Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Electronic Supplementary Information

Recovery of gold from wastewater using nanoscale zero-valent iron

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Figure S2 XRD of nZVI after reaction with Au(III) solution (Au(III): 200 mg/L; nZVI: 0.5 g/L). (a) nZVI after reaction (Au-nZVI); (b) Au-nZVI after acid wash.

Figure S3 HR-XPS spectrum of nZVI after reaction with Au(III) solution (Au(III): 200 mg/L, nZVI: 0.5 g/L).

Figure S4 Gold recovery using nanoscale iron oxide (nFe_2O_3) and using the combination of nFe_2O_3 and $NaBH_4$. Initial Au(III) concentration: 50 μg/L; initial solution pH=9.0. The dosages of nFe_2O_3 were all 1.0 g/L, and that of $NaBH_4$ was 1.0 g/L.

Figure S5 Experiment demonstrating the long-lasting reactivity of nZVI in aqueous solution. (A) Schematics of the experiment setup; (B) Changes of the Fe(0) content of nZVI as a function of reaction time. Embedded in Figure S5B: pressure increase of upper space of the beaker.

Figure S6 Photos of nZVI settling in a 40-mL vial in aqueous solution.

Figure S7 (a) Overview of nZVI reactor; (b) influent, nZVI suspension and nZVI reactor.

Figure S8 Recovery of the trace gold using Na_2SO_3 solution.

Figure S9 Batch experiment of gold recovery from the leaching wastewater.

Figure S10 Raw data of the characterizations of the dewatered nZVI in Figure 6: (A) STEM image; (B) elemental mapping; (C) Au mapping; (D) EDX spectrum.

