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Cobaltocene Reduction of Cu and Ag Salts and Catalytic Behavior of the Nanoparticles Formed

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Abstract

The modes of generation of nanoparticles (NPs) are of great interest for multiple applications in catalysis, optics, sensing and nanomedicine. Here, fast reduction of $CuSO_4 \cdot 5H_2O$ and Ag salts by commercial cobaltocene yields small stable water-soluble Cu and Ag nanoparticles (NPs) with narrow size distribution without any other ligand or support. The variation of the Ag salt counter anion (NO_3^-, F^-, BF_4^-) strongly influences both the plasmonic absorption of the AgNPs synthesized in this way and the high apparent rate constant of the AgNP-catalyzed 4-nitrophenol reduction by $NaBH_4$, showing that the precursor counter anion binds the AgNP surface. The CuNPs synthesized from $CuSO_4$ and cobaltocene are a recyclable catalyst for CuAAC reactions in water that is extended to various azides and alkynes, including functionalization of compounds of biomedical interest. Both CuNP and AgNP catalytic activities are also very promising signs for further extension to a variety of other truly efficient metal NP-catalyzed reactions.

Keywords: copper nanoparticles; silver nanoparticles; nanocatalyst; click reaction; CuAAC; nitrophenol; surface plasmon band; cobaltocene

Introduction

Transition metal nanoparticles (TMNPs) are an essential part of the nanoworld because of their fundamental aspects and multiple applications in biomedicine, sensing, optoelectronics,[1-4] and particularly in catalysis.[5-14] Although organometallic chemistry has provided efficient transition-metal catalysts, they include expensive and sometimes toxic ligands.[15] The advantages of TMNP catalysts are the lack of such ligands and the simplicity of preparation and fixation onto supports.[16-19] It is necessary, however, that the synthesis be well controlled and that for efficiency the TMNPs be small enough so that most atoms are located at the periphery.[20] Usually, the TMNPs are synthesized by reduction of TM salts using reducing agents such as H_2, $NaBH_4$, $(SiMe_2)_6$, Mg, Li or Na in liquid NH_3 and Li or Na naphthalenide in the presence of a stabilizer.[20-23] Key parameters in the TMNP synthesis are the control of the reductant stoichiometry, its driving force and the nature of the stabilizer that define the size, shape and protection type of the TMNPs. Very often the oxidized form of the reductant is not removed and its combination with the TMNP is uncertain, so that it can partly inhibit the TMNP surface activity.

We propose the use of cobaltocene, $CoCp_2$[24,25] ($Cp = \eta^5\text{-}C_5H_5$), because it presents many advantages that solve the above problems. It is a commercially available electron-reservoir compound,[26-28] and its amount and reaction product, $[CoCp_2][X]$,[24,25,29] are well controlled. $CoCp_2$ provides a strong driving force with a standard redox potential of -1.4 V vs. SCE [27,28] for the reduction of $CuSO_4{\cdot}5H_2O$ and Ag salts insuring the fast formation of very small CuNPs and AgNPs respectively.

