Facile Fabrication of Ordered Component-Tunable Heterobimetallic Self-Assembly Nanosheet for Catalyzing “Click” Reaction

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ABSTRACT: How to maximize the number of desirable active sites on the surface of the catalyst and minimize the number of sites promoting undesirable side reactions is currently an important research topic. In this study, a new way based on the synergism to achieve the successful fabrication of an ordered heterobimetallic self-assembled monolayer (denoted as BMSAM) with a controlled composition and an excellent orientation of metals in the monolayer was developed. BMSAM consisting of phenanthroline and Schiff-base groups was prepared, and its novel heterobimetallic (Cu and Pd) self-assembled monolayer anchored in silicon (denoted as Si-Fmp-Cu-Pd BMSAM) with a controlled composition and a fixed position was fabricated and characterized by UV, cyclic voltammetry, Raman, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), X-ray diffraction (XRD), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and water-drop contact angle (WDCA) analyses. The effects of Si-Fmp-Cu-Pd BMSAM on its catalytic properties were also systematically investigated using “click” reaction as a template by WDCA, XPS, SEM, XRD, ICP-AES and in situ Fourier transform infrared analyses in a heterogeneous system. The results showed that the excellent catalytic characteristic could be attributed to the partial (ordered or proper distance) isolation of active sites displaying high densities of specific atomic ensembles. The catalytic reaction mechanism of the click reaction interpreted that the catalytic process mainly occurred on the surface of the monolayer, internal active site (Pd) and rationalized that the Cu(I) species and Pd(0) reduced from the Cu(II) and Pd(II) catalyst were active species, which had a proper distance between two different metals. The cuprate-triazole intermediate and the palladium intermediate, whose production is the key step, should lie in a proper position between the copper and active palladium sites, with which the reaction rate of transmetalation would be improved to increase the amount of the undesired Sonogashira coupling product.

1. INTRODUCTION

Catalysis based on transition-metal materials has emerged as a powerful synthetic tool in the synthesis of simple to complex molecules and the development of industrial processes, especially in fine chemicals.1,2 Among the many transition-metal catalysts reported to date, palladium catalysts are known to be very powerful and are often used as active transition metals, with extensive applications in organic catalysis.3 Copper has been recognized to have a catalytic activity different from that of their mononuclear analogues.4 This is because when a number of substrates are placed in a single reaction vessel containing several catalysts, the selectivity of these metallic components is challenging but necessary if a single product is to emerge. Over the last decades, tremendous efforts have been made to synthesize structurally defined polynuclear complexes, in particular heterobimetallic complexes.7 Bimetallic catalysts show obvious advantages compared to those of the monometal counterparts, such as enhanced catalytic activity and improved stability and selectivity due to synergistic effects.8 They have recently attracted much attention because they represent an important class of catalytic materials9 as well as they can enhance the performance of metal catalysts by tuning the stabilization degree of key intermediates in different reactions for the construction of various bonds.10 In particular, Pd-based bimetallic catalysts11 and Cu-based bimetallic catalysts12 have been successfully used for the construction of different bonds in...
many applications.\textsuperscript{13} Palladium–copper\textsuperscript{14} or copper–palladium\textsuperscript{15} bimetallic catalysts designed for a combined effect of two metals exhibited higher activities for the same reaction than those of the mononuclear catalyst.\textsuperscript{16}

The control over the well-defined structure of bimetallic catalysts is of more interest in the fields of chemistry and physics mainly due to their new and enhanced properties that are superior to those of their monometallic counterparts. Previous studies have shown that the performance of a catalyst can be improved by tuning its size, feature, and composition.\textsuperscript{29}

From the papers reported above, some of the catalysts are usually homogeneous, which are often very efficient. However, their preparation often is tedious and expensive, with difficulties in handling and recycling. To solve these problems, considerable efforts have been devoted to develop suitable supports, especially in the field of heterogenization of homogeneous catalysts.\textsuperscript{18} It should be mentioned that the ratio of metallic components in a catalyst is essential to enhance its catalytic activity, which must be readily tuned by deposition, mixing,\textsuperscript{19} self-assembly, and functional molecular-based ligands.\textsuperscript{20} On the other hand, the activity of the Cu-based catalysts was reported to strongly depend on their structure and morphology.\textsuperscript{21}

The copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction, which is the most widely recognized example of click chemistry,\textsuperscript{22} has been used in a wide range of new syntheses and applications in scientific research.\textsuperscript{23} Moreover, studies on various nitrogen or carbon ligand/Cu(I) complexes covalently immobilized on solid substrates for the CuAAC reaction were reported.\textsuperscript{24}

Recently, a new heterobimetallic catalyst containing nickel or palladium and copper immobilized on supports has emerged as a multitask catalyst for catalyzing sequential Sonogashira–click and click–Heck reactions and the multicomponent reaction of terminal alkynes, sodium azide, and benzyl bromide derivatives because of its positive and synergetic effect of the metallic species.\textsuperscript{19g,25}

Although considerable progress has been made in this field,\textsuperscript{6} methods to fabricate a large amount of defined heterobimetallic catalyst at the molecular level are in high demand. To date, there are only very few reports on the rational fabrication of the ordered self-assembled monolayer (SAM) of a component-tunable bimetallic catalyst (Cu–Pd) related to CuAAC, Sonogashira coupling or Heck reactions, or other reactions, with which the catalytic mechanism can be investigated deeply.

In the design of molecular-based ligands, functional groups, which can coordinate with certain metals, are usually introduced into molecules to get mono- or bi-metallic complexes for catalyzing reactions, such as the Schiff-base\textsuperscript{26} and 1,10-phenanthroline\textsuperscript{27} groups, which have attracted considerable attention due to their facile synthesis, diversity in structural topology, and ability to produce stable complexes with a large number of transition-metal ions and present efficient catalytic properties,\textsuperscript{28} especially suppressing the catalytic effect in some reactions,\textsuperscript{1c,28a,b} in which the cooperative effect must be considered also in reactions that are catalyzed by both metals, whose mechanisms are different from each other.\textsuperscript{29}

SAMs offer customized design, ease of recovery, recyclability, stability, and superior activity,\textsuperscript{30} as well as can potentially combine the advantages of homogeneous and heterogeneous catalysis in a single platform through structural maneuvers.\textsuperscript{31} Our group has got a series of cyclopalladated ferrocenylinines used for Heck, Suzuki, Sonogashira, Kamata, and other reactions in a homogeneous or immobilized substrate in self-assembled films, wherein they showed a highly efficient catalytic ability.\textsuperscript{32,33}

In the reports mentioned above, bulk copper–metal alloys,\textsuperscript{31c–h} bimetallic copper–metal nanooalyts,\textsuperscript{3a, d, 9a, b, d,10,11b,c,e,12b,d,13c,g,14a,b,16a,17a,b,19a,d,20a,25} core–shell-type nanoparticles,\textsuperscript{19e–g} nanowires,\textsuperscript{1a,d,19b} nanosponges,\textsuperscript{19n} nanorods,\textsuperscript{13i} nanowheels, nanodendrites,\textsuperscript{13f} and bimetallic copper–metal molecular catalysts,\textsuperscript{6,7b,8g,9e,13o,14c,15a,b,16b,20a,28a,29} are well-known and much developed systems, but ordered, component-tunable, distribution-controllable, and position-controllable bimetallic self-assembled monolayers anchored on substrates by engineering of molecules have received relatively little attention. At the same time, it is quite challenging to achieve fundamental insights into how each of these factors affect the catalytic performance due to the interplay between the structural and chemical factors, which are crucial for the rational design of a catalyst with high activity, selectivity, and durability.\textsuperscript{10c,12} To the best of our knowledge, this is the potential design in which the electronic properties of a ligand and the strategy effect of heterobimetalts in an ordered self-assembled monolayer have been shown to influence the activity of the incorporated bimetallic catalysts in predictable ways. Therefore, much needs to be known how to control the relative distributions of the different metals or active sites on the surface of the self-assembled monolayer for optimal performance.

