

1 **Supporting Information for**

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3 **Comparative study on the characteristics, operational life and**
4 **reactivity of Fe/Cu bimetallic particles prepared by electroless and**
5 **displacement plating process**

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16 **Summary:**

17 Page 2-18: Optimization of operational parameters

18 Page 19: Table S1

19 Page 20: Table S2

20 Page 21: Fig.S1

21 Page 22: Fig.S2

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22 Page 23: Fig.S3

23 Page 24: Fig.S4

24 Page 25: Fig.S5

25 Page 26: Fig.S6

26 Page 27: Fig.S7

27 Page 28: Fig.S8

28 Page 29: Fig.S9

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1. Experimental

1.1 Reagents

In the experiment, the analytical reagents including PNP, Na_2SO_4 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, H_3BO_3 , $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, TCD (trisodium citrate dehydrate, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), PSTT (potassium sodium tartrate tetrahydrate, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), EDTA (disodium ethylenediaminetetraacetate dehydrate, $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$), En (ethylenediamine, $\text{C}_2\text{H}_8\text{N}_2$), TEA (triethanolamine, $\text{C}_6\text{H}_{15}\text{NO}_3$) were purchased from Chengdu Kelong chemical reagent factory. Meanwhile, zero valent iron (Fe^0) particles used in this study have a mean particle size of approximately 120 μm , and their Fe content is above 98%. Other chemicals used in the experiment were of analytical grade. Deionized water was used in all experiments.

1.2 Preparation of the Fe/Cu bimetallic particles by electroless plating

The micron-scale Fe^0 particles were used as the substrates to prepare Fe/Cu bimetallic particles, and copper was deposited on Fe^0 surface by electroless plating. The bath composition and plating operating conditions are summarized in Table S1 (Supporting Information). In particular, the main ingredients of the plating bath were $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (11.25 g/L), sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, 50 g/L), boracic acid (H_3BO_3), $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and complexants (e.g., TCD, PSTT, EDTA, En or TEA). There were excessive Cu^{2+} and sodium hypophosphite in the plating bath. The Fe/Cu bimetallic particles were prepared by adding the Fe^0 particles in 400 mL plating bath, and the slurry was mixed by a mechanical agitator (300 rpm). In addition, the whole prepared process was performed at 70 ± 1 °C by water batch heating[1, 2].

Effects of the key parameters, such as reaction time (0.5, 0.75, 1.0, 1.5, 2.0 and 3.0 min), initial pH (8.0, 9.0, 9.5, 10.0 and 11.0), H_3BO_3 (5.0, 15.0, 22.5, 25.0, 27.5, 30.0, 37.5 and 45.0 g/L), $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (0.250, 0.375, 0.500, 0.625, 0.750, 1.000 and 2.000 g/L) and complexants (i.e., TCD (6.00, 8.00, 9.00, 10.00, 11.00, 12.00 and 14.00 g/L), PSTT (25.0, 27.5, 30.0, 31.5, 33.0, 35.0 and 37.5 g/L), EDTA (5.00, 7.50, 8.75, 10.00, 11.25, 12.50 and 15.00 g/L), En (2.50, 5.00, 6.25, 7.50, 8.75 and 10.00 g/L), TEA (7.50, 8.50, 10.00, 11.00, 12.50 and 15.00 g/L)), on the reactivity of the prepared Fe/Cu bimetallic particles were investigated, respectively. Under the obtained optimal parameters, effect of the pretreatment of Fe^0 particles before the electroless plating on the reactivity of the Fe/Cu bimetallic particles was also investigated thoroughly. In particular, the Fe^0 particles were first added to 400 mL Na_2SO_4 aqueous solution (50 mmol/L), and then they were aerated for 2.5 min with a air flow rate of 1.5 L/min. Subsequently, the separated Fe^0 particles were acid-washed by using HCl (5%, w/w) solution. Finally, the pretreated Fe^0 particles were used to prepare Fe/Cu bimetallic particles with electroless plating.

2 Results and discussion

2.1 Effect of the operating parameters of the electroless plating

In electroless copper plating process, Cu mass loading of the prepared Fe/Cu bimetallic particles could be directly affected by the plating time. In addition, nickel (Ni) is mandatory for the electroless copper deposition with sodium hypophosphite as a reducing agent due to its catalytic effect on the anodic oxidation reaction[2, 3]. Furthermore, the copper deposition rate could be affected by the initial pH, and the

concentration of H_3BO_3 , Ni^{2+} and complexants in the plating bath[1, 4]. Therefore, it is necessary to optimize the key parameters including plating time, initial pH, and the concentration of Ni^{2+} , H_3BO_3 and complexants.

2.1.1 Effects of the plating time

According to the previous study, the reactivity of Fe/Cu bimetallic particles was primarily attributed to the number of galvanic cells formed between Fe and Cu on Fe^0 surface[5, 6]. In other words, the high reactivity of Fe/Cu bimetallic particles was resulted from the high potential difference between Fe and Cu (0.777 V)[7]. However, the number of galvanic cells depends on the Cu mass loading on Fe^0 surface. The electroless copper deposition was performed through the reduction of Cu^{2+} by hypophosphite (Eq. (2))[2]. Since there were excessive Cu^{2+} and H_2PO_2^- in plating bath, the Cu mass loading on Fe^0 surface mainly depended on the plating time.



The Fe/Cu bimetallic particles prepared with different plating time (0.5-3.0 min) were used to remove 500 mg/L PNP in aqueous solution, respectively. The logarithmic plots of residual concentration of PNP in solutions versus the reaction time are shown in Fig.S1(a). The results illustrate that a good linear fitting ($R^2 > 0.93$) was observed in each of the batch experiments with the different Fe/Cu bimetallic particles. In other words, the PNP removal rates obtained by using the prepared Fe/Cu bimetallic particles with different plating time all were described by the pseudo-first-order as shown in Eq. (1). K_{obs} values obtained by the Fe/Cu bimetallic particles prepared with different plating time are shown in Fig.S1(b). In particular, K_{obs} rapidly

reached the maximum (0.061 min^{-1}) when the plating time increased to 1.0 min, and then it began to decrease with the further increase of the plating time. The results suggest that the short or long plating time (i.e., low or high Cu mass loading) would limit the reactivity of Fe/Cu bimetallic particles.

