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Uptake, Translocation, and Transformation of Metal-based Nanoparticles in Plants: Recent Advances and Methodological Challenges

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List of Acronyms:

Light microscope (LM), Fluorescence microscope (FM), Confocal laser scanning microscopy (CLSM), Scanning electron microscopy (SEM), (high resolution) transmission electron microscopy ((HR)TEM), Energy dispersive spectrum (EDS), Scan transmission electron microscopy (STEM), Inductively coupled plasma optical emission spectrometer (ICP-OES), Inductively coupled plasma mass spectrometry (ICP-MS), Single-particle ICP-MS (SP-ICP-MS), Laser ablation ICP-MS (LA-ICP-MS), Multicollector ICP-MS (MC-ICP-MS), Micro-X-ray fluorescence microscopy (μ-XRF), Micro-X-ray absorption near edge structure (μ-XANES), Micro-proton induced X-ray emission (μ-PIXE), X-ray absorption spectroscopy (XAS), Scan transmission X-ray microscopy (STXM), Synchrotron Fourier transform infrared microspectroscopy (SR-FTIR), X-ray computed nanotomography (nano-CT), Nano secondary ion mass spectrometry (nano-SIMS), Confocal Raman mapping (CRM), Hyperspectral microscopy (HSI)

Table S1 Literature summary of Ag NPs and Au NPs uptake and translocation, transformation in plants

NPs	Plants	Size/nm	Exposure concentration	Exposure media and time	Analytical methods	Uptake and translocation, transformation[ref]
GA-Ag	Ryegrass	6, 25	1- 40 mg/L	Hydroponic, 5-7d	LM, ICP-OES, μ-XRF, μ-XANES	AgNPs adsorb to plant root surfaces, that oxidative dissolution leads to the insertion of Ag across the cell membrane, and that once internalized Ag can be translocated between tissues. Silver is oxidized within plant tissues.[1]
PVP-Ag GA-Ag	*P. diversifolius,* *E. densa*	12, 50		Microcosm, 90d	AF4-ICP-MS, XANES	In the presence of plant, 25% of the Ag present as an oxidized form resembling Ag-cysteine.[2]
Bare Ag	Wheat	10	0-5 mg/kg	Sand, 14d	TEM	Ag NPs were observed in shoots of plants.[3]
Ag	Arabidopsis	20, 40, 80	67-535 mg/L	Hydroponic, 28d	TEM, STEM, CLSM	AgNPs accumulated in: border cells, root cap, columella and columella initials. NPs were apoplastically transported in the cell wall and found in plasmodesmata.[4]
PEG-Ag C-Ag	Poplars, Arabidopsis	5, 10, 25	0.1-100 mg/L	Hydroponic, 42d	ICP-MS	Arabidopsis accumulated silver primarily in leaves, whereas poplars accumulated silver at similar concentrations in leaves and stems. [5]
Ag_2S	Cucumber, wheat	20-25	10 mg/L	Hydroponic, 7d	SP-ICP-MS, XANES, μ-XRF	Plants take up Ag_2S NPs without a marked selectivity in regard to particle size and without substantial transformation during translocation from roots to shoots.[6]
(-, +) Au	Arabidopsis	12	10 mg/L	Agar, 10d	Nano-CT, HSI	(-) NPs were able to translocate into the apoplast, (+) NPs produced higher mucilage which prevented NPs translocation into the root tissue.[7]
CA-, CYS-, TGA- Au	Rice, tomato	8-12	500 ug/L	Hydroponic, 1d	ICP-MS, HRTEM	Negatively charged CYS-AuNPs were more efficiently absorbed in roots and transferred to shoots. CYS ligand probably facilitated the endocytosis of AuNPs and increased the internalization of NPs in plants. [8]
Au	Arabidopsis, alfalfa	7-108	25-100 mg/L	Agar, 8d	TEM	5-100 nm NPs are not directly accumulated by plants. Au NPs were only observed in plants exposed to ionic gold in solution.[9]

