

## Electronic Supplementary Information

### Elemental mapping of Pd-Fe bimetallic nanoparticles at 0.1 nm resolution

#### Experimental Details

**Materials** All reagents used [i.e.,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NaBH}_4$ ,  $\text{Pd}(\text{C}_2\text{H}_3\text{O}_2)_2$ , ethanol] were of analytical grade or higher. Ultrapure deionized (DI) water was used in all the solutions. nZVI was prepared by the method of reduction of Fe(III) with sodium borohydride.

**Preparation of nanoparticles.** Iron nanoparticles (nZVI) were prepared using a sodium borohydride reduction method as described previously. The nanoparticles were used as freshly prepared in their moist forms without further drying. The mass of the nZVI indicated in this work refers to the dry mass, which was calculated by subtracting the mass in the moist form by its moisture content measured with a moisture analyzer. The nanoparticles were previously characterized and found to have a median diameter of 60 nm and the BET surface area was found to be  $30 \text{ m}^2/\text{g}$ .<sup>1-3</sup>

Pd-Fe bimetallic nanoparticles (Pd-nZVI) were prepared by reacting the freshly prepared iron nanoparticles with an ethanol solution containing palladium chloride ( $\text{Pd}(\text{C}_2\text{H}_3\text{O}_2)_2$ , 99.9 %, Alfa Aesar) at a concentration of 200 mg/L. The mixture was sonicated for 10 min, and the resulting particles were collected by vacuum filtration. In this study, the nominal loading of Pd with respect to iron was fixed at a mass fraction of 1.0 %.<sup>3</sup>

**Aging Experiments.** The aging experiment was performed in 120-mL serum bottles containing 100 mL of deionized water. An appropriate amount of freshly made nZVI or Pd-nZVI nanoparticles were added into 100 mL of DI water to reach a concentration of 5 g/L. The bottles were sealed with crimp caps having a Teflon-lined septum and placed on a mechanical shaker at 25 °C for 24 h. The solid residues were harvested by vacuum filtration and dried in a glovebag containing high purity  $\text{N}_2$  before STEM analysis.

Iron nanoparticles for the STEM analysis were collected from batch reactors and rinsed twice with high-purity nitrogen-purged ethanol and stored in a nitrogen-purged sample vial before the STEM analysis.

**STEM Analysis.** A Hitachi HD-2700 STEM with cold field emission gun operated at 200 kV was

used in this work.<sup>4,5</sup> This instrument was equipped with a hexapole transfer lens spherical aberration (Cs) corrector, and fitted with secondary electron (SE), high-angle annular dark-field (HAADF), bright-field (BF) detectors, as well as EDS (EDAX, USA) (energy resolution < 129 eV) and EELS (Gatan, UK) spectrometers. With a STEM image aperture inserted between the BF and DF detectors, it can simultaneously acquire SE, BF and DF images from the same specimen under optimal optical conditions. Plus, adding a Cs corrector allowed an electron beam with large current to converge to a finer electron probe and achieved high sensitivity, high speed and high spatial resolution.<sup>4,5</sup> By correcting the spherical aberration, resolution of less than 0.105 nm can be attained in the HAADF mode. To minimize the effect of specimen drift, a drift-correction mode was applied during the acquisition of EDS maps. Samples for STEM analysis were prepared by allowing a single drop of a dilute ethanol suspension of nanoparticles to dry on lacey-carbon film supported on a 200-mesh copper TEM grid (Ted Pella, Inc.) in a N<sub>2</sub>-filled glovebox.

**XRD characterizations.** XRD characterizations were performed with a Bruker AXS D8 Advanced X-ray diffractometer. The instrument used Cu K<sub>α</sub> radiation to produce X-rays with a wavelength of 0.1540 nm. Test samples were scanned for 2θ of 20–80 ° at the rate of 2 °/min. This scan range covered all major species of interests in this work, i.e., iron, palladium, Pd/Fe alloys, iron oxides.