In literature, PNP was reduced by three pathways, (i) indirect reduction by the generated reactive atomic H ($[\text{H}]_{\text{abs}}$)[6, 8-11], (ii) indirect reduction by the new generated Fe^{2+} [12], (iii) direct reduction on the catalytic activity sites (Cu) by the accepting electrons from the oxidation of Fe^0 [5]. Cu coated on Fe^0 surface could efficiently catalyze H_2 dissociation to reactive atomic H and facilitate the hydrogenation effect of the pollutants[11, 13]. It also could enhance the corrosion rate of Fe^0 to release a plenty of electrons, which would facilitate the direct reduction of the pollutants by accepting the electrons[5].

Therefore, the Cu mass loading on Fe^0 surface played a leading role in the reactivity of Fe/Cu bimetallic particles. Only an appropriate amount of Cu mass loading (i.e., plating time of 1.0 min) could obtain the highest reactivity ($K_{\text{obs}}=0.061 \text{ min}^{-1}$) of Fe/Cu bimetallic particles. This phenomenon can be explained from two aspects, (i) When Cu mass loading is lower (e.g., plating time $< 1 \text{ min}$), the increase of Cu mass loading caused by longer plating time can enhance the contact area between Cu and Fe, which would facilitate the $[\text{H}]_{\text{abs}}$ production, electron transport, and the formation catalytic sites and Fe-Cu galvanic cells. (ii) When Cu mass loading is higher (e.g., plating time $> 1 \text{ min}$), the contact area between Cu and Fe will be oversize. In other words, a large-scale copper layer would be formed on Fe^0 surface,

and it would increase quickly with the increase of plating time, which would begin to protect the Fe⁰ substrate from corrosion. Limit of the Fe⁰ corrosion would seriously reduce the reactivity of Fe/Cu bimetallic particles. In our previous work, we also found that the Fe/Cu bimetallic particles lose their reactivity completely when the Fe⁰ substrate was completely covered by Cu layer[5]. Therefore, the plating time of 1 min was chosen as the optimal condition in the following experiments.

2.1.2 Effects of H₃BO₃ dosage

In electroless copper plating process, the deposition rate of Cu can be obviously affected by the H₃BO₃ concentration in plating bath[1]. When the H₃BO₃ concentration was above 25 mmol/L, it would transfer into B₅O₆(OH)₄⁻ that could accelerate the electron transfer of copper deposition reaction. Furthermore, it would improve the copper deposition rate obviously. In addition, the Cu distributed characteristics on Fe⁰ surface would be influenced by the Cu deposition rate, which would affect the reactivity of Fe/Cu bimetallic particles.

Fig.S2 shows the K_{obs} for the PNP reduction by the prepared Fe/Cu bimetallic particles with different H₃BO₃ dosages. It is clear that K_{obs} increased gradually to the maximum (0.061 min⁻¹) when H₃BO₃ dosage in plating bath increased from 5 to 30 g/L. And then it began to decrease with the further increase of H₃BO₃ dosage. The results could be explained from two aspects, (i) positive function: when H₃BO₃ dosage was below 30 g/L, its increase could improve the copper deposition rate and facilitate the formation of Fe-Cu galvanic cells. In other words, the deposited Cu layer in this phase could catalyze the corrosion of Fe⁰ substrate. (ii) negative function: when

H₃BO₃ dosage was above 30 g/L, its increase would be resulted in the excessive Cu deposition on Fe⁰ substrate, and form a thick Cu layer which would protect Fe⁰ from corrosion. In addition, the too high copper deposition rate would cause the abscission of copper coating during the preparation process. Therefore, the optimal H₃BO₃ dosage of 30 g/L was selected for the subsequent experiments.

2.1.3 Effects of the catalyst (Ni²⁺)

Ni²⁺ added in the plating bath could be reduced into Ni⁰, which has a strong catalytic activity for the oxidizing reaction of NaH₂PO₂ (Eq. (2))[2]. In other words, copper was hard to be deposited on the Fe⁰ surface if there was not enough Ni²⁺ in the plating bath. In addition, nickel, initially added to the electrolytes in order to improve deposition speed and throwing power, has increasingly become important to promote good film adhesion[3]. Meanwhile, the added nickel could prevent changes of the Cu film strain after deposition[14]. In other words, nickel could enhance the bonding force between Fe⁰ substrate and Cu layer, which could prevent the abscission of Cu on the Fe⁰ surface during the wastewater treatment process by using Fe/Cu bimetallic particles.

Fig.S3 shows K_{obs} for the PNP reduction by the prepared Fe/Cu bimetallic particles with different NiSO₄·7H₂O dosage. It is clear that K_{obs} increased gradually to the maximum (0.061 min⁻¹) when NiSO₄·7H₂O dosage in plating bath increased from 0.25 to 0.50 g/L. And then it began to decrease with the further increase of NiSO₄·7H₂O dosage. The results could be explained from three aspects, (i) the lower nickel content could catalyze the reduction of Cu²⁺ by NaH₂PO₂ (Eq. (2)), which

facilitate copper deposition on Fe⁰ surface and generate a plenty of Fe-Cu galvanic cells. (ii) the higher nickel (>0.50 g/L) content would obviously accelerate the copper deposited rate, which might be resulted in the rapid formation of uniform, less porous, compact and thick copper layer on Fe⁰ surface. On the contrary, this copper layer would inhibit the formation of Fe-Cu galvanic cells and decrease the reactivity of Fe/Cu bimetallic particles. Yang and his colleagues have also found that when the concentration of nickel sulfate was 0.5 g/L, the deposition rate of only 0.11 μm/h; however, when the concentration was above 0.5 g/L, the copper deposition rate increased rapidly[2]. (iii) The nickel ion not only intensively catalyzed the hypophosphite oxidation but also codeposited with the copper ion to form the Cu-Ni alloy[2]. The higher Ni²⁺ content in plating bath would be resulted in the more Cu-Ni alloy generated in deposition film, which might inhibit the reactivity of Fe/Cu bimetallic particles. In addition, the reactivity of Fe/Cu was higher than that of Fe/Ni[15]. Therefore, only the appropriate Ni²⁺ content (i.e., NiSO₄·7H₂O = 0.50 g/L) could improve the reactivity of the prepared Fe/Cu bimetallic particles.