Table S1 Literature summary of Ag NPs and Au NPs uptake and translocation, transformation in plants (Continued)

NPs	Plants	Size/nm	Exposure concentration	Exposure media and time	Analytical methods	Uptake and translocation, transformation[ref]
Au	*A. caroliniana* *M. simulans* *Egeria densa*	4, 18	250 mg/L	Hydroponic, 1d	TEM, SEM, STEM	Absorption of AuNPs through root uptake was size and species dependent. 4-nm and 18-nm AuNPs were absorbed by *A. caroliniana*, whereas only 4-nm AuNPs were absorbed by *M. simulans*. *Egeria densa* did not absorb AuNPs of either size.[10]
T-Au C-Au	Tomato, wheat	10, 30, 50	30 mg/L	Hydroponic, 3-7d	LA-ICP-MS, μ-XRF	All AuNPs were bioaccumulated in tobacco, but no bioaccumulation of AuNPs was observed for any treatment in wheat. [11]
C-Au	Tomato	3.5, 18	48, 76 mg/L	Hydroponic, 12d	SEM, HRTEM, EDS, μ-XANES, μ-XRF	Au NPs entered plants through the roots and moved into the vasculature. The uptake was size selective, 3.5 nm NPs were detected in plants but 18 nm NPs not.[12]
(+,0,-) Au	Rice	2	1.6, 0.14 mg /L	Hydroponic, 5d, 90d	LA-ICP-MS	Surface charge greatly affected the AuNP uptake into plant tissues. (+) AuNPs preferential accumulated in roots but (-) AuNPs were preferential to translocation from roots to shoots.[13]
PVP-Au	Tomato	40	0.2, 5 mg/L	Hydroponic, 4d	SP-ICP-MS	Tomato can uptake AuNPs as intact particles without alternating the AuNP properties.[14]
Bare Au	Poplar	15, 25, 50	250-500 μg/L	Hydroponic, 6d	ICP-MS, TEM	AuNPs were observed in the cytoplasm and various organelles of root and leaf cells.[15]

Table S2 Literature summary of metallic oxide NPs uptake and translocation, transformation in plants

NPs	Plant	Size/nm	Exposure concentration	Exposure media and time	Analytical methods	Uptake and translocation, transformation[ref]
ARS-TiO_2	Arabidopsis	2.8	1 μM	Hydroponic, 24h	FM, μ-XRF	TiO_2 NPs capable of passing the cell walls of plant cells, and capable of penetrating deeper into the plant tissues, beyond the surface cell layers.[16]
TiO_2	Wheat, Arabidopsis	12	100 mg/L	Hydroponic, 7d	SEM, μ-XRF, XANES	TiO_2 NPs were transferred from the exposure suspension to vegetal tissues.Ti is still in the TiO_2 chemical form inside plants.[17]
TiO_2 ZnO	Wheat	20 40	4307.5 mg/kg 214.5 mg/kg	Soil, 6m	SEM, TEM	TiO_2 NPs were retained in the soil for long periods and primarily adhered to root cell walls. ZnO NPs dissolved in the soil, thereby enhancing the uptake of toxic Zn by wheat.[18]
TiO_2	Cucumber	27	100-4000 mg/L	Hydroponic, 15d	μ-XRF, μ-XANES	TiO_2 NPs were not biotransformed inside plant, and were transported from the roots to the leaf trichomes.[19]
TiO_2	Rice	19-37	5, 50 mg/L	Hydroponic, 3d	STEM-EDS, SP-ICP-MS, ICP-OES	TiO_2 NPs penetrated into the plant root and resulted in Ti accumulation in above ground tissues.[20]
TiO_2	Wheat	14-655	100 mg/L	Hydroponic, 7d	μ-XRF, μ-XANES μ-PIXE, TEM	Below 36 nm, NPs accumulate in roots and distribute through whole plant tissues without dissolution or transformation; 36-140 nm, NPs are accumulated in wheat root parenchyma but do not reach the stele and consequently do not translocate to the shoot; above 140 nm, NPs are no longer accumulated in wheat roots.[21]
ZnO	Ryegrass	20	10-1000 mg/L	Hydroponic, 12d	SEM, TEM, ICP-MS	ZnO NPs were observed present in apoplast and protoplast of the root endodermis and stele. Little (if any) ZnO nanoparticles could translocate up in the ryegrass in this study.[22]
ZnO	Maize	30	0-100 mg/L	Hydroponic, 7d	ICP-OES,TEM, FM, μ-XRF, XAS	ZnO NPs were observed in the cortex, root tip cells, vascular, and primary root-lateral root junction. No ZnO nanoparticle was observed to translocate to shoots. Zn accumulated in plant mainly as the form of Zn phosphate similar to Zn ion exposure.[23]
ZnO CeO_2	Soybean	8 7	500-4000 mg/L	Hydroponic, 5d	XANES	CeO_2 NPs were presented in roots, whereas ZnO NPs were not present, Zn appeared coordinated in the same manner as Zn-nitrate or Zn-acetate. [24]
ZnO	Phaseolus	40	100, 1000 mg/L	Hydroponic, 2d	μ-XRF, XANES	Phaseolus takes up Zn bound to both citrate and malate, while entire NPs were only absorbed when roots were injured. [25]