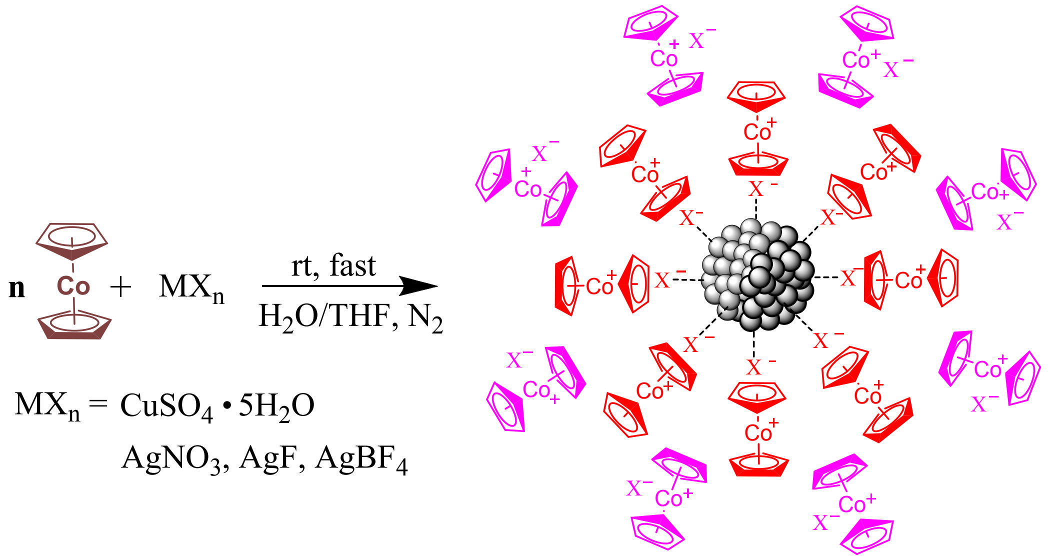
Following immediate reactions between $CoCp_2$ and $CuSO_4{\cdot}5H_2O$ or Ag salts, the cationic groups $[CoCp_2]^+$ obtained along with the metal NP form an encapsulating network around the NP that is an excellent NP stereoelectronic and electrostatic stabilizer. This protecting network does not bind the NP surface atoms that remain available for catalytic substrate binding and activation. The activity of the NP surface will be investigated in order to know if it is appropriate for excellent catalytic conditions. The AgNP plasmonic absorption and kinetics of AgNP-catalyzed 4-nitrophenol reduction by $NaBH_4$ are both therefore excellent tests. Overall the major interest is the facile, fast and clean reduction under ambient conditions of standard commercial salts to catalytically very efficient CuNPs for alkyne azide cycloaddition (CuAAC) reaction.[30]

"Click" reactions were highlighted by Sharpless as a privileged way to couple two molecular fragments for practical use in organic chemistry, biochemistry and nanomaterials science.[30] The most currently used "click" reaction, Cu(I)-catalyzed alkyne azide cycloaddition (CuAAC),[31] was proposed with high amount of $CuSO_4$ that is toxic for biomedical usage[32] or with sophisticated nitrogen ligands.[33,34] CuNPs can also work as catalyst, although the catalytic amounts are usually far higher than those of the reported molecular Cu(I) catalysts.[34-38]

Here we have used $CoCp_2$ to reduce and stabilize CuNPs with small particle size and narrow histogram in water and tetrahydrofuran (THF). The CuNPs are characterized by UV-vis. spectroscopy, Transmission Electron Microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The CuNPs are examined for their catalytic activity in the CuAAC reaction in neat water with low catalytic amounts, and their use is extended to various alkynes and organic azides for CuAAC "click" reactions. Interestingly these CuNPs are in particular successfully used to prepare functional biomedical substrates in neat water.

Results and discussion

Synthesis and Characterizations of the AgNPs. Quick addition of cobaltocene in THF to an aqueous solution of the commercial salt $AgNO_3$ at room temperature (rt) under N_2 results in instantaneous color change (*vide infra*) indicating the formation of AgNPs (Scheme 1, see details in Experimental section). The cobaltocene stoichiometry matches that of the number of electrons necessary to reduce the metal cation of the precursor salt to metal (0) atoms precursors of nanoparticles. Thus no additional stabilizing agent is needed, and these AgNPs are more stable than other non- or less-protected TMNPs synthesized by other means, which shows the protecting role of the cobalticinium salt network.



Scheme 1. Synthesis of CuNPs and AgNPs by reaction of $CuSO_4{\cdot}5H_2O$ or an Ag salt with cobaltocene. For CuNPs, n = 2 and $MX_n = CuSO_4$. For AgNPs, n = 1, and MX_n = AgX (X = NO_3, F or BF_4).

