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# Truncated concave octahedral Cu<sub>2</sub>O nanocrystals with {*hkk*} highindex facets for enhanced activity and stability in heterogeneous catalytic azide-alkyne cycloaddition

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We report a facile synthesis of Cu<sub>2</sub>O truncated concave octahedral nanocrystals mainly with {511} high-index facets in a system of oil in water emulsion. In azide-alkyne cycloaddition with water as a green solvent, Cu<sub>2</sub>O truncated concave octahedra showed greatly enhanced activity with turnover frequency (TOF) as high as 2413 h<sup>-1</sup>, which was about two and four times, respectively, as compared to Cu<sub>2</sub>O rhombic dodecahedra with {110} facets and cubes with {100} facets. After 10 rounds of recycle experiments, Cu<sub>2</sub>O truncated concave octahedra still exhibited good catalytic and structural stability.

Cu-catalyzed azide-alkyne cycloaddition (CuAAC), as a paradigm of click reactions, has been used in organic synthesis, surface and polymer chemistry, and biomedical field due to its high regioselectivity and reactivity.<sup>1-4</sup> During the last decade, CuAAC was mainly studied in the field of homogeneous catalysis by using copper (I) salts.<sup>3</sup> However, in homogeneous

CuAAC, it is difficult to separate copper complexes in the end products and reuse catalysts, which limits the wide application of CuAAC.<sup>5</sup> In recent years, heterogeneous CuAAC (Table S1<sup>+</sup>) has attracted more and more attention due to its green and characters.6-11 environmentally friendly Cu-based nanocatalysts were investigated in heterogeneous CuAAC, but the main issues existed were the dissolution of copper element and/or stability of catalysts during the reaction, thereby preventing their reuse.<sup>5,7</sup> Although the detail mechanism of the CuAAC still needs further exploration, Cu(I) was considered as the active species in the reaction.<sup>12</sup> Compared with other cuprous catalysts, the readily available and inexpensive Cu<sub>2</sub>O is one of most promising catalysts with good activity and recyclability for heterogeneous CuAAC.<sup>13-16</sup>

It is well known that surface structure of a nanocrystal is one of the most important factors that determines its activity.<sup>17-21</sup> Huang and co-workers found that (110) surface of Cu<sub>2</sub>O was more active than (100) and (111) surfaces of Cu<sub>2</sub>O toward heterogeneous CuAAC.<sup>14</sup> Owing to high density of atomic steps, edges, and unsaturated coordination sites, nanocrystals with high-energy (high-index) facets usually exhibit higher reactivity relative to that with low-energy facets.<sup>22-24</sup> However, high-energy facets usually diminish or even disappear during growth to minimize surface energy of crystals.<sup>25</sup> In last decade, Cu<sub>2</sub>O nanocrystals with various as cubes, octahedra, morphologies such rhombic dodecahedra, multipods, and nanowires have been synthesized, but all of these Cu<sub>2</sub>O nanocrystals were enclosed by low-energy facets.<sup>26,27</sup> There are some reports about the synthesis of Cu<sub>2</sub>O crystals with high-index facets,<sup>28-32</sup> whereas the sizes of these Cu<sub>2</sub>O crystals are within micrometer-scale with very low specific surface areas, which is against the improvement of catalytic activity.<sup>15</sup> Taken together, we believe that the fabrication of Cu<sub>2</sub>O nanocrystals enclosed by highindex facets will be in favor of the enhancement of the activity of Cu<sub>2</sub>O toward heterogeneous CuAAC.

In this paper, we have successfully synthesized  $Cu_2O$  truncated concave octahedral nanocrystals mainly enclosed by