Table S2 Literature summary of metallic oxide NPs uptake and translocation, transformation in plants **(**Continued**)**

NPs	Plant	Size/nm	Exposure concentration	Exposure media and time	Analytical methods	Uptake and translocation, transformation
ZnO	Velvet mesquite	10	500-4000 mg/L	Hydroponic, 15d	ICP-OES, μ-XRF, XANES	ZnO NPs were not present in mesquite tissues, Zn was found resembe to the spectra of $Zn(NO_3)_2$. Zn was presented in the vascular system of roots and leaves in ZnO NP treated plants. [26,27]
ZnO	Maize	--	100-800 mg/kg	Soil, 30d	ICP-OES, CLSM	ZnO NPs aggregates penetrated the root epidermis and cortex through the apoplastic pathway and passed the endodermis through the symplastic pathway.[28]
ZnO, CeO_2	Soybean	10 8	500 mg/kg 1000 mg/kg	Soil, 48d	ICP-MS, μ-XRF, μ-XANES	No presence of ZnO NPs within plant tissues, Zn presented in plant in a form resembling Zn-citrat. Ce remained mostly as CeO_2 NPs within the plant, a small percentage of CeO_2 NPs was biotransformed to Ce(III).[29]
ZnO	Cowpea	20-30	500 mg/kg	Soil, 28d	μ-XRF, XAFS	No upward translocation of ZnO NPs from roots to shoots was observed. Zn were similar in stem and leaf tissues regardless of Zn-treatments, with Zn mainly bound to citrate, histidine, and phytate.[30]
CuO	Maize	20−40	100 mg L/1	Hydroponic, 15d	ICP-MS, TEM, EDS	CuO NPs were transported from roots to shoots via xylem and could translocate from shoots back to roots via phloem. During this translocation, CuO NPs could be reduced from Cu (II) to Cu (I). [31]
CuO	Rice	40	100 mg/L	Hydroponic, 14d	μ-XRF, μ-XANES, XANES, STXM	CuO NPs were transported from the roots to the leaves, and that Cu (II) combined with cysteine, citrate, and phosphate ligands and was even reduced to Cu (I).[32]
CuO	Elsholtzia splendens.	43	100-1000 mg/L	Hydroponic, 14d	ICP-MS, HRTEM, EDS, XANES	Accumulated Cu species existed predominantly as CuO NPs in the plant tissues. CuO NPs-like deposits were found in the root cells and leaf cells.[33]
CuO ZnO	Wheat	＜50 ＜100	500 mg/kg	Sand, 14d	ICP-MS, XANES	Bioaccumulation of Cu, mainly as CuO and Cu(I)-sulfur complexes, and Zn as Zn-phosphate was detected in the shoots of NP-challenged plants. [34]
SiO_2	Arabidopsis	14, 50, 200	250, 1000 mg/L	Hydroponic, 21,42d	TEM, ICP-OES	Significant uptake of SiO_2 NPs (14, 50, and 200 nm) into the root system of A. thaliana was observed, and the contents of uptake were size-dependent.[35]
Fe_3O_4	Pumpkin	20	500mg/L	Hydroponic, 20d	VSM	Magnetite NPs can absorb, translocate, and accumulate the particles in the plant tissues.[36]
γ-Fe2O3	Maize	21	20-100mg/L	Hydroponic, 14d	TEM, CLSM	NPs could enter roots and migrate apoplastically from the epidermis to the endodermis and the vacuole. But most of NPs existed around the epidermis and did not transport from roots to shoots.[37]

