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Facile synthesis of copper ions chelated sand via dopamine chemistry for recyclable and sustainable catalysis

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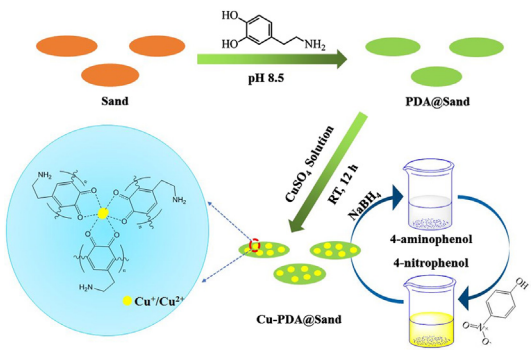
HIGHLIGHTS

- Cu ions chelated sand (Cu-PDA@Sand) was simply synthesized through dopamine chemistry.
- Low-cost Cu-PDA@Sand exhibited efficient catalytic reduction properties towards organic dyes in the presence of $NaBH_4$.
- Cu-PDA@Sand could be recovered by self-sedimentation and reused for 20 cycles.
- Cu-PDA@Sand presented long-term high catalytic activities.

GRAPHICAL ABSTRACT



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ABSTRACT

Metal-based catalysts present highly efficient catalytic activities towards organic dyes and their intermediates for color removal. However, several issues are needed to be addressed urgently for their large-scale practical applications, such as the cost, stability and recyclable use of these catalysts. In this work, we developed a facile approach to chelate Cu ions on the polydopamine-coated sand (Cu-PDA@Sand) and investigated their catalytic properties towards the decoloration of organic dyes or intermediate including 4-nitrophenol (4-NP), methylene blue (MB), and congo red (CR). Our results found that the copper ions from Cu-PDA@Sand were the mixture of Cu (I) and Cu (II), and the molar fraction of Cu (I) over Cu (II) was increased from the original 3:2 to 4:1 in the presence of $NaBH_4$. The reduction of these organic dyes or intermediate followed the first order kinetics, and the apparent reduction rate k_{app} of CR was larger than that of MB and 4-NP under similar conditions. Additionally, the optimized k_{app} of 4-NP could reach to 1.28 min^{-1}, which is much higher than the reported results from literature. The recyclability test of Cu-PDA@Sand showed that the reduction efficiency of Cu-PDA@Sand maintained 100% during the successive 20 cycles. Additionally, Cu-PDA@Sand was demonstrated to present long-term stability and catalytic activities after soaking Cu-PDA@Sand in water for 30 days. Our research demonstrated that the easy-prepared low-cost Cu-PDA@Sand catalyst would have a great potential in the practical applications for color removal of the dye-containing wastewater.

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1. Introduction

Organic dyes are widely used not only in the textile industry but also in papers, plastics, rubbers, drugs, foods, paints, printings, and cosmetics (Ali, 2012; Okesola and Smith, 2016). However, tons of colored wastewaters containing organic dyes were produced every year and thus caused a serious aquatic ecosystem pollution, particularly, most of the organic dyes are carcinogenic, bright-colored, and un-degradable (de Luna et al., 2014; Eggen et al., 2014; Subair et al., 2016). In the past few years, different strategies have been developed to treat organic dyes in aqueous environment, including adsorption (Ayati et al., 2016; Hassan and Carr, 2018; Lipatova et al., 2018; Wang et al., 2018; Zhang et al., 2019), membrane separation (Kurt et al., 2012; Ong et al., 2014), chemical coagulation (Verma et al., 2012), biological methods (Laszlo, 2000), electrochemical processes (Szpyrkowicz et al., 2001), photochemical oxidation process (Sun et al., 2014), and catalytic reduction (Bastús et al., 2014; Panáček et al., 2014; Yao et al., 2014). The catalytic reduction of organic dyes using the metallic catalysts is considered as one of the most effective ways to remove color due to its fast and efficient performances. A variety of noble metals such as Au (Li et al., 2012; Yao et al., 2014), Ag (Zheng and Wang, 2012; Gao et al., 2016), and Pd (Chaplin et al., 2012) exhibit high catalytic activities of removing the color of organic dyes in the presence of reducing agents, because the noble metals can shift the Fermi level of electron donor to more negative potentials and thereby enhance the interfacial electron transfer to reduce organic dyes (Subramanian et al., 2004). Due to the expensive cost of noble metals, however, it is highly desired to develop cheap metallic catalysts with high activity and good stability.

Cu-based catalysts have received increasing interests due to their outstanding catalytic properties and much low cost compared with noble metallic catalysts (Sun et al., 2013; Zhang et al., 2013; Zhang et al., 2014; Wang et al., 2017). Cu (0) nanoparticles exhibited a 0.39 min^{-1} of the high apparent rate constant (k_{app}) towards 4-nitrophenol (Sun et al., 2013), which is similar or even higher than that of Au (Zhang et al., 2011; Luo et al., 2014), and Ag nanoparticles (Dong et al., 2014; Tang et al., 2015), respectively. Meanwhile, Cu_xO nanoparticles or clusters such as Cu (I) and Cu (II) oxides also have been demonstrated to promote the electron transfer from the donor to the acceptor, and then decolorate organic dyes efficiently in the presence of sodium borohydride (Sun et al., 2013). Unfortunately, nanoparticles, because of their high surface energy, easily clumped to form aggregation and difficultly recycled to use in the practical applications, and the agglomerate often destroyed their characteristic nanostructured properties and then severely deteriorated their catalytic activities (Xie et al., 2014).

