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Boosting chemoselective reduction of 4-nitrostyrene *via* photoinduced energetic electrons from *in situ* formed Cu nanoparticles on carbon dots[†]

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Chemoselective hydrogenation of structurally diverse nitroarenes is a challenging process that often requires precious metal catalysts and proceeds in an organic solvent. Herein, a convenient and stable hybrid nanocatalyst combining carbon dots and copper nanoparticles is developed as an ideal alternative for this transformation. The as-prepared nanocatalyst achieves over 99% selectivity for the formation of 4-aminostyrene at 100% conversion of 4-nitrostyrene in an aqueous solvent under visible light irradiation. Compared with other reported catalysts, our presented catalyst shows more superior hydrogenation selectivity and stability as well as lower material cost. This high efficiency could be originated from the nanocatalyst's ability to synergistically control surface hydrogen species released from ammonia borane and energetic "hot" electrons induced by visible light irradiation for the selective reduction reaction. Compared with other reported catalysts, our presented nanocatalyst is better for the realization of energy-saving chemical processes by introducing solar energy.

Enhancing the selectivity and activity of catalysts is of paramount importance for the realization of energy-saving chemical processes.^{1,2} For instance, the manufacture of functionalized anilines, which are pivotal intermediates for the pharmaceutical, polymer, agrochemical, and fine chemical industries,^{1,3,4} highly depends on noble metal catalysts that can selectively reduce aryl nitro groups without affecting other easily reducible functionalities.^{3,5,6} However, these precious metals possess the disadvantages of high cost and limited availability. Therefore, using more Earth-abundant alternatives to catalyze the same reaction is attracting much interest.^{1,7} Non-noble metal Cu nanostructures are not only cheap but can also capture visible light via the localized surface plasmon resonance (LSPR) effect.^{8,9} Unfortunately, nanometer Cu usually suffers from poor chemical stability during catalytic processes. In this context, various substrate-supported Cu nanoparticles (CuNPs),^{8,10-12} such as graphene-supported CuNPs,⁸ WO_{2.72}-supported CuNPs,¹⁰ and Sm₂Co₁₇-supported CuNPs,¹¹ have been developed to inhibit their oxidation in the presence of molecular oxygen, and they have been applied for chemoselective hydrogenation of aryl nitro to amine groups.^{8,10,11} Nevertheless, these developed catalysts only work in organic solvents, exerting huge pressure on the environment and cost of manufacturing.¹³ In contrast, water is of low cost and has relative abundance and ecological advantages. As a solvent with many unique properties such as a large temperature window in which it keeps in the liquid state, high heat capacity, and extensive hydrogen bonding, water may be also endowed with inherent functions to enhance the rates and affect the selectivity of organic reactions. Besides, the supports also possess some unique nanomaterial properties, providing a synergistic platform for catalytic reaction.^{10,11} Thus, exerting external stimuli to improve both selectivity and activity of the as-prepared heterogeneous catalysts simultaneously is highly desirable.

Ammonia borane (AB) and borohydrides are regarded as safe, mild and inexpensive reagents for applications in reduction processes of modern organic chemistry.^{14,15} Hydrogen species are released from AB or borohydrides to the surface of catalysts and then are utilized to reduce nitro-aromatics to aromatic amines for the realization of hydrogenation reaction under ambient conditions.¹⁶ When another reducible functional group, *e.g.* vinyl group, is present in the structure of nitro-aromatics, this hydrogenation process becomes complex since there is competition between two reduction reactions,¹⁰ thereby often giving rise to poor selectivity.

