



Discovery of nano-sized gold particles in natural plant tissues

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Abstract

Biological effects of nanoparticles have attracted widespread attention. However, the interaction between plants and nanoparticles remains unclear. The purpose of this study was to investigate characteristics of nano-sized metal particles in two representative plant species, *Erigeron canadensis* and *Boehmeria nivea*, in the Guangdong Province, China. The stems of the plants were sliced and placed on Ni–C grids for field-emission transmission electron microscopy (TEM). The metal-bearing nanoparticles were further analysed for their size, shape, composition, content and other characteristics using X-ray energy spectrum analysis, scanning TEM and selected-area electron diffraction pattern. The results revealed that the plants contain nano-sized Au-bearing particles with a diameter of 5–50 nm, ellipsoid, spherical and bone-rod shapes or irregular morphology with smooth edges. These nanoparticles primarily consisted of Au, Cu, O and Cl. The discovery of Au-bearing nanoparticles in natural plant tissues is of great significance for biological nanoscience. Here, we discuss the function and absorption mechanism of Au-bearing nanoparticles in plants and present the influence of the discovery of Au-bearing nanoparticles in natural plants.

Keywords Au nanoparticles · Plant tissues · TEM study · Characteristic · Absorption mechanism · Environment

Introduction

Scanning tunnelling microscopy has facilitated the visualisation of the microatomic world since 1981 and is the base on which the field of nanotechnology has gradually developed. With the rapid development of nanotechnology, nanoparticles will present some environmental risks (Meyer et al. 2009; Yang et al. 2016). Nanoparticles are natural products, but the widespread use of nano-materials, which have a very wide range of applications in fields such as electronics, magnetism, optics, biomedicine, pharmacology, cosmetics, energy resources, sensors, catalysis and materials science, has enhanced the growth of synthetic, engineered nanoparticles (Bhatt and Tripathi 2011). There is little doubt regarding the artificial nanoparticles entering the ecosystem and

concomitantly presenting a series of potential environmental risks. Plants, which are an important part of the ecosystem, are the fundamental route for nanoparticles to enter the food chain and accumulate in organisms (Rico et al. 2011). However, little is known about the interactions between nanoparticles and plants, let alone between nanoparticles and the environment.

Two articles have discussed biological effects of nanoparticles (Brumfiel 2003; Service 2003). As a result, this topic has attracted widespread attention among researchers. The characteristic of nano-materials has been of tremendous value for scientific and technological development, and their safety is paramount to their further development. The special physical and chemical properties of nanoparticles, such as the small size effect, surface effect, quantum size effect and macroscopic quantum tunnelling effect, make nanoparticles easily absorbable by organisms; thus, these nanoparticles affect the growth and health of organisms by interacting with them (Nel et al. 2006). In addition, metallic nanoparticles have the dual adverse effects of metal- and nano-toxicity. Their biological toxicity and ecological risk have, therefore, become an important topic in nano-toxicology.

A lot of research on interactions between plants and metals has been conducted, but research on the interactions

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between plants and metal nanoparticles is still inadequate. Because of differences among different types of plants and nanoparticles, the mechanisms underlying and extent of their actions vary (Andreotti et al. 2015). For instance, Ag, Fe, Cu, Al and Zn nano-materials may present toxicological risks for the growth of plants (Lin and Xing 2007; Lee et al. 2008, 2012; Kumari et al. 2009; Stampoulis et al. 2009; Yin et al. 2011; El-Temsah and Joner 2012; Liu et al. 2016). In contrast, Au nanoparticles could be beneficial to growth, leading to an increased yield (Kumar et al. 2013). Each of these studies consisted of observations made using cultures. To date, studies reporting types and characteristics of metal nanoparticles present in natural plant tissues are rare. We, therefore, conducted this study to determine the presence of noble metal (such as Au) nanoparticles in plants growing in the natural environment.

Experimental

Erigeron canadensis and *Boehmeria nivea* were the plants chosen for this study. *B. nivea* is a perennial subshrub or shrub, whereas *E. canadensis* is an annual or biennial weed. Both have a very wide distribution in Guangdong Province, China. Stems of *E. canadensis* and *B. nivea* were sampled in their flourished period, cleaned using ultrapure water and cut into strips measuring 2–4 mm in length prior to storage in 5-ml centrifuge tubes containing aldehyde fixative (5% glutaraldehyde + 4% paraformaldehyde). The centrifuge tubes were refrigerated at 0–4 °C throughout the experimental course. Samples were fixed, dehydrated and embedded as described previously (Glauert 1975). Ultrathin sections were prepared from the embedded samples (Hagler 2007). Ni–C grids were used to support the sample slices. The samples were not dyed to ensure that clear images were obtained under the mirror, and the entire procedure was performed while maintaining high standards of cleanliness.