Most recent investigations have been focused on the fabrication of substrate-supported catalysts to distribute the metal nanoparticles on the support for the prevention of their aggregation and the realization of their recyclable use. A variety of supports, including boron nitride (h-BN) (Huang et al., 2014), Fe_3O_4 (Feng et al., 2013), Al_2O_3 (Bradu et al., 2010), chitosan (Šuláková et al., 2007), mesoporous silica (SBA-15) (Ghosh et al., 2015), and graphene oxide (GO) (Hu et al., 2013) have been used as support materials to load copper nanoparticles. Among these various substrates, magnetic nanoparticles such as Fe_3O_4 could help to recover nanomaterials from wastewater in the presence of an external magnetic field (Feng et al., 2013; Zhu et al., 2013; Xie et al., 2014; Yao et al., 2014). Regretfully, the added extra separation and recovery process was not well engaged in the practical applications in industry or required high cost. Meanwhile, the fabrication procedure of these substrate supported catalysts often involves complicated processes, enduring time, rigorous conditions such as strong acid and base, organic solvents, high temperature, and so on. In addition, these supports were very expensive to be used for treating wastewater containing organic dyes. Therefore, it is urgently needed to select a support with low-cost and easy recovered properties and to develop a facile method of fabricating the Cu-based catalyst on this support for the catalytic reduction of organic dyes.

In this work, we fabricated a cheap sand supported copper catalyst (Cu-PDA@Sand) and investigated the catalytic performances of Cu ions to remove the color of dye-containing water. Sand was selected as a support to chelate Cu ions because of its cheap cost and easy sedimentary properties from the aqueous environment. Cu ions were chosen as the metal catalyst due to its outstanding catalytic performance, very low cost, and non-aggregation properties in aqueous solution, compared with other noble metallic catalysts. The long-term catalytic activity and recyclability of Cu-PDA@Sand were estimated to develop its practical application possibility for the color removal of dyes in the water system.

2. Experimental section

2.1. Chemicals

Dopamine hydrochloride, Cupric sulfate ($CuSO_4$), *p*-nitrophenol (4-NP, $C_6H_5NO_3$), methylene blue (MB, $C_{16}H_{18}ClNS$), Congo red (CR, $C_{32}H_{22}N_6Na_2O_6S_2$), and sodium borohydride ($NaBH_4$) were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received. Sand (collected from Yantai coast, China) was thoroughly washed with deionized water and filtered through 50 mesh size to remove large aggregates after 24 h dry in a vacuum oven at 80 °C.

2.2. Preparation of polydopamine-coated sand (PDA@Sand) and Cu ions-chelated PDA@Sand (Cu-PDA@Sand)

100.0 g of sand was added in 2 L of DI water under magnetic stirring. After 30 min, 1.0 g of dopamine hydrochloride were added and 10 mM Tris-HCl buffer was titrated to tailor the pH value of the above mixture at 8.5. With the continuous stirring of 8 h at room temperature, the color of the sand suspension was turned from brown to dark with the polymerization of dopamine, and after 10 min sedimentation, the darken sand were collected followed by at least five times thorough washing with 25% isopropyl alcohol. Afterward, the dark solid dried at 80 °C for 12 h. Then 50.0 g of as-prepared PDA@Sand was dispersed in 0.5 L $CuSO_4$ aqueous solution (50 mM) under 12 h of stirring. Finally, the samples filtrated was repeatedly rinsed using DI water and dried at 60 °C for at least 24 h.

2.3. Characterizations

Samples were characterized with Fourier transform infrared spectrometer (FT-IR, Perkin-Elmer 2000, USA), Surface Area and Pore Analyzer (Nova 2200e, USA), scanning electron microscopy (SEM, S-4800, HITACHI, Japan) coupled with Energy-dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS, Thermo EscaLab 250Xi, Thermo Fisher Scientific, USA) (High-resolution scans were carried out for analysis of Cu element.), and UV–Vis spectrometer (PERSEE UT 1810, Shanghai, China).

2.4. Catalytic reduction experiments

The catalytic reduction capacity of the prepared Cu-PDA@Sand catalyst was fully examined by testing the catalytic reduction efficiency of organic dyes or intermediate, including 4-NP, MB, and CR. In general, 200 mg Cu-PDA@Sand, dye solution (1 mL of 1 g/L), and

$NaBH_4$ (2 mL of 0.1 M) aqueous solutions were completely mixed with 7 mL DI water under stirring. The time-dependent concentration of dye in the reacting solution was monitored by the UV–visible absorption spectra. The calibration curves of 4-NP, MB, and CR are shown in Fig. S1. Three key factors such as the concentrations of Cu-PDA@Sand, dye, and $NaBH_4$ were investigated to study the reduction efficiency of dyes. Three key factors such as the concentrations of Cu-PDA@Sand, dye, and $NaBH_4$ were investigated to study the reduction efficiency of dyes. The adsorption of the prepared Cu-PDA@Sand was investigated by monitoring the color removal of dyes in the absence of $NaBH_4$, and the procedure is similar to the above catalytic reduction.

The apparent reduction rate constant k_{app} of dyes was calculated through fitting a pseudo-first-order kinetic behavior based on the following Eq. (1) (Zeng et al., 2013):

$$\ln\left(\frac{C_t}{C_0}\right) = -k_{\mathrm{app}}t \tag{1}$$

where k_{app} is the apparent reduction rate constant (min^{-1}), and t is the equilibrium time. C_t and C_o are the concentration of the dyes at time t and 0, respectively.