Figure S1

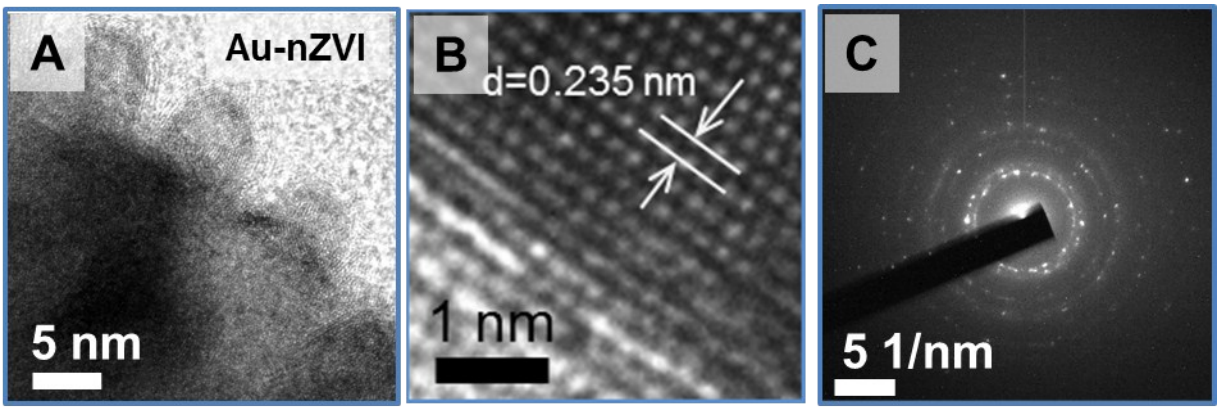


Figure S2

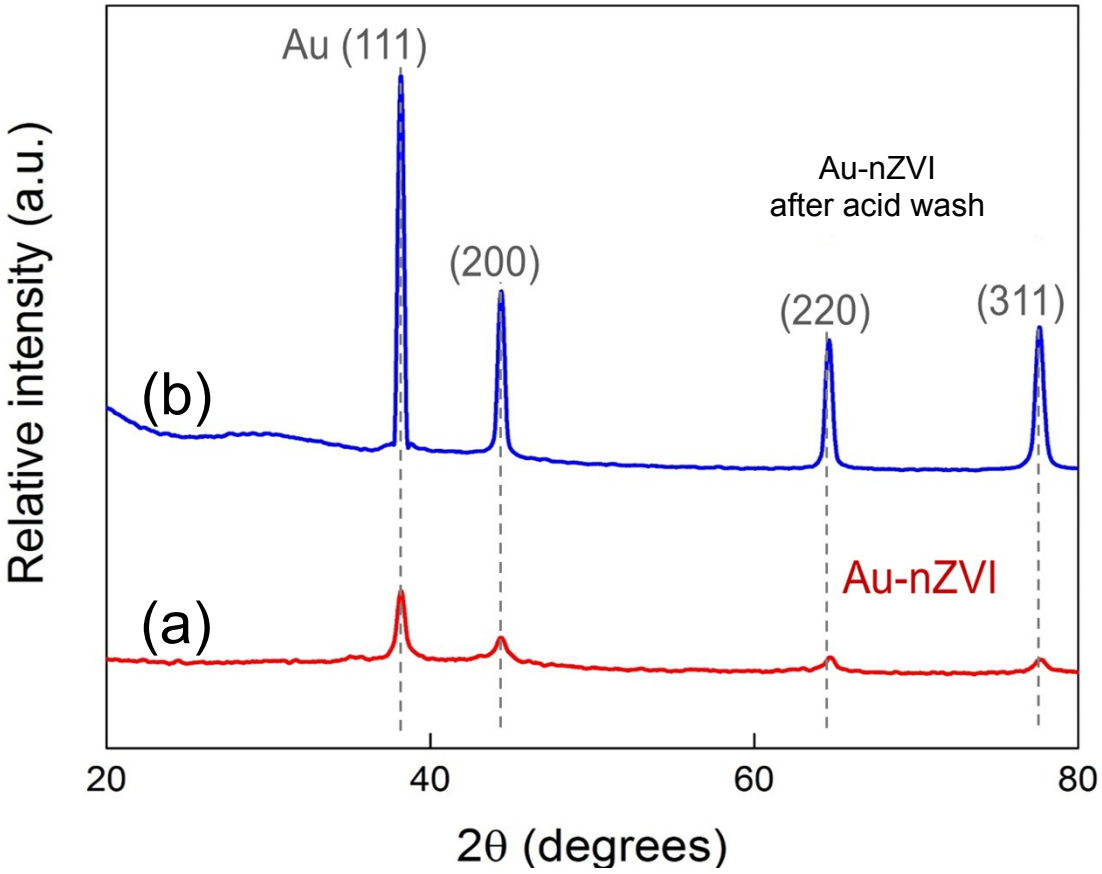

Au (111)
(200)
(220)
(311)
Au-nZVI
after acid wash
(b)
(a)
Au-nZVI
Relative intensity (a.u.)
20
40
60
80
2θ (degrees)