Following pretreatment, plant tissue sections on Ni–C grids were examined using a field-emission transmission electron microscope (TEM; Tecnai G2 F30 S-TWIN instrument) at the Testing Center at Yangzhou University, China. Energy-dispersive X-ray spectroscopy (EDS) and selected-area electron diffraction (SAED) data or high-resolution TEM (HRTEM) images were obtained for each detected particle. The maximum magnifications of TEM and scanning TEM (STEM) were 1 and 2.3 million, respectively. The dot resolution was 0.20 nm, and the line resolution was 0.102 nm. The High-Angle Annular Dark Field STEM resolution was 0.17 nm. This meant that the size, shape, composition, content and other characteristics of metal nanoparticles could be displayed. In addition, particles primarily composed of metallic elements (metal-bearing particles) appeared dark under TEM and bright under STEM (Hu et al.

2017). C and Ni content measurements were eliminated from the measured values for Ni–C grids, and H and O could not be determined because plant cells mostly consist of organic matter.

Results and discussion

Characteristics of Au nanoparticles within plant tissues

Au-bearing nanoparticles were observed in both *E. canadensis* and *B. nivea* using HRTEM (Figs. 1, 2). Some common nanoparticles were rejected because they are ubiquitously present in air. The results revealed that Au-bearing nanoparticles in *E. canadensis* primarily consisted of Au, O, Cu and Cl (Fig. 1c) or only Au and O (Fig. 1d). These Au-bearing particles were approximately 20–50 nm in diameter and had an irregular morphology. EDS analysis revealed that components of one particle were mainly O (44.81%), Cl (5.27%), Cu (17.52%) and Au (32.40%; Table 1), whereas another one only consisted of Au (50.05%) and O (49.95%; Table 2). In addition, the diffraction pattern shown in Fig. 1d revealed a number of relatively regular spots, indicating that this particle was crystalline in nature. Nanoparticles found in *B. nivea* mainly consisted of Au (54.46%) and O (45.54%; Table 3 and Fig. 2e) and were circular, elliptical or bone-rod shaped with smooth edges. Au nanoparticles in *B. nivea* were 5–15 nm in size. The clear diffraction spots in the diffraction pattern (Fig. 2e) indicated that these Au-bearing nanoparticles were also likely to be crystalline. The Au-bearing nanoparticles found in *B. nivea* were more abundant and more regular shaped than those found in *E. canadensis*. Furthermore, most of these Au-bearing nanoparticles were distributed around the plant cytoskeleton, as assessed by TEM and STEM.

The source of Au nanoparticles

It is likely that the Au-bearing nanoparticles found in these plants were accumulated by enrichment given that the abundance of Au in the crust is very low. In plants, gold exists as an ultra-trace element and is a non-essential element for plant growth. The natural baseline level of gold in plants is usually as low as 10 ng/g dry weight (10 ppb), and its concentration in hyperaccumulator plants is 100 times more than that in normal vegetation, i.e. up to 1 mg/g dry weight (1 ppm; Brooks et al. 1977). Besides the concentration of metal elements in the environment, the entry and accumulation of metals is also related to their availability, pH and other physicochemical properties of the soil and the interaction between various elements (antagonism and synergy) and other ecological factors, such as light, temperature and