Carbon dots (CDs) are composed of carbon cores that are surrounded by shells containing surface functional groups and they have been found to possess excellent optical and luminescence properties, photo-induced electron transfer, and elec-

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tron reservoir properties.^{17–22} Accordingly, CDs are emerging as ideal nanocatalytic platforms for the transformation of valuable organic compounds and artificial photosynthesis under mild operating conditions.^{19–21} In this contribution, we first utilized CDs to directly reduce Cu ions to CuNPs under hydrothermal conditions, leading to *in situ* combination of CDs and CuNPs (namely CDs@CuNPs). Using the CDs@CuNPs as a catalyst then catalyzes AB for selective hydrogenation of 4-nitrostyrene to 4-vinylaniline in aqueous solution under ambient conditions. Under visible light irradiation, CDs@CuNPs exhibit significantly enhanced activity and selectivity to reduce 4-nitrostyrene to 4-aminostyrene. We have achieved >99% chemoselectivity from 100% conversion within 20 min at 298 K under one sun irradiation.

Under the same hydrothermal conditions, a control sample (namely Cu₂O) was also synthesized following the same procedure and processes as that for CDs@CuNPs but without adding CDs. Fig. 1a shows the X-ray diffraction (XRD) patterns



Fig. 1 XRD patterns (a) and XPS Cu 2p spectra of samples (b).

of both samples, revealing two different sets of diffraction peaks that correspond to cubic phases of Cu (PDF#85-1326) and Cu₂O (PDF#78-2076), respectively. The valence states of Cu element in samples were further characterized by X-ray photoelectron spectroscopy (XPS). A shift difference in binding energy was observed from both samples (Fig. 1b), indicating the presence of Cu⁰ in CDs@CuNPs and Cu⁺ in the contrast sample.^{12,23} All of the above results confirm that the formation of Cu is attributed to the presence of CDs.

The transmission electron microscopy (TEM) image of the Cu_2O sample shows a large structure with micron sizes (Fig. 2a). The corresponding high-resolution TEM (HRTEM) image illustrates the lattice fringe of Cu_2O with a spacing distance of 0.24 nm, which can be assigned to the interplanar spacing of (111) planes of Cu_2O . Differently, the TEM image of CDs@CuNPs depicts spheroidal shapes assembled from small nanoparticles. By further HRTEM characterization, one can observe the distinct hetero-nanostructure that consists of a carbon dot with a planar spacing of 0.21 nm. The energy-dispersive X-ray spectroscopy (EDS) maps exhibit that Cu, C and O elements are distributed uniformly in the spheroidal shapes. This implies that numerous hybrid nanoparticles of CDs and CuNPs constitute a large spheroidal structure.

Catalytic hydrogenation of 4-nitrostyrene (4-NS) may achieve three typical products, *i.e.* 4-aminostyrene (4-AS), 4-nitroethylbenzene (4-NE) and 4-ethylbenzenamine (4-EA).² For chemoselective hydrogenation of 4-nitrostyrene into 4-aminostyrene, the vinyl group is one of the most competitive to the formation of functional amines. Fig. 3a shows the UV-Vis absorption spectra of three products as well as 4-NS for com-



Fig. 2 TEM and HRTEM images of Cu₂O (a, b) and CDs@CuNPs (c, d), and EDS mappings of CDs@CuNPs (e).



Fig. 3 UV-Vis absorption spectra: (a) the solution of pure 4-NS (1), 4-AS (2), 4-NE (3) and 4-EA (4); (b) the evolution of 4-NS reduction over CDs@CuNPs with time under dark conditions; (c and d) the evolution of 4-NS reduction over CDs@CuNPs with time in the absence of EDTA-2Na (c) and in the presence of EDTA-2Na (d) under illumination; (e and f) the evolution of 4-NS reduction over Cu_2O with time under dark conditions (e) and illumination (f).

parison. Clearly, each molecule is endowed with its own characteristic absorption peak. Thus, catalytic transformation processes of 4-NS and the products formed with time can be monitored using UV-Vis spectroscopy. The addition of CDs@CuNPs to a solution of 4-NS and AB resulted in a gradual decrease in the 311 nm band, and simultaneous appearance of a peak centered at 273 nm (Fig. 3b) corresponding to the formation of the 4-AS product. The generation of 4-AS was verified by gas chromatography-mass spectrometry (GC-MS, Fig. S1[†]). The catalytic reaction was stopped in 12 min. Under visible light irradiation (the corresponding spectrum shown in Fig. S2[†]), the characteristic peak at 273 nm increases slightly in absorbance (Fig. 3c), but it enhances remarkably with irradiation time after adding ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) as a hole scavenger^{24,25} (Fig. 3d). The transformation from 4-NS to 4-AS was complete in 20 min (Table 1). Similarly, CDs@CuNPs also showed good selectivity in the reduction of 4-nitrophenylacetylene under the same conditions (Fig. S3[†]). The control experiment with Cu₂O added to a solution of 4-NS and AB showed no evidence of the formation of 4-AS (Fig. 3e), but instead 4-EA. Additionally, the product is unchanged under visible light irradiation (Fig. 3f and Table 1).