In this study, on the basis of our previous studies on monometallic self-assembled catalytic monolayer,\textsuperscript{35} we designed the framework for preparing complexes with two different metal ions that would be sufficiently close to ensure an interaction between the coordinated metals.\textsuperscript{14} Schiff base and 1,10-phenanthroline moiities were selected and introduced into one molecule as the binding site for palladium ion, copper ion, or other metal ion. It is based on the assumption that the character of the phenanthroline and Schiff-base group could provide suitable sterics, electronics, and coordination demands, which are needed along the different steps of the catalytic reaction. Then, the monolayer of the ligand and its self-assembled monolayer linked to a functional substrate with different ratios of palladium and copper were fabricated via self-assembly, which may offer a super control over the orientation, distribution, and composition of metals and even the locations where the atoms are fixed, with which a powerful and highly versatile tool for the orientation and component-controlled fabrication of multimetal catalytic films may be provided.

2. RESULTS AND DISCUSSION

2.1. Preparation and Characterization of Si-Fmp-Cu-Pd Heterobimetallic Self-Assembled Monolayer (BMSAM) Self-Assembled Monolayer. In this section, we are interested in developing a system in which two different metals brought into close proximity by an appropriately selected ligand act in a cooperative manner, which can allow for cooperative effects at inter- or intra-molecular levels, both improving their efficiency in catalysis and promoting reactions that are not possible using a single metal center. The targeted catalysts are heterobimetallic complexes, in which both metals are capable of activating small-molecule substrates.\textsuperscript{29,34} To date, many examples of “heterobimetallic” compounds showing some cooperative effect on their catalytic properties have been
reported. However, reports on the cooperative effect for a heterobimetallic catalyst in an ordered, self-assembled monolayer are still scarce. This is due to the lack of rational synthetic methods to incorporate two different kinds of metal ions into a single molecule in a certain position. To overcome this problem, we have developed a multifunctional molecular approach, in which a self-assembled molecule having several sites coordinates in a stepwise fashion to the second and third metal ions to form the desired bimetallic coordination compounds. Scheme 1 shows the preparation route of Si-Fmp-Cu-Pd BMSAM.

2.1.1. Water-Drop Contact Angle (WDCA) Analysis. WDCA analysis was carried out on SAM to determine the wettability of functionalized surfaces. To some extent, the free energy of the functionalized surface can be related to the molecular composition and structure of the monolayer.36 The hydrophilic silicon (Si-OH) gave a WDCA of 2.0° (Figure S10). The results indicated that the surface changed from a hydrophilic to hydrophobic state when treated with APTES (Si-APTES), followed by Fmp (Si-Fmp) (from 43.6 to 60.8°). Its transition was caused by the monolayer surface covered with a hydrophobic phenanthroline ring. However, the WDCA on the surface of Cu-phenanthroline imine (Si-Fmp-Cu) decreased to 50.1° due to its hydrophilic moiety of the copper complex structure, but WDCA had a little change (from 50.1 to 47.8°) after coordinating with palladium (Si-Fmp-Cu-Pd BMSAM). The results indicated that the surface configuration had significantly changed, which could clearly exhibit the chemical gradient of each step. It also meant that the catalyst monolayer on solid substrates was fabricated via self-assembly.

2.1.2. Electronic Absorption Spectroscopy. The UV−vis spectra of modified quartz along with the immobilizing process offered further evidences of the preparation of Si-Fmp-Cu-Pd BMSAM (Figure S11). Hydrophilic quartz plates (black line) and those modified with APTES (red line) showed almost no absorption, and the absorption intensity of the modified quartz plates gradually increased with different degrees of functionality. A peak at ~229 and peaks at ~287 and ~336 nm of quartz plates modified with the Schiff-base phenanthroline derivative had also been observed (blue line), consistent with the literature, which revealed two peaks, at ~229 nm due to the imine group (attributed to the π−π* and n−π* transitions of the −C≡N group)37 and ~287 and 336 nm due to phenanthroline.27 The absorption peak at 287 nm gradually shifted to longer wavelengths due to the coordination interaction between phenanthroline and copper (pink line). In the spectrum of Si-Fmp-Pd-Cu BMSAM (pink line), a broad band ranging from 280 to 360 nm attributed to the π−π* electronic transfer of conjugated double bond of Schiff base, benzene, and imidazophenanthroline27 and a peak at 226 nm appeared due to the coordination interaction of the Schiff base with Li2PdCl4 (yellow line),38 suggesting a stronger interaction between the molecules and the metal ion.

2.1.3. Vibrational Spectroscopy. Raman spectroscopy is an important technique that is considered to be a powerful tool for characterizing the structures of catalyst molecules.39 Figure S12 presents the Raman spectra of the bimetallic catalytic monolayer compared to those of its precursors. The stretching vibrations of −CH2 groups for grafted APTES could be observed at 2992−2895 cm−1 (Figure S12A), and the imine moiety grafting onto the silicon surface could also be monitored at 1609 cm−1 (Figure S12B),40 suggesting the successful grafting of the phenanthroline derivative onto the silicon surface,41 in which the shifting frequency and line width were caused by the interactions between molecules and metals. After the Cu-phenanthroline imine grafting (Figure S12C), the C≡N band at 1609 cm−1 shifted to about 1599 cm−1 (Figure S12B),40 the imine moiety grafting onto the silicon surface could also be monitored at 1609 cm−1 (Figure S12B),40 suggesting the successful grafting of the phenanthroline derivative onto the silicon surface,41 in which the shifting frequency and line width were caused by the interactions between molecules and metals. After the Cu-phenanthroline imine grafting (Figure S12C), the C≡N band at 1609 cm−1 shifted to about 1599 cm−1, indicating that the structure of the molecules in the monolayer changed due to the complexing between phenanthroline and copper.42 Finally, the C≡N band at 1599 cm−1 shifted to about 1586
were assigned to Cu(II) (Figure S14c). The high-resolution peaks of Cu 2p at 963.07, 963.47, 943.07, and 933.07 eV, which suggest that Cu or Pd was not reduced in the sample, indicating that the novel Si-Fmp-Cu-Pd BMSAM monolayer was successfully grafted onto the substrate. The survey XPS and detailed Pd 3d and Cu 2p XPS analyses of the Si-Fmp-Cu-Pd BMSAM are shown in Figure S14a. The high-resolution XPS spectrum of the Si-Fmp-Cu-Pd BMSAM monolayer shows only the N 1s signals at 399.6 eV in the XPS spectrum of the Si-Fmp-Cu-Pd BMSAM, which suggests that N is present in the monolayer.