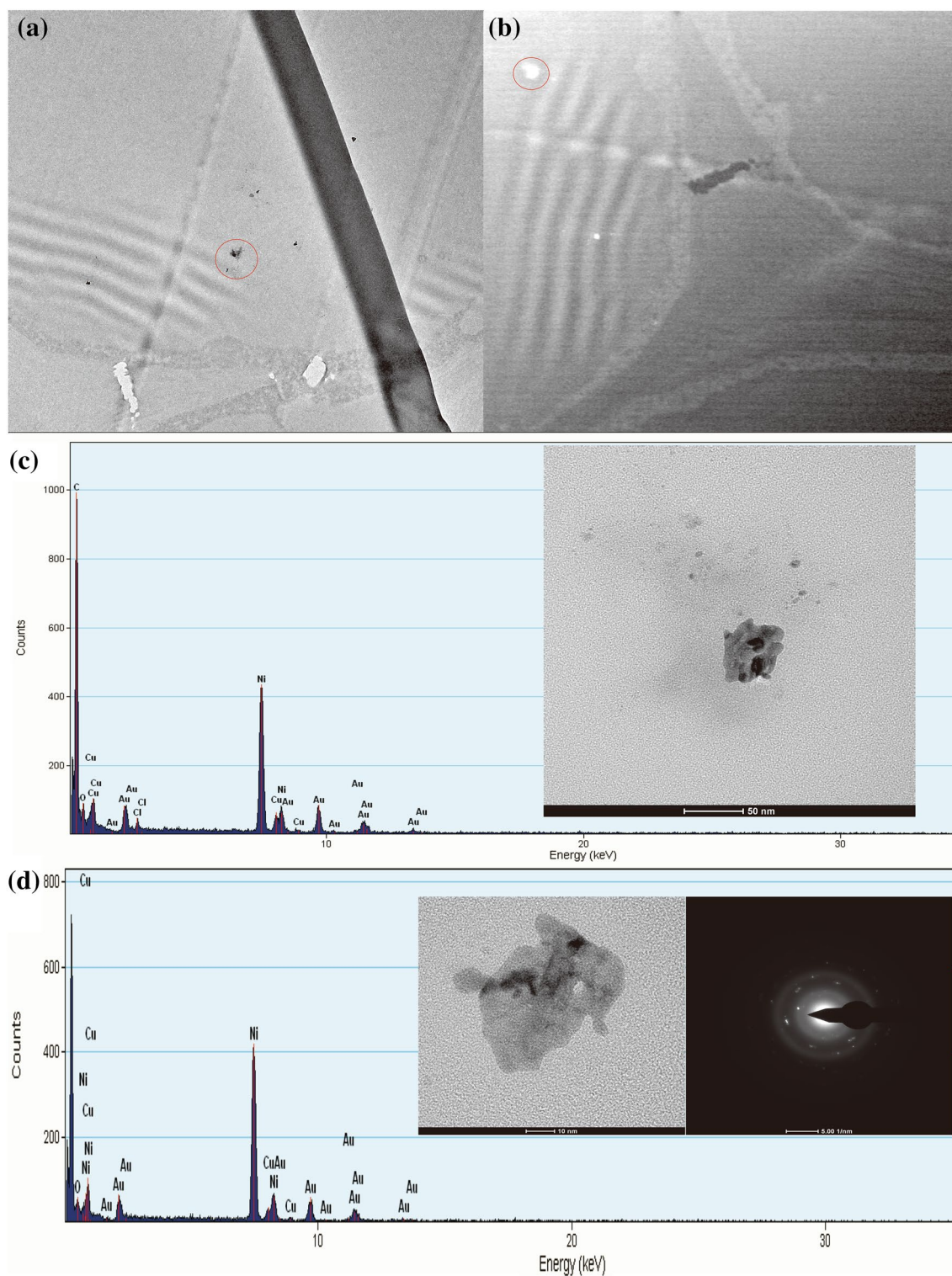


Fig. 1 Au-bearing nanoparticles in the plant *E. canadensis*. Transmission electron microscope (TEM) photomicrograph (a) and scanning TEM (STEM) photomicrograph (b) of nanoparticles. TEM images,

particle electron diffraction pattern and energy-dispersive X-ray spectroscopy (EDS) results of irregular Au-bearing particles (c, d)