Catalytic hydrogenation of 4-NS could be determined by the hydrogen evolution reaction of AB in an aqueous solution that relies on the activity of the catalyst. First of all, it should be noted that CDs@CuNPs can't reduce 4-NS in the absence of AB whether the reaction system is irradiated or not (Fig. S4[†]).

Due to the low hydrogen species release rate from AB in the ethanol solution, CDs@CuNPs also exhibited a low catalytic activity in the selective reduction of 4-NS when the aqueous solution was replaced with the mixed solution of water and ethanol without changing other conditions (Fig. S5[†]). When the concentration of AB was held in large excess (Fig. S6[†]) or AB was replaced with NaBH₄ (Fig. S7^{\dagger}) or N₂H₄·H₂O (Fig. S8^{\dagger}) without changing the amount of catalysts, CDs@CuNPs lost their selective reduction ability or exhibited low catalytic rate in the transformation of 4-NS into 4-AS. Similarly, different products were formed after the addition of the Cu₂O sample to a solution of 4-NS and NaBH₄ (Fig. S9[†]). We then chose 4-nitrophenol (4-NP) as a model molecule to further explore the effect of hydrogen releasing rates on catalytic hydrogenation. Under the same conditions, the CDs@CuNPs is much more active than Cu₂O for the reduction of 4-NP to 4-aminophenol (4-AP) in the presence of AB no matter whether irradiated with visible light or not (Fig. S10[†]). Besides, its activity and conversion efficiency in NaBH₄ solution become more superior to those in AB solution while reducing 4-NP to 4-AP (Fig. S11[†]). According to the above results, both CDs@CuNPs and Cu₂O are all active in the reduction of -NO₂ and their activities increase with the hydrogen releasing rates. Therefore, we inferred that the selectivity of CDs@CuNPs could be ascribed to its control ability of hydrogen species released by AB. More interestingly, light energy input is able to boost the reduction of -NO₂ in the styrene structure, while inactivating the -C=C group in the presence of hole scavengers.

 Table 1
 Selective hydrogenation of 4-NS to 4-AS with different catalysts^a

Entry	Catalyst	Reductant	Solvent	T/t^b (K min ⁻¹)	Yield (%)	Selectivity (%)
1	CDs@CuNPs	AB	H_2O	298/20	>99	100
2	Cu_2O	AB	H ₂ O	298/20	0	0
3	Cu ₂ O@Cu	AB	H_2O	298/20	0	0

^{*a*} Reaction conditions: 2 mg of 4-NS, 3 mg of catalyst, 2 mg of AB, 20 mL of H_2O , 4 mg of EDTA-2Na, 100 mW cm⁻² of light intensity. ^{*b*} Reaction temperature/reaction time.



Fig. 4 (a) Adsorption amounts of 4-NS over Cu₂O and CDs@CuNPs versus time at different temperatures; (b) UV-Vis absorption spectra of Cu₂O, Cu₂O@Cu and CDs@CuNPs; (c) MS plots of Cu₂O, Cu₂O@Cu and CDs@CuNPs; (d) photocurrent responses of Cu₂O, Cu₂O@Cu and CDs@CuNPs.

Since the first hydrogenation process is endothermic and the rate-limiting step,^{3,10} the affinity of catalysts to 4-NS plays an important role in the catalytic reaction. As shown in Fig. 4a, the adsorption amount of 4-NS on the surface of both catalysts is increased with shaking time at the given initial concentration and temperature. After the adsorption reaches a maximum value, it remains constant. More importantly, the adsorption reaction can speed up with an increase in reaction temperature.