2.1.4. Charge-Transfer Resistance (Rct). As illustrated in Figure S13, the behavior of impedance with different monolayers was presented. For Si-OH, Si-APTES, and Si-Fmp monolayers, the impedance behavior is dependent on the molecular structure grafted onto the electrode, in which the resistance increased in the procedure steps (Figure S13a–c). With the Si-Fmp-Cu monolayer, the impedance behavior is a strong function of the complexed metals, as depicted in Figure S13d, in which the resistance decreased due to the coordination between SAM and copper. This behavior is thought to be due to the introduction of copper ion, making electron transfer easy from the surface to ITO. However, the impedance found for the Si-Fmp-Cu-Pd monolayer increases by a factor of nearly as five times as compared to the behavior of the Si-Fmp-Cu monolayer. This phenomenon observed in the electrodes can be explained by the electron transfer between the ITO electrode and the redox species in the solution phase through the SAM was destroyed due to the introduction of palladium. This interpretation suggests that the charge density of the interface may affect the magnitude of the experimental Rct observed.

2.1.5. X-ray Photoelectron Spectroscopy (XPS) Studies. The survey XPS and detailed Pd 3d and Cu 2p XPS analyses of Si-Fmp-Cu-Pd BMSAM are shown in Figure S14a–d. The survey spectrum shows only the N 1s signals at 399.6 eV in the preparation of films fabricated with APTES (Figure S14a) and then grafted with Fmp (Figure S14b). The high-resolution XPS spectrum of the Si-Fmp-Cu film showed the characteristic peaks of Cu 2p at 963.07, 963.47, 943.07, and 933.07 eV, which were assigned to Cu(II) (Figure S14c). The high-resolution XPS spectrum of Si-Fmp-Cu-Pd BMSAM not only showed two peaks of Pd 3d at 338.15 and 343.47 eV assigned to Pd(II) (Figure S14d) but also the Cu2p peaks and the peak of Cl 2p at 200.10 eV (Figure S14d). XPS analysis of the Si-Fmp-Cu-Pd BMSAM catalyst also showed the presence of Cu(II) and Pd(II) in the sample, suggesting that Cu or Pd was not reduced during the self-assembly process. These results demonstrate that the intermetallic catalyst (Si-Fmp-Cu-Pd BMSAM) was successfully prepared. The X-ray diffractograms for the preparation procedure of Si-Fmp-Cu-Pd BMSAM on quartz were measured as shown in Figure S15. As depicted in Figure S15a, two characteristic peaks were observed at 0.6 and 1.025° after grafting with APTES. The same peak at 0.6° and a slightly shifted peak at 1.080° appeared when L was grafted (Figure S15b). The diffractogram of films modified with Cu also showed two peaks, in which the peak at 1.125° could be observed (Figure S15c), indicating that phanenthroline and copper coordinated to form Si-Fmp-Cu. However, after Pd(II) coordinated with Si-Fmp-Cu to yield Si-Fmp-Cu-Pd BMSAM, two peaks shifted to a low angle of 1.075° were obtained (Figure S15d). Although the position of the peaks changed significantly during the preparation process, their width and intensity had a little change, which demonstrated that the films fabricated above maintained a crystalline nature. Obvious layered structures of the fabricated catalyst monolayers proved by LAXD indicated that the ordered heterobimetallic self-assembled catalytic monolayer was grafted onto the surface of the solid substrate.

2.1.7. Scanning Electron Microscopy (SEM) Investigation. SEM images of the catalyst-grafted surface presented the evidence of high-density arrays and ordered structure (Figure S16). As shown in Figure S16A, a very smooth surface can be obtained after hydrophilic treatment, and a similar flat surface in the next procedure with silanization is shown in Figure S16B. Granules appeared after reaction with the ligand (Figure S16C), and more granules were observed after complexing with copper (Figure S16D). The surface of the resultant samples (Si-Fmp-Cu-Pd BMSAM) shown in Figure S16E is also relatively smooth with a little coarse feature due to a little agglomeration, which is proved clearly by the X-ray diffraction (XRD) results (Figure S15). The ordered structure and the stability of Si-Fmp-Cu demonstrated by these characterizations may impact the catalytic performance, which prompted us to explore the surface chemical reactions in the heterogeneous system.
2.2. Contrast Experiment and Characterization. As we know, it is important to determine the position and distribution of metals complexed with certain functional groups in the molecular surface or interior, which helps determine the factors affecting the catalytic properties and the catalytic mechanism. To determine whether copper only coordinated with the 1,10-phenanthroline group, as shown in Scheme 2, the test depicted in Scheme S1 was designed and characterized.

UV spectra were recorded during the fabrication process, as shown in Figure S17. Hydrophilic quartz plates (black line) or those modified with APTES (red line) showed almost no absorption, and the absorption intensity of the modified quartz plates gradually increased with different degrees of functionality. Quartz plates modified with p-bromo benzaldehyde (Si-BBA, blue line) showed peaks at ca. 203, 258, 284, and 294 nm, consistent with the literature, which revealed two peaks (at ∼229 nm) of the imine group (attributed to the π−π* and n−π* transitions of the −C≡N group), and the four peaks did not change when the self-assembled monolayer (Si-BBA) was put into copper(II) acetate solution at different times (green and purple lines), indicating that the coordination interaction of Si-BBA with copper(II) did not occur. On the other hand, there were two broad peaks at about 223 nm, attributed to the coordination interaction of Schiff base with Li2PdCl4, and 302 nm, due to the π−π* electronic transfer of the conjugated double bond of the Schiff base. Benzene

| entry | solvent | T (°C) | time (h) | yield (%)a | yield (%)b |
|-------|---------|--------|----------|-------------|-------------|
| 1     | H2O     | 80     | 12       | 92          | 85          |
| 2     | EtOH    | 80     | 12       | 7           | trace       |
| 3     | THF     | 80     | 12       | trace       | 7           |
| 4     | DMF     | 80     | 12       | 11          | 15          |
| 5     | toluene | 80     | 12       | trace       | trace       |
| 6     | EtOAc   | 80     | 12       | trace       | 10          |
| 7     | MeOH    | 80     | 12       | trace       | trace       |
| 8     | H2O/MeOH = 1:1 | 80 | 12 | 20 | 17 |
| 9     | H2O/MeOH = 2:1 | 80 | 12 | 46 | 18 |
| 10    | H2O/MeOH = 3:1 | 80 | 12 | 37 | 38 |
| 11    | H2O/MeOH = 4:1 | 80 | 12 | 95 | 61 |
| 12    | H2O/MeOH = 5:1 | 80 | 12 | 86 | 10 |
| 13    | H2O     | 80     | 16       | 92          | 85          |
| 14    | H2O     | 80     | 24       | 91          | 86          |
| 15    | H2O     | 100    | 12       | 85          | 82          |
| 16    | H2O     | 70     | 12       | 86          | 69          |
| 17    | H2O     | 55     | 12       | 82          | 60          |
| 18    | H2O     | RT     | 4        | 55          | 7           |
| 19    | H2O     | RT     | 8        | 66          | 10          |
| 20    | H2O     | RT     | 12       | 80          | 15          |
| 21    | H2O     | RT     | 16       | 96          | 17          |
| 22    | H2O     | RT     | 20       | 93          | 20          |
| 23    | H2O     | RT     | 16       | 98a        |
| 24    | H2O     | RT     | 16       | 95b        |
| 25    | H2O     | RT     | 16       | 94c        |
| 26    | H2O     | RT     | 16       | 93d        |
| 27    | H2O     | RT     | 16       | 93e        |
| 28    | H2O     | RT     | 16       | 94f        |
| 29    | H2O     | RT     | 16       | 92g        |
| 30    | H2O     | RT     | 16       | 95h        |
| 31    | H2O     | RT     | 16       | 92i        |
| 32    | H2O     | RT     | 16       | 87m        |
| 33    | H2O     | RT     | 16       | 95n        |
| 34    | H2O     | RT     | 16       | 92o        |
| 35    | H2O     | RT     | 16       | 57l        |
| 36    | H2O     | RT     | 16       | 45p        |
| 37    | H2O     | RT     | 16       | 26q        |