Table S3 Literature summary of rare-earth oxides NPs uptake and translocation, transformation in plants

NPs	Plant	Size/nm	Exposure concentration	Exposure media and time	Analytical methods	Uptake and translocation, transformation
CeO_2	Alfalfa, maize, cucumber, tomato	7	500-4000 mg/L	Hydroponic, 6-9d	ICP-OES, XAS	CeO_2 were found within root tissues of the four plant species without transformation.[38]
$^{141}CeO_2$	Cucumber	7, 22	2-200 mg/L	Hydroponic, 7d	Autoradiography, TEM	Only very limited amounts of CeO_2 NPs could be transferred from the roots to shoots. However, once they have entered into the vascular cylinder, NPs could move smoothly to the end of the vascular bundle along with water flow.[39]
CeO_2	Tomato	20	0.1–10 mg/L	Hydroponic, 70d	ICP-MS	CeO_2 NPs were taken up by tomato roots and translocated to shoots and edible tissues. In particular, substantially higher Ce concentrations were detected in the fruits.[40]
CeO_2	Cucumber	7	2000 mg/L	Hydroponic, 21d	ICP-MS, STXM, XANES, TEM, EDS	CeO_2 NPs were likely dissolved and reducing to Ce(III) by root exudates. Ce(III) ions were precipitated on the root surfaces and in intercellular spaces with phosphate, or form complexes with carboxyl compounds during translocation to the shoots. [41]
CeO_2	Cucumber	25	20-2000 mg/L	Hydroponic, 7d	STXM, XANES, TEM, EDS	Root surfaces are the sites, and the physicochemical interaction between the NPs and root exudates at the nanobio interface is the necessary condition for the transformation of CeO_2 NPs in plant systems.[42]
CeO_2	Cucumber	25	200, 2000 mg/L	Hydroponic, 3d	ICP-MS, μ-XRF, μ-XANES	About 15% of Ce was reduced from Ce(IV) to Ce(III) in the roots). Ce was transported as a mixture of Ce(IV) and Ce(III) from roots to shoots through xylem, while it was transported almost only in the form of CeO_2 from shoots back to roots through phloem.[43]
(+,0,-)CeO_2	Wheat	4nm	20 mg/L	Hydroponic, 34h	ICP-MS, μ-XRF, XANES	A 15−20% reduction from Ce(IV) to Ce(III) was observed in both roots and leaves, independent of NP surface charge. (+) CeO_2 NPs exposed plants had lower Ce leaf concentrations.[44]

Table S3 Literature summary of rare-earth oxides NPs uptake and translocation, transformation in plants **(**Continued**)**