Tab. S1. Common Halogenated Contaminants Treated by Pd-Fe Bimetallic Nanoparticles and Selected Field Applications

Contaminants		Pd-Fe materials			References	
Carbon tetrachloride (CT)		0-2 mol % via a solution deposition process, hydrogen reduction process, or hydrogen reduction of ferrihydrite coprecipitated with the metal cations			3	
Chlorinated methanes		As-synthesized Pd(0.05-1% by mass)-Fe nanoparticles			4	
Tetrachloroethene(PCE), Trichloroethene (TCE), Cis-dichloroethene(cis-DCE), Vinyl chloride (VC)		as-synthesized Pd-Fe nanoparticles			5	
Trichloroethene (TCE)		Pd(10% by mass)-Fe nanoparticles embedded in PAA/PES membrane			6	
		Starch stabilized Pd(0.1% by mass)-Fe nanoparticles			7	
		as-synthesized Pd(0.3% by mass)-Fe nanoparticles for field evaluation			8,9	
		as-synthesized Pd(1.5% by mass)-Fe nanoparticles			10	
Chlorophenols		encapsulated Pd-Fe in magnetic stabilized fluid bed reactor			11	
		Pd(0.68% by mass)-Fe nanoparticles supported on reactive activated carbon			12	
		as-synthesized Pd(0.585% by mass)-Fe nanoparticles			13	
Polychlorinated biphenyls (PCB)		as-synthesized Pd(0.68% by mass)-Fe on granular activated carbon support			14	
		Pd-Fe bimetallic nanotubes			15,16	
		as-synthesized Pd(0.25% by mass)-Fe nanoparticles			17	
		as-synthesized Pd (0.31% by mass)-Fe on activated carbon			17	
		Pd(10% by mass)-Fe nanoparticles embedded in PAA/PES membrane			19	
		Pd(0.68% by mass)-Fe nanoparticles supported on granular activated carbon			20	
Chlorobenzenes		as-synthesized Pd(0.1% by mass)-Fe nanoparticles and particles regenerated by acid or NaBH <sub>4</sub>			21	
γ-hexachlorocyclohexane		as-synthesized Pd(0.01% by mass)-Fe nanoparticles			21	
Polybrominated diphenyl ethers (PBDEs)		as-synthesized Pd(0.25% by mass)-Fe nanoparticles			17	
		as-synthesized Pd (0.31% by mass)-Fe on activated carbon			17	
		as-synthesized Pd(0.3% by mass)-Fe nanoparticles			22	
Site location	Contaminants	Total iron used (kg)	Degradation efficiency	Operation duration (mon)	Treated volume (m <sup>3</sup> )	References
Lakehurst, NJ, USA	PCE, TCE, TCA, DCE, VC	135	74% (total VOC)	—	—	24,25,26
Jacksonville, FL, USA	PCE, TCE, TCA	135	65–99%	9	740	24,25,26
Research Triangle Park, NC, USA	PCE, TCE, DCE, VC	11.2	>90% (total VOC)	3	—	24,25,26
Quebec, Canada	TCE, DCE, VC	4550	98% (TCE)	12	4500	24,25
Kaohsiung, Taiwan	TCA, DCA, TCE, DCE, VC	40	50–99% (VC)	3	2400	24,25