aReaction condition: benzyl bromide (0.125 mmol), phenylacetylene (0.15 mmol), sodium azide (0.15 mmol), SAB (5 mg), solvent (7 mL), under N2 atmosphere, substrate: 3 cm × 0.6 cm × 0.8 cm. Si-Fmp-Cu-Pd BMSAM (1:1) isolated yield. "Si-Fmp-Cu BMSAM (1:0) isolated yield. Si-Fmp-Cu-Pd BMSAM (1:0.15) isolated yield. Si-Fmp-Cu-Pd BMSAM (1:0.31) isolated yield. Si-Fmp-Cu-Pd BMSAM (1:0.37) isolated yield. SAB (5 mg). SAB (7 mg). SAB (10 mg). SAB (20 mg). Si-Fmp-Cu-Pd BMSAM (1:0.74). Si-Fmp-Cu-Pd BMSAM (1:0.61). Si-Fmp-Cu-Pd BMSAM (1:0.36). TTO-Fmp-Cu-Pd (1:1). SG-Fmp-Cu-Pd BMSAM (1:1). Fmp/Cu(OAc)2/Li2PdCl4. Cu(OAc)2/Li2PdCl4. Cu(OAc)2.
appeared when the self-assembled monolayer (Si-BBA) was immersed in the Li,PdCl₄ solution, suggesting the stronger interaction between the Schiff-base group in the molecules with copper (orange line).

WDCAs shown in Figure S18 were also measured. The hydrophilic silicon substrate presented a WDDA value of 3.0°, which indicated that the surface transformed from hydrophilic to hydrophobic when treated with APTES and imine (from 38 to 60°) due to the coverage of the surface of the monolayer with a phenyl ring. The WDDA of the surface treated with copper acetate showed a little change (59°). However, WDDA decreased (from 59 to 54°) after coordinating with palladium. The result indicated that only palladium could coordinate with the Schiff-base group. Furthermore, the survey XPS and detailed Pd 3d, Cu 2p, N 1s, Cl 2p, and Br 3d analyses of Si-BBA immersed in copper acetate and palladium solution are shown in Figure S19a–d. The high-resolution XPS spectrum of the Si-BBA-Cu(OAc)₂ monolayer showed only a Br3d peak and no characteristic peaks of Cu 2p at 936.07, 963.47, 943.07, and 933.07 eV. However, the high-resolution XPS spectrum of Si-BBA-Li₂Pd Cl₄ not only showed two peaks of Pd 3d at 338.15 and 343.47 eV assigned to Pd(II) (Figure S14d) but also the Br3d peak and the peak of Cl 2p at 200.10 eV, which is an evidence that palladium can be complexed with the Schiff-base group under adopted conditions. Using the current synthetic protocol, the composition of Si-Fmp-Cu-Pd BMSAM in the location of the metallic ion with an ordered structure can be readily tuned by simply controlling the initial molar ratio of the Cu and Pd salts.

2.3. Catalytic Performance for Three-Component Click Reaction. Click chemistry is one of these methods based on reactions which have a wide scope, give high yields, and use highly energetic reactants to form irreversible carbon–carbon or carbon–heteroatom bonds. In this section, we took into account that the combined effect of copper and palladium is fixed in the self-assembled monolayer, possibly by coordination. On the basis of our experience with self-assembled systems, we selected to examine the fixation and activity of copper(II)–palladium(II) on silicon.

2.3.1. Screening of Catalytic Condition. To evaluate the effectiveness of Si-Fmp-Cu-Pd BMSAM containing different ratios of Cu/Pd as a heterogeneous catalyst, a three-component cycloaddition of benzyl bromide, phenylacetylene, and sodium azide was chosen as a model for the synthesis of 1,2,3-triazole derivatives mentioned above. The reaction was investigated under various conditions (Table 1). In the preliminary experiment, various solvents were used as media for screening their suitability in a fixed amount of catalyst and reaction time (12 h) and sodium ascorbate (SAB) (5 mg) at 80 °C. As evidenced in Table 1 (entries 1–12), a significant effect on time and yield was observed with the different solvents, of which water presented the greatest effect, giving the desired product in a yield of about 92%. However, better yield was also obtained using a mixture of H₂O and EtOH (4:1). Considering the cost and green nature, we selected pure water. Also, the yields obtained with water as solvent had a little change when the reaction time was prolonged (entries 13 and 14). Optimization for the amount of catalyst was then explored with an equimolar ratio of the reactant and SAB. Their yield decreased to 85% with increasing the temperature to 100 °C (entry 15). Decreasing the reaction temperature to 70, 50 °C, and room temperature (RT) results in the decrease of yield (entries 16, 17, and 20).

It is also observed that increasing the reaction time enhanced the yield of product up to 96% until 16 h (entries 18–22), whereas the yield slightly changed (entries 26–29) on increasing the amount of SAB. Si-Fmp-Cu-Pd BMSAM with different ratios exhibited similar results (entries 23–25). Consequently, in the presence of Si-Fmp-Cu-Pd BMSAM (1:1), the best yield of 1,2,3-triazole could be obtained in the reaction of benzyl bromide, phenylacetylene, and sodium azide (ratio 1:1:5:1) with 5 mmol % SAB at room temperature after 16 h. These were used as the optimum conditions (entry 21). This supported Cu/Pd bimetallic catalyst (Table 1, entry 21) is among the most active catalysts for the three-component click reaction, proceeding in 16 h at room temperature.

On the basis of the higher catalytic activity of Si-Fmp-Cu-Pd BMSAM in the model reaction, the substrate scope of the synthesis of 1,4-disubstituted 1,2,3-triazoles was evaluated, and the results are summarized in Table S2. A wide range of different substituted benzyl and allyl groups were subjected to the click reaction. It was found that all reactions produced triazole; however, in the case of chlorides, only moderate yield could be obtained (entry 7). It was also found that benzyl halides containing electron-donating or electron-deficient groups all can give desired products in high yield (entries 1–6). Aromatic acetylenes were also quantitatively converted to the corresponding triazoles. It was noted that acetylenes having electron-deficient groups, which were normally inactive groups, which were normally inactive groups, could react to give a higher yield of desired triazoles (entries 8–14). Compared to that of the Si-Fmp-Cu catalyst under high reaction temperature with middle yield of product, Si-Fmp-Cu-Pd BMSAM showed higher catalytic activity due to the cooperation between copper and palladium. These results showed that Si-Fmp-Cu-Pd BMSAM was an active heterogeneous copper–palladium catalyst, which could effectively catalyze the three-component cycloaddition of aromatic halide, azide, and alkyne for the synthesis of triazole derivatives.