Dependence of the AgNP surface plasmon band and 4-nitrophenol reduction rate constants on the precursor counter anion

Various Ag salts (NO_3^-, F^- and BF_4^-) were probed for reduction by $CoCp_2$ in order to characterize the effects of the coordination of the anions on a plasmonic NP surface by variations of the AgNP surface plasmon band (SPB).[39] XPS analysis (Figure S1) and UV-vis. spectroscopy show that the AgNPs are in the zero oxidation state, and the average size of the AgNPs prepared by $AgNO_3$, AgF and $AgBF_4$ are 3.0, 3.1 and 3.2 nm respectively according to the measurements made by TEM (Figures S5-7). The variations of color and SPB maximum are dramatic upon anion variation. Reduction of the precursor salts $AgNO_3$, AgF and $AgBF_4$ respectively yield orange, dark-brown and light brown AgNPs (Figure 1) with SPB maxima at 423, 439 and 410 nm respectively (Figures S2-4). These strong anion effects are best taken into account as suggested above by the coordination of a good proportion of the anions onto the AgNP surface that differently perturbs the electronic state of the surface.

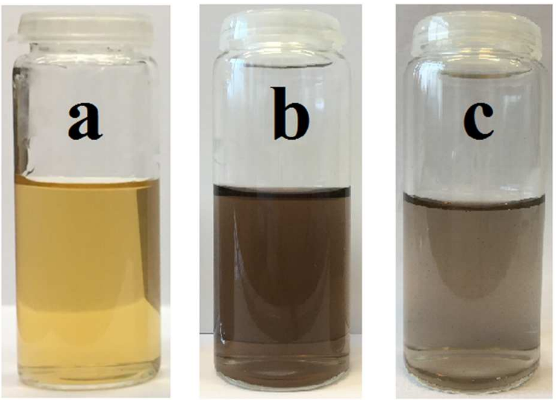


Figure 1. Photographs of the AgNPs obtained using cobaltocene for the reduction of AgX precursor salts: (a) $AgNO_3$; (b) AgF; (c) $AgBF_4$

This coordination of the anion is corroborated by the variation of the effects of the nature of anion coordination in the surface restructuring involved in surface catalysis as shown below. The nature of this anion also influences the AgNP-catalyzed 4-nitrophenol reduction by $NaBH_4$[40] as anticipated from the influence of the anion coordination on the SPB (*vide supra*). This reaction is a useful test to investigate the restructuration of the NP surface during a catalytic reaction according to a Langmuir-Hinshelwood model that involves adsorption of the substrates on the NP surface as shown by Ballauff's group.[41] Indeed starting from $AgBF_4$, $AgNO_3$ and AgF, the k_{app} values of the pseudo-first order rate constant of this reaction measured by the disappearance of the nitrophenolate absorption band at 400 nm are respectively 0.0010 s^{-1}, 0.0017 s^{-1} and 0.0036 s^{-1} without any retention time (Figures S8-10). These rate constants are very different from an anion to another. Their comparison indicates that the catalytic reaction with the small F^- anion is more favorable than those involving other larger anions. Also the reaction is fast with the three anions, even compared to the best catalysts, i. e. the reported classic PdNPs and AuNPs, confirming the excellent catalytic properties of the NPs synthesized using this method

Synthesis and Characterizations of the CuNPs

Reduction of $CuSO_4{\cdot}5H_2O$ by cobaltocene at rt under N_2 results in instantaneous color change from colorless to black indicating the formation of the CuNPs (Scheme 1, see details in Experimental section). The stoichiometry is 2 equivalents of cobaltocene per Cu atom. The CuNPs obtained by this method are stable as the AgNPs above and are characterized by TEM pictures showing the very small NP core size and narrow histogram with a distribution around 1.7 nm (Figure 2). The very small CuNP size results from the strong driving force provided by the reducing agent resulting in fast reduction of Cu(II) to Cu(0) followed by efficient electrostatic and anion ligand stabilization by cobalticinium sulfate.