Figure S3

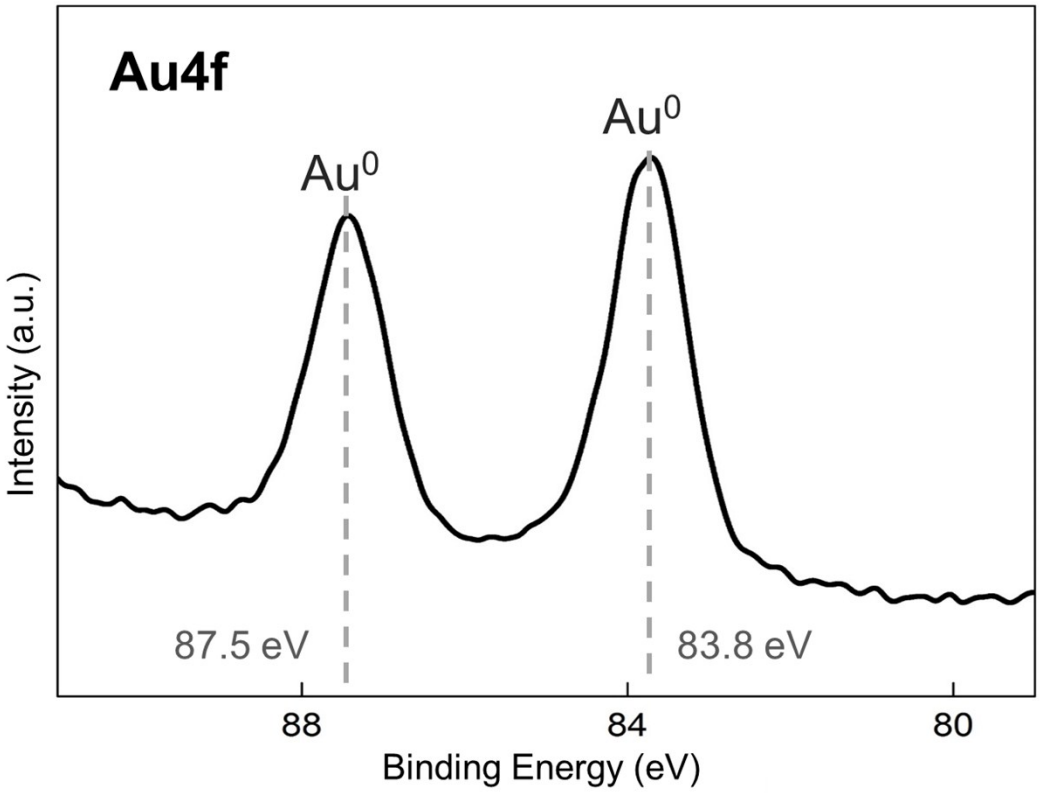

Au4f
Au0
Au0
87.5 eV
83.8 eV
Intensity (a.u.)
88
84
80
Binding Energy (eV)