As demonstrated previously,^{26,27} the interaction of LSPR with adsorbate orbitals will make energetic charge carriers inject into the adsorbate. Plasmon-generated energized carriers provide not only electrons and holes but also thermal energy for the chemical reaction,²⁷ so they can influence the energetics of adsorbates and enhance the net reaction rate of chemical transformations. As illustrated in Fig. 4b, the absorption band at around 560 nm for CDs@CuNPs can be assigned to the LSPR absorption of CuNPs.⁸ In contrast, the LSPR absorption at 560 nm is absent in the Cu₂O sample, but it is observed from the nanocomposite of Cu₂O and Cu (named Cu₂O@Cu, its XRD pattern is shown in Fig. S12†). We then conducted Mott–Schottky (MS) plots (Fig. 4c), revealing a posi-

tive slope that represents an n-type semiconductor. Clearly, the MS plot slope of CDs@CuNPs is the smallest one among the three samples. Based on the below equation,¹²

$$N_{\rm d} = 2(e_0 \varepsilon \varepsilon_0)^{-1} |d(C^{-2})/dV|^{-1} \tag{1}$$

where $N_{\rm d}$, e_0 , ε and ε_0 represent the carrier density, the electron charge, the dielectric constant and the vacuum permittivity, respectively. The carrier density of CDs@CuNPs was calculated as 12×10^{21} cm⁻³, which is dramatically higher than that of Cu₂O@Cu ($5.1 \times 10^{21} \text{ cm}^{-3}$). When N_d is beyond 10^{21} cm^{-3} , the collective oscillations of free conduction band (CB) electrons (for n-type semiconductors) could give rise to the LSPR effect under visible light irradiation. This confirms that the energetic electrons can be generated from CDs@CuNPs while being excited by visible light. Fig. S13a[†] shows the time-dependent UV-Vis absorbance spectra for the selective reduction of 4-NS irradiated with the fixed excitation wavelength at 560 \pm 10 nm without adding the EDTA-2Na hole scavenger. The characteristic absorption peak of 4-AS obtained using the LSPR frequency of the CDs@CuNPs as the input light source shows higher intensity than that from visible light irradiation (Fig. S13b[†]). Particularly, the intensity of the characteristic absorption peak increases linearly with the input energy of the fixed excitation wavelength at 560 ± 10 nm in the presence of EDTA-2Na, indicating the specific role of energetic electrons in light-mediated selective reduction reactions (Fig. S13c[†]).

Besides the role of LSPR, the Schottky barrier (ϕ_{SB}) at the interface of CuNPs and CDs could help trap the transferred energetic electrons in the CB of CDs by delaying them from traveling back to CuNPs.^{26,28} This effectively prolongs their lifetimes and fosters surface chemical reactions.^{26,27} Fig. 4d shows the photocurrent responses of three samples under visible light irradiation. Due to the presence of interfacial ϕ_{SB} , the photocurrent response of CDs@CuNPs and Cu₂O@Cu does not display a rectangular shape like that of the Cu₂O sample. Among them, CDs@CuNPs produce the highest photocurrent density under the same conditions, suggesting that they possesses a superior ability to suppress the recombination of photogenerated electron-hole pairs through a heterogeneous interface of CuNPs and CDs.

Particularly, the role of CDs in CDs@CuNPs is unique and irreplaceable. For instance, we employed Cu₂O@Cu as a contrast catalyst to reduce 4-NS and found its poor selectivity to the hydrogenation of $-NO_2$ to $-NH_2$ in the presence of the -C=C group under the same conditions as CDs@CuNPs (Table 1 and Fig. S14[†]). However, Cu₂O@Cu exhibited higher

Communication

activity to reduce 4-NP in contrast to the Cu_2O sample (Fig. S15†). Moreover, the energy level structures of the samples were analyzed using their XPS valence band spectra together with their MS plots (Fig. S16†). We found that the introduction of CDs can elevate the CB bottom position of catalysts (Fig. S17†). This behavior could be helpful for improving the activity and selectivity in AB-initiated hydrogenation of 4-NS.