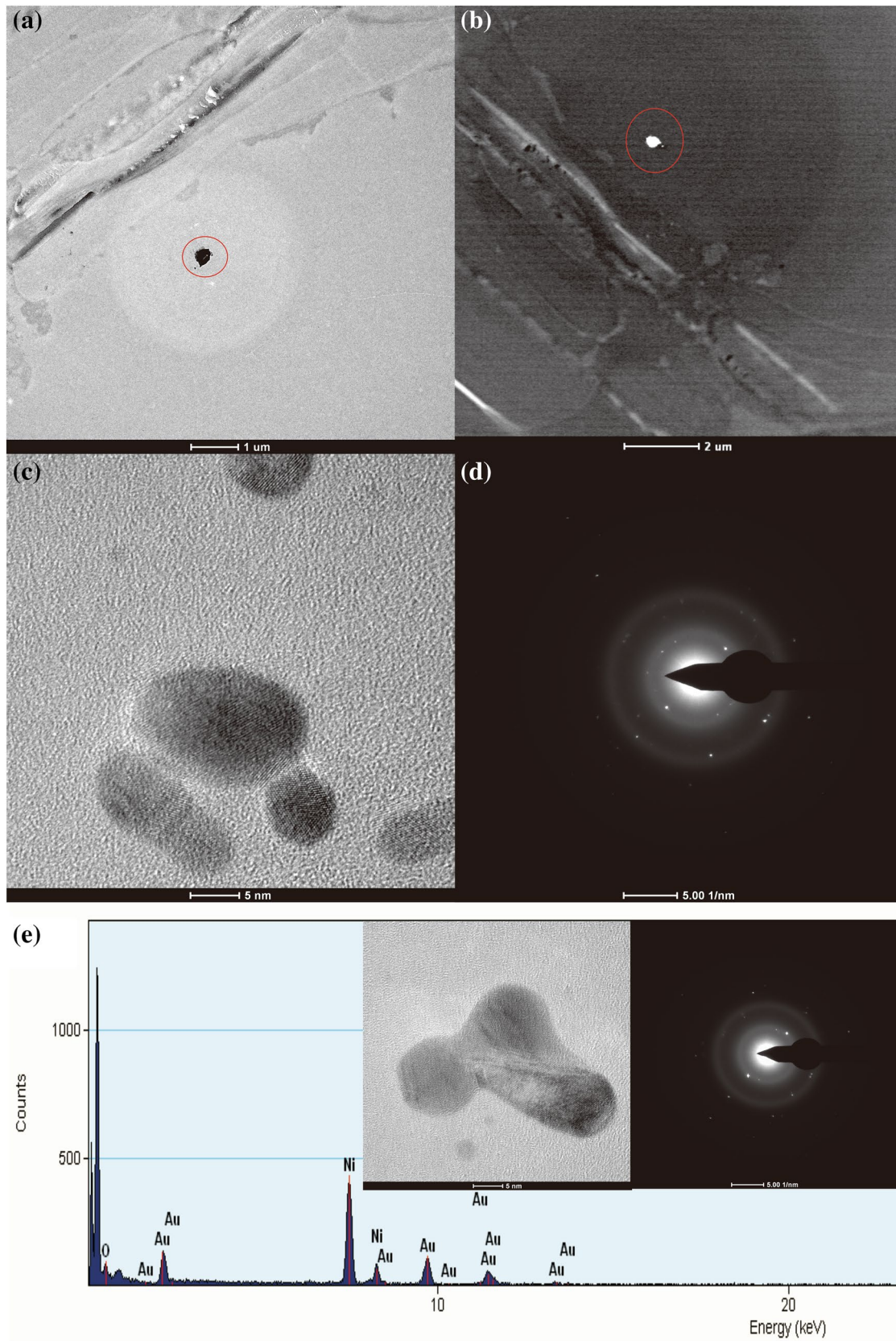


Fig. 2 Au-bearing nanoparticles in the plant *B. nivea*. Transmission electron microscope (TEM) photomicrograph (a) and scanning TEM (STEM) photomicrograph (b) of nanoparticles. High-resolution TEM photomicrographs (c, e), their electron diffraction patterns (d, e) and an energy-dispersive X-ray spectroscopy (EDS) result (e) of irregular Au-bearing particles

humidity. No metal deposits were identified in the sampling area; however, there was an electroplating plant nearby. The pollution of the electroplating plant is very serious because it not only discharges heavy metal pollutants and eluates, but also the discharged acid gas can corrode the metal articles. The surrounding air, water and soil were more or less polluted by waste from the factory, which included metal nanoparticles. Therefore, we theorised that the factory would have an effect on the formation of gold nanoparticles in the plant tissues.

The mechanism of nanoparticles entry and accumulation within the plant body

It is uncertain how these Au nanoparticles were absorbed by the plants. Previous investigations have revealed that there are two ways by which metal elements enter plant tissues. One is by root absorption (Bali et al. 2010; Lintern et al. 2013; Fontes et al. 2014). In general, dissolved metal elements in plants are primarily absorbed from the soil by the roots, where they gradually accumulate and are then transferred to other plant tissues. It is generally recognised that gold is imbibed through roots in the biogeochemical cycle and then combined with organic compounds to form organic complexes or chelates. Separating border cells (border cells separated from the root) and mucus can accumulate and capture metal nanoparticles regardless of particle charge (Avellan et al. 2017). Plants have previously been induced to accumulate gold from ores (Cwn et al. 1998; Robinson et al. 1997), which supports the possibility of root absorption. A previous study has shown that gold ions accumulated by plants (Alfalfa) and stored in leaf and stem biomass can be reduced to form discrete nanoparticles of pure metal (Gardea-Torresdey et al. 2002). So one possibility is that gold ions absorbed by roots can be reduced in the plant tissues (Anand et al. 2016; Lintern et al. 2013). And it has been proved that nanoparticles could be absorbed directly by the plant body through root uptake also and then translocated through the plant tissues (Stone 2010; Cifuentes et al. 2010). Some studies have shown that nanoparticles can be absorbed and transported by plants, but their storage locations vary (Lin et al. 2009; Parsons et al. 2010; Wild and Jones 2009; Zhang et al. 2011; Zhu et al. 2008).