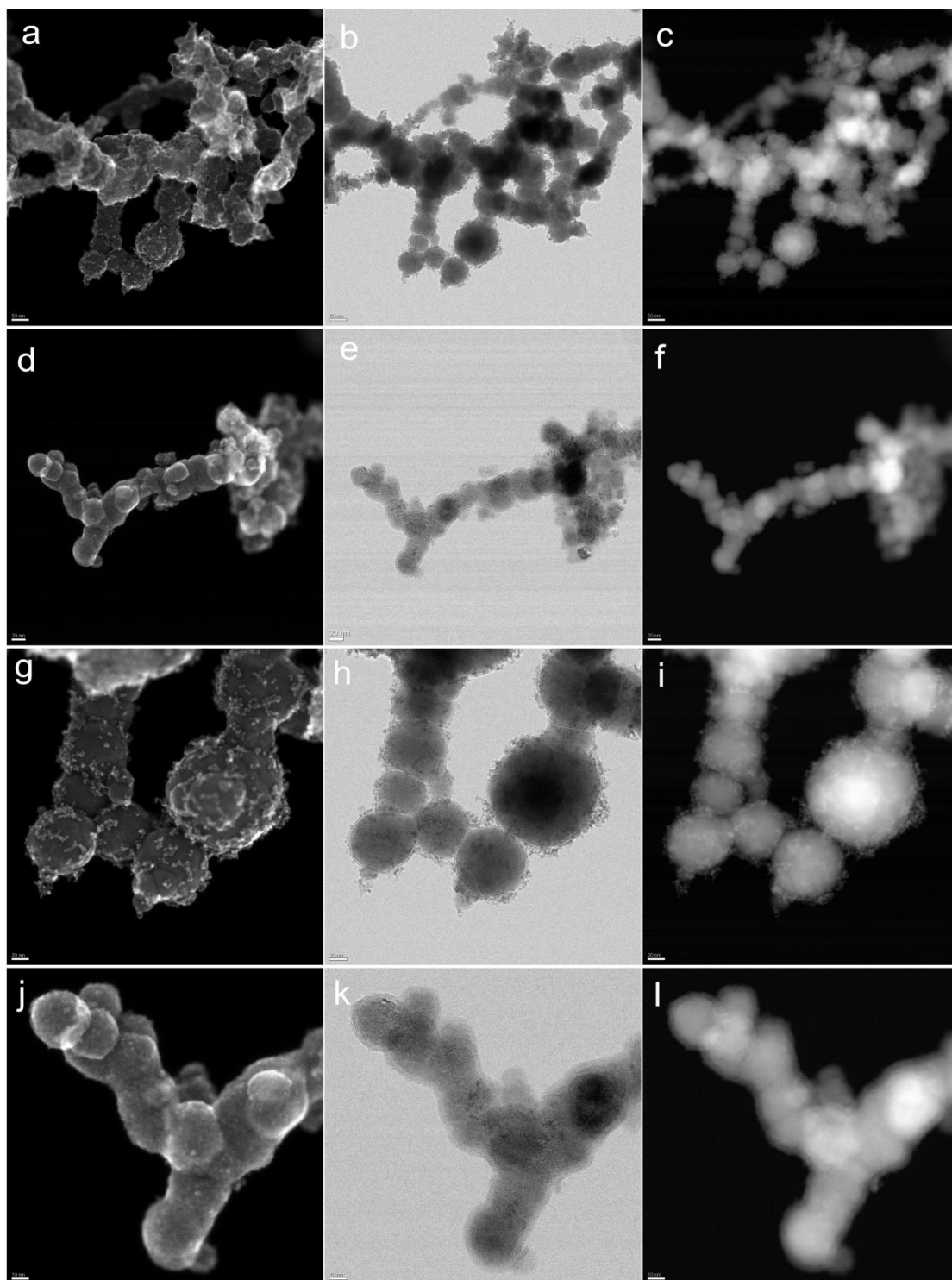


Fig. S1. Low magnification SE, BF and HAADF of freshly prepared Pd-nZVI (a-c) and 24-hour aging Pd-nZVI (d-f). High magnification SE, HAADF and BF image of freshly prepared Pd-doped(g-i) nZVI and 24 h aged Pd-doped nZVI (j-l).