2.1.4 Effects of initial pH

In literature, it is clear that electroless copper plating could be carried out only when pH of plating bath was higher than 7[1, 2]. According to the anodic half electrode reaction (Eq. (3)), the increasing pH value (i.e., increasing OH⁻) can minimize the H⁺ concentration, which could accelerate the oxidation rate of sodium hypophosphite[2, 16].

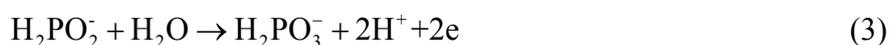
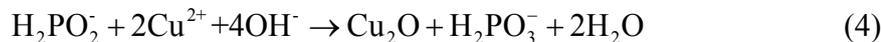
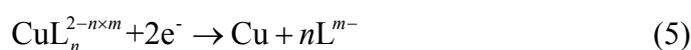


Fig.S4 shows K_{obs} for PNP reduction by the prepared Fe/Cu bimetallic particles with different initial pH. It is clear that K_{obs} increased rapidly when pH augmented from 8.0 to 9.5. This is because that OH^- is the reactant of the anodic reaction (Eq. (3)) which is the controlling step of electroless plating[2, 16]. The reaction rate increased as pH rose. In the second stage, the increasing tendency became slow, when pH value further increased from 9.5 to 11.0. Meanwhile, this tendency seriously decreased when pH was above 9.5. The augmentation of pH could promote the process of side reaction (Eq. (4)), which would cause the increase of Cu_2O content in the copper coating[4]. The results would be resulted in the decrease of conductivity for the Cu coating, which would seriously affect the formation of Fe-Cu galvanic cells. Therefore, the optimal pH value of the plating bath should be kept in about 9.5.



2.1.5 Effects of the type and dosage of complexants

Electroless copper plating can be generally described by anodic (Eq. (3)) and cathodic (Eq. (5)) reactions.



Where L represents the chelating agent, such as EDTA, TEA, PSTT, TCD, or En, and m denotes the charge of the chelating agent[17]. When the complexants are added to the plating bath, the very stable metal complexes are formed, which would represent inhibition of the deposition process[18, 19]. The metal complexes have low diffusion coefficients, while the metal ions without complexants have the faster diffusion rate[19]. Sieben and his colleagues found that the deposited metals prepared

with the complexants have a lower average particles size and crystallite size, and a higher active surface area than that of the plating metals without complexants[20]. In other words, a high true surface area with low catalyst loading on the substrate materials could be obtained when the complexants were added to the plating bath. They also found that the catalysts prepared using the chelating compounds exhibit greater activity per mass unit of the catalyst than when it synthesized without complexant are used[20]. Thus, the complexants could improve the reactivity of the prepared materials.

Fig.S5 show that when the different complexants (i.e., EDTA, TEA, PSTT, TCD, or En) were used for the electroless copper plating, K_{obs} for the PNP removal obtained by the different Fe/Cu bimetallic particles had a similar variation law with the increasing of complexant dosage. In particular, K_{obs} rapidly increased to the maximum with the increase of the complexant dosage at the initial phase, and then it began to decrease with the further increase of the complexant dosage. The results suggest that the appropriate complexant could improve the reactivity of the prepared Fe/Cu bimetallic particles, while the excessive complexant could inhibit its reactivity seriously. The phenomenon could be explained from two aspects, (i) The complexant could inhibit the copper deposition rate[18]. In other words, it could block metal ion deposition and crystal growth on the substrate surface, which would influence the distribution and morphology (e.g., average particle size, crystallite size and active surface area) of the deposited metal[20]. Thus, it would indirectly affect the reactivity of the Fe/Cu bimetallic particles. (ii) The excessive complexants can be adsorbed on

the surface of substrate materials, blocking metal ions deposition and crystal growth[20], which would be resulted in the decrease of copper mass loading on the Fe⁰ surface. Subsequently, it would greatly reduce the number of active sites and Fe-Cu galvanic cells on the Fe⁰ surface, which would limit the reactivity of the prepared Fe/Cu bimetallic particles[5]. In addition, if the bimetallic materials were prepared without complexant, a relatively compact and rough deposit displaying a “tree cortex” structure would be formed on the substrate materials, which would seriously affect the reactivity of the prepared bimetallic materials[20]. Therefore, it is very important for the appropriate complexants to prepare the high reactivity Fe/Cu bimetallic particles.

The maximum K_{obs} (i.e., 0.061, 0.041, 0.070, 0.052 and 0.047 min⁻¹) were obtained by the Fe/Cu bimetallic particles prepared with different complexants (i.e., TCD (10 g/L), PSTT (30 g/L), EDTA (10 g/L), En (7.5 g/L) and TEA (11 g/L)), respectively. The results suggest that the highest reactive Fe/Cu bimetallic particles (0.070 min⁻¹) could be prepared when the lower EDTA dosage (10 g/L) was added to the plating bath. In other words, EDTA was the optimal complexant for the electroless copper plating to prepare the Fe/Cu bimetallic particles. The different behavior of the different complexants can be linked to differences in the stability of the metal ion complexes formed after organic compounds additions. It is clear that more stable complexes of Cu²⁺ are formed with EDTA specie due to the high complexation constant ($\lg K_{MY} = 18.8$) between Cu²⁺ and EDTA[21]. Reported that Cu(II)-EDTA required more energy than Cu(II)-TEA or Cu(II)-En to accomplish Cu(II) reduction, meanwhile EDTA played an important role in chelating for a dual-chelating-agent

system (EDTA+TEA)[17]. Sieben and his colleagues found that the complexes formed with EDTA were more stable than those formed with trisodium citrate, exerting an important influence on the reactivity of the prepared catalyst[20]. Ivanov and Tsakova reported that the best results in terms of number, shape and size distribution of the crystals were obtained by combining the silver-EDTA complex solution with electroless precipitation[22]. Braun and his colleagues also found that EDTA could inhibit the deposition efficiency, and the PdRu films with dendritic morphologies and cracks were obtained if the samples were performed without EDTA[23]. Thus, the EDTA in plating bath seems to play a special role for the characteristics of the coating in the course of metal electroless precipitation.