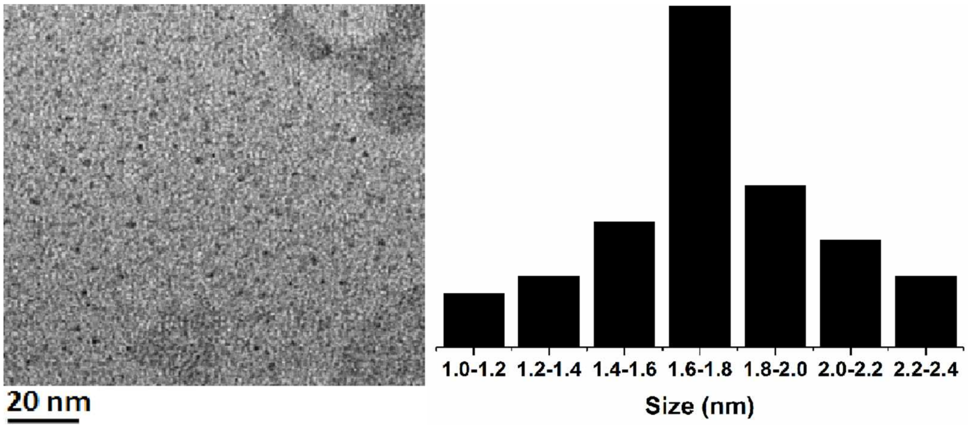


Figure 2. TEM picture (left) and histogram (right) of the 1.7 nm CuNPs prepared by reduction of $CuSO_4$ by cobaltocene.

The XPS spectrum of the CuNPs essentially confirms their zero oxidation state in the core and on the surface. The Cu 2p spectrum shows the Cu $2p_{3/2}$ and $2p_{1/2}$ peaks. The fitting of the Cu 2p3/2 part of the spectrum reveals the presence of Cu(0) at around 932.5 eV, without Cu(II) species (Figure 3).

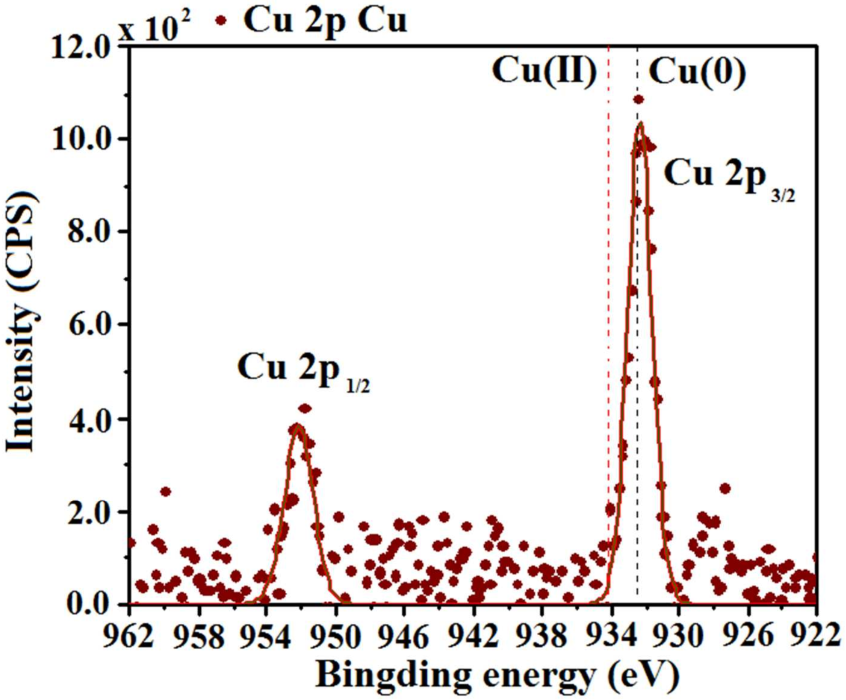


Figure 3. XPS spectrum of the CuNPs prepared from $CuSO_4$ and cobaltocene.