Figure S4

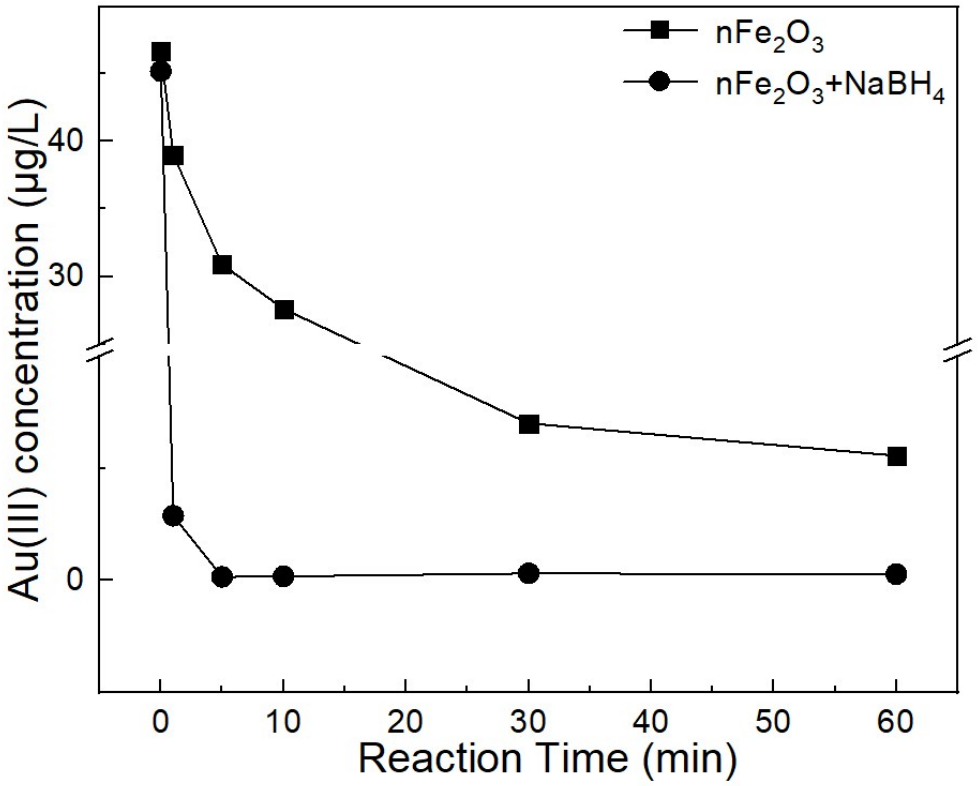
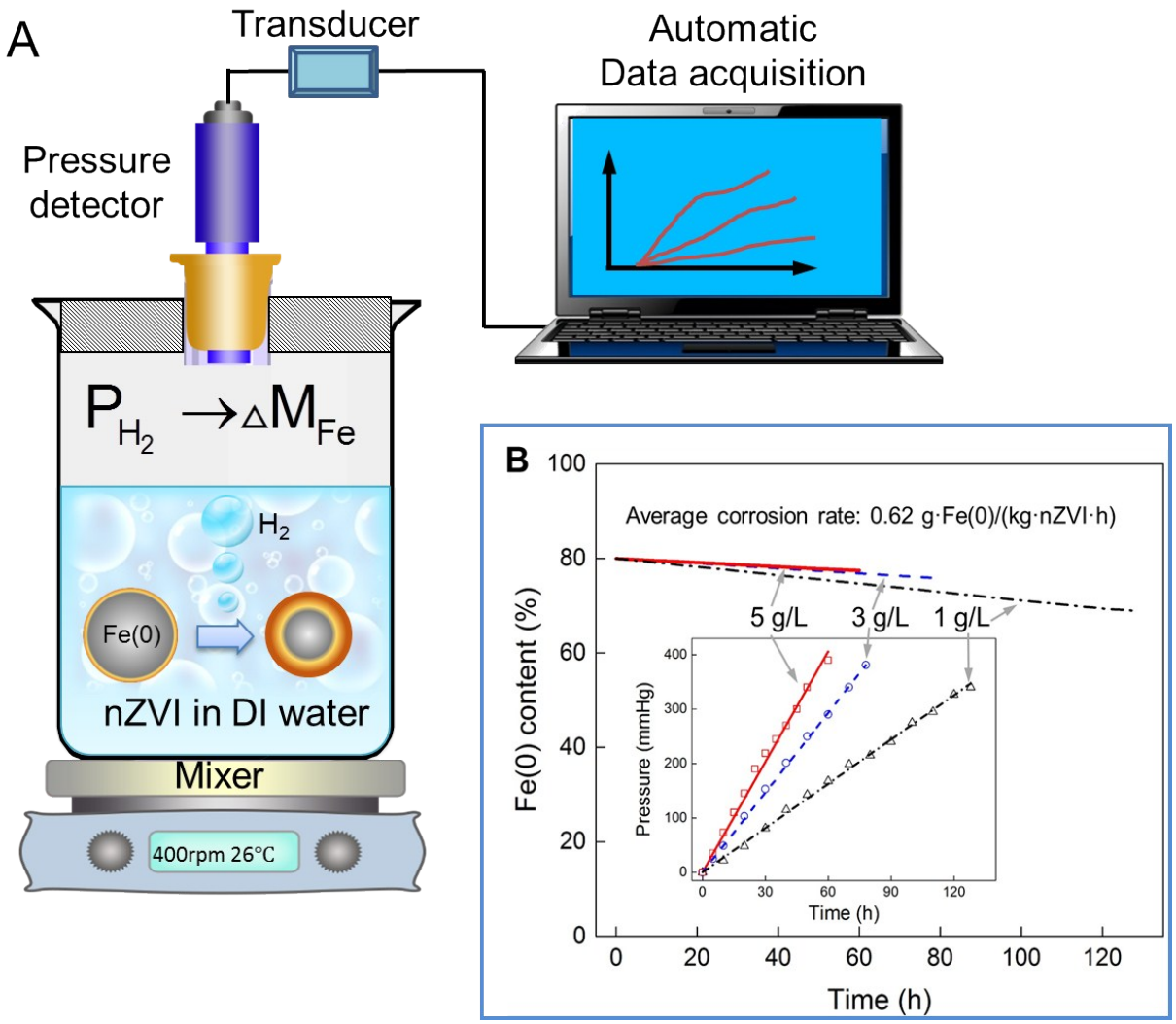

nFe2O3
nFe2O3+NaBH4
Au(III) concentration (μg/L)
40
30
0
0
10
20
30
40
50
60
Reaction Time (min)

Figure S5



The long-lasting reactivity of nZVI was evaluated by measuring Fe(0) reaction rates of nZVI in water, in an extended period of 120 h under anoxic condition (Figure S5). The fresh nZVI has Fe(0) content of ~78%, as determined using the Fe(III)-Fe(0) method reported elsewhere[1]. The reaction rate was determined by measuring the amount of the H_2 produced in the following equation.