According to the above discussion, the optimal key plating conditions (i.e., $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O} = 10 \text{ g/L}$, $\text{H}_3\text{BO}_3 = 30 \text{ g/L}$, $\text{NiSO}_4\cdot 7\text{H}_2\text{O} = 0.5 \text{ g/L}$, $\text{pH} = 9.5$ and plating time = 1 min) could be concluded. Under the optimal conditions, a high PNP removal efficiency of 94.1% was obtained by the prepared Fe/Cu bimetallic particles, and its K_{obs} reached 0.070 min^{-1} . Furthermore, the optimal key conditions and the other conditions (i.e., $\text{CuSO}_4\cdot 5\text{H}_2\text{O} = 11.25 \text{ g/L}$, $\text{Fe} = 30 \text{ g/L}$, $\text{NaH}_2\text{PO}_2\cdot \text{H}_2\text{O} = 50 \text{ g/L}$, $T = 70 \text{ }^\circ\text{C}$ and stirring speed = 300 rpm) were chosen for the subsequent experiments.

2.2 Effect of pretreatment process

Prior to the electroless plating process, pretreatment of the substrate materials was required to increase the surface roughness of the substrate materials[24, 25]. After the proper pretreatment, the evenly distributed concave holes could be formed on the surface of substrate materials, which could improve the adhesion between the metal

plating and substrate materials by the anchor effect[26, 27].

Fig.S6 shows that the PNP removal efficiency (98.1%) and K_{obs} (0.095 min^{-1}) obtained by the Fe/Cu bimetallic particles with pretreatment were higher than those (94.1% and 0.070 min^{-1}) without pretreatment. The results suggest that the pretreatment of Fe^0 particles before the electroless copper plating could significantly improve the reactivity of the prepared Fe/Cu bimetallic particles. It could be seen from Fig.S7 that plenty of concave holes and irregular bulges were formed on the surface of Fe^0 particles. In other words, their smooth surface was become very rough after the pretreatment process (i.e., aeration oxidation and acid-washing). In the pretreatment process, many corrosion products (e.g., iron oxide) were generated on the smooth surface of Fe^0 particles under the aeration oxidation phase, and then the rough surface would be formed after the corrosion products were acid-washed by the HCl (5%, w/w) solution. The rough surface could facilitate the adhesion between the deposited copper and substrate materials (Fe^0 particles).

2.3 Operational life of the electroless plating bath

In order to evaluate the stability of the electroless plating bath, 5 batches Fe/Cu bimetallic particles were continuously prepared by using the same electroless plating bath. During this process, only appropriate Cu^{2+} ions were complemented in the electroless plating bath according to its consumption in each electroless copper plating process. Fig.S8 shows the change of PNP removal obtained by the 5 batches Fe/Cu bimetallic particles prepared by the same plating bath. Although the obtained K_{obs} gradually decreased from 0.095 to 0.088 min^{-1} with the increasing number of

cycles for the electroless plating bath, their PNP removal efficiencies always maintained about 98%. The results suggest that the reactivity of Fe/Cu bimetallic particles did not be affected seriously by the recycling of the electroless plating bath. It also represents that the discharge of electroless plating wastewater could be decreased as much as possible. In addition, treatment of wastewater contaminated with EDTA could be performed by the advanced oxidation processes (AOPs)[28-30]. Therefore, electroless copper plating was an effective and robust process to prepare the Fe/Cu bimetallic particles.

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Table S1. Composition and operation parameters of electroless copper plating

Component	Concentration (g/L)	Operating conditions	
H₃BO₃	5-45	pH	8.0-11.0
NaH₂PO₂·H₂O	50	Time	0.5-3.0 min
CuSO₄·5H₂O	11.25	Temperature	70±1 °C
NiSO₄·7H₂O	0.25-2.00	Stirring speed	300 rpm
Complexant	TCD (6-14 g/L), PSTT (25-37.5 g/L), EDTA (5-15 g/L), En (2.5-10.0 g/L), TEA (7.5-15.0 g/L)		

Table S2. Changes of TFe and [Cu²⁺] in the bath before and after copper plating when the Fe/Cu bimetallic particles with same TML_{Cu} were prepared by two different methods.

No.	Item	Unit	Electroless plating*	Displacement plating*
1	TFe	g/L	0.012	0.471
2	[Cu ²⁺] ₀	g/L	2.890	0.527
3	[Cu ²⁺]	g/L	2.356	No detection
4	TML _{Cu}	%(w/w)	1.74	1.75

* 12 g Fe⁰ particles were added in 400 mL plating solution to prepared Fe/Cu bimetallic particles.

TFe: Total Fe²⁺/Fe³⁺ ions concentration in the bath after the preparation of Fe/Cu bimetallic particles.

[Cu²⁺]₀: Cu²⁺ concentration in the bath before the preparation of Fe/Cu bimetallic particles.

[Cu²⁺]: Cu²⁺ concentration in the bath after the preparation of Fe/Cu bimetallic particles.

TML_{Cu}: Theoretical Cu mass loading on the Fe⁰ surface.

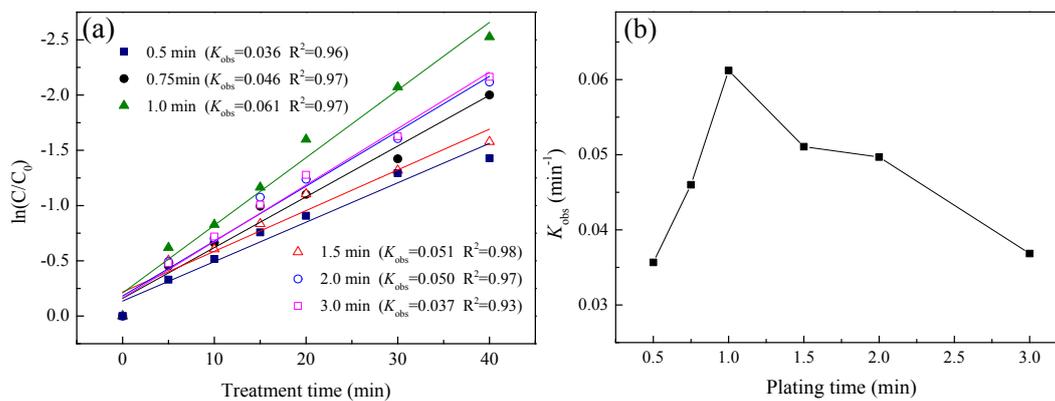


Fig.S1. Degradation kinetics for PNP by the Fe/Cu bimetallic particles prepared with different plating time. Other plating conditions: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 11.25$ g/L, $\text{Fe} = 30$ g/L, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} = 50$ g/L, $T = 70 \pm 1$ °C, stirring speed = 300 rpm, TCD = 10 g/L, $\text{H}_3\text{BO}_3 = 30$ g/L, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O} = 0.50$ g/L and pH = 9.5.