2.3.2. Component-Tunable Investigation. The ratio of heterobimetallic or multimetallic components in the catalyst was essential to enhance the catalytic activity, which must be readily tuned by deposition in step or by mixing way. Although modification of the functional groups in the self-assembled monolayer and the ratio in the catalyst can be utilized to optimize the catalytic activity, the research on such modifications can be a challenging task. In fact, it is often even more difficult to predict what structure of the molecule is suitable and how changes to the ratio of the heterobimetallic catalyst will influence its catalytic activity. Herein, we investigated the ratio and distribution of supported Cu–Pd bimetallic self-assembled catalysts (Si-Fmp-Cu-Pd BMSAM) through optimization approach, in which both the ratio of M1/M2 and distribution in the self-assembled monolayer contribute to the catalyst activity in click reaction, wherein the reaction path for the formation of alkylene copper and cuprate trizole on the surface of the sample could be → RC = CCu → cuprate trizole → transmetalation → elimination to get TM. Meanwhile, the incorporation of Pd was done to facilitate the absorption of Ph-X to form Ph-Pd-X, resulting in an enhanced transmetalation. However, the atomic ratio of Cu to Pd should be optimized, as too much Pd on the surface means a low density of adsorbed alkynes and azo, which can be used to
produce cuprate–triazole intermediates. It certainly limits the catalytic performance of Si-Fmp-Cu−Pd BMSAM.50

To find the ratio of certain metals in an ordered self-assembled film, the self-assembled monolayer was immersed in different concentration ratios of the Cu/Pd mixture solvent in a stepwise coordination way, that is, first complexing with copper and then with palladium. Catalytic monolayers with different compositions could be obtained by mixing or stepwise route (presented in Table S1). It is easy to determine the desired ratio in a catalytic reaction with the above procedure. Next, we probed into the effect of the ratio of Cu/Pd on catalysis (Table 1, entries 21, 23−29, and 30−32). The results showed that the higher the percentage of copper to palladium, the higher the activity of the catalyst when the total loading of copper was held (entries 21, 23−29, and 30−32) compared to that of monometallic copper catalysts (entry 21, yieldd) at room temperature, indicating that palladium had a profound effect on the catalytic properties. This supported Cu/Pd bimetallic catalyst (entry 21, yieldd) is the most active catalyst for the three-component click reaction, proceeding in just 16 h at room temperature. Different supports were used for fabricating functional catalysts (Table 1, entries 33 and 34), such as ITO and silica gel (denoted as ITO-Fmp-Cu−Pd BMSAM and SG-Fmp-BMSAM, respectively), also with higher yields. In the case of only Fmp ligand coordinated with the Cu(OAc)2/Li3PdCl4 mixture, Cu(OAc)2/Li3PdCl4 mixture, or only Cu(OAc)2 utilized for catalyzing, higher yields could not be achieved (Table 1, entries 35−37), indicating that not only the structure of the ligand but also the orientation and density of the catalyst and palladium coexist are very important for fixing the catalytic active sites and their distribution, which will have an impact on its catalysis.

Having demonstrated the wide scope of the catalyst prepared, we want to explore the impact of the structure of the ligand and the distribution of the metal at the interface on the catalytic activity. It has been based on the hypothesis that interactions between the metals on the surface and the electrons of the aromatic rings having nitrogen atom in the ligand facilitate the formation of the controlled nanocatalyst and stabilize the resulting nanoactive species toward oxidation.51 At the same time, if the groups complexed with different metals are too far apart, they cannot cooperate; however, if they are too close, they may interact in an intramolecular fashion and thus prevent the association of the substrate. This strategy has the potential to simplify catalyst optimization in heterogeneous catalysis, similar to what is accomplished by a modified ligand in homogeneous transition-metal catalysis.52 Therefore, catalysts consisting of fitting distributions with well-defined composition and defined position with proper distance between two different catalytic metals can be conceived in this way.53 Thus, we thought that the differences in the catalytic activities of Si-Fmp-Cu−Pd BMSAM should relate to a combination of variations in different molecular structures, density, orientation, and strength of the metal–functional group interaction.54 Therefore, another self-assembled monolayer of ligands containing only phenanthroline or terpyridine functional group without a Schiff-base group (denoted as Si-HOP and Si-TPy, Scheme 3),55,24j which has different complexing abilities to Cu or Pd, was designed and fabricated (Scheme 3), with which heterobimetallic complex monolayers (denoted as Si-HOP-Cu−Pd and Si-TPy-Cu−Pd) were formed and characterized (Schemes S2 and S3 and Figures S20−S25) and their catalytic properties influenced by the effect of the structure of the ligand and the distribution of the catalyst on the surface were investigated compared to those of Si-Fmp-Cu−Pd BMSAM.

Catalytic monolayers with different compositions are listed in Table S3. More palladium ions were incorporated in Si-Fmp-Cu−Pd BMSAM (Table S1, entries 3−5) compared to those in Si-HOP-Cu−Pd (Table S3, entries 1−3) or Si-TPy-Cu−Pd (Table S4, entries 1−3) due to the lack of the Schiff-base group. The complexing ability of copper and palladium with phenanthroline or terpyridine is different, in which more copper was incorporated on the surface. We also investigated the catalytic properties of Si-HOP-Cu−Pd and Si-TPy-Cu−Pd for click reaction, and the results are presented in Table S3 (entries 1−3 and 6) and Table S4 (entries 1−4), in which the catalytic yields were lower than those of Si-Fmp-Cu−Pd BMSAM under the same condition.

A higher percentage of copper to palladium in Si-HOP-Cu−Pd or Si-TPy-Cu−Pd also led to a mediated activity (Table S3, entries 1−3; Table S4, entries 1−3) but lower than that of Si-
Cu-Pd BMSAM (Table 1, entries 21, 23–25), indicating that not only palladium on the surface but also internal palladium located with the Schiff-base group should have a profound effect on the catalytic properties. Not surprisingly, the yield of the obtained products increased with increasing Cu content used for Si-Fmp-Cu-Pd BMSAM. However, in the case of Si-HOP-Cu-Pd, the yield decreased with increasing palladium content (Table S3, entries 1–3), which showed that the ratio, orientation, density, and distribution were not the only factors affecting the catalytic properties. Therefore, the distance between the two different catalytic sites (Cu–Pd distance) on the surface or between Cu on the surface with the internal palladium must be considered (as depicted in Scheme 4), which may have a significant impact on its catalytic efficiency according to different catalytic mechanisms, such as the metal transformation step. Therefore, if the cuprate–triazole intermediate and the palladium intermediate lie exactly between the copper and active palladium sites, then the reaction rate of transmetalation would be improved, and the facility of transmetalation would increase the amount of the undesired Sonogashira coupling product, which is the most challenging issue of the proposed three-component cycloaddition coupling reaction. We presumed that the number of real synergistic sites having a proper distance between different metals also had a significant impact on the catalytic activity. On the other hand, Si-TPy-Cu-Pd with different ratios had the catalytic activity opposite to the results (Table S4, entries 1–3), which showed that the yields decreased with decreasing palladium content due to the decrease of real synergistic sites, which was also the evidence that the performance of catalysts can be enhanced by engineering their surface, internal structure, or surroundings. Meanwhile, phenanthroline introduced in this research onto the surface showed that it could potentially prevent the metal nanoparticles from oxidation, with which a good concentration of the catalytically active complexes will be maintained throughout the reaction and also have an effect on both the equilibrium distribution and the rate of equilibration among the active sites to substantially enhance the rate of reaction on its own by promoting the presence of the most active sites, which was sufficient to allow molecules to diffuse to/from the internal catalyst. It also provided the absorbed configuration of reactant molecules, dissociated species, intermediates, and even products, which influences the selection of a specific reaction pathway to give the desired product.