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \qquad (S1)$$

This H_2-releasing reaction (Eq. S1) leads to the pressure build-up in the upper space of beaker (Fig. S5A). Since the reaction (Eq. S1) is the only gas source in such system, the total amount of the H_2 ($H_{2(t)}$) produced can be calculated using the sum of $H_{2(g)}$ and $H_{2(l)}$, which represent H_2 in the gas phase (upper space) and in the dissolved phase respectively (Eq. S2):

$$H_{2(t)} = H_{2(g)} + H_{2(l)} \quad \text{(S2)}$$

$H_{2(g)}$ is calculated from the total pressure increase in the upper space of the flask using the ideal gas law (Eq.S3), where ΔP is the total pressure increase (kPa), V is the headspace volume (90 mL) of the flask, and T is the temperature (299 K).

$$H_{2(g)} = \frac{2\Delta PV}{8.314T} \quad \text{(S3)}$$

$H_{2(l)}$ is calculated using Henry's law.

$$H_{2(l)} = 1.503 \times 10^{-5} \Delta P M_{H_2O} \quad \text{(S4)}$$

where M_{H_2O} is the water mass in the beaker (kg). The Fe(0) loss (ΔM_{Fe}) is calculated based on the Fe(0)/ H_2 molar ratio (1:1) in Eq. S1,

$$\Delta M_{Fe} = 28 \times H_{2(t)} \quad \text{(S5)}$$

The Fe(0) reaction (corrosion) rate ($R_{corrosion}$) is calculated by dividing the loss of Fe(0) with the corrosion time(*t*).

$$R_{Corrosion} = \frac{\Delta M_{Fe}}{t} \quad \text{(S6)}$$

The steady increase of the pressure indicates the continuous built-up of H_2 (Figure S5B, embedded) in the upper space, suggesting that nZVI remains reactive after days in contact with water. The average Fe(0) reaction rate obtained was 0.62 g-Fe(0)/(kg-nZVI·h), suggesting the Fe(0)-water reaction in nZVI solution is rather slow process. More than 80% of the Fe(0) remains after 5 days, and consuming 50% of the Fe(0) in nZVI would take approximately 1300 h.

Figure S6

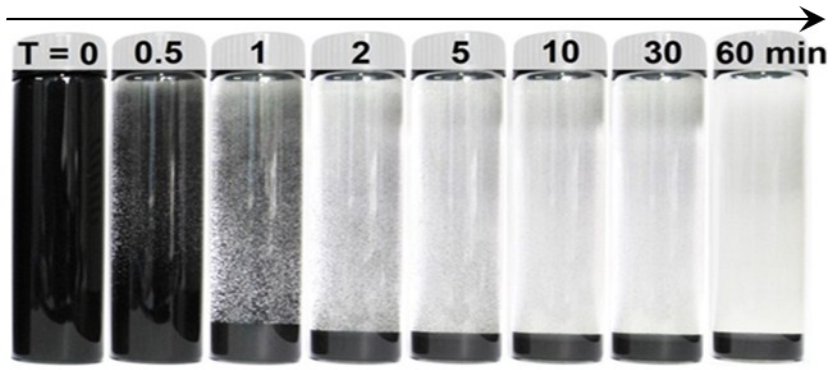


Figure S6 shows the gravitational settling of nZVI (5 g-nZVI/L) in aqueous solution in a 40-mL vial. It is found that floc-like particles, which are visible via bare eyes and have sizes close to millimeter, emerge immediately after the settling. The particles settle quickly, forming a sludge-water interface at 1 min. Most of the particles settle to the vial bottom in 5 min. The entire slurry becomes transparent after 10 min of settling.