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<sup>†</sup> Electronic Supplementary Information (ESI) available: experimental section; SEM image and size distribution plot of truncated concave octahedral  $\mathsf{Cu}_2\mathsf{O}$ nanocrystals; XPS spectra of the synthesized Cu<sub>2</sub>O; TEM image, SAED pattern, and schematic model of a truncated concave octahedron viewed along [001] direction; schematic model of Cu<sub>2</sub>O (511) surface projected along  $[01\overline{1}]$  direction; particle size distribution histograms of as-prepared Cu<sub>2</sub>O nanocrystals: SEM image and particle size distribution histograms of Cu<sub>2</sub>O nanocystals prepared by adjusting pH using H<sub>2</sub>SO<sub>4</sub> or KOH; SEM image of Cu<sub>2</sub>O nanoparticles prepared in the absence of oleic acid; photographs showing the color change of solution during the synthesis of Cu<sub>2</sub>O nanocrystals with different morphologies: FT-IR spectra of Cu<sub>2</sub>O nanocrystals; the amounts of produced BPT normalized with surface areas of Cu<sub>2</sub>O; XRD patterns and SEM images of Cu<sub>2</sub>O nanocrystals before and after catalytic reaction; schematic models of Cu $_2O$  (100), (110), and (511) surfaces; SEM, TEM HRTEM images, SAED pattern, XRD pattern, and XPS spectra of truncated concave octahedral  $Cu_2O$  nanocrystals after 10 recycles of catalytic reaction; tables of reported Cu-based nanocatalysts in azide-alkyne cycloaddition, the calculated crystallite sizes of Cu<sub>2</sub>O nanocrystals using Scherrer equation, BET results for Cu<sub>2</sub>O nanocrystals, mole percentages of surface Cu(I) over the total Cu(I) in the Cu<sub>2</sub>O catalysts, and yields of different types of triazoles derived from benzyl azide / benzyl azide derivative and different types of alkynes; NMR data of all synthesized compounds. See DOI: 10.1039/x0xx00000x

#### COMMUNICATION

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{511} high-index facets through a system of oil in water emulsion. We have systematically investigated experimental conditions and morphologies of Cu<sub>2</sub>O nanocrystals evolved from rhombic dodecahedra, to truncated concave octahedra, and cubes by increasing solution pH. As predicted, Cu<sub>2</sub>O truncated concave octahedral nanocrystals showed much enhanced activity in azide-alkyne cycloaddition, as well as good stability, relative to Cu<sub>2</sub>O rhombic dodecahedral and cubic nanocrystals.



Fig. 1 (a) Typical SEM image and (b) powder X-Ray diffraction pattern of the Cu<sub>2</sub>O truncated concave octahedra. (c) SEM images, (d) TEM images, (e) the corresponding selective area electron diffraction (SAED) patterns, and (f) schematic models of a truncated concave octahedron enclosed by twenty-four {511}, twelve {110}, and six {100} facets viewed along [ $\overline{1}$ 11], [ $01\overline{1}$ ], and [001] directions, respectively. Scale bars in (c) and (d): 100 nm.

In the standard synthesis of Cu<sub>2</sub>O truncated concave octahedral nanocrystals, the aqueous solutions of CuSO<sub>4</sub>, NaOH, and sodium ascorbate (SA) were successively added in a two-phase solution of water and oleic acid. The final solution reacted at 50 °C for 1 h. Fig. 1a showed scanning electron microscopy (SEM) image of as-prepared Cu<sub>2</sub>O truncated concave octahedral nanocrystals. The truncated concave octahedra had an average diameter of about 158 nm (Fig. S1<sup>†</sup>). As shown in Fig. 1b, the powder X-ray diffraction (XRD) pattern of the truncated concave octahedral nanocrystals can be indexed to the cubic phase Cu<sub>2</sub>O (JCPDS No. 05-0667). SEM and transmission electron microscopy (TEM) images of Cu<sub>2</sub>O truncated concave octahedra along [111], [011], and [001] directions could match well with a model of truncated concave octahedra with twenty-four {511}, twelve {110}, and six {100} facets (Fig. 1c-f and Fig. S2<sup>†</sup>), demonstrating that the asprepared Cu<sub>2</sub>O truncated concave octahedra nanocrystals

were mainly exposed with {511} high-index facets, together with {110} and {100} facets. Atomic model of (511) surface showed that (511) surface can be seen as a combination of (100) terraces and (011) steps (Fig. S3<sup>+</sup>).