NPs	Plant	Size/nm	Exposure concentration	Exposure media and time	Analytical methods	Uptake and translocation, transformation
CeO_2	Tall fescue, tomato	3.9	1-50 mg/kg	Soil, 8d	XANES	Soil properties controlled Ce uptake. The clay fraction enhanced the retention of the CeO_2 nanoparticles and hence reduced Ce uptake, whereas the organic matter content enhanced Ce uptake.[45]
Yb_2O_3	Cucumber	15	0.32-2000 mg/L	Hydroponic, 14d	ICP-MS, TEM, EDS, STXM, NEXAFS	In the intercellular regions of the roots, Yb_2O_3 NPs and $YbCl_3$ were all transformed to $YbPO_4$.[46]
La_2O_3	Cucumber	22	2-2000 mg/L	Hydroponic, 5d	TEM, EDS, STXM	La_2O_3 NPs and $LaCl_3$ were both transformed to needle-like LaPO4 nanoclusters in the intercellular regions of the cucumber roots. [47]

References

1 L. Y. Yin, Y. W. Cheng, B. Espinasse, B. P. Colman, M. Auffan, M. Wiesner, J. Rose, J. Liu and E. S. Bernhardt, *Environ. Sci. Technol.*, 2011, **45**, 2360-2367.

2 A. J. Bone, B. P. Colman, A. P. Gondikas, K. M. Newton, K. H. Harrold, R. M. Cory, J. M. Unrine, S. J. Klaine, C. W. Matson and R. T. Di Giulio, *Environ. Sci. Technol.*, 2012, **46**, 6925-6933.

3 C. O. Dimkpa, J. E. McLean, N. Martineau, D. W. Britt, R. Haverkamp and A. J. Anderson, *Environ. Sci. Technol.*, 2013, **47**, 1082-1090.

4 J. Geisler-Lee, Q. Wang, Y. Yao, W. Zhang, M. Geisler, K. Li, Y. Huang, Y. Chen, A. Kolmakov and X. Ma, *Nanotoxicology*, 2013, **7**, 323-337.

5 J. Wang, Y. Koo, A. Alexander, Y. Yang, S. Westerhof, Q. B. Zhang, J. L. Schnoor, V. L. Colvin, J. Braam and P. J. J. Alvarez, *Environ. Sci. Technol.*, 2013, **47**, 5442-5449.

6 P. Wang, E. Lombi, S. K. Sun, K. G. Scheckel, A. Malysheva, B. A. McKenna, N. W. Menzies, F. J. Zhao and P. M. Kopittke, *Environ.-Sci. Nano*, 2017, **4**, 448-460.

7 A. Avellan, F. Schwab, A. Masion, P. Chaurand, D. Borschneck, V. Vidal, J. Rose, C. Santaella and C. Levard, *Environ. Sci. Technol.*, 2017, **51**, 8682-8691.

8 H. Li, X. Ye, X. Guo, Z. Geng and G. Wang, *J Hazard Mater*, 2016, **314**, 188-196.

9 A. F. Taylor, E. L. Rylott, C. W. Anderson and N. C. Bruce, *PLoS One*, 2014, **9**, e93793.

10 J. B. Glenn, S. A. White and S. J. Klaine, *Environ. Toxicol. Chem.*, 2012, **31**,

194-201.

11 J. D. Judy, J. M. Unrine, W. Rao, S. Wirick and P. M. Bertsch, *Environ. Sci. Technol.*, 2012, **46**, 8467-8474.

12 T. Sabo-Attwood, J. M. Unrine, J. W. Stone, C. J. Murphy, S. Ghoshroy, D. Blom, P. M. Bertsch and L. A. Newman, *Nanotoxicology*, 2012, **6**, 353-360.

13 J. Koelmel, T. Leland, H. H. Wang, D. Amarasiriwardena and B. S. Xing, *Environ. Pollut.*, 2013, **174**, 222-228.

14 Y. B. Dan, W. L. Zhang, R. M. Xue, X. M. Ma, C. Stephan and H. L. Shi, *Environ. Sci. Technol.*, 2015, **49**, 3007-3014.