Figure S7

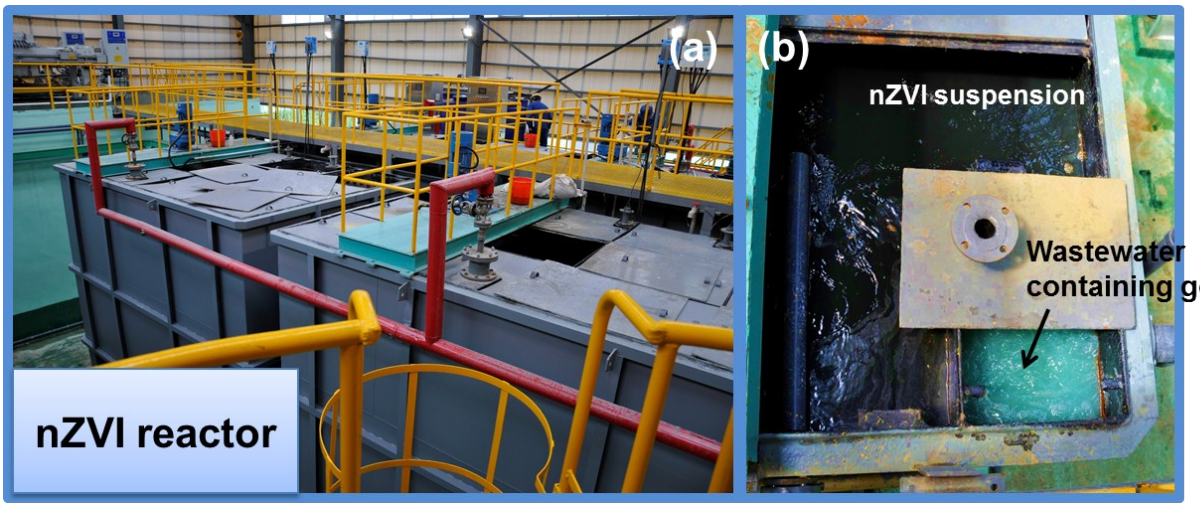
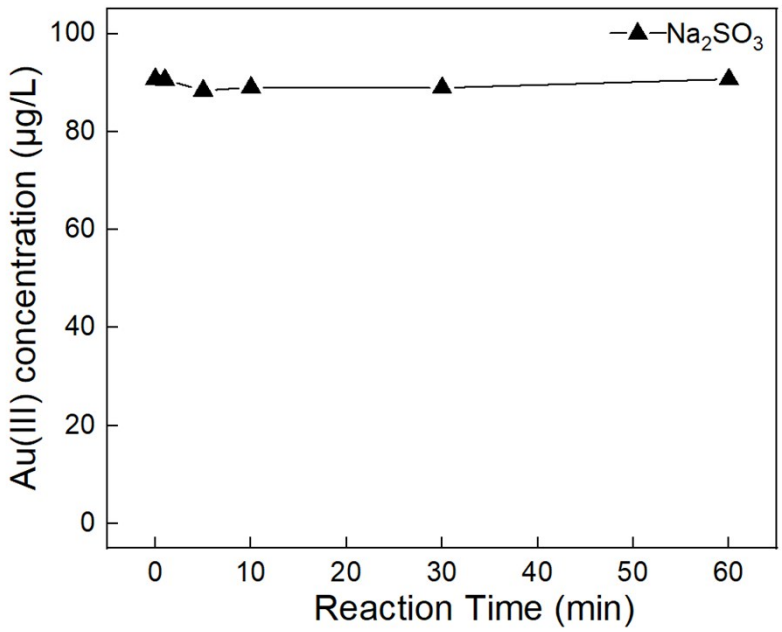
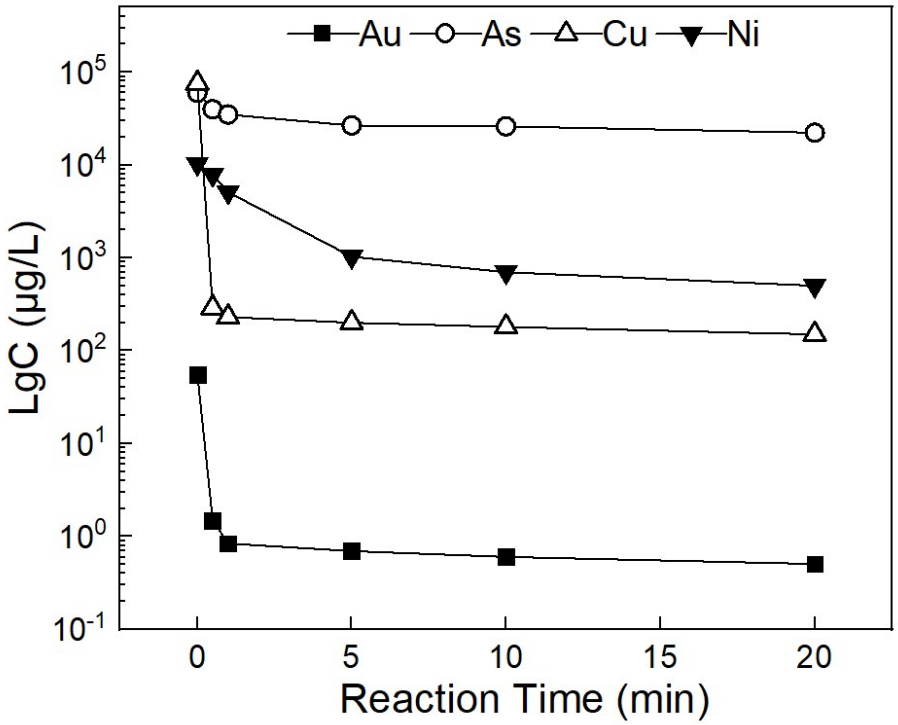