Solution pH is critical to the formation of truncated concave octahedral Cu2O nanocrystals. In this synthesis system, the relative amount of NaOH and oleic acid is the main factor determining solution pH. Solution pH was measured immediately after adding SA. In the standard synthesis of truncated concave octahedra, the amounts of added oleic acid and NaOH solution (1.0 M) were 0.5 and 1.3 mL, respectively, and the solution pH after adding SA was 9.0. Then we modified the amount of oleic acid added while keeping other conditions unchanged. Without oleic acid, the solution pH was 12.9 and the product mainly consisted of Cu<sub>2</sub>O cubic microcrystals (Fig. 2a). When 0.3 mL of oleic acid was added, the solution pH decreased to 11.3 and Cu<sub>2</sub>O cubic nanocrystals with {100} facets could be obtained (Fig. 2b). Further increasing the amount of oleic acid to 0.6 mL with solution pH 8.2, the morphology of Cu<sub>2</sub>O nanocrystals evolved to rhombic dodecahedra with {110} facets (Fig. 2c). The average diameters of obtained cubic and rhombic dodecahedral nanocrystals were around 168 and 145 nm, respectively (Fig. S4a and b<sup>+</sup>), which are close to the calculated crystallite sizes based on XRD using Scherrer equation (Table S2<sup>+</sup>). To further confirm the important role of solution pH, we then adjusted solution pH by changing the amount of NaOH solution (1.0 M) on the basis of standard synthesis method for truncated concave octahedra. When solution pH was adjusted to 8.3 and 11.6 by adding 1.05 and 1.85 mL of NaOH solution, respectively, we could also obtain Cu<sub>2</sub>O rhombic dodecahedral and cubic nanocrystals (Fig. 3a and b). The average diameters of rhombic dodecahedra and (a) cubes derived from different amounts of NaOH solution (Fig. S4c and d<sup>+</sup>) are also close to that derived from different amounts of oleic acid. To further confirm the role of solution pH, KOH or H<sub>2</sub>SO<sub>4</sub> was further introduced to control the solution pH. Based on the synthetic protocol of truncated concave decahedra, when 0.55 mL of KOH solution (1.0 M) or 58  $\mu$ L of H<sub>2</sub>SO<sub>4</sub> solution (2.0 M) were added in the system, respectively, solution pH can be adjusted to 11.4 and 8.3, and cubes and rhombic dodecahedra still can be obtained (Figure S5<sup>†</sup>).



Fig. 2 SEM images of Cu<sub>2</sub>O nanoparticles synthesized using the standard method for Cu<sub>2</sub>O truncated concave octahedra, except for different amounts of oleic acid: (a) 0 mL, (b) 0.3 mL, and (c) 0.6 mL.

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Fig. 3 SEM images of Cu<sub>2</sub>O nanoparticles synthesized using the standard method for  $Cu_2O$  truncated concave octahedra, except for different amounts of 1.0 M NaOH solution: (a) 1.05 mL and (b) 1.85 mL.

In addition to solution pH, oleic acid is also indispensable for the synthesis of Cu<sub>2</sub>O truncated concave octahedral nanocrystals. When keeping the solution pH 9.0 with the absence of oleic acid, only spherical like nanocrystals with rough surface appeared (Fig. S6<sup>+</sup>), rather than truncated concave octahedra, demonstrating the important role of oleic acid for the synthesis of Cu<sub>2</sub>O truncated concave octahedral nanocrystals.



Fig. 4 Schematic of shape-controlled synthesis of Cu<sub>2</sub>O nanocrystals by adjusting solution pH. Scale bars in SEM images: 100 nm.