The reduction efficiency (E_{dye}) was calculated according to the Eq. (2):

$$E_{\mathrm{dye}} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100\% \tag{2}$$

where E_{dye} is the reduction efficiency of dye, and C_t and C_o are the concentration of the dyes at time t and 0, respectively.

2.5. Long-term catalytic activity measurement

After soaking in DI for 30 days, the catalytic activity of Cu-PDA@Sand was examined. Typically, 1.0 g Cu-PDA@Sand and 40 mL of deionized water were mixed under shaking, and the as-formed suspension was taken out and subsequently collected through self-sedimentation after 30 days. Upon the complete dry of Cu-PDA@Sand in a vacuum oven at 60 °C for at least 24 h, 200 mg Cu-PDA@Sand were mixed with dyes (1 mL of 1 g/L) (4-nitrophenol, Congo red, and methylene blue, respectively), $NaBH_4$ (2 mL of 0.1 M), and 7 mL DI water to measure its catalytic activity following the above-mentioned approach.

2.6. Recyclability experiments

The recyclability of Cu-PDA@Sand was explored to remove the color of 4-nitrophenol by successive 20 cycles. For the first cycle, 200 mg Cu-PDA@Sand, dye solution (1 mL of 1 g/L), and $NaBH_4$ (2 mL of 0.1 M) aqueous solutions were completely mixed with 7 mL DI water under stirring. The k_{app} of dyes were successively measured and calculated based on the above-mentioned method. After the one cycle of reduction reaction was finished to completely remove the color of dyes, Cu-PDA@Sand was easily collected to regenerate through self-sedimentation, and then repeatedly utilized in the next cycle of reduction reaction, following the above conditions. The total recycles were extended to 20 times, and the E_{dye} was carefully examined every five cycles.

3. Results and discussion

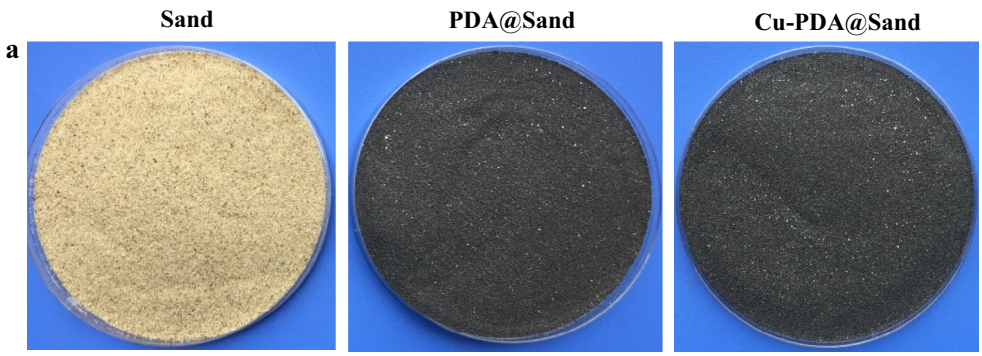
3.1. Synthesis and characterization of Cu-PDA@Sand

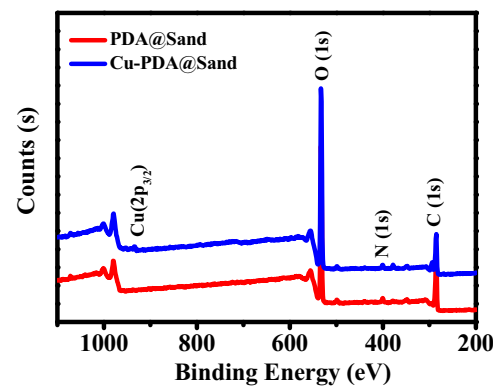
Dopamine chemistry provides a universal, facile, and green chemistry to coat polydopamine and thus chelate Cu ions on most of the support materials (Liu et al., 2014; Zhang et al., 2015; Zhang et al., 2017). Therefore, the fabrication scheme of Cu-PDA@Sand through dopamine chemistry is shown in Scheme 1. This procedure involved two steps: Firstly, the self-polymerization polydopamine occurred on the sand to obtain the PDA coated sand (PDA@Sand). Secondly, the as-prepared PDA@Sand chelated Cu ions through incubation with $CuSO_4$ to synthesize Cu-PDA@Sand. In addition, upon the self-polymerization of dopamine on the sand (Scheme 1), the color of sand turned from pale yellow to dark as shown in Fig. 1a, which is a typical phenomenon to indicate that polydopamine was coated on the sand (Liu et al., 2016). In addition, the color of Cu-PDA@Sand did not change much upon 12 h immersion in the $CuSO_4$ aqueous solution, which did not present a shiny color of metals upon the generation of metal nanoparticles on the PDA coated supports after incubation with inorganic salts (Liu et al., 2016; Wang et al., 2017).