2.3.3. Recycling Experiment. For recycling experiments, the catalyst was recovered from the reaction mixture by drawing and made ready for reuse after washing with solvents. The reusability of Si-Fmp-Cu-Pd BMSAM was tested through the one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles from alkyl halides, alkyne, and sodium azide. As shown in Figure 1, Si-Fmp-Cu-Pd BMSAM (1:1) showed a higher stability upon reuse than Cat. 1−3 (Table S1, entries 3−5) and Si-Fmp-Cu. Although, for four cycles, the catalyst could maintain a high activity without discernible activity. However, a significant decrease in yield was observed during the fifth cycle. The amount of Cu and Pd in the substrate is measured (ICP: Cu: 1.40 × 10−10 mol/cm2; Pd: 0.14 × 10−10 mol/cm2), which suggested that catalyst deactivation occurred as the reaction progressed. However, the recyclability may be influenced by the amount of palladium, that is to say, Si-Fmp-Cu-Pd BMSAM has not only palladium on the surface but an internal monolayer, which is likely a container.

2.4. Investigation on the Mechanism of Catalyzing Click Reaction. The problem of distinguishing homogeneous catalysis from heterogeneous catalysis is an important question that arises more and more often. Heterogeneous catalytic systems may partly dissolve to yield a homogeneous component, which might be much more reactive than the parent metal surface. Therefore, it is necessary to investigate whether or not the leaching of the catalyst during the reaction process, careful kinetic studies, hot filtration tests, and catalyst poisoning tests are very helpful to solve the question of heterogeneity, in which the surface function of the nanomonomer is a well-designed way to bridge the gap between heterogeneous and homogeneous catalysis. In heterogeneous catalysis, the surface and structural understanding of the well-
defined catalyst material is important for the optimization and mechanism of the catalyst systems.

2.4.1. Water Contact Angle Analysis. Wettability is an important property of solid materials that is governed by both surface chemical composition and geometrical structure, and a suitable wettability in principle can enhance the catalytic activity.60 Figure 2 shows the changes of WDCA in Si-Fmp-Cu-
Pd BMSAM during the catalytic process. The hydrophilic silicon substrate generates a WDCA value of 4.0°. The water contact angles of Si-Fmp-Cu-Pd BMSAM changed from 49° (0 h) to 55° (1 h), 57° (2 h), 63° (3 h), 67° (5 h), 62° (7 h), 60° (10 h), and 53° (16 h), which demonstrates that catalysis occurred on the surface of Si-Fmp-Cu-Pd BMSAM and reveals that the surface nature of the catalyst monolayer maintained after catalysis.

2.4.2. Kinetic Studies and Hot Filtration Experiment. As shown in Figure 3, the yield increased rapidly within a 4 h reaction time. After 4 h, the yield increased slowly. For catalyst loading, the reaction completed after 16 h and led to a 96% yield. The high efficiency of the Si-Fmp-Cu-Pd BMSAM catalyst can be attributed to the favorable orientation and dispensability on the surface. The filtration test relies on a comparison of catalytic activities before and after drawing the active catalyst from solution. This test is probably most useful to check whether the bulk metal is responsible for the catalysis.61 To explore if the leaching of catalyst occurred during the reaction process, the Si-Fmp-Cu-Pd BMSAM catalyst was removed from the reaction system after 4 h and the reaction kinetics was monitored from then on. As shown in Figure 3, after the catalyst was removed, the yield slightly increased, which was the evidence that few palladium ions leached during the reaction process.

2.4.3. XRD Patterns of Si-Fmp-Cu-Pd BMSAM for Catalyses. The LAXRD patterns of Si-Fmp-Cu-Pd BMSAM used for catalyzing at different times were measured (Figure 4).

Initially, Si-Fmp-Cu-Pd BMSAM showed a good XRD pattern, which proved that the structure is ordered. The diffraction peak shifted to a lower angle although the pattern types had no change during catalyzing (from 1 to 16 h), indicating that the thickness of the catalyst monolayer increased and finally became a certain pattern. It was the evidence that the structure was not damaged before and after reaction, demonstrating that the heterobimetallic catalyst was durable and maintained its orientation under the adopted conditions.

2.4.4. XPS of Si-Fmp-Cu-Pd BMSAM in Catalyzing Process. The XPS spectrum of Si-Fmp-Cu-Pd BMSAM obtained during the catalytic reaction showed not only two peaks of Pd 3d at 338.15 and 343.47 eV assigned to Pd(II) (Figure S5)33 but also Cu 2p peaks at 298.10 eV. The survey XPS and detailed Cu 2p and Pd 3d XPS analyses of Si-Fmp-Cu-Pd BMSAM during the catalytic process are shown in Figure 5. The high-resolution XPS spectrum of Si-Fmp-Cu-Pd BMSAM showed the characteristic peaks of Cu 2p at 963.07, 963.47, 943.07, and 933.07 eV, assigned to Cu(II),62 without catalysis (Figure 5A). New peaks appeared in the Cu(I) spectrum at 953.77 and 932.17 eV during catalysis, and their densities increased with increasing time and became the main state, indicating that Cu(II) was reduced to Cu(I), which could
catalyze the cycloaddition to form the cuprate-triazole intermediate. Finally, the main state of copper turned into Cu(II) with a little Cu(I) after 16 h.

The result of the high-resolution XPS spectrum of Pd 3p in Si-Fmp-Cu-Pd BMSAM was similar to that of Cu 2p, as shown in Figure 5B, in which Pd(0) appeared and increased with increasing time and disappeared at the end. These results demonstrate that the intrabimetallic catalyst (Si-Fmp-Cu-Pd BMSAM) could catalyze the click reaction successful by a synergic way.

The survey spectrum shows the N 1s signal at 399.6 eV (0 h), the peak of Cl 2p at 199.8 eV (0 h), and Br 3d with no signal (0 h) before catalyzing, as shown in Figure 6. The positive shifts of the N 1s peak from 399.7 eV (1 h) to 401.1 eV (5 h) and to 400.8 eV (10 h) indicated that the N-metal bond changed during the catalytic process, which suggested that the intermolecular coordination of different copper and palladium ions with the nitrogen occurred. Then, it almost returned to the original position (399.7 eV) when finished (Figure 6A). In the case of Br 3d, the appearance of Br 3d peaks changed from 69.2 eV (1 h) to 69.5 and 69.4 eV during the catalytic process, indicating that the Pd(0) oxidative addition with Br-Ph occurred to form Br-Pd-Ph on the catalytic surface or interior. The peak of Br 3d was not detected after completion of the reaction (Figure 6C). According to the result of Cl 2p shown in Figure 6B, no change of Cl 2p was observed, indicating that a Pd−Cl bond existed during the catalytic procedure.