Based on the above experiments, it can be found that both solution pH and oleic acid are responsible for morphology control of  $Cu_2O$  nanocrystals. Fig. 4 shows the schematic of shape-controlled synthesis of Cu<sub>2</sub>O nanocrystals with different solution pH. When oleic acid was added into the aqueous solution of CuSO<sub>4</sub>, Cu<sup>2+</sup> in water phase gradually moved into oil phase and oil phase turned to blue, as  $\mbox{Cu}^{2+}$  tended to coordinate with oleic acid to generate  $Cu(C_{17}H_{33}COO)_2$ according to reaction (1).<sup>33</sup> After introducing NaOH solution, the oil in water (O/W) emulsion with uniform blue was formed. Then Cu<sub>2</sub>O nanocrystals were generated based on the reaction (2). With the increase of solution pH, the morphology of obtained Cu<sub>2</sub>O nanocrystals evolved from rhombic dodecahedra with pH 8.2, to truncated concave octahedra with pH 9.0, and cubes with 11.3. The different morphologies of Cu<sub>2</sub>O nanocrystals under different solution pH could be attributed to the different growth rates of Cu<sub>2</sub>O, which could be accelerated with the increase of solution pH. In the growth process of rhombic dodecahedra, truncated concave octahedra, and cubes, the color of solutions turned from blue to light yellow in 35 min, 10 min, and 15 s, respectively (Fig. S7-S9<sup>†</sup>). These results demonstrate that the medium growth rate is benefit for the generation of truncated concave dodecahedra with {511} high-index facets, while a faster or slower growth rate, respectively, leads to the formation of cubes and rhombic dodecahedra.

$$Cu^{2+}+2C_{17}H_{33}COOH \leftrightarrow Cu(C_{17}H_{33}COO)_2+2H^+$$
 (1)

$$2Cu(C_{17}H_{33}COO)_{2}+2OH^{-} \rightarrow Cu_{2}O+4C_{17}H_{33}COO^{-}+H_{2}O$$
 (2)

SΑ



Fig. 5 (a) Time courses of azide-alkyne cycloaddition for BPT catalyzed by  $Cu_2O$ nanocrystals with different morphologies at 40 °C. (b) Comparison of TOFs of different  $\text{Cu}_2\text{O}$  catalysts calculated based on surface Cu(I) and BPT yields below 20% (for truncated concave octahedra, BPT yield: 18.0% at 10 min; for rhombic dodecahedra, BPT yield: 15.5% at 15 min; for cubes, BPT yield: 16.6% at 45 min). BPT yields achieved with truncated concave octahedra over ten rounds of successive reaction at 40 °C for (c) 70 min and (d) 30 min. Error bars refer to the standard deviation based on three repeated experiments.

The catalytic properties of Cu<sub>2</sub>O truncated concave octahedral, cubic, and rhombic dodecahedral nanocrystals were evaluated by azide-alkyne cycloaddition in water as a green solvent. Herein Cu<sub>2</sub>O cubes and rhombic dodecahedra used in the catalytic reaction were synthesized using standard synthesis method for Cu<sub>2</sub>O truncated concave octahedra, except for different amounts of NaOH solution. Before reaction, the as-obtained Cu<sub>2</sub>O nanocrystals were washed nine times with ethanol and hexane to remove the adsorbed oleic acid from the surface. From Fourier transform IR (FT-IR) spectra (Fig. S10<sup>+</sup>), no stretching frequencies of C-H bonds and carboxylate groups could be observed in the range of 2850-2960 and 1400-1600 cm<sup>-1</sup>, demonstrating that the surfaces of Cu<sub>2</sub>O nanocrystals were free from oleic acid.<sup>14,34</sup> Fig. 5a showed the yields of 1-benzyl-4-phenyl-1H-1,2,3-triazole (BPT) catalyzed by Cu<sub>2</sub>O nanocrystals with different morphologies in the reaction of benzyl azide and phenylacetylene for various times. Under the same conditions, BPT yields catalyzed by different Cu<sub>2</sub>O nanocatalysts followed the sequence truncated concave octahedra > rhombic dodecahedra > cubes. When the reaction was performed at 40 °C for 70 min, truncated concave octahedra gave a BPT yield as high as 98%, while rhombic dodecahedra and cubes gave BPT yields of 70% and 25%, respectively. To eliminate the size effects of different types of Cu<sub>2</sub>O, the amount of produced BPT were normalized with their