Another alternate route for the absorption of metal nanoparticles is via plant surfaces. Nanoparticles in the atmosphere may settle on leaves or upper roots and enter through

trichomes or stomata before being transported to other tissues of plant (Nair et al. 2010; Eichert et al. 2008; Navarro et al. 2008). It is well known that plants possess natural barriers to absorption and transport, such as cutin, a cork layer and the Casparian strip, which makes it difficult for nanoparticles to enter plant cells (Schreiber 2010). Above the ground, nanoparticles may enter the plant through the non-cuticle parts, such as drainage holes, stomata and stigma, but they would have to pass through the cork layer and Casparian strip before reaching the vascular cylinder (Kurepa et al. 2010; Lee et al. 2008; Lin and Xing 2008; Wang et al. 2012). The plant cell wall is porous, with a pore diameter of 5–20 nm; consequently, nanoparticles smaller than this diameter can commonly enter the cell. However, new and larger pores created by smaller nanoparticles enable the larger nanoparticles to enter (Navarro et al. 2008). The diameter of Au nanoparticles found in the plant tissues ranges from 5 to 50 nm, so these nanoparticles were most likely to be absorbed through pores directly.

In the present study, Au-bearing nanoparticles in the stems were found around the plant microtubules instead of in the microtubules, and EDS analyses corroborated that these nano-sized particles were not of pure gold. The irregular shape of Au-bearing particles was different from the morphology of natural Au reported in a previous study (Cao et al. 2009; Hu et al. 2015). They were also not very crystalline, as evidenced by SAED analysis, indicating that these Au-bearing nanoparticles were artificial and absorbed by plants directly through the stoma and that the electroplating factory may be the primary source of pollution.

The influence of the discovery of Au-bearing nanoparticles in natural plants

Gold has been used for centuries as currency, hedge and in jewellery production, and Au nanoparticles hold a great potential for use in medicine and biology because of their characteristic high electron density, dielectric properties and catalysis and their lack of influence on biological activities of macromolecules (Dykman and Khlebtsov 2012; Liu and Ye 2013; Sotnikov et al. 2015). Over the last decade or so, a number of studies have been conducted on the use of plants for the synthesis of gold nanoparticles (Avellan et al. 2017; Gan and Li 2012; Kumar et al. 2013; Mubarakali et al. 2011; Shankar et al. 2003, 2004). However, most of them involved the production of gold nanoparticles using plant extracts instead of intracellular reduction. To the best of our knowledge, this is the first report on the presence of gold nanoparticles in plants growing in a natural environment without a gold-containing substrate, and the detailed characteristic of Au nanoparticles has been presented using TEM for the first time. We hope that the findings of this study can be put to use in the treatment of nano-material pollution

Table 1 Energy-dispersive X-ray spectroscopy (EDS) analysis of metal-bearing particles in the plant *E. canadensis* (Fig. 1c)

Element	Weight (%)	Atomic percentage (%)
O(K)	8.52	44.81
Cl(K)	2.22	5.27
Cu(K)	13.26	17.52
Au(L)	76.00	32.40

Table 2 Energy-dispersive X-ray spectroscopy (EDS) analysis of Au-bearing particles in the plant *E. canadensis* (Fig. 1e)

Element	Weight (%)	Atomic percentage (%)
O(K)	7.46	49.95
Au(L)	92.54	50.05

Table 3 Energy-dispersive X-ray spectroscopy (EDS) analysis of Au-bearing particles in the plant *B. nivea* (Fig. 2e)

Element	Weight (%)	Atomic percentage (%)
O(K)	6.35	45.54
Au(L)	93.65	54.46

and the enrichment of Au nanoparticles using plants. The safety effect of nanotechnology and nano-materials is an important social issue closely related to human society. As an important component of the ecosystem, plants can influence the environmental fate, migration and ecotoxicity of nanoparticles through absorption and bioaccumulation, and may become potential pathways for nanoparticle migration and bioaccumulation in the food chain. Therefore, the study of the absorption, transport and toxicity effects of plants on nanoparticles has an important role in the evaluation of the biological effects of nanoscale substances, the impact on human health and environmental risks.

Conclusion

In this study, Au-bearing nanoparticles were discovered in plant tissues (*E. canadensis* and *B. nivea*) using TEM. These Au-bearing nanoparticles were nearly 20–50 nm in diameter and had an irregular morphology in *E. canadensis*. EDS analysis revealed that components of some particles were mainly O (44.81%), Cl (5.27%), Cu (17.52%) and Au (32.40%), while others only consisted of Au (50.05%) and O (49.95%). In *B. nivea*, particles mainly consisted of Au

(54.46%) and O (45.54%) and were 5–15 nm in size and circular, elliptical or bone-rod shaped with smooth edges. In addition, particle electron diffraction patterns indicated that most of these nanoparticles were nearly crystalline. Based on our discussion of the absorption mechanism, we concluded that these Au-bearing nanoparticles were directly absorbed by the plants through their stomata. The discovery of Au-bearing nanoparticles in natural plant tissues is of great significance, providing new insights with respect to the accumulation of dispersed nanoparticles in contaminated areas and enrichment of Au nanoparticles using plants.