Fig. 5a illustrates the catalytic mechanism of CDs@CuNPs for chemoselective hydrogenation of 4-NS. There are two cases: the appropriate amount of AB (Case 1) and the excessive amount of AB (Case 2). AB can be catalyzed at the surface of CDs@CuNPs to release the surface hydrogen species for involving the reduction reaction.¹⁶ Concomitantly, 4-NS molecules adsorb onto the unoccupied sites of the surface of CDs@CuNPs. The reduction of 4-NS to 4-AS with the surface hydrogen species generated on the surface of CDs@CuNPs react preferentially with $-NO_2$ groups in the styrene structure. For case 2, the excessive hydrogen species will attack vinyl groups simultaneously, thereby making selectivity become poor.

Under visible light irradiation, LSPR-generated energetic electrons with sufficient energy are transferred to the CB of CDs and then are injected into the unpopulated electronic orbitals of 4-NS.²⁶ The 4-NS adsorbed on the surface of the catalyst could be moved to a different potential energy surface.²⁷ The forces induced on atoms in the 4-NS result in nuclear motion of atoms or vibration energy, causing the activation of specific chemical bonds of $-NO_2$.²⁷ This process



Fig. 5 (a) Schematic illustration of the catalytic mechanism of CDs@CuNPs for chemoselective hydrogenation of 4-NS under visible light irradiation and (b) the cycling stability of CDs@CuNPs.

facilitates more surface hydrogen species to participate in the reduction of 4-NS to 4-AS. The EDTA-2Na scavenger not only suppresses the recombination of electrons and holes but also impedes the occurrence of the hole-induced oxidation reaction. Therefore, CDs@CuNPs offer a desired synergistic effect on the surface hydrogen species released from AB and boosting selective hydrogenation of $-NO_2$ in the styrene structure through energetic electrons induced by visible light irradiation.

We further performed the stability test of CDs@CuNPs in the reaction solution of chemoselective hydrogenation of 4-NS. The sample was recovered by centrifugation followed by washing with ethanol and water. The CDs@CuNPs maintain their initial selectivity and show only a slight decrease in activity after five catalytic cycles (Fig. 5b). The high stability also verifies that CDs are able to stabilize CuNPs during selective hydrogenation of 4-NS to 4-AS. Compared with other reported catalysts,^{3,4,7,29,30} our presented catalyst shows more superior hydrogenation selectivity and stability as well as lower material cost (Table S1[†]). What's more, the chemoselective catalytic hydrogenation performance of CDs@CuNPs was almost unchanged when simulated AM 1.5G solar light (100 mW cm^{-2}) replaced visible light as a light source (Fig. S18[†]). This indicates that taking advantage of the inexhaustible solar energy source can effectively drive CDs@CuNPs to fulfill the reactions of selective hydrogenation of nitroarenes, reducing the pressure of energy consumption and carbon emission.

In conclusion, we have used CDs as reducing agents for in situ formation of CuNPs on their surface under hydrothermal conditions. The obtained heterogeneous nanocomposites of CDs@CuNPs show a highly active and selective reduction of nitrostyrene, achieving over 99% selectivity for the formation of 4-AS at 100% conversion of 4-NS within 20 min of reaction time in the presence of AB under visible light irradiation. The high efficiency of CDs@CuNPs is originated from its ability to simultaneously control surface hydrogen species released from AB and energetic electrons induced by visible light irradiation for the selective reduction of 4-NS to 4-AS in an aqueous solution. We also found that CDs in CDs@CuNPs not only stabilize CuNPs, but also prolong the lifetimes of energetic electrons to boost the selective activation of chemical bonds in nitrostyrene. Therefore, this work opens a novel pathway for the rational design of ideal nanocomposite catalysts for the realization of energy-saving chemical processes.

Conflicts of interest

The authors declare no conflicts of interest.

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Green Chemistry

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