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surface areas determined by Brunauer-Emmett-Teller (BET) results (Table S3<sup>+</sup>). It was found that truncated concave octahedra still showed the highest activity while Cu2O cubic catalyst exhibited the lowest activity among these types of Cu<sub>2</sub>O nanocatalysts (Fig. S11<sup>+</sup>). To compare the catalytic activities accurately, the turnover frequencies (TOFs) of different Cu<sub>2</sub>O catalysts then were calculated on the basis of BPT yields below 20% and surface Cu(I) of catalysts determined by carbon monoxide temperature programmed desorption (Table S4<sup>†</sup>).<sup>35,36</sup> The calculated TOF value of Cu<sub>2</sub>O truncated concave octahedral nanocrystals was 2413 h<sup>-1</sup>, which was 1.9 and 3.9 times than that of Cu<sub>2</sub>O rhombic dodecahedral and cubic nanocrystals, respectively (Fig. 5b). After azide-alkyne cycloaddition, the compositions and morphologies of different Cu<sub>2</sub>O nanocatalysts were analyzed. As confirmed by XRD and SEM images, both bulk phases and morphologies of Cu<sub>2</sub>O truncated concave octahedral, rhombic dodecahedral, and cubic nanocrystals were well maintained after azide-alkyne cycloaddition (Fig. S12 and S13<sup>†</sup>).

When the reaction was conducted at 40 °C for 70 min, the reaction solution after removing Cu<sub>2</sub>O catalyst was analyzed by inductively coupled plasma mass spectrometer (ICP-MS). The concentration of copper in the final solution was negligible (less than 180 ppb), indicating that copper contamination was averted in the reaction. Furthermore, control experiment based on the concept of hot filtration experiment was performed to exclude that the observed activity of Cu<sub>2</sub>O nanocrystals might be resulted from homogeneous process catalyzed by dissolved Cu(I).14 Herein we modified the procedure by conducting the reaction in the absence of benzyl azide and phenylacetylene in the first step, as product BPT could not be completely removed from the reaction solution and the residual BPT in the solution may influence the measurement results in the followed step. Firstly, 2 mg (13.9  $\mu mol)$  of  $Cu_2O$  nanocatalyst was dispersed in 1 mL of deionized (DI) water and the solution was heated at 40 °C for 70 min with stirring under N<sub>2</sub>. After removal of Cu<sub>2</sub>O nanocatalyst by centrifugation, 0.25 mmol of benzyl azide and 0.25 mmol of phenylacetylene were added into the remaining solution and the obtained solution was reacted at 40 °C for 70 min under N<sub>2</sub>. No BPT product could be detected in the reaction solution by high performance liquid chromatography. The result revealed the observed activity in the azide-alkyne cycloaddition resulted from the heterogeneous process catalyzed by Cu<sub>2</sub>O catalysts, rather than homogeneous process.

Although there is much debate about the mechanism of CuAAC, Cu(I) acetylides was considered as the true species.' intermediate Single-molecule spectroscopy investigation confirmed that the formation of Cu-acetylide on the surface of heterogeneous catalysts was the first step of heterogeneous CuAAC.<sup>37</sup> Cu-acetylide was formed when Cu atoms with positive charge replaced the terminal protons of alkynes.<sup>38</sup> For bulk Cu<sub>2</sub>O, the coordination number (CN) of Cu-O for Cu atoms is 2. On Cu<sub>2</sub>O (511) surface, part of Cu atoms is coordinatively unsaturated, whereas all the Cu atoms on Cu<sub>2</sub>O (110) and (100) surfaces are coordinatively saturated (Fig.

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S14†). The low-coordinated Cu atoms on the (511) surface could be favorable for adsorption of alkynes, thereby promoting catalytic activity.<sup>39,40</sup> We further measured  $\zeta$  potentials of Cu<sub>2</sub>O catalysts in aqueous solution. The  $\zeta$  potentials of Cu<sub>2</sub>O truncated concave octahedral, rhombic dodecahedral, and cubic nanocrystals were +0.49, +13.1, and +16.6 mV, respectively. Cu<sub>2</sub>O surface with higher positive charge has stronger adsorption capacity of deprotonated alkynes with negative charge, which is favourable for the formation of Cu-acetylide and the improvement of catalytic activity.<sup>14</sup> Therefore, Cu<sub>2</sub>O truncated concave octahedra mainly with {511} facets exhibited the highest activity while Cu<sub>2</sub>O cubes with {100} facets displayed the lowest activity in azide-alkyne cycloaddition.