2.4.5. SEM of Si-Fmp-Cu-Pd BMSAM in Catalyzing Process. Figure 7 presents the SEM images of the surface of the Si-Fmp-Cu-Pd BMSAM catalyst. As shown in Figure 7A, individual morphologies are small and round in shape, dispersing without any obvious agglomeration phenomenon. Figure 7B,C shows the SEM images of the catalyst surface after 1 and 5 h, respectively, which reveals that the surface of the sample has more substrates due to the main factor of adsorption. In Figure 7D, the surface exhibits a rough feature owing to the adsorption and resultant phenomenon of more similar particles. Furthermore, these particles are uneven in size due to the mixture of the substrate and resultants, in which the adsorption and desorption of resultants are equivalent. Figure 7E confirms that the desorption of resultant is the main factor because of the appearance of a uniform surface, which is proved clearly by the XPS results (Figures 5 and 6). The SEM image of the Si-Fmp-Cu-Pd BMSAM catalyst after 16 h is shown in Figure 7F. The surface of samples is relative smooth, with a slight agglomeration phenomenon compared to that of Figure 7A. It can be inferred that the catalytic mechanism is heterogeneous.

2.4.6. Catalyst Poisoning Experiment. To ensure that our catalytic mechanism is whether or not heterogeneous, catalyst poisoning tests were carried out. As shown in Table S5, when a
drop of mercury was added to the reaction mixture before starting the model reaction (Table S4, entry 2), the catalytic activity could be effectively inhibited. However, the catalyst could not be poisoned completely due to the fact that mercury could not come in sufficient contact with the catalytically active site because of its poor dispersibility in the reaction solvent.33 After that, PPh3 ligand was added to the reaction mixture and a significant loss of catalytic activity was not observed (Table S5, entry 1). This phenomenon is probably attributed to the strong coordination ability of PPh3, which led to ligand exchange with chlorine. Therefore, PPh3 is not an effective poisoning additive for our catalytic system. It is noteworthy that when poisoning a catalyst with thiophene additives even with less than 1.0 equiv per metal atom, no significant activity was noted due to the coverage of the active sites by thiophene. The results obtained above were the evidence that the catalyzing process mainly occurred on the surface and that Si-Fmp-Cu-Pd BMSAM acted as a heterogeneous catalyst. The result indicates that the Si-Fmp-Cu-Pd BMSAM catalyst was stable under the experimental conditions.

2.4.7. In Situ Fourier Transform Infrared (FTIR) Spectroscopy Monitoring. ReactIR is a suitable tool for monitoring reactions and investigating catalytic mechanisms.34 As shown in Figures 8 and 9, the ReactIR 3D maps over time catalyzed by Si-Fmp-Cu-Pd BMSAM (Figure 8) and homogeneous Cu(OAc)2/Li2PdCl4 (Figure 9) showed a marked difference. For the ReactIR 3D maps over time catalyzed by Si-Fmp-Cu-Pd BMSAM, the intensity of the peak at 2095 cm−1 assigned to acetylene showed a slowly decreasing trend with increasing time during the reaction process (Figure 8B). However, the ReactIR 3D maps over time catalyzed by Cu(OAc)2/Li2PdCl4 showed a rapidly decreasing peak intensity within 2 h (Figure 9B). The marked differences indicated different catalytic mechanisms when catalyzed by Si-Fmp-Cu-Pd BMSAM and Cu(OAc)2/Li2PdCl4. For homogeneous Cu(OAc)2/Li2PdCl4, the catalyst can be evenly dispersed in the reaction solution and the environment of isotropy allows the reactants to attack the catalyst from all directions. Therefore, the reaction intermediates are also evenly dispersed in the reaction solution. As such, at the beginning of the reaction, reaction intermediates generated rapidly. For this reason, a rapidly decreasing peak intensity trend was observed from the ReactIR 3D map within 1 h. The reaction intermediates gradually converted into product through the reaction process, so rapidly declining peak intensities were observed. For the Si-Fmp-Cu-Pd BMSAM catalyst, a heterogeneous catalytic mechanism was suggested. The surface of a heterogeneous catalyst contains a limited number of active metal atoms. Therefore, a surface reaction mechanism was considered.34 The reactants were adsorbed onto the internal catalytic surface, and reaction intermediates were generated at specific active sites during the reaction process. After that, the products are diffused to the reaction solution by desorption of the products from the catalytic surface, so few reaction intermediates diffused to the reaction solution. Therefore, the ReactIR 3D maps of the coupling reaction catalyzed by Si-Fmp-Cu-Pd BMSAM showed that the
characteristic peaks of the substrate decreased during the reaction process. To ensure our conclusion, FTIR spectra at different times during catalysis by Si-Fmp-Cu-Pd BMSAM and Cu(OAc)$_2$/Li$_2$PdCl$_4$ were selected, as shown in Figure 7c. We assigned the band at 1486 cm$^{-1}$ to the skeleton vibration of the benzene ring and the band at 1069 cm$^{-1}$ to the flexural vibration of the C–H bond. The bands at 823, 754, and 696 cm$^{-1}$ are well known as the flexural vibration of para-substituted benzene.$^{65}$ All of the peak intensities showed an increasing trend during the reaction process. The kinetic analysis of the reaction was carried out using the band at 2095 cm$^{-1}$ assigned to acetylene (Figure 10) because the high intensity would give less error. For the reaction catalyzed by Si-Fmp-Cu-Pd BMSAM, the yield decreased slowly within 16 h, indicating that full conversion was achieved (Figure 10, red line), in which some intermediates were produced during 4−7 h. In the case of homogeneous Cu(OAc)$_2$/Li$_2$PdCl$_4$ a rapid decrease in absorbance was observed, indicating a different catalytic mechanism (Figure 10, black line).

On the basis of the results obtained above, a proposed process during the catalytic reaction was presented (Scheme 5).

First, the Cu$^{II}$ and Pd$^{II}$ precursors were reduced in situ to active Cu$^+$ and Pd$^0$ on the surface and interior of the molecular monolayer and efficiently stabilized by phenanthroline. Subsequently, copper(I) acetylide and sodium azide quickly formed a cuprate−triazole intermediate on the surface and the catalytic activation of Ph-Br was realized on the Pd$^0$ species to produce a palladium intermediate on the surface or interior, which should lie at a proper distance between the copper and active palladium sites, followed by a quick transmetalation to afford a palladated intermediate on the surface. A reductive elimination of these intermediates yielded the desired product, accompanied by the generation of Cu$^+$ and Pd$^0$ species. Si-Fmp-Cu-Pd BMSAM is a true heterogeneous catalysts and acts as a reservoir of molecular species. In this latter case, either “naked copper and palladium atoms” may leach from the monolayer or the first step of the reaction, namely, the cycloaddition and the oxidative addition, occurred at the surface of Si-Fmp-Cu-Pd BMSAM, followed by leaching of the cuprate−triazole intermediate and the [Pd(Ar)X] species, which could be transmetalated with the cuprate−triazole intermediate on the surface of the catalyst or an internal molecule. The picture emerged is one where catalytic conversion occurs on surface sites or internal sites, which are made out of well-defined local ensembles of atoms on the surface and interior of Si-Fmp-Cu-Pd BMSAM.