FT-IR measurement was firstly performed to characterize the fabricated process. For the spectrum of PDA@Sand, the presentation of the strong peak at 1630 cm^{-1} was the typical adsorption peak of the amide groups, providing the evidence of the coating of PDA layer on sand (Fig. S2) (Wang et al., 2017). SEM coupled with EDX was employed to observe the surface morphologies of PDA@Sand and Cu-PDA@Sand, and to determine their surface elemental compositions, respectively. No obvious morphology change was found in their SEM images before and after PDA coating on sand (Fig. S3), which may due to a very thin layer of PDA coating formed on the sand. In addition, no particles were observed on the sand surface after incubating PDA@sand with the $CuSO_4$ solution, which illustrates that PDA could not reduce Cu ions to generate Cu nanoparticles, agreeing with the reported results (Hu et al., 2013; Liu et al., 2016). As expected, nitrogen peak and Cu peak were detected upon PDA coating and Cu chelation based on their EDX spectra (Fig. S4). Furthermore, TGA results are shown in Fig. S4 to illustrate that sand is stable even under 800 °C with a weight loss of only 1.5 wt%, and PDA can fully degrade at 800 °C with a weight loss of 100 wt%. The content of PDA coating on the sand was calculated to be 3.3 wt%, and the content of Cu ions on the PDA coated sand was 0.85 wt% (See supporting information). The specific surface areas of sand, PDA@sand, and Cu-PDA@sand were quantified by BET to be 1.3 m^2 g^{-1}, 0.16 m^2 g^{-1}, and 0.04 m^2 g^{-1}. Their pore volumes were quantified to be 0.005 cm^3-g^{-1}, 0.0004 cm^3g^{-1}, and 0.0003 cm^3g^{-1}, respectively. All these results from N_2 adsorption reflect the pore-less structure and weak adsorbability of these sand-based catalysts towards dyes.

Furthermore, the valence state of Cu ions on the sand was further characterized by XPS. The characteristic shakeup satellite peaks (943–963 eV) confirmed the presence of Cu (II) (Fig. 1b) (Fan et al., 2009), and the peaks from 925 eV to 938 eV were assigned to Cu $2p_{3/2}$ (Fig. 1c). The lower peak at 934.2 eV was attributed to Cu (II) from the prepared Cu-PDA@sand, and the

Scheme 1. The fabrication process of Cu-PDA@Sand catalyst through dopamine chemistry including the polydopamine coating and the chelation of Cu ions on the sand support.





Element (%)	PDA@Sand	Cu-PDA @Sand
Cu	---	0.76
C	33.62	24.81
O	41.78	46.65
N	2.46	1.78
Si	16.48	19.67
Al	4.92	4.84
K	0.22	1.24
Na	0.52	0.53

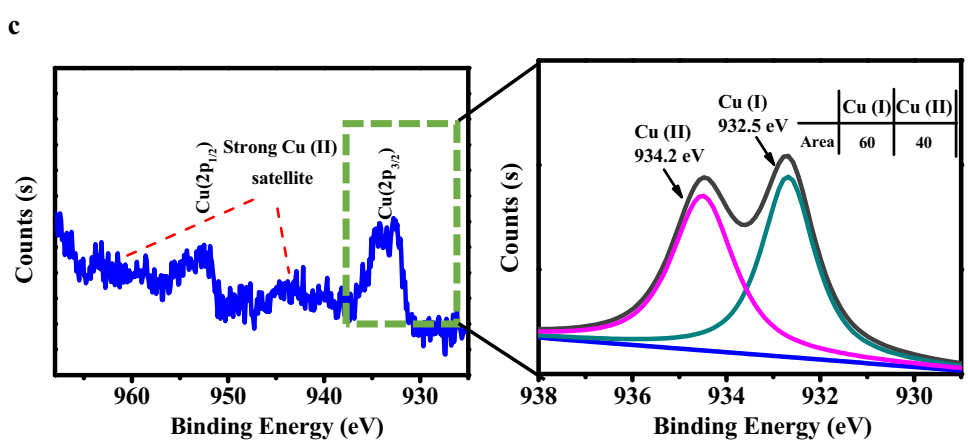


Fig. 1. Photographs of pristine sand, PDA@Sand, and Cu-PDA@Sand (a), and the XPS spectra of PDA@Sand, and Cu-PDA@Sand (b) with their surface elemental compositions. The enlarged spectra from 925 eV to 970 eV and the peak fitting of the Cu $2p_{3/2}$ spectrum of the Cu-PDA@Sand (c).

higher peak at 932.5 eV indicated the presence of Cu (0) or Cu (I) in the Cu-PDA@sand. To further distinguish Cu (0) and Cu (I) species, X-ray-induced auger electron spectroscopy was used and then confirmed the peak at 574 eV from the characteristic Cu (I) peak (Fig. 2a). In addition, no characteristic peak of Cu (0) could be detected from the Cu-PDA@sand sample, indicating that Cu (II) was not reduced to Cu (0) through polydopamine. Therefore, it can conclude that the copper ions chelated on the PDA-coated sand is the mixture of Cu (I) and Cu (II) with 3:2 M fraction of Cu (I) over Cu (II) (Fig. 1c). Moreover, the content of Cu was determined to be 0.76 wt%, which is almost the same with the results obtained from TGA (Fig. S5) and lower than 1.40% of Cu chelated on other substrates through dopamine chemistry in our previous work (Liu et al., 2016), probably due to the less surface area of sand for less PDA coating to support Cu. Besides, the content fraction of Si and O elements was high up to 46.65% and 19.67%, respectively, while that of Al element decreased to 4.84% after immobilization of Cu ions, probably due to the uneven chemical composition of natural sea sand.