15 G. S. Zhai, K. S. Walters, D. W. Peate, P. J. J. Alvarez and J. L. Schnoor, *Environ. Sci. Tech. Let.*, 2014, **1**, 146-151.

16 J. Kurepa, T. Paunesku, S. Vogt, H. Arora, B. M. Rabatic, J. J. Lu, M. B. Wanzer, G. E. Woloschak and J. A. Smalle, *Nano Lett.*, 2010, **10**, 2296-2302.

17 C Larue, H Khodja, N Herlin-Boime, F Brisset, AM Flank, B Fayard, S Chaillou and M. Carrière, *J. Phy. Conf. Ser.*, 2011, **304**.

18 W. C. Du, Y. Y. Sun, R. Ji, J. G. Zhu, J. C. Wu and H. Y. Guo, *J. Environ. Monitor.*, 2011, **13**, 822-828.

19 A. D. Servin, H. Castillo-Michel, J. A. Hernandez-Viezcas, B. C. Diaz, J. R. Peralta-Videa and J. L. Gardea-Torresdey, *Environ. Sci. Technol.*, 2012, **46**, 7637-7643.

20 Y. Deng, E. J. Petersen, K. E. Challis, S. A. Rabb, R. D. Holbrook, J. F. Ranville, B. C. Nelson and B. Xing, *Environ. Sci. Technol.*, 2017, **51**, 10615-10623.

21 C. Larue, J. Laurette, N. Herlin-Boime, H. Khodja, B. Fayard, A. M. Flank, F. Brisset and M. Carriere, *Sci . Total. Environ.*, 2012, **431**, 197-208.

22 D. H. Lin and B. S. Xing, *Environ. Sci. Technol.*, 2008, **42**, 5580-5585.

23 J. T. Lv, S. Z. Zhang, L. Luo, J. Zhang, K. Yang and P. Christie, *Environ.-Sci. Nano*, 2015, **2**, 68-77.

24 M. L. Lopez-Moreno, G. de la Rosa, J. A. Hernandez-Viezcas, H. Castillo-Michel, C. E. Botez, J. R. Peralta-Videa and J. L. Gardea-Torresdey, *Environ. Sci. Technol.*, 2010, **44**, 7315-7320.

25 T. N. M. da Cruz, S. M. Savassa, M. H. F. Gomes, E. S. Rodrigues, N. M. Duran, E. de Almeida, A. P. Martinelli and H. W. P. de Carvalho, *Environ.-Sci. Nano*, 2017, **4**, 2367-2376.

26 J. A. Hernandez-Viezcas, H. Castillo-Michel, A. D. Servin, J. R. Peralta-Videa and J. L. Gardea-Torresdey, *Chem. Eng. J.*, 2011, **170**, 346-352.

27 M. Kumari, S. S. Khan, S. Pakrashi, A. Mukherjee and N. Chandrasekaran, *J. Hazard Mater.*, 2011, **190**, 613-621.

28 L. J. Zhao, J. R. Peralta-Videa, M. H. Ren, A. Varela-Ramirez, C. Q. Li, J. A. Hernandez-Viezcas, R. J. Aguilera and J. L. Gardea-Torresdey, *Chem. Eng. J.*, 2012, **184**, 1-8.

29 J. A. Hernandez-Viezcas, H. Castillo-Michel, J. C. Andrews, M. Cotte, C. Rico, J. R. Peralta-Videa, Y. Ge, J. H. Priester, P. A. Holden and J. L. Gardea-Torresdey, *ACS Nano*, 2013, **7**, 1415-1423.

30 P. Wang, N. W. Menzies, E. Lombi, B. A. McKenna, B. Johannessen, C. J.

Glover, P. Kappen and P. M. Kopittke, *Environ. Sci. Technol.*, 2013, **47**, 13822-13830.