(a)
nZVI reactor
(b)
nZVI suspension
Wastewater
containing gold.

Figure S8



Na_2SO_3 in the commercial processes are to reduce Au(III) at high concentration (e.g., >500 mg/L)—acid condition and high temperature (e.g., pH<1 and >50^{o}C) are also required. To study whether it is applicable in the current system (low concentration, near neutral pH and ambient temperature), an experiment is conducted using Na_2SO_3 (1.0 g/L) to recovery the trace gold (90 μg/L) (Figure S8). Results show that Na_2SO_3 is not able to recover Au at such condition.

Figure S9



A batch experiment was conducted about assessing the competing effect of other wastewater metal ions on gold recovery (Figure S9). The results show the fast and complete recovery of the gold and copper ions in less than 2 min, and the slower recovery of the rest two ions (As(V) and Ni(II)). The recovered gold and copper on nZVI are expected to enhance reactivity of the remaining Fe(0) in the nZVI, due to their galvanic effect. The recovered copper, which is cheaper but much abundant in quantity, (~10%, w/w; Figure 6B), elevates the value of the reacted nZVI after recovery.

Figure S10

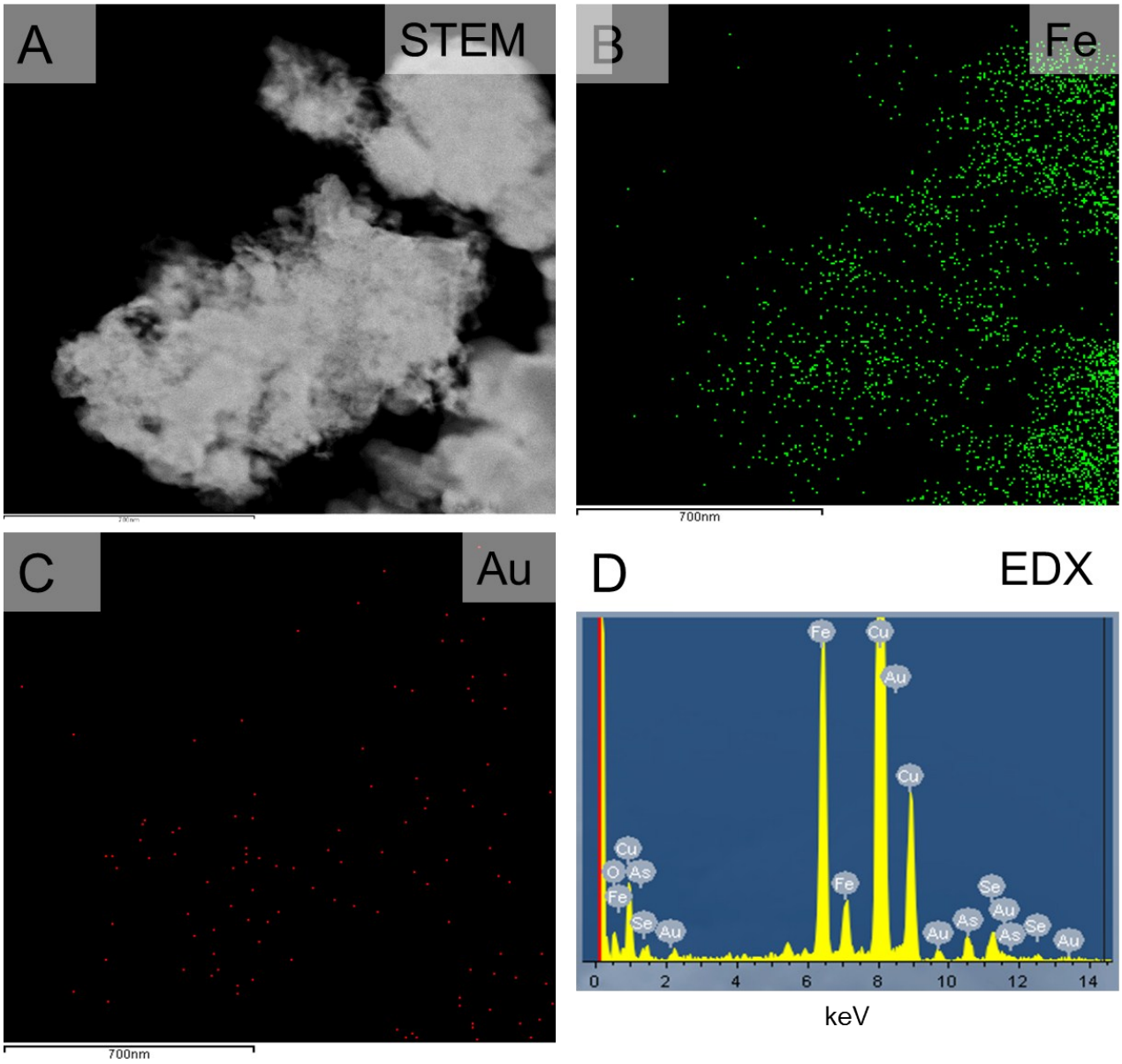

A
STEM
B
Fe
700nm
C
Au
700nm
D
EDX
Fe
Cu
Au
Cu
Cu
O
As
Fe
Se
Au
Fe
Se
Au
Au
As
As
Se
Au
0
2
4
6
8
10
12
14
keV

Table S1 Chemicals

Items	Size	Grade	Source
$FeCl_3 \cdot 6H_2O$	/	ACS	Aladdin industrial Co.
$HAuCl_4 \cdot 4H_2O$	/	AR	Sinopharm Chemical Reagent Co.
$NaBH_4$	/	98%	Shanghai Macklin Biochemical Co.
nFe_2O_3	20 nm	99.5%	Aladdin industrial Co.
NaCl	/	AR	Sinopharm Chemical Reagent Co
nZVI	60-200 nm	70%-83%	Lab made

Table S2 Composition of the wastewater

Item	Concentration (mg/L, average)	Item	Concentration (mg/L, average)
As	~100	NH_3-N	~500
Cu	~100	NaCl	80 000
Ni	~1	TOC	~500
Zn, Pb, Cr, Co	<3	Sb Se	< 30

References

1. S. L. Li, Y. Y. Ding, W. Wang and H. Lei. A facile method for determining the Fe(0) content and reactivity of zero valent iron. *Analytical Methods*, 2016, **8**, 1239-1248.