3.2. Catalytic properties of Cu-PDA@Sand

The catalytic properties of the prepared Cu-PDA@Sand were investigated using organic dye intermediate 4-NP as a model. The reduction process of 4-NP was monitored by the change of absorbance at 400 nm. With the reduction of 4-NP progressing, the

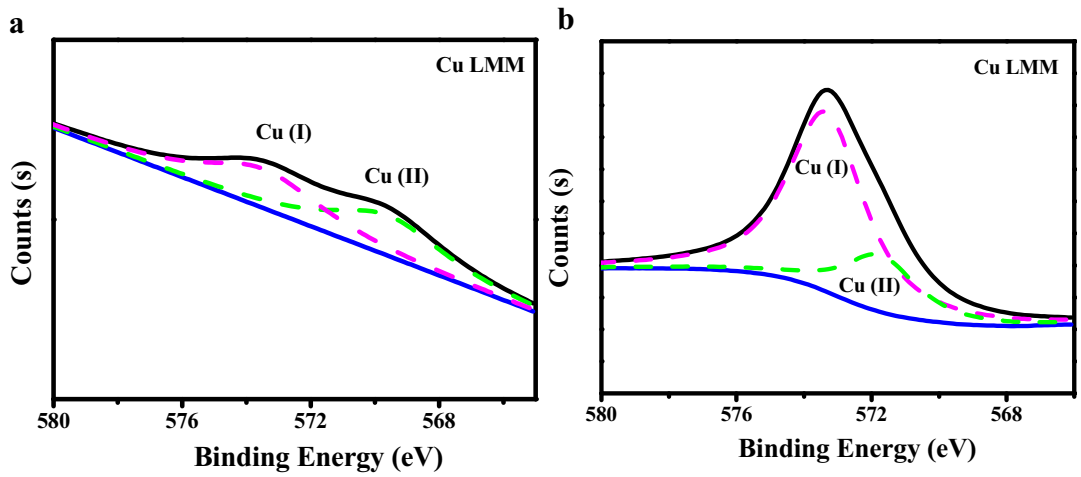


Fig. 2. Cu LMM XPS spectrum of Cu ions chelated onto the PDA@Sand (a) and the Cu-PDA@Sand after incubation with $NaBH_4$ (b).

green-yellow color of 4-NP solution completely disappeared as shown in Fig. 3a. The characteristic absorbance of 4-NP at 400 nm rapidly decreased to zero in 13 min, indicating the complete degradation of 4-NP, but its absorbance at 300 nm gradually increased due to the formation of 4-aminophenol (4-AP) (Fig. 3b) (Zhang et al., 2014; Subair et al., 2016). To identify the valence state of Cu ions in the system after reaction with $NaBH_4$, the X-ray-induced Auger electron spectroscopy was also employed to detect no Cu (0) from Cu-PDA@Sand, but to observe the molar fraction of Cu (I) over Cu (II) on Cu-PDA@Sand increased from 3:2 to 4:1 (Fig. 2b). As literature reported that the catalytic rate of Cu (I) towards the reduction of 4-NP (12 min) (Huang et al., 2014) was much faster than that of Cu (0) (18 min) (Tang et al., 2014; Zhang et al., 2014). The k_{app} (0.308 min^{-1}) in the Cu-PDA@Sand is much higher than the value of Cu (0) microspheres (0.182 min^{-1}, Zhang et al., 2014) reported in the literature. The k_{app} over Cu content was calculated as 202 min^{-1}/g Cu, which is much higher than the reported results (36 min^{-1}/g Cu, Zhang et al., 2014). The per-