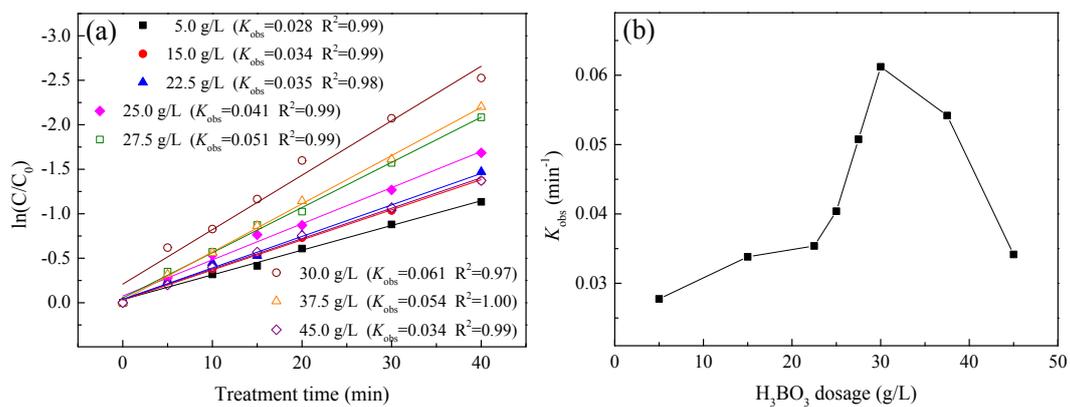


Fig.S2. Degradation kinetics for PNP by Fe/Cu bimetallic particles prepared with different H_3BO_3 dosages in plating bath. Other plating condition: $CuSO_4 \cdot 5H_2O = 11.25$ g/L, Fe = 30 g/L, $NaH_2PO_2 \cdot H_2O = 50$ g/L, $T = 70 \pm 1$ °C, stirring speed = 300 rpm, TCD = 10 g/L, $NiSO_4 \cdot 7H_2O = 0.50$ g/L, pH = 9.5 and plating time = 1 min.

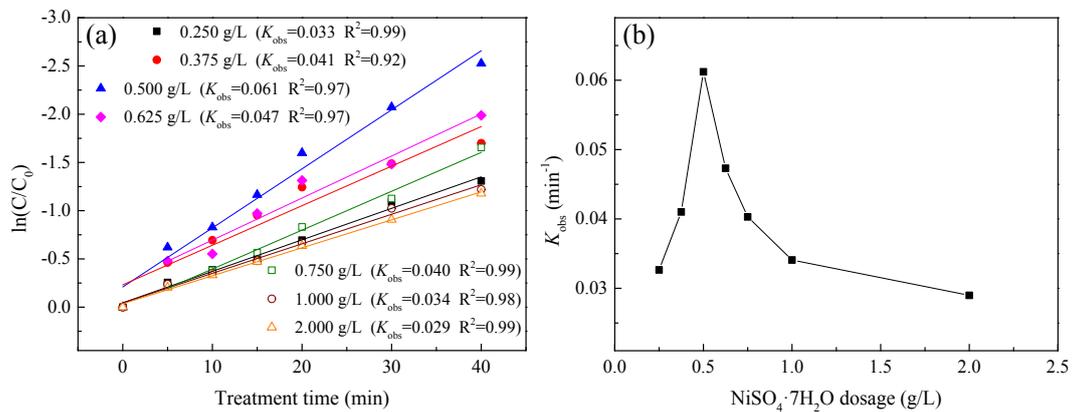


Fig.S3. Degradation kinetics for PNP by Fe/Cu bimetallic particles prepared with different $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ dosages in plating bath. Other plating condition: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 11.25$ g/L, $\text{Fe} = 30$ g/L, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} = 50$ g/L, $T = 70 \pm 1$ °C, stirring speed = 300 rpm, TCD = 10 g/L, $\text{H}_3\text{BO}_3 = 30$ g/L, pH = 9.5 and plating time = 1 min.

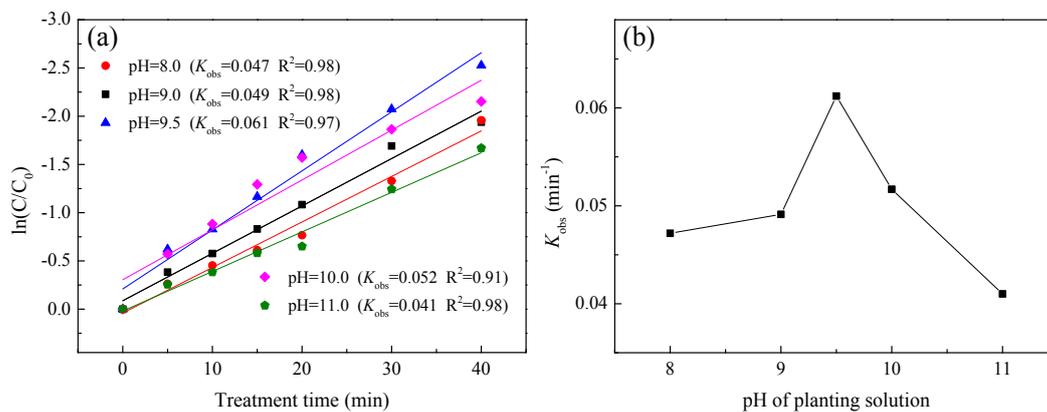


Fig.S4. Degradation kinetics for PNP by Fe/Cu bimetallic particles prepared with different initial pH of plating bath. Other plating condition: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 11.25$ g/L, $\text{Fe} = 30$ g/L, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} = 50$ g/L, $T = 70 \pm 1$ °C, stirring speed = 300 rpm, TCD = 10 g/L, $\text{H}_3\text{BO}_3 = 30$ g/L, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O} = 0.500$ g/L and plating time = 1 min.