31 Z. Wang, X. Xie, J. Zhao, X. Liu, W. Feng, J. C. White and B. Xing, *Environ. Sci. Technol.*, 2012, **46**, 4434-4441.

32 C. Peng, D. Duan, C. Xu, Y. Chen, L. Sun, H. Zhang, X. Yuan, L. Zheng, Y. Yang, J. Yang, X. Zhen, Y. Chen and J. Shi, *Environ. Pollut.*, 2015, **197**, 99-107.

33 C. Peng, C. Xu, Q. Liu, L. Sun, Y. Luo and J. Shi, *Environ. Sci. Technol.*, 2017, **51**, 4907-4917.

34 C. O. Dimkpa, J. E. McLean, D. E. Latta, E. Manangon, D. W. Britt, W. P. Johnson, M. I. Boyanov and A. J. Anderson, *J. Nanopart Res.*, 2012, **14**.

35 Danielle L. Slomberg and M. H. Schoenfisch, 2012.

36 H. Zhu, J. Han, J. Q. Xiao and Y. Jin, *J. Environ. Monitor.*, 2008, **10**, 713-717.

37 J. Li, J. Hu, C. Ma, Y. Wang, C. Wu, J. Huang and B. Xing, *Chemosphere*, 2016, **159**, 326-334.

38 M. L. Lopez-Moreno, G. de la Rosa, J. A. Hernandez-Viezcas, J. R. Peralta-Videa and J. L. Gardea-Torresdey, *J. Agr. Food Chem.*, 2010, **58**, 3689-3693.

39 Z. Y. Zhang, X. He, H. F. Zhang, Y. H. Ma, P. Zhang, Y. Y. Ding and Y. L. Zhao, *Metallomics*, 2011, **3**, 816-822.

40 Q. Wang, X. M. Ma, W. Zhang, H. C. Pei and Y. S. Chen, *Metallomics*, 2012, **4**, 1105-1112.

41 P. Zhang, Y. H. Ma, Z. Y. Zhang, X. He, J. Zhang, Z. Guo, R. Z. Tai, Y. L. Zhao

and Z. F. Chai, *ACS Nano*, 2012, **6**, 9943-9950.

42 Y. H. Ma, P. Zhang, Z. Y. Zhang, X. He, J. Z. Zhang, Y. Y. Ding, J. Zhang, L. R. Zheng, Z. Guo, L. J. Zhang, Z. F. Chai and Y. L. Zhao, *Environ. Sci. Technol.*, 2015, **49**, 10667-10674.

43 Y. Ma, X. He, P. Zhang, Z. Zhang, Y. Ding, J. Zhang, G. Wang, C. Xie, W. Luo, J. Zhang, L. Zheng, Z. Chai and K. Yang, *Environ. Sci. Technol.*, 2017, **51**, 5215-5221.

44 E. Spielman-Sun, E. Lombi, E. Donner, D. Howard, J. M. Unrine and G. V. Lowry, *Environ. Sci. Technol.*, 2017, **51**, 7361-7368.

45 C. Layet, M. Auffan, C. Santaella, C. Chevassus-Rosset, M. Montes, P. Ortet, M. Barakat, B. Collin, S. Legros, M. N. Bravin, B. Angeletti, I. Kieffer, O. Proux, J. L. Hazemann and E. Doelsch, *Environ. Sci. Technol.*, 2017, **51**, 9756-9764.

46 P. Zhang, Y. H. Ma, Z. Y. Zhang, X. He, Z. Guo, R. Z. Tai, Y. Y. Ding, Y. L. Zhao and Z. F. Chai, *Environ. Sci. Technol.*, 2012, **46**, 1834-1841.

47 Y. H. Ma, X. He, P. Zhang, Z. Y. Zhang, Z. Guo, R. Z. Tai, Z. J. Xu, L. J. Zhang, Y. Y. Ding, Y. L. Zhao and Z. F. Chai, *Nanotoxicology*, 2011, **5**, 743-753.