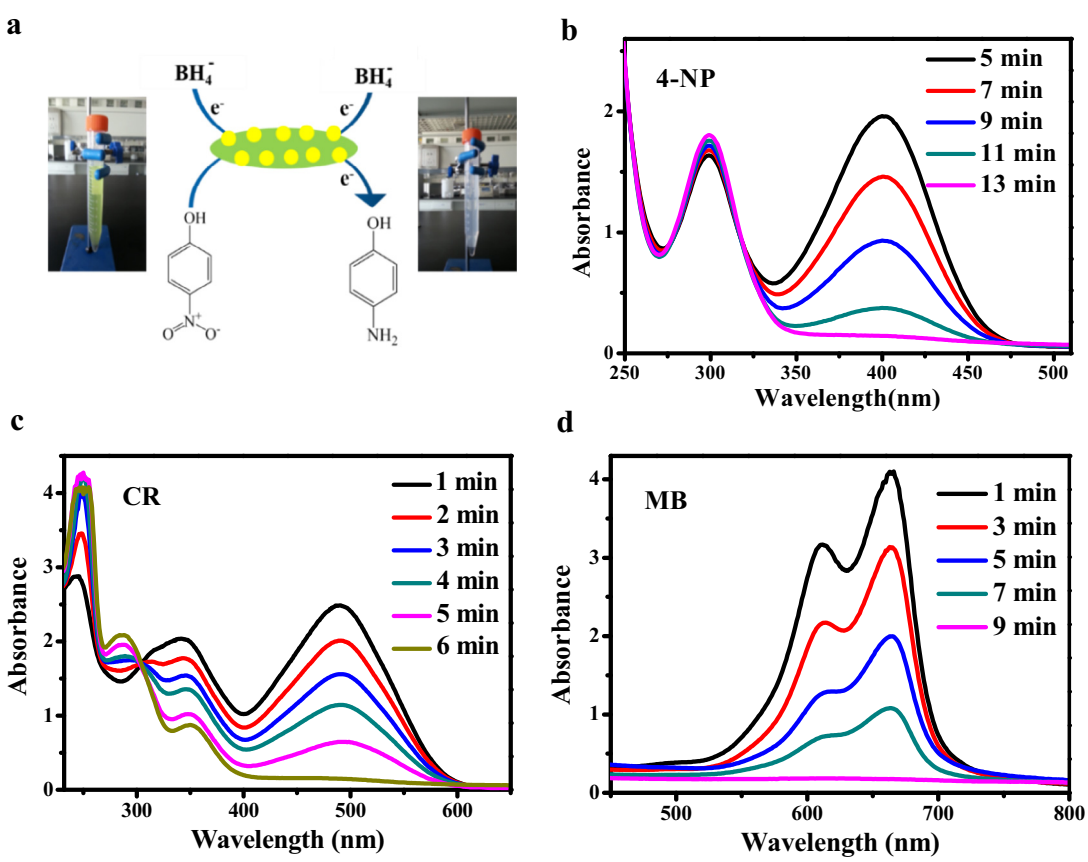


Fig. 3. Schematic presentation of the catalytic reduction process of 4-NP with Cu-PDA@Sand in the presence of $NaBH_4$ (a) and the time-resolved UV–Vis spectra of dyes solutions containing (b) 4-NP (100 mg L^{-1}), (c) CR (100 mg L^{-1}), and (d) MB (100 mg L^{-1}) with $NaBH_4$ (0.02 M) and Cu-PDA@Sand (20 g L^{-1}).

centage of Cu (I) in the Cu-PDA@Sand is 80 wt%. We, therefore, propose that the high catalytic rate of Cu-PDA@Sand may be due to the high Cu (I) loading on the sand and a high efficiency of Cu (I).

To confirm the universality of the Cu-PDA@Sand as a catalyst for the reduction of organic dyes or intermediate, congo Red (CR) and methylene blue (MB) were also chosen as the model dyes. The catalytic reductions of CR and MB were also monitored by their solution optical density changes at their corresponding maximum absorbance wavelengths of CR ($\lambda_{510\ nm}$) and MB ($\lambda_{665\ nm}$ and $\lambda_{614\ nm}$), respectively. Fig. 3c illustrates that the absorption peak of CR solution at 510 nm significantly decreased within 6 min, indicating a very rapid reduction of CR in the presence of Cu-PDA@Sand and $NaBH_4$. The UV–Vis spectrum of MB (Fig. 3d) exhibited two absorption peaks at 665 nm and 614 nm, which are originated from the π-p* transition and a shoulder peak, respectively. The color of the MB solution quickly faded within 9 min after reduced by Cu-PDA@Sand. No obvious new peak was observed in the spectrum, suggesting the complete reduction of MB to LMB (Zhang et al., 2014; Subair et al., 2016). All these results reveal that the prepared Cu-PDA@Sand exhibited high effective and universal catalytic activities, and reduced CR and MB in a much faster rate than 4-NP under similar conditions.

The reduction kinetics of organic dyes were monitored and measured as the plot of dye concentration versus reaction time. Fig. 4a presents that the concentration of all dyes decreased exponentially with the reaction time and Fig. 4b illustrates that ln (C_t/C_o) decreased linearly with the reaction time, which confirms that the catalytic reduction of organic dyes or intermediate follows the first order kinetics. The apparent reduction rates k_{app} of three dyes or intermediate were calculated as the intercept of the plot of ln (C_t/C_o) verse the reaction time following the reported Eq. (1). The k_{app} of CR was 0.55 min^{-1}, larger than 0.43 min^{-1} of MB and 0.34 min^{-1} of 4-NP, in the catalytic system of 20 g L^{-1} Cu-PDA@Sand, 0.02 M $NaBH_4$, and 100 mg L^{-1} dyes. In addition, the control experiment using PDA@Sand rather than Cu-PDA@Sand, both the absorbance of the 4-NP solution at 400 nm and the solution color did not change with time in the presence of $NaBH_4$.

The catalytic reduction process of copper ions is an electrochemical mechanism where copper ions work as an electron relay from $NaBH_4$ to organic dyes, and the concentrations of Cu-PDA@Sand, dyes, and $NaBH_4$ may greatly affect the reduction rate. The dependences of k_{app} on the concentrations of Cu-PDA@Sand, dyes, and $NaBH_4$ were investigated, and these results are shown in Fig. 5 and Fig. S6, using the 4-NP and CR as the models. Fig. 5a finds that the k_{app} of 4-NP increased linearly as the concentration of Cu-PDA@Sand increased to 40 g L^{-1}, and then almost unaltered with the further increased concentration of Cu-PDA@Sand. Our previous work has demonstrated that the unaltered k_{app} was due to the lack of reductant $NaBH_4$ (Wang et al., 2017). Moreover, it was also found that the k_{app} decreased rapidly with the increasing 4-NP concentration and then reached to a plateau when 4-NP was more than 200 mg L^{-1} (Fig. 5b), and the k_{app} increased obiviously with the $NaBH_4$ concentration (Fig. 5c). Additionally, the catalytic reduction of CR also exhibited very similar phenomena as shown in Fig. S6. It can be concluded that the catalytic activity of Cu-PDA@Sand could be well optimized to simply tailor the concentration of Cu-PDA@Sand, dyes, and $NaBH_4$. Generally, the concentration of the reductant $NaBH_4$ was added significantly more than enough to allow the catalytic rate of dyes depend entirely on the concentration of catalysts. For example, k_{app} of 1.28 min^{-1} is obtained through optimizing the condition with 20 g L^{-1} Cu-PDA@Sand, 100 mg L^{-1} 4-NP, and 0.04 M $NaBH_4$, which is much higher than those (0.18 min^{-1} (Zhang et al., 2014), 0.35 min^{-1} (Huang et al., 2014), and 0.50 min^{-1} (Huang et al., 2012)) reported elsewhere. The high catalytic rate of Cu-PDA@Sand is probably due to the high Cu(I) ions loading on the sand.