The absence of the absorption band in the UV-*vis*. spectra confirms that these CuNPs are zero-valent Cu species, the CuNP plasmon band being only observable for large CuNPs, contrary to those of AgNPs and AuNPs.[4] On the other hand, the cobalticinium moiety is well characterized by the broad absorption band at 397 nm in the UV-vis. spectrum (Figure 4).[42]

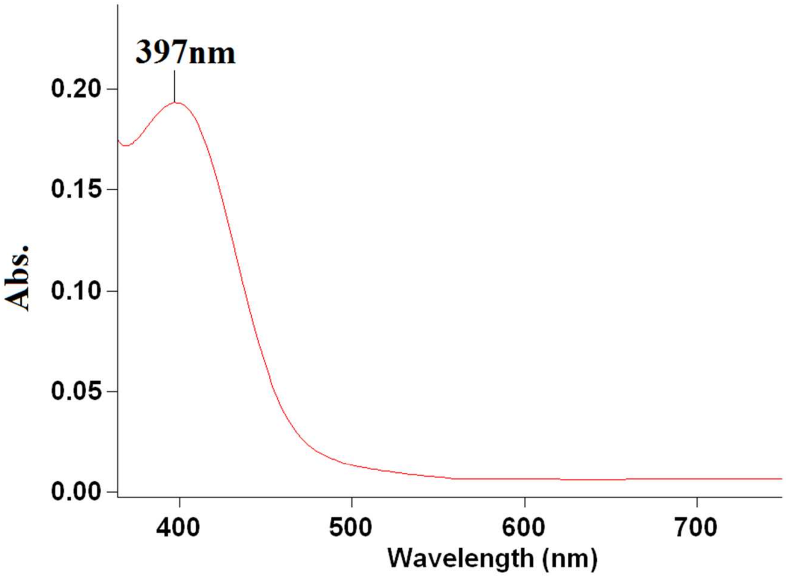
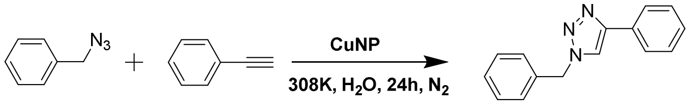


Figure 4. UV-vis. spectrum of the CuNPs obtained by reduction of $CuSO_4$ by cobaltocene.

Some of the SO_4^{2-} anions formed in these reactions are week "L_2-type" (formally 4e) ligands[25] for the zero-valent surface metal atoms in order to equilibrate the cobalticinium charges (*vide infra*). The number of SO_4^{2-} ligands is limited by the number of surface metal atoms. Since there are more SO_4^{2-} species than surface metal atoms many SO_4^{2-} anions remain only electrostatically bonded to cobalticinium groups without binding the CuNP surface. The SO_4^{2-} anions weakly bonded to the surface electrostatically attract cobalticinium counter cations that are close to the NP surface to form the stabilizing network. These considerations are confirmed by the above experiments for AgNPs.

Efficient Cu(NP)-catalyzed alkyne azide cycloaddition in water. The CuNPs obtained by reduction of $CuSO_4$ by cobaltocene were probed for their catalytic activity in CuAAC reaction between benzyl azide and phenylacetylene in neat water (eq 1 and Table 1). This reaction produced 99% isolated yield with 0.1% catalytic amount for 24 h at 35°C and a TOF of 250 with 50 ppm of CuNP catalyst. The scope of the application of this low level amount of the water-soluble CuNP catalyst was explored with other CuAAC reactions between various alkynes and organic azides in water. Good isolated yields were achieved in the CuAAC reaction of a wide variety of alkynes with organic azides using 0.1% or 0.2% catalysts (Table 2). Moreover, one-pot three-components "click" reactions have been conducted from benzyl bromide, sodium azide and phenylacetylene yielding 93% isolated yield with 0.2% Cu of this CuNP nanocatalyst (Supporting Information). The water-soluble CuNP catalyst was also easily recycled by simple filtration at least 4 times with only very slight yield decrease, the click products being insoluble in water (Supporting Information).