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References

- Anand RR, Aspandiar MF, Noble RRP (2016) A review of metal transfer mechanisms through transported cover with emphasis on the vadose zone within the Australian regolith. *Ore Geol Rev* 73:394–416. <https://doi.org/10.1016/j.oregeorev.2015.06.018>
- Andreotti F, Mucha AP, Caetano C, Rodrigues P, Gomes CR, Almeida CMR (2015) Interactions between salt marsh plants and Cu nanoparticles—effects on metal uptake and phytoremediation processes. *Ecotoxicol Environ Saf* 120:303–309. <https://doi.org/10.1016/j.ecoenv.2015.06.017>
- Avellan A, Schwab F, Masion A, Chaurand P, Borschneck D, Vidal V et al (2017) Nanoparticle uptake in plants: gold nanomaterial localized in roots of *Arabidopsis thaliana* by X-ray computed nanotomography and hyperspectral imaging. *Environ Sci Technol* 51:8682–8691. <https://doi.org/10.1021/acs.est.7b01133>
- Bali R, Siegele R, Harris AT (2010) Phytoextraction of Au: uptake, accumulation and cellular distribution in *Medicago sativa* and *Brassica juncea*. *Chem Eng J* 156(2):286–297. <https://doi.org/10.1016/j.cej.2009.10.019>
- Bhatt I, Tripathi BN (2011) Interaction of engineered nanoparticles with various components of the environment and possible strategies for their risk assessment. *Chemosphere* 82:308–317. <https://doi.org/10.1016/j.chemosphere.2010.10.011>
- Brooks RR, Lee J, Reeves RD, Jaffre T (1977) Detection of nickeliferous rocks by analysis of herbarium specimens of indicator plants. *J Geochem Explor* 7:49–57. [https://doi.org/10.1016/0375-6742\(77\)90074-7](https://doi.org/10.1016/0375-6742(77)90074-7)
- Brumfiel G (2003) Nanotechnology: a little knowledge. *Nature* 424:246–248. <https://doi.org/10.1038/424246a>
- Cao JJ, Hu X, Jiang D (2009) Transmission electron microscopy study of adsorption of colloidal gold nanoparticles on lepidocrocite and kaolinite. *Micro Nano Lett* 4:95–98. <https://doi.org/10.1049/mnl.2009.0023>
- Cifuentes Z, Custardoy L, de la Fuente JM, Marquina C, Ibarra MR, Rubiales D et al (2010) Absorption and translocation to the aerial part of magnetic carbon-coated nanoparticles through the root of different crop plants. *J Nanobiotechnol* 8(1):26. <https://doi.org/10.1186/1477-3155-8-26>
- Cwn A, Brooks RR, Stewart RB, Simcock R (1998) Harvesting a crop of gold in plants. *Nat Lond* 395:553–554