In addition, the dependence of k_{app} on pH was investigated using MB as a model dye. Results are shown in Fig. S7. k_{app} decreased from 0.75 min^{-1} to 0.31 min^{-1} as the increasing of pH value from 3, 5, 7, to 9, which may be attributed to the strong binding capabilities of polydopamine towards Cu ions at high pH conditions ((Liu et al., 2014).

3.3. Long-term catalytic activity and recyclability of Cu-PDA@Sand

The long-term catalytic activity and recyclability of the catalysts are key properties to determine their potentials in practical applications (Dong et al., 2014). The long-term stability and catalytic activity of Cu-PDA@Sand were investigated upon soaking it in water for 30 days. As shown in Fig. 6a, all the k_{app} of Cu-PDA@Sand towards organic dyes or intermediate did not change much after 30 days soaking. The k_{app} decreased slightly within 6% with no statistical difference for 4-NP, CR, and MB, respectively, which confirms that the catalytic performances of Cu-PDA@Sand were efficient and stable in the long-term.

Cu-PDA@Sand was found to be easily collected and reused for the next cycle just by self-sedimentation in aqueous solution because of the high density of sand, which provides a very simple and convenient process to recover it (Fig. 3a). Successive 20 cycles of Cu-PDA@Sand were tested to measure its catalytic properties for

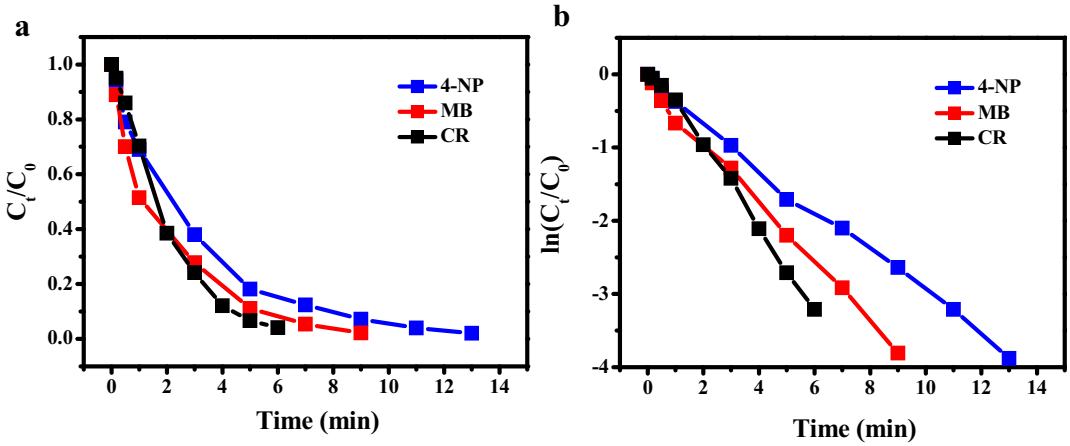


Fig. 4. The plot of C_t/C_0 versus reaction time (a) and ln (C_t/C_0) versus reaction time (b) for the reduction of 4-NP, CR, and MB. The solution had 100 mg L^{-1} organic dyes, 0.02 M $NaBH_4$, and 20 g L^{-1} Cu-PDA@Sand.

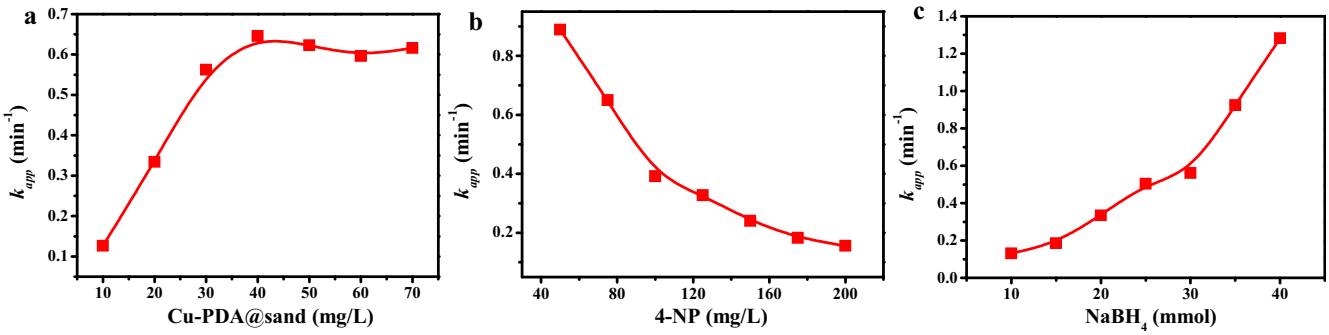


Fig. 5. The apparent reduction rate constant (k_{app}) of 4-NP as a function of the concentration of Cu-PDA@Sand (a), 4-NP (b), and $NaBH_4$ (c), respectively.