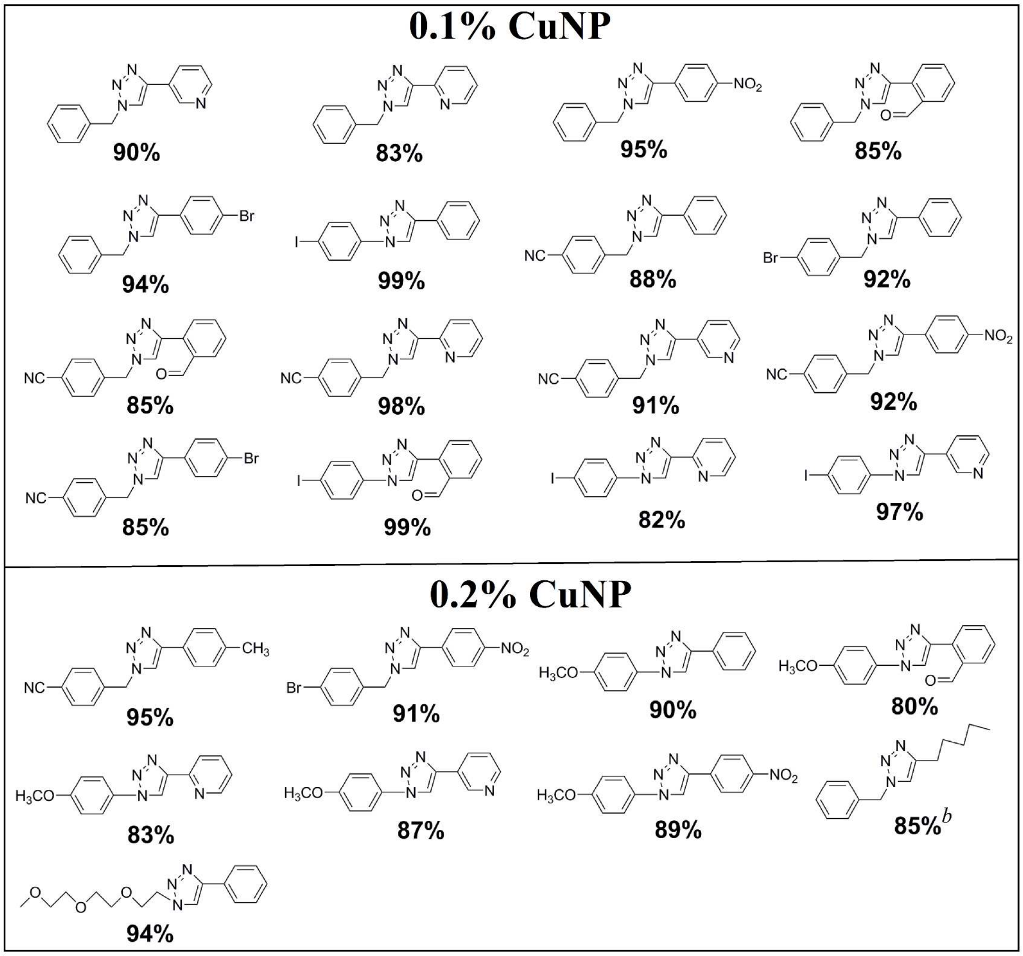
(eq 1)

Table 1. “CuAAC” reaction of eq 1catalyzed by the CuNPs [a]

Entry	Amount (%) [b]	Yield (%) [c]	TON	TOF (h^{-1})
1	0.005	30	6000	250
2	0.01	48	4800	200
3	0.05	76	1520	63.3
4	0.1	99	990	41.3
5	0.2	99	495	20.6

[a] Reaction conditions: 0.5 mmol of benzyl azide, 0.505 mmol of phenylacetylene, and 2 mL of H_2O, 35°C, 24 h, under N_2. [b] Amount of catalysts used in the “CuAAC” reduction. [c] Isolated yield.

Table 2. “CuAAC” reactions between various azides and alkynes using the 0.1% or 0.2% CuNP catalyst.[a]

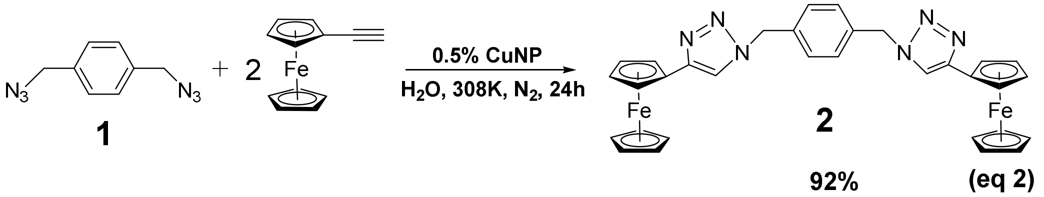


[a] Reaction conditions: 0.5 mmol of azide, 0.505 mmol of alkyne, 2 mL H_2O, 35°C, 24 h, under N_2. [b] Solvent: 1 mL H_2O and 1 mL *tert*-butanol.