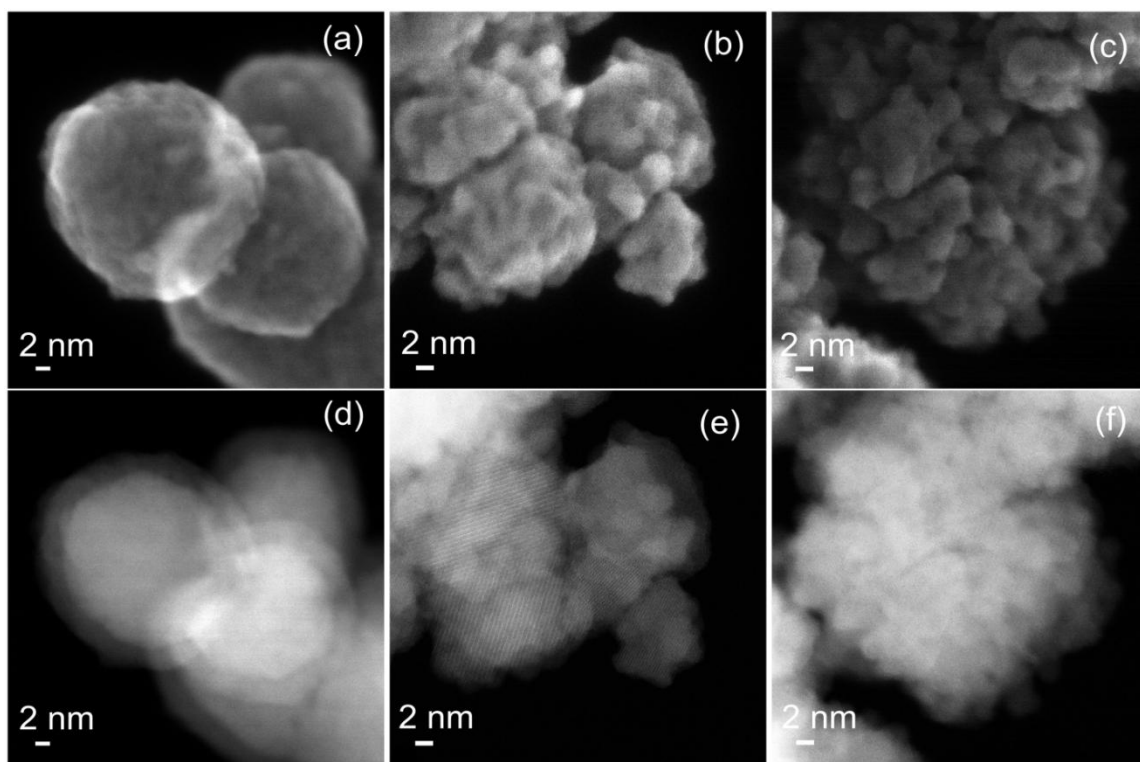


Fig. S2. (a-c) SE images and (d-f) corresponding HAADF images of the spent (24 h) Pd- nZVI particles.

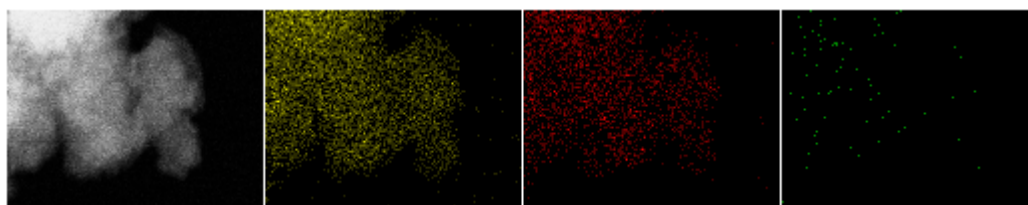


Fig. S3. HAADF (a) and STEM-EDS elemental maps of the Fe(b) ,O(c),Pd(d) of typical particle found in 24-hour aged Pd-nZVI.