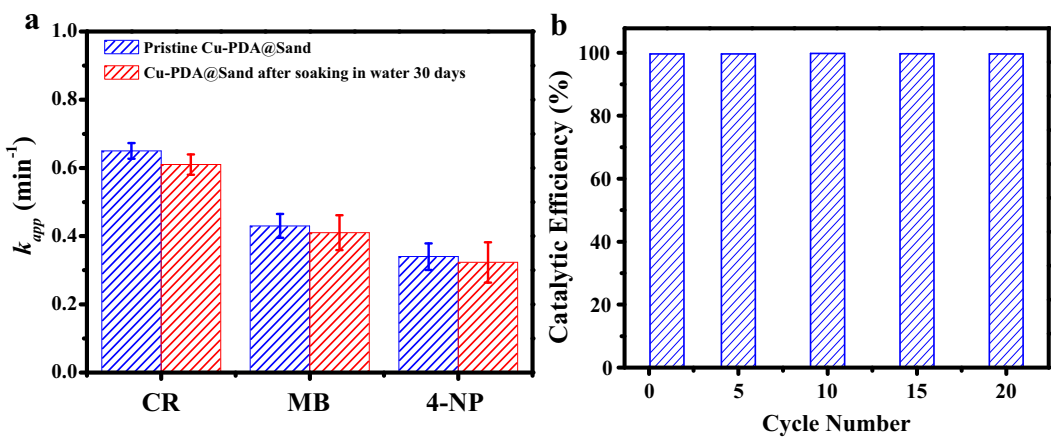


Fig. 6. The apparent reduction rate constant of CR, 4-NP, and MB after soaking Cu-PDA@Sand in water for 30 days (a) and the catalytic reduction efficiency of Cu-PDA@Sand towards 4-NP during the tested successive 20 cycles (b). The catalytic conditions: 20 g/L Cu-PDA@Sand, 0.02 M $NaBH_4$, and 100 mg/L organic dyes.

recyclable and sustainable use, 4-NP was selected as a model dye. Fig. 6b shows that Cu-PDA@Sand kept highly effective and stable catalytic efficiency of 100% towards 4-NP during the tested 20 cycles and could completely fade the 4-NP solution in each cycle, which was much better than the reported unstable $CuFe_2O_4$ catalyst during the catalytic process without recyclability (Feng et al., 2013). Overall, the easy-prepared low-cost Cu-PDA@Sand catalyst showed not only highly effective and sustainable catalytic activities but also recyclable and long-term stable properties, exhibiting a great potential of practical applications for color removal of the dye-containing wastewater.

4. Conclusion and implication

Our work has demonstrated that Cu ions could be successfully chelated onto the sand (Cu-PDA@Sand) through the facile and universal dopamine chemistry, followed by the incubation with a cupric salt solution. The copper ions chelated on the PDA-coated sand are the mixture of Cu (I) and Cu (II) w and the molar fraction of Cu (I) over Cu (II) was increased from the initial 3:2 to 4:1 but with no Cu (0) found during the catalytic reduction process in the presence of $NaBH_4$. 4-Nitrophenol, methylene blue, and congo red were selected as the model dyes to confirm the universality of the Cu-PDA@Sand as a catalyst towards their decoloration. The catalytic reduction of these organic dyes or intermediate follows the first order kinetics. The apparent reduction rate k_{app} of CR was 0.65 min^{-1}, larger than 0.43 min^{-1} of MB and 0.34 min^{-1} of 4-NP, in the catalytic system of Cu-PDA@Sand (20 g L^{-1}), $NaBH_4$ (0.02 M), and dyes with initial dye concentration 100 mg L^{-1}. Furthermore, k_{app} was highly dependent on the concentrations of Cu-PDA@Sand, dyes, and $NaBH_4$ when using the 4-NP and CR as the model dyes. The k_{app} of 4-NP increased with the concentration of Cu-PDA@Sand and $NaBH_4$, but decreased with the concentration of dyes, and may reach to a plateau when either Cu-PDA@Sand or $NaBH_4$ was significantly less than the required amount to reduce dyes. The optimized k_{app} of 4-NP could reach to 1.28 min^{-1} (20 g L^{-1} Cu-PDA@Sand, 100 mg L^{-1} 4-NP, and 0.04 M $NaBH_4$), which is much higher than the reported results from literature. The high catalytic rate of Cu-PDA@Sand is probably due to the high Cu (I) ions loading on the sand.

Meanwhile, the recyclability of Cu-PDA@Sand was tested and the reduction of 4-NP was measured when Cu-PDA@Sand was used for 5, 10, 15, and 20 cycles, the results suggest that the reduction efficiency of Cu-PDA@Sand maintained 100% during the tested successive 20 cycles. Additionally, the long-term stability and catalytic activities of Cu-PDA@Sand were also evaluated after soaking Cu-PDA@Sand in water for 30 days, the results confirm that the catalyst did not show a statistical decrease towards the reduction of 4-NP, MB, and CR. All these results illustrate that Cu-PDA@Sand can be easily prepared with low cost and simply recovered through self-sedimentation, and reused for long-term stable and efficient catalytic performances, which presents a great potential of Cu-PDA@Sand in the practical applications for color removal of the dye-containing wastewater.

As literature study confirmed the versatile and universal PDA coatings could be deposited on the surface of diverse substrates through dopamine chemistry including organic, inorganic, and other materials, the copper ions chelation is mainly through the PDA coating, and thus copper ions can be chelated on diverse sub-

strates through dopamine chemistry and then used as catalysts, biocides, and other functional materials. Our facile and universal approach of copper ions chelation may open a new avenue to fabricate the low-cost copper-based materials on a large scale for practical applications.

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Declaration of interest statement

This manuscript is solely the work of the authors and the authors declare no competing financial interest.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ces.2019.04.009.

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