### 3. CONCLUSIONS

A solution to achieve the successful fabrication of heterobimetallic self-assembled monolayer (BMSAM) with a controlled composition of different metals was developed. BMSAM containing phenanthroline and Schiff-base groups was prepared, and its novel heterobimetallic (Cu and Pd) self-assembled monolayer anchored on silicon (denoted as Si-Fmp-Cu-Pd BMSAM) with controlled composition and fixed position was also fabricated and in-depth characterized by UV, Raman, XPS, SEM, XRD, inductively coupled plasma atomic emission spectrometry (ICP-AES), and WDCA analyses. The effects of Si-Fmp-Cu-Pd BMSAM on its catalytic
properties were also systematically investigated. The preferred orientation and composition of the heterobimetallic monolayer can be controlled by means of selecting a material containing certain functional groups and coordinating way. The catalytic properties of Si-Fmp-Cu-Pd BMSAM for the three-component click reaction were studied, and the catalytic mechanism of the click reaction in a heterogeneous system was proposed preliminarily. The results showed that the partial (ordered) isolation of active sites played a great role in the catalytic performance. The catalytic reaction mechanism of click reaction interpreted that the catalytic process mainly occurred on the surface of the film and the internal active site (Pd) and rationalized that the Cu(I) species and Pd(0) reduced from the Cu(II) and Pd(II) catalysts were active species. The cuprate—triazole intermediate and the palladium intermediate, whose formation was the key step, should lie in proper positions between copper and active palladium sites, with which the rate of transmetalation would be accelerated to increase the amount of the undesired Sonogashira coupling product. We presumed that the number of real synergistic sites having a proper distance between the different metals also played a great role in the catalytic activity. These variations in the structure of ligand lead to predictable changes in the catalyst activity that can be used to optimize catalyst efficiency and provide an effective route to obtain an ordered heterobimetallic self-assembled monolayer, which represents a new intraheterometallic nanocatalyst with potential applications in a wide range of heterogeneous catalyzed reactions.

4. EXPERIMENTAL SECTION

4.1. Chemicals and Reagents. All chemicals, silicon wafer, and ITO conductive glass (<10 Ω/sq) were purchased from commercial sources. Solvents were distilled before use.

4.2. Apparatus. 1H NMR and 13C NMR spectra were recorded on a Bruker DPX-400 spectrometer in CDCl3 with tetramethylsilane as an internal standard. Mass spectra were obtained with an ESCALab220i-XL electron spectrometer using KBr pellets. Raman spectra were measured using a Hitachi S-4800 system. UV–vis absorption spectra were recorded on a PerkinElmer Lambda 35 UV–vis spectrophotometer.

4.3. Preparation of Compounds. 1,10-Phenanthroline imine derivative and terpyridine derivative, 2-(4-formylphenyl)-imidazo[4,5-f][1,10]phenanthroline (Fmp), 4-(1H-imidazo-[4,5-f]-1,10-phenanthrolin-2-yl)phenol (HOP), and 4-(4-carboxyphenyl)-2,2,6,2-terpyridine (TPy) were prepared according to the literature. 1H and 13C NMR spectra were recorded on a Bruker DPX-400 spectrometer. FTIR measurements were carried out on a BRUKER TENSOR FTIR spectrometer using KBr pellets. Raman spectra were measured with a Thermo Scientific DXR Raman microscope with an excitation laser wavelength of 532 nm. SEM images were recorded using a Hitachi S-4800 system. UV–vis spectra were recorded on a PerkinElmer Lambda 35 UV–vis spectrophotometer.

4.4. Preparation of Catalytic Monolayer. Surface hydrophilic treatment and surface modification of 3-aminopropyltrimethoxysilane, ITO, quartz, and glass were treated according to the literature. 1H and 13C NMR spectra were recorded on a Bruker DPX-400 spectrometer. FTIR measurements were carried out on a BRUKER TENSOR FTIR spectrometer using KBr pellets. Raman spectra were measured with a Thermo Scientific DXR Raman microscope with an excitation laser wavelength of 532 nm. SEM images were recorded using a Hitachi S-4800 system. UV–vis spectra were recorded on a PerkinElmer Lambda 35 UV–vis spectrophotometer.

4.4.1. Monolayer Preparation of 1,10-Phenanthroline Imine or Terpyridine Derivative on the Wafer. A 3-aminopropylated wafer and 2 mmol of 1,10-phenanthroline carboxaldehyde or triptycine carboxaldehyde were placed in dry toluene (20 mL). The entire mixture was heated at 80 or 25 °C for 24 h in a nitrogen stream. The functionalized wafer was carefully washed by petroleum ether, ethyl acetate, ethanol, and deionized water.

4.4.2. Preparation of a Si-Fmp-Cu-Pd BMSAM Monolayer on the Wafer with Certain Ratio of Pd/Cu. Route 1: Appropriate amounts of copper acetate were dissolved in water. The functionalized wafer was put into the prepared solution for 16 h and then washed by sonication in ethanol, to give a Si-Cu BMSAM self-assembled monolayer. The Cu BMSAM slide was added to the solution of Li2PdCl4 for 16 h and washed with ethanol to yield the Si-Fmp-Cu-Pd BMSAM monolayer. Route 2: The functionalized wafer was added to the mixture of copper acetate and Li2PdCl4 at room temperature for 3 or 16 h, and the physisorbed species were removed by sonication in ethanol to give Si-Fmp-Cu-Pd BMSAM, Si-Fmp-Cu-Pd BMSAM, and Si-TPy-Cu-Pd, with different ratios of Pd/Cu.

4.5. Electrochemical Measurements. Voltammetric detection was performed on a CHI650A electrochemical work station (CH Instruments, Inc., Shanghai, China). The ITO electrode linked with catalyst was used as the working electrode. A Pt wire and a Ag/AgCl wire were used as the counter electrode and reference electrode, respectively. The voltammetric measurements were recorded with cyclic potential scans between −1.0 and 0 V in a 0.1 mol L−1 Tris–HCl buffer solution.

6. General Procedure for the Three-Component Click Reactions. Organic azide (0.15 mmol), benzyl bromide (0.125 mmol), and alkyne (0.15 mmol) were added into a glass vessel equipped with a magnetic stir bar under a nitrogen atmosphere. Catalysts immobilized on the substrates were added into the vessel under N2, and degassed water was added to obtain 5–7 mL as the total volume of water. The reaction mixture was stirred for 16 h at 25 °C. Then, the mixture was extracted using ethylacetate (3 × 10 mL). The solvent was removed in vacuo and chromatographed with petroleum ether/ethylacetate (1:1,v/v) as an eluent to give the corresponding 1,2,3-triazole derivatives.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00364.

Synthesis of ligands; characterization of Si-Fmp-Cu-Pd BMSAM; contrast experimental and characterization; preparation and characterization of Si-HOP-Cu-Pd and Si-TPy-Cu-Pd; substrate scope of synthesis catalyzed by Si-Fmp-Cu-Pd and BMSAM (PDF)

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