through the reaction suspension. In addition, the mass or heat transfer may also influence the reaction after amplification. Therefore, there are many experiments to do before the industrial scale-up.

3.4 Proposed mechanism

Several controlled experiments were performed to elucidate the reaction mechanism of the photocatalytic Sonogashira. SiC had no catalytic activity for the Sonogashira reation and the conversion of iodobenzene was 2% without visible light irradiation for Pd_3Cu_1/SiC catalyst. This indicates that Pd_3Cu_1 alloy nanoparticles and light irradiation are indispensable for the photocatalytic Sonogashira reaction. To investigate the roles of photogenerated electrons and holes in photocatalytic reaction process, 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) and triethanolamine (TEA) were employed. When DMPO was added to the reaction system as the electron-trapping agent, the conversion of iodobenzene was only 5%. It was very close to that in the dark reaction, indicating the light-driven reaction was quenched. This is in accordance with our previous work that photo-generated electrons can facilitate the cleavage of carbon-halogen bond in the Pd/SiC catalyzed Sonogashira reaction.[19] While TEA was added to trap the photogenerated holes, the conversion of iodobenzene decreased to 77%. TEA lowered the catalytic activity of the Pd_3Cu_1/SiC catalyst. It was much different from the results of Pd/SiC reaction system, since the photo-generated holes of SiC has no influence to the photocatalytic Sonogashira reaction.[19] According to the literature,[27-28] Cu(I) state easily reacts with phenylacetylene to form phenylethynylcopper(I) compound. We supposed that the addition of TEA quenched the positively charged sites at the surface of Cu particles and thus lowered the catalytic activity of Pd_3Cu_1/SiC catalyst. Since Pd nanoparticles on SiC can catalyze Sonogashira reaction alone, the photocatalytic Sonogashira reaction over Pd_3Cu_1/SiC could still proceed when Cu failed to activate phenylacetylene in the presence of TEA. Thus, a reaction mechanism for the photocatalytic Sonogashira reaction over Pd_3Cu_1/SiC catalyst is proposed as shown in Figure 5. Under the visible light irradiation, the photogenerated electrons on SiC surface and excited electrons of Cu in PdCu alloy are transferred to Pd. The electron-rich Pd can facilitate the cleavage of carbon-halogen bond in aryl halides. At the same time, the positively charged sites of Cu react with phenylacetylene to form phenylethynylcopper compound. Finally, the target products are achieved by cross-coupling reaction.

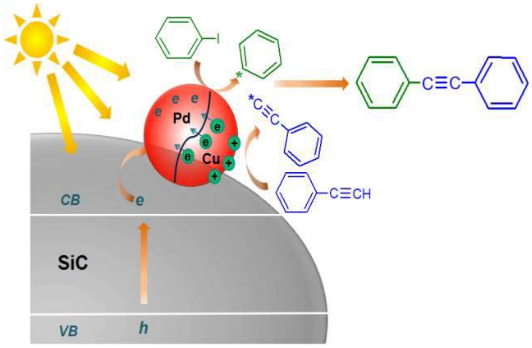

Fig. 5 Proposed mechanism for the photocatalytic Sonogashira reaction of aryl halides and phenylacetylene over Pd_3Cu_1/SiC.

3.5 Stability

The recyclability is an important parameter to evaluate the heterogeneous catalyst. The Pd_3Cu_1/SiC photocatalyst was reused for up to 5 cycles under the same reaction condition and there was no evident loss in the catalytic activity, suggesting the superior stability of this catalyst (Figure 6 A). TEM image of the used catalyst indicates that PdCu alloy nanoparticles are still in homogeneous distribution and have no obvious morphology change after five cycles as shown in Figure 6 B.

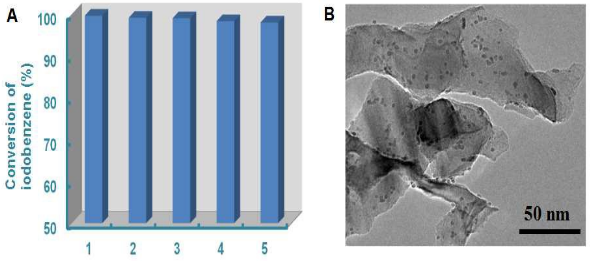

Fig. 6 (A) Recycle stability of the Pd_3Cu_1/SiC catalyst in five cycles, (B) TEM image of Pd_3Cu_1/SiC catalyst after five cycles.

4. Conclusions

SiC supported Pd_3Cu_1 alloy nanoparticles showed excellent performance for the Sonogashira cross-coupling reaction in visible light irradiation under ligand-free and mild condition. The alloying of Cu into Pd can increase the activity of PdCu alloy nanoparticles. The photogenerated electrons of SiC surface and excited electrons of Cu particles in PdCu alloy are transferred to Pd under light irradiation. Due to the synergistic effect of PdCu alloy nanoparticles, the electron-rich Pd can activate carbon-halogen bond in aryl halides and the positively charged sites of Cu react with phenylacetylene to form

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DOI: 10.1039/C8CY00618K

phenylethynylcopper compound where the final products are achieved by reductive elimination processes. Besides, light intensity and wavelength had the great influence on the reaction rate. The Pd_3Cu_1/SiC catalyst also possessed excellent stability and can be recycled for five runs without significant activity loss. The Pd_3Cu_1/SiC catalyst for the photocatalytic Sonogashira reaction provides a new direction for the application of alloy nanoparticles and a new route for synthetic chemistry.

Acknowledgements

The work was financially supported by NSFC (21473232, 21403270, 21673271 and U1710112).

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DOI: 10.1039/C8CY00618K

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ARTICLE

Photocatalytic Sonogashira Reaction over Silicon Carbide Supported Pd-Cu Alloy Nanoparticles under Visible Light Irradiation

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PdCu alloy nanoparticles supported on SiC can efficiently catalyze the Sonogashira reaction by visible light irradiation under ligand-free and mild condition. Among the prepared alloy catalysts, Pd_3Cu_1/SiC catalyst exhibited the highest catalytic performance for the Sonogashira reaction, and the conversion of iodobenzene and selectivity of diphenylacetylene were 99.7% and 98.7%, respectively. The superior catalytic activity of PdCu alloy catalysts was caused by synergistic effect of PdCu alloy nanoparticles.