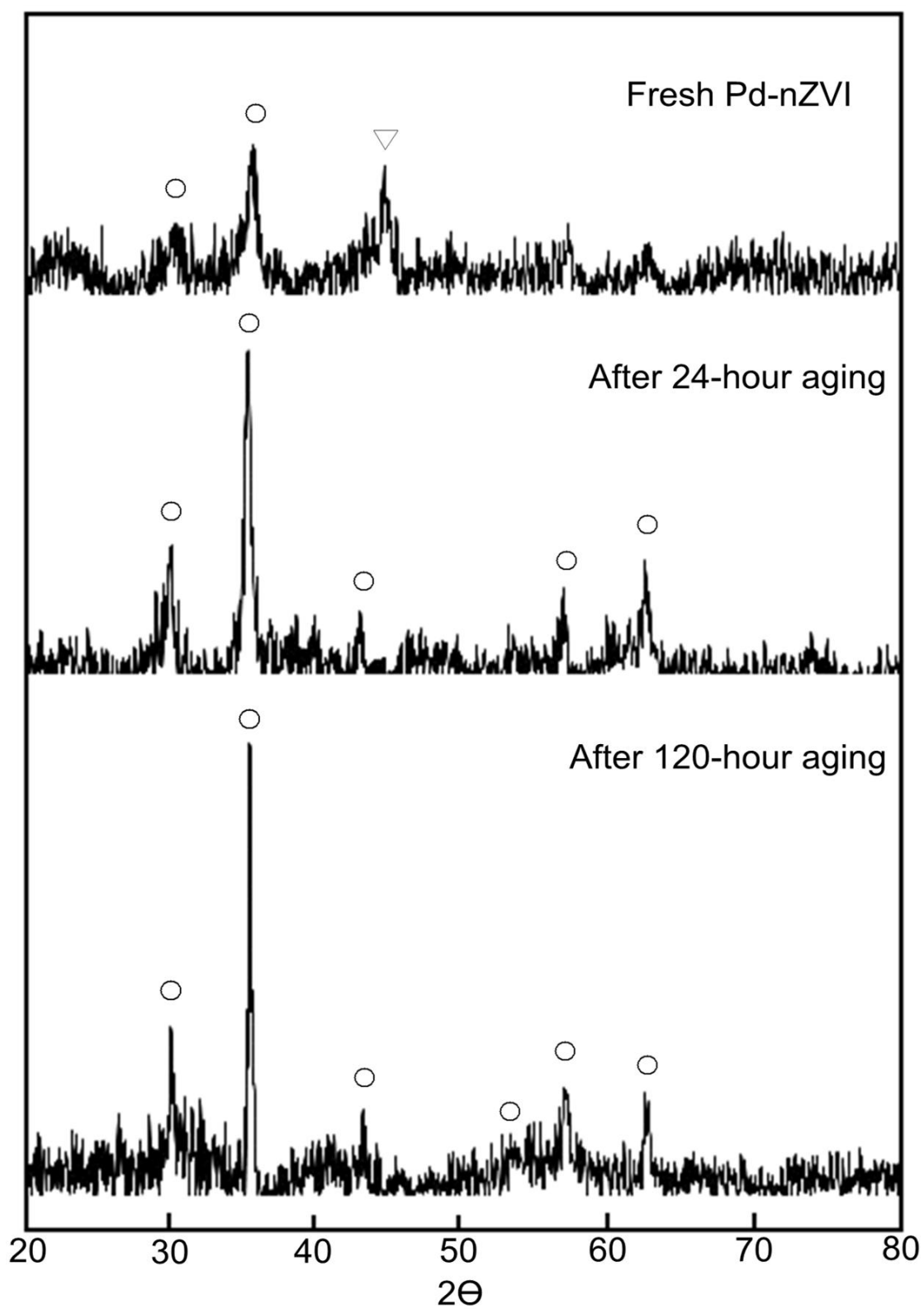


Fig. S4. XRD pattern of freshly prepared Pd-nZVI (a), 24-hour aging (b) and 120-hour aging (c) (▽ represents metallic iron; ○ represents iron oxide).