- Dykman L, Khlebtsov N (2012) Gold nanoparticles in biomedical applications: recent advances and perspectives. *Chem Soc Rev* 41(6):2256–2282. <https://doi.org/10.1002/chin.201224275>
- Eichert T, Kurtz A, Steiner U, Goldbach HE (2008) Size exclusion limits and lateral heterogeneity of the stomatal foliar uptake pathway for aqueous solutes and water-suspended nanoparticles. *Physiol Plant* 134(1):151–160. <https://doi.org/10.1111/j.1399-3054.2008.01135.x>
- El-Temsah YS, Joner EJ (2012) Impact of Fe and Ag nanoparticles on seed germination and differences in bioavailability during exposure in aqueous suspension and soil. *Environ Toxicol* 27(1):42–49. <https://doi.org/10.1002/tox.20610>
- Fontes RLF, Pereira JMN, Neves JCL, Fontes RLF, Pereira JMN, Neves JCL (2014) Uptake and translocation of Cd and Zn in two lettuce cultivars. *Anais Acad Bras Cienc* 86:907–922. <https://doi.org/10.1590/0001-37652014117912>
- Gan PP, Li SFY (2012) Potential of plant as a biological factory to synthesize gold and silver nanoparticles and their applications. *Rev Environ Sci Bio/Technol* 11(2):169–206. <https://doi.org/10.1007/s1157-012-9278-7>
- Gardea-Torresdey JL, Parsons JG, Gomez E, Peralta-Videa J et al (2002) Formation and growth of Au nanoparticles inside live alfalfa plants. *Nano Lett* 2(4):397–401. <https://doi.org/10.1021/nl015673>
- Glauret AM (1975) Fixation, dehydration and embedding of biological specimens. North-Holland Pub. Co, Oxford
- Hagler HK (2007) Ultramicrotomy for biological electron microscopy. *Methods Mol Biol* 369:67–96. https://doi.org/10.1007/978-1-59745-294-6_5
- Hu G, Cao JJ, Lai PX, Hopke PK, Holub RF, Zeng JN, Wang ZH, Wu ZQ (2015) Characteristics and geological significance of particles on fractures from the Dongshengmiao polymetallic pyrite deposit, Inner Mongolia, China. *Geochem Explor Environ Anal* 15:373–381. <https://doi.org/10.1144/geochem2014-312>
- Hu G, Cao J, Jiang T, Wang Z, Yi Z (2017) Prospecting application of nanoparticles and nearly nanoscale particles within plant tissues. *Resour Geol* 67(3):316–329. <https://doi.org/10.1111/rge.12130>
- Kumar V, Guleria P, Kumar V, Yadav SK (2013) Gold nanoparticle exposure induces growth and yield enhancement in *Arabidopsis thaliana*. *Sci Total Environ* 461–462:462–468. <https://doi.org/10.1016/j.scitotenv.2013.05.018>
- Kumari M, Mukherjee A, Chandrasekaran N (2009) Genotoxicity of silver nanoparticles in *Allium cepa*. *Sci Total Environ* 407:5243–5246. <https://doi.org/10.1016/j.scitotenv.2009.06.024>
- Kurepa J, Paunesku T, Vogt S, Arora H, Rabatic BM, Lu J et al (2010) Uptake and distribution of ultrasmall anatase TiO₂ Alizarin red S nanoconjugates in *Arabidopsis thaliana*. *Nano Lett* 10(7):2296–2302. <https://doi.org/10.1021/nl903518f>
- Lee WM, An YJ, Yoon H, Kweon HS (2008) Toxicity and bioavailability of copper nanoparticles to the terrestrial plants mung bean (*Phaseolus radiatus*) and wheat (*Triticum aestivum*): plant agar test for water-insoluble nanoparticles. *Environ Toxicol Chem* 27:1915–1921. <https://doi.org/10.1897/07-481.1>
- Lee WM, Kwak JI, An YJ (2012) Effect of silver nanoparticles in crop plants *Phaseolus radiatus* and *Sorghum bicolor*: media effect on phytotoxicity. *Chemosphere* 86:491–499. <https://doi.org/10.1016/j.chemosphere.2011.10.013>
- Lin D, Xing B (2007) Phytotoxicity of nanoparticles: inhibition of seed germination and root growth. *Environ Pollut* 150:243–250. <https://doi.org/10.1016/j.envpol.2007.01.016>
- Lin D, Xing B (2008) Root uptake and phytotoxicity of ZnO nanoparticles. *Environ Sci Technol* 42:5580–5585. <https://doi.org/10.1021/es800422x>
- Lin S, Reppert J, Hu Q, Hudson JS, Reid ML, Ratnikova TA, Ke PC (2009) Uptake, translocation, and transmission of carbon nanomaterials in rice plants. *Small* 5:1128–1132. <https://doi.org/10.1002/sml.200801556>
- Lintern M, Anand R, Ryan C, Paterson D (2013) Natural gold particles in Eucalyptus leaves and their relevance to exploration for buried gold deposits. *Nat Commun* 4(4):2614. <https://doi.org/10.1038/ncomms3614>
- Liu A, Ye B (2013) Application of gold nanoparticles in biomedical researches and diagnosis. *Clin Lab* 59(1–2):23. <https://doi.org/10.7754/clin.lab.2012.120614>
- Liu R, Zhang H, Lal R (2016) Effects of Stabilized nanoparticles of copper, zinc, manganese, and iron oxides in low concentrations on lettuce (*Lactuca sativa*) seed germination: nanotoxicants or nanonutrients? *Water Air Soil Pollut* 227(1):1–14. <https://doi.org/10.1007/s11270-015-2738-2>
- Meyer DE, Curran MA, Gonzalez MA (2009) An examination of existing data for the industrial manufacture and use of nanocomponents and their role in the life cycle impact of nanoproducts. *Environ Sci Technol* 43(5):1256–1263. <https://doi.org/10.1021/es8023258>
- Mubarakali D, Thajuddin N, Jeganathan K, Gunasekaran M (2011) Plant extract mediated synthesis of silver and gold nanoparticles and its antibacterial activity against clinically isolated pathogens. *Colloids Surf B* 85(2):360–365. <https://doi.org/10.1016/j.colsurfb.2011.03.009>
- Nair R, Varghese SH, Nair BG, Maekawa T, Yoshida Y, Kumar DS (2010) Nanoparticulate material delivery to plants. *Plant Sci* 179(3):154–163. <https://doi.org/10.1016/j.plantsci.2010.04.012>
- Navarro E, Baun A, Behra R, Hartmann NB, Filser J, Miao AJ, Sigg L (2008) Environmental behavior and ecotoxicity of engineered nanoparticles to algae, plants, and fungi. *Ecotoxicology* 17(5):372–386. <https://doi.org/10.1007/s10646-008-0214-0>
- Nel A, Xia T, Mädler L, Li N (2006) Toxic potential of materials at the nanolevel. *Science* 311(5761):622–627. <https://doi.org/10.1126/science.1114397>
- Parsons JG, Lopez ML, Gonzalez CM, Peralta-Videa JR, Gardea-Torresdey JL (2010) Toxicity and biotransformation of uncoated and coated nickel hydroxide nanoparticles on mesquite plants. *Environ Toxicol Chem* 29(5):1146–1154. <https://doi.org/10.1002/etc.146>
- Rico CM, Majumdar S, Duarte-Gardea M (2011) Interaction of nanoparticles with edible plants and their possible implications in the food chain. *J Agric Food Chem* 59(8):3485–3498. <https://doi.org/10.1021/jf104517j>
- Robinson BH, Brooks RR, Howes AW, Kirkman JH, Gregg PEH (1997) The potential of the high-biomass nickel hyperaccumulator *Berkheya coddii* for phytoremediation and phytomining. *J Geochem Explor* 60(2):115–126. [https://doi.org/10.1016/s0375-6742\(97\)00036-8](https://doi.org/10.1016/s0375-6742(97)00036-8)
- Schreiber L (2010) Transport barriers made of cutin, suberin and associated waxes. *Trends Plant Sci* 15(10):546–553. <https://doi.org/10.1016/j.tplants.2010.06.004>
- Service RF (2003) Nanomaterials show signs of toxicity. *Science* 300:243. <https://doi.org/10.1126/science.300.5617.243a>
- Shankar SS, Ahmad A, Pasricha R, Sastry M (2003) Bioreduction of chloroaurate ions by geranium leaves and its endophytic fungus yields gold nanoparticles of different shapes. *J Mater Chem* 13(7):1822–1826. <https://doi.org/10.1039/b303808b>
- Shankar SS, Rai A, Ahmad A, Sastry M (2004) Rapid synthesis of Au, Ag, and bimetallic Au core–Ag shell nanoparticles using Neem (*Azadirachta indica*) leaf broth. *J Colloid Interface Sci* 275(2):496–502. <https://doi.org/10.1016/j.jcis.2004.03.003>
- Sotnikov DV, Zherdev AV, Dzantiev BB (2015) Development and application of a label-free fluorescence method for determining the composition of gold nanoparticle–protein conjugates. *Int J Mol Sci* 16(1):907–923. <https://doi.org/10.3390/ijms16010907>