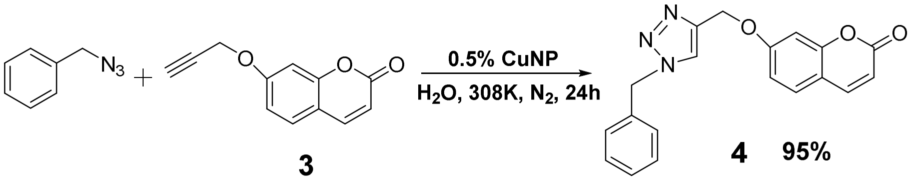
Functional substrates of biomedical interest were also successfully prepared using this CuNP catalyst. In eq 2, *p*-bis (ferrocenyl-1,2,3-triazolylmethyl) benzene (**2**) was synthesized by the click reaction between compound **1** and ethynylferrocene[43] using 0.25% per branch at 35 °C for 24 h with 92% isolated yield in water. This product **2** is of interest, because host-guest molecular interactions between β-CD and ferrocene derivatives[44] are currently used to synthesize nanocatalysts and AuNPs for photothermal therapy.[45]

Coumarin derivatives are often used in the perfume industry. They also are fluorophores and have been applied as fluorescent probes to visualize the metabolism of cysteine in living cells.[46] Thus the click-triazole functionalized 7-(propargyloxy)-coumarin **4** was synthesized from **3** in H_2O in 95% isolated yield upon using this CuNP catalyst (0.5% Cu) for 24 h at 35 °C.

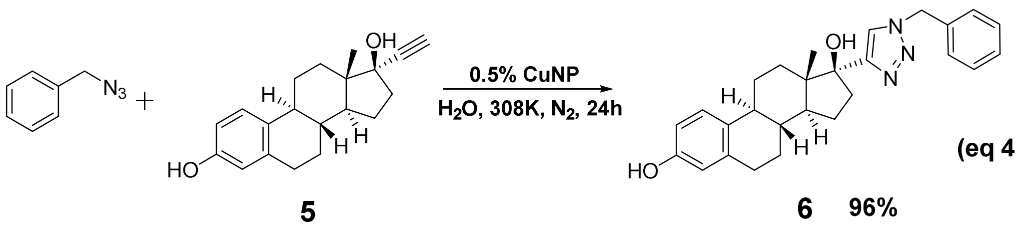
Another key natural product, estradiol, is known as a medication and naturally occurring steroid hormone. Estradiol is an estrogen that is mainly used in menopausal hormone therapy and to treat low sex hormone levels in women. It has several biological functions such as sexual development, reproduction, skeletal system, and nervous system. Besides, the natural alkyne of estradiol also discloses various medicinal applications. Here, the CuAAC click reaction between ethynyl estradiol (**5**) and benzyl azide using CuNP (0.5%) in water at 35 °C for 24 h provides **6** in 96% isolated yield (eq 4).



(eq 2)



(eq 3)



(eq 4)

Concluding remarks

The reduction of Cu and Ag salts to metal NPs by cobaltocene, a common commercial product, provides a range of possibilities for further use of CuNPs and AgNPs that have large catalytic applications. The reduction of these salts to NPs shows that cobaltocene should in fact reduce a good number of transition metal salts to zero-valent metal NPs. Cobaltocene being a neutral 19-electron complex is an electron-reservoir system that indeed provides a large driving force leading to the formation of very small NPs ideal for catalysis. This stands in contrast with isostructual ferrocene providing a weak driving force that produces large NPs that have little catalytic activity.[47,48] Another advantage of cobaltocene here is that its oxidized cobalticinium form is perfectly defined and robust, contrary to the oxidized forms of most other reductants.