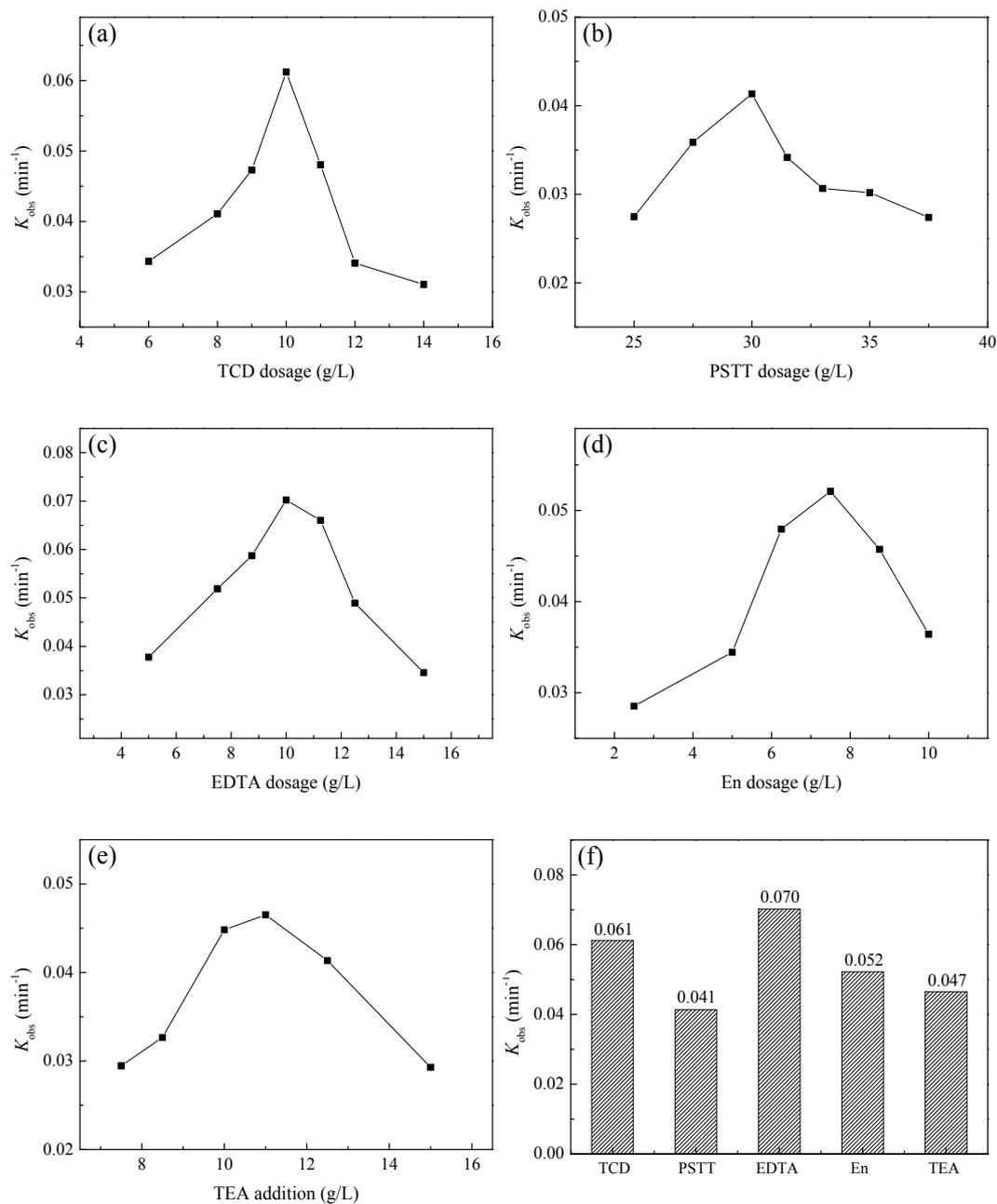


Fig.S5. Degradation kinetics for PNP by Fe/Cu bimetallic particles prepared with different complexants in plating bath. Other plating condition: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 11.25 \text{ g/L}$, $\text{Fe} = 30 \text{ g/L}$, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} = 50 \text{ g/L}$, $T = 70 \pm 1 \text{ }^\circ\text{C}$, stirring speed = 300 r/min , $\text{H}_3\text{BO}_3 = 30 \text{ g/L}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O} = 0.500 \text{ g/L}$, $\text{pH} = 9.5$ and plating time = 1 min .

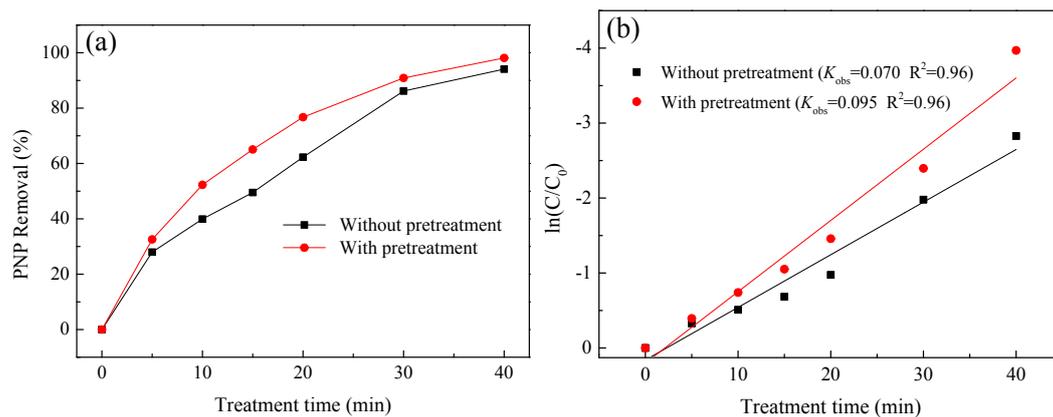


Fig.S6. PNP removal by Fe/Cu bimetallic particles prepared with or without pretreatment.