- Stampoulis D, Sinha SK, White JC (2009) Assay-dependent phytotoxicity of nanoparticles to plants. *Environ Sci Technol* 43(24):9473–9479. <https://doi.org/10.1021/es901695c>
- Stone MB (2010) Differential uptake of carbon nanoparticles by plant and Mammalian cells. *Small* 6(5):612–617. <https://doi.org/10.1002/smll.200901911>
- Wang Z, Xie X, Zhao J, Liu X, Feng W, White JC, Xing B (2012) Xylem- and phloem-based transport of CuO nanoparticles in maize (*Zea mays* L.). *Environ Sci Technol* 46(8):4434–4441. <https://doi.org/10.1021/es204212z>
- Wild E, Jones KC (2009) Novel method for the direct visualization of in vivo nanomaterials and chemical interactions in plants. *Environ Sci Technol* 43(14):5290–5294. <https://doi.org/10.1021/es900065h>
- Yang X, Pan H, Wang P, Zhao FJ (2016) Particle-specific toxicity and bioavailability of cerium oxide (CeO₂) nanoparticles to *Arabidopsis thaliana*. *J Hazard Mater* 322(Pt A):292–300. <https://doi.org/10.1016/j.jhazmat.2016.03.054>
- Yin L, Cheng Y, Espinasse B, Colman BP, Auffan M, Wiesner M, Bernhardt ES (2011) More than the ions: the effects of silver nanoparticles on *Lolium multiflorum*. *Environ Sci Technol* 45(6):2360–2367. <https://doi.org/10.1021/es103995x>
- Zhang Z, He X, Zhang H, Ma Y, Zhang P, Ding Y, Zhao Y (2011) Uptake and distribution of ceria nanoparticles in cucumber plants. *Metallomics Integr Biometal Sci* 3(8):816. <https://doi.org/10.1039/c1mt00049g>
- Zhu H, Han J, Xiao JQ, Jin Y (2008) Uptake, translocation, and accumulation of manufactured iron oxide nanoparticles by pumpkin plants. *J Environ Monit JEM* 10(6):713–717. <https://doi.org/10.1039/b805998e>