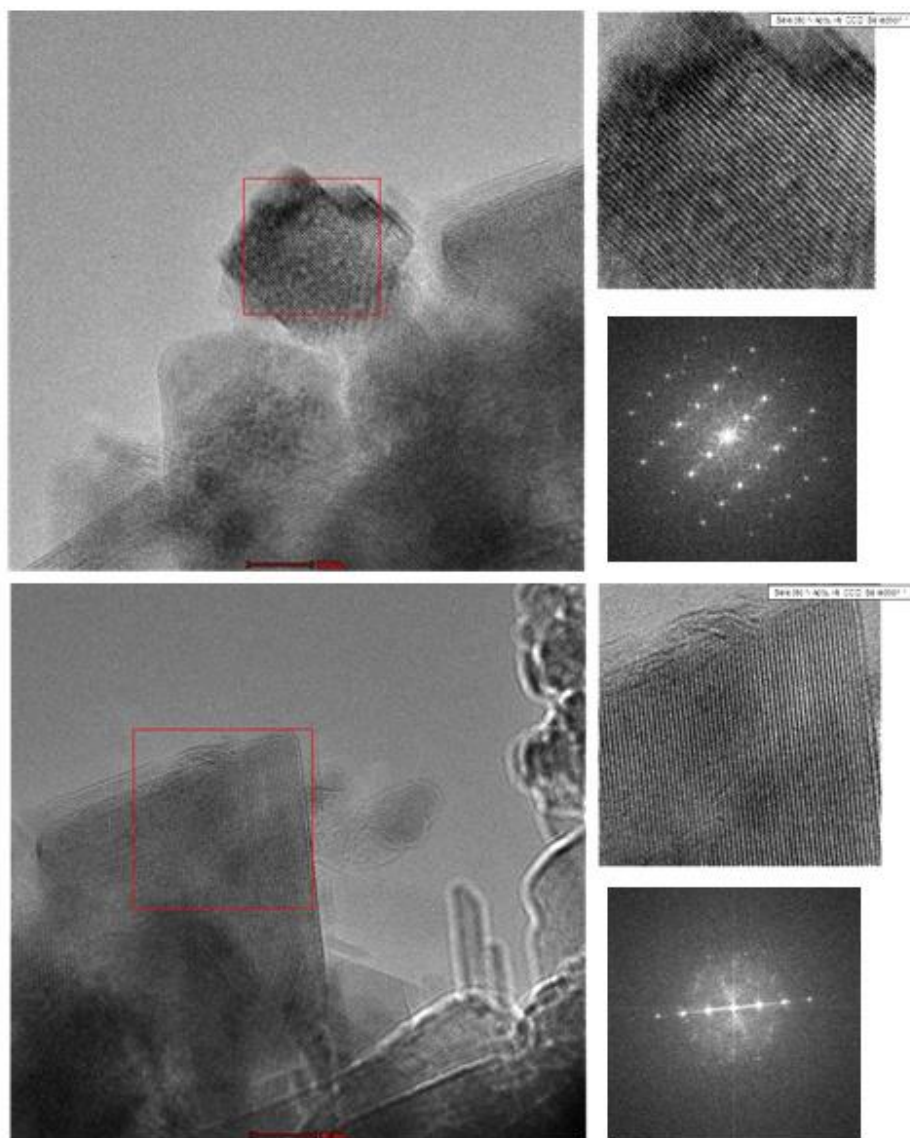


Fig. S5. Top-view HAADF image, high-resolution HAADF image, and selected area diffraction patterns of the 120-h-aged Pd-nZVI particles.

## References

1. D. M. Cwiertyny, S. J. Bransfield, K. J. T. Livi, D. H. Fairbrother and A. L. Roberts, *Environ. Sci. Technol.*, 2006,**40**, 6837–6843.
2. W. X. Zhang, C. B. Wang, H. L. Lien, *Catal.Today*, 1998, **40**, 387–395.
3. W. L. Yan, A. A. Herzing, X. Q. Li, C. J. Kiely, W. X. Zhang, *Environ. Sci. Technol.*, 2010, **44**, 4288–4294.
4. L. Ling and W. X. Zhang, *Anal. Method.*, 2014, **6**, 3211–3214.
5. Y. Zhu, H. Inada, K. Nakamura and J. Wall, *Nat. Mater.*, 2009, **8**, 808–812.