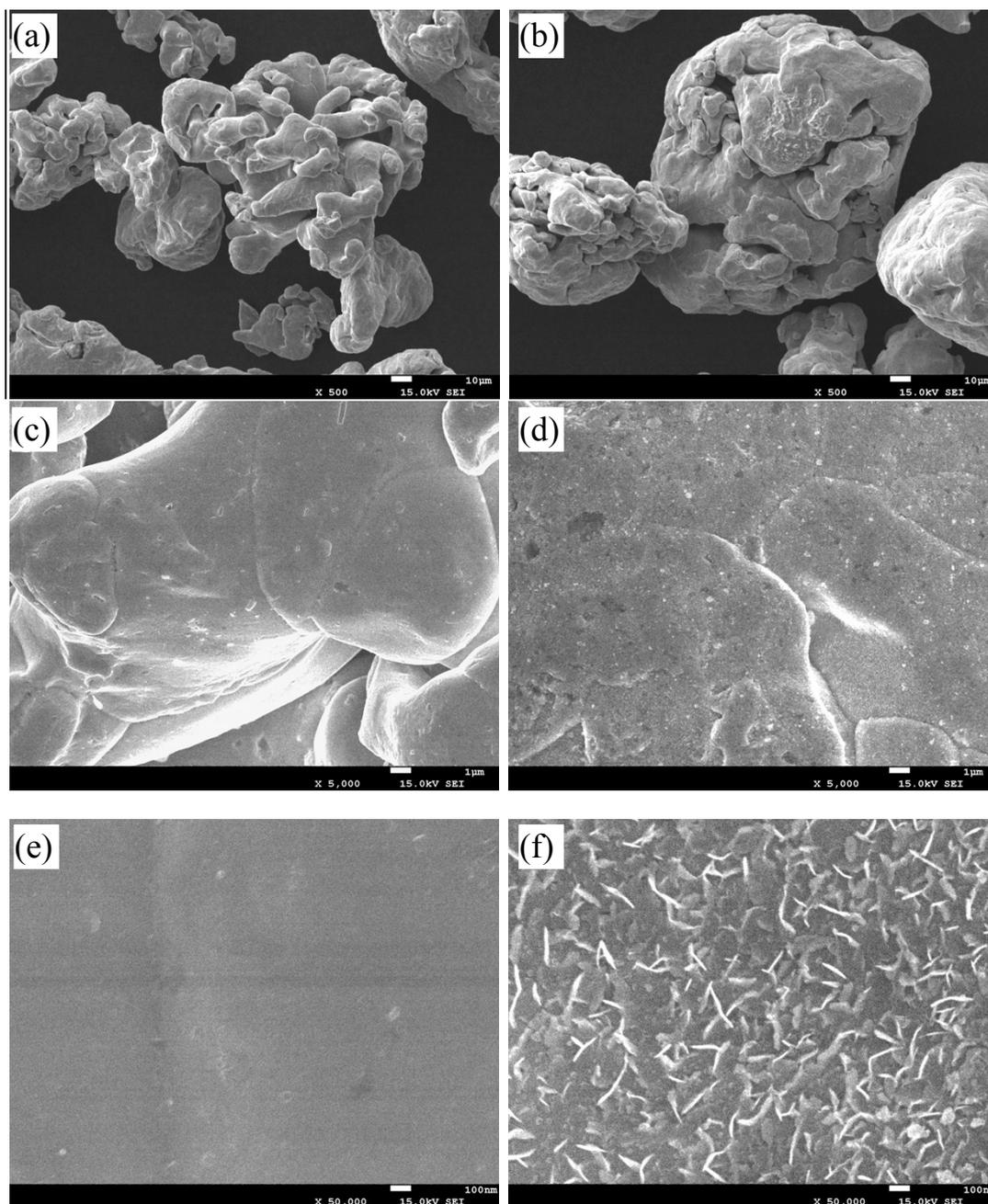


Fig.S7. SEM of the Fe⁰ particles with (a, c and e) or without (b, d and f) pretreatment (pretreatment process: the Fe⁰ particles were first added to the aqueous solution, and then they were aerated for 2.5 min with a air flow rate of 1.5 L/min. Subsequently, the separated Fe⁰ particles were acid-washed by using HCl (5%, w/w) solution).

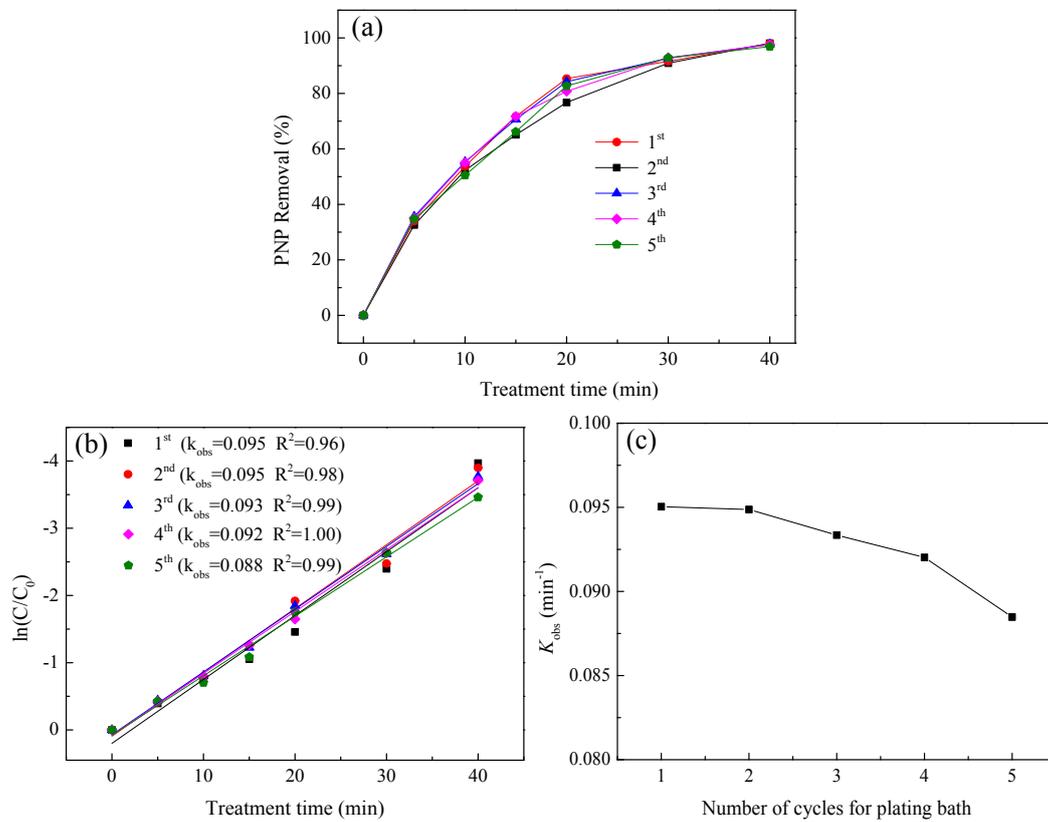


Fig.S8. Operational life of the electroless copper plating bath, (a) PNP removal efficiency, (b-c) degradation kinetics for PNP.