The high activity of Cu<sub>2</sub>O truncated concave octahedral nanocrystals was further confirmed in the azide-alkyne cycloaddition reaction of benzyl azide with different types of terminal alkynes (Table S5<sup>†</sup>). When using aromatic alkynes containing electron-donating groups, 4-ethynyltoluene (Entry 1) and 3-ethynyltoluene (Entry 2) as substrates, excellent triazole yields around 99% and 97% could be obtained, respectively. By using aromatic alkynes with electrongroups withdrawing (3-chlorophenylacetylene, 4chlorophenylacetylene, and 4-fluorophenylacetylene) as substrates, the target triazole yields are around 95% (Entries 3, 4, and 5). Apart from aromatic alkynes, the reaction of benzyl azide with aliphatic alkynes such as 1-hexyne, could also give a high yield of 85% 1-benzyl-4-butyl-1H-1,2,3-triazole (Entry 6). In addition, the 1-(azidomethyl)-3-methoxybenzene was also used to react with phenylacetylene and 4-ethynyltoluene, and the target triazole yields still could achieve as high as 98% and 97%, respectively (Entries 7 and 8).

In addition to superior activity, Cu<sub>2</sub>O truncated concave octahedral nanocrystals also displayed good catalytic stability in azide-alkyne cycloaddition. The recyclability of Cu<sub>2</sub>O truncated concave octahedra was evaluated in the cycloaddition reaction at 40 °C. After 10 recycles, truncated concave octahedra remained to achieve BPT yield of 97% when every round was performed for 70 min (Fig. 5c). Based on the analysis of XRD, SEM, TEM, high-resolution TEM (HRTEM) images, and SAED pattern after 10 recycles (Fig. S15 and S16<sup>†</sup>), the bulk phase and morphology of Cu<sub>2</sub>O truncated concave octahedra were also well preserved. The surface composition of the catalyst before and after 10 recycles were further analysed by X-ray photoelectron spectrometer (XPS). From the XPS results before and after 10 recycles (Fig. S17 and S18†), the peaks located at 932.5 and 952.3 eV in XPS can be assigned to Cu(I) feature in Cu<sub>2</sub>O.<sup>41,42</sup> The peak at 916.2 eV kinetic energy in Cu LMM Auger spectra can also be attributed to  $Cu_2O$ . These results demonstrated that  $Cu_2O$  truncated concave octahedra maintained good structural stability after 10 recycles. To better illustrate the recyclability of present Cu<sub>2</sub>O catalyst, recycle experiment was also conducted by reducing reaction time to 30 min for each round. Under this condition, BPT yield was all about 60% without obvious loss of catalytic activity, further demonstrating good recyclability and green feature of catalyst (Fig. 5d).

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## Conclusions

In summary, we have fabricated Cu<sub>2</sub>O truncated concave octahedral nanocrystals enclosed by twenty-four {511} highindex facets, twelve {110}, and six {100} facets through a system of O/W emulsion. In this synthesis system, both oleic acid and solution pH are crucial for the formation of Cu<sub>2</sub>O truncated concave octahedra. The morphologies of  $Cu_2O$ nanocrystals could be controlled by adjusting solution pH. With the increase of solution pH, morphologies of Cu<sub>2</sub>O evolved from rhombic dodecahedra, to truncated concave octahedra, and cubes. In azide-alkyne cycloaddition, Cu<sub>2</sub>O truncated concave octahedra showed much enhanced activity, when compared to Cu<sub>2</sub>O rhombic dodecahedra with (110) facets and cubes with (100) facets. The enhancement in activity could be attributed to the low-coordinated Cu atoms on (511) surface of Cu<sub>2</sub>O, as well as higher positively charged (511) surface relative to (110) and (100) surfaces. In recycle experiment, Cu<sub>2</sub>O truncated concave octahedra also displayed good catalytic and structural stability. The high activity and good recyclability of Cu<sub>2</sub>O truncated concave octahedra demonstrated the green feature of this work. All these results demonstrate an effective pathway to the development of heterogeneous catalysts for CuAAC by controlling surface structure.

## **Conflicts of interest**

There are no conflicts to declare.

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Truncated concave octahedral Cu<sub>2</sub>O nanocrystals with high-index  $\{hkk\}$  facets exhibited superior activity and stability toward azide-alkyne cycloaddition.