The remarkable variation of the SPB wavelength and kinetics of the AgNP-catalyzed 4-nitrophenol reduction as a function of the nature of the counter anion of the precursor Ag(I) salt shows the stabilization of the AgNPs by this counter anion acting as a weak ligand for the AgNP surface. This means that the cobalticinium salts works as a nanoreactor around the NPs, leaving the NP surface rather free for catalytic interactions with substrates at this NP surface. This is corroborated by the high catalytic activity of the AgNP surface in 4-nitrophenol reduction by $NaBH_4$.

Application of this principle to CuNPs synthesized by reduction of $CuSO_4$ by cobaltocene provides new possibilities in useful catalysis that have already been partly exploited in this work. A variety of heterogeneous click CuAAC reactions have been shown to proceed very efficiency with water-insoluble substrates using the water-soluble CuNP catalyst synthesized in this way including click CuAAC synthesis of biologically relevant compounds.

Such CuNP catalysis is advantageous compared to that using sophisticated pre-synthesized Cu(I) complexes. Yet the mechanism of CuAAC reactions is well known to proceed via Cu(I) active species, whereas the CuNPs synthesized here have been shown by UV-vis. and XPS spectroscopy to involve Cu(0) atoms on the CuNP surface as well as in the core. It is probable, however, that terminal alkynes, whose coordination in complex Cu species has been demonstrated earlier, react with the Cu(0)NP surface to form surface Cu(I)-alkynyl intermediate species.[49-51] These principles of nanocatalyst design should be extended to various other very efficient mono- and polymetallic nanocatalysts in the close future.

Experimental Section

Nanoparticle synthesis. $CuSO_4{\cdot}5H_2O$ (1 mg, 4×10^{-3} mmol) was dissolved in 19 mL milli-Q water under nitrogen in a standard Schlenk flask and degassed for 10 min., then $[CoCp_2]$[52] (1.5 mg, 8×10^{-3} mmol) in dry THF (1 mL) was quickly injected under nitrogen into the Schlenk flask. The color of the solution changed from colorless to black indicating the formation of the CuNPs. This synthesis has also been scaled up 10 times. AgNPs were synthesized similarly.

4-Nitrophenol reduction kinetics: 4-NP (7 mg, 5×10^{-2} mmol) was mixed with $NaBH_4$ (154 mg, 4.0 mmol) in water under nitrogen. The color of the solution changed from light yellow to dark yellow due to the formation of the sodium 4-nitrophenolate salt. Then a solution containing 2 mol% Ag nanoparticles was added to the mixture under nitrogen. Then the solution lost its dark yellow color with time, and the progress of the reaction kinetics was monitored by UV-*vis*. spectroscopy (40 s for each run).

CuAAC reactions: A Schlenk flask equipped with a magnetic stir bar was charged with benzyl azide (66.5 mg, 0.5 mmol) and phenylacetylene (51.5 mg, 0.505 mmol) under N_2. The catalyst was added into the Schlenk flask under N_2, and degassed water was added in order to obtain a 2 mL volume of aqueous solution. The reaction heterogeneous mixture was then stirred for 24 h at 35 °C under N_2, then the product was extracted with CH_2Cl_2 (3 x 15 mL). The organic layer was dried over Na_2SO_4 and filtered, and the solvent was removed *in vacuo* to give crude 1-benzyl-4-phenyl-1H-[1,2,3]triazole. This product was then purified by silica gel column chromatography using petroleum ether/ethyl acetate: 10/1 for elution to give a 99% isolated yield (116 mg). ^1H NMR (300 MHz, $CDCl_3$): δ 7.89 – 7.77 (m, 2H), 7.68 (s, 1H), 7.49 – 7.37 (m, 5H), 7.38 – 7.30 (m, 3H), 5.60 (s, 2H) (SI). The other CuAAC reactions were conducted analogously, the reaction being carried out on 0.5 mmol or 0.2 mmol scale. The products were purified by silica gel column chromatography using petroleum ether/ethyl acetate: 10/1 for elution or washed with pentane. The yields are given in tables 1 and 2, and the data and spectra for all the products are provided in the SI.

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Notes

The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxx. General data, characterizations, catalytic procedures, kinetics graphs, and spectra.

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