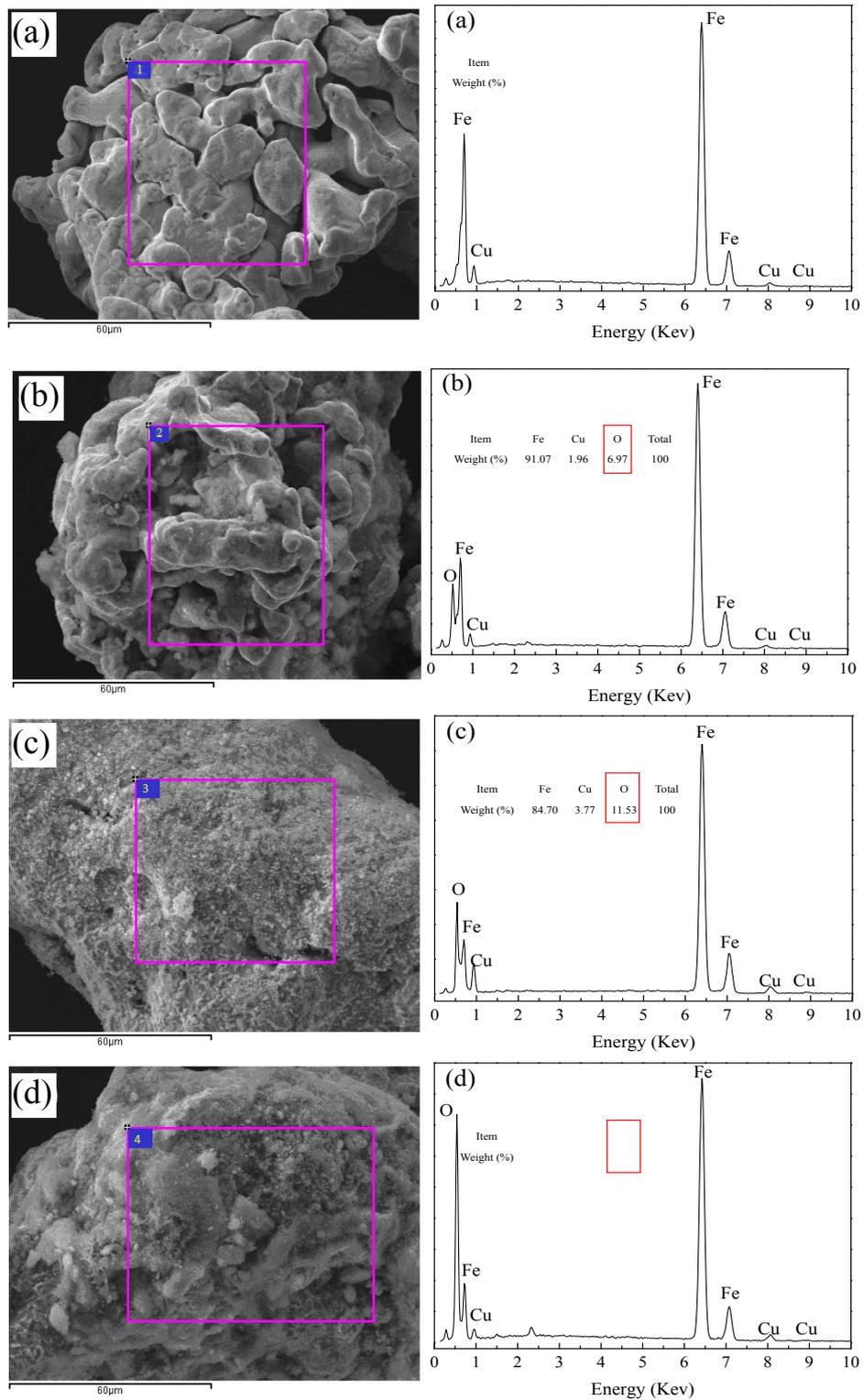


Fig.S9. SEM-EDS of Fe/Cu bimetallic particles: (a) prepared by electroless plating; (b) prepared by displacement plating, (c) Fe/Cu (a) after five employments, (d) Fe/Cu (b) after five employments.

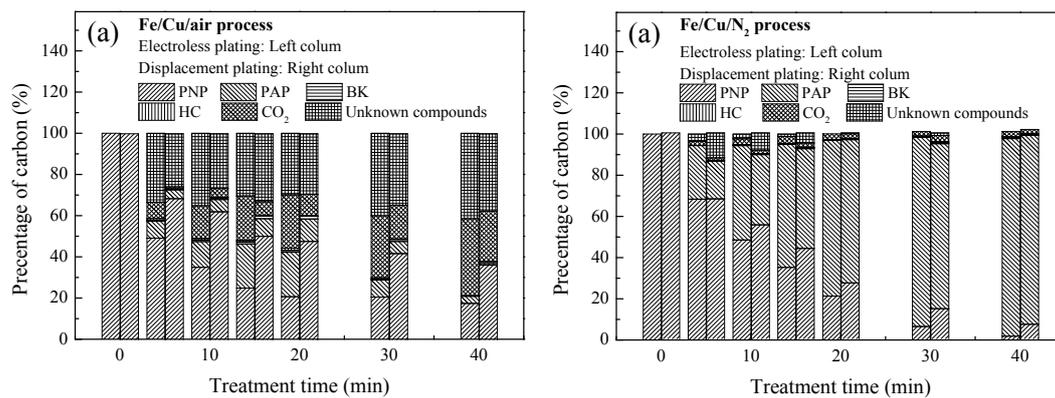


Fig.S10. Carbon mass balance during 40 min treatment process by Fe/Cu/air or Fe/Cu/N₂ process, (a) Fe/Cu/air process, (b) Fe/Cu/N₂ process ([PNP]₀=500 mg/L, initial pH=7.0, Fe/Cu dosage=30 g/L, TML_{Cu}=1.74%, stirring speed=300 rpm and air or N₂ flow rate=1.5 L/min).