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

Supplementary information

Applications of Surface-Enhanced Raman Spectroscopy on Nanoparticle Analysis in the Environment

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Table S1. Current analytical techniques for NP detection and their pros/cons.

Techniques		Information provided	Pros	Cons	Ref
Light scattering techniques	Dynamic light Scattering	Hydrodynamic diameter	Quick, no sample consumption	Matrix interference, disability to measure smaller particles in polydispersed samples	[1,2]
	Multi-angle light-scattering	Particle shape	Shape measurement, no sample consumption	Matrix interference	[3,4]
	Nanoparticle tracking analysis	Hydrodynamic diameter, particle number concentration	Quick, sensitive, suitable to measure polydispersed samples, minimal sample disturbance	Matrix interference, reduced sensitivity for small particles and/or materials of low refractive index.	[5]
Electron microscopy	Transmission electron microscopy (TEM)	Size, shape, elemental composition (+EDS[a]), crystal structure (+SAED[b])	Accurate size and shape measurement	Complex sample preparation, matrix interference, highly localized sampling area	[1,6]
	Scanning electron microscopy	Size, shape, elemental composition	Accurate size and shape measurement	Complex sample preparation, matrix	[1,6]

	(SEM)	(+EDS)		interference, highly localized sampling area	
Atomic spectrometry	Inductively coupled plasma mass spectrometry (ICP-MS)	Elemental concentration	High sensitivity (ng/L)	Laborious sample digestion and dilution, speciation disability	[4,6]
	Single particle ICP-MS	Size and concentration (number and mass) of NPs	High sensitivity (ng/L or 10^6/L), size discrimination	Matrix interference, high size detection limit (>40 nm) for Ti, Zn, Cu and their oxide NPs, inaccurate measurement upon incomplete vaporization	[7–9]
	Field flow fractionation ICP-MS (FFF-ICP-MS)	Size and concentration (number and mass) of NPs	Separation and detection of a wide size range of NPs, protection of the native states of NPs	Interference of the NPs elution by biomolecules, low recovery (<80%), complicated optimization of working conditions	[10–12]
	Graphite furnace atomic absorption spectrometry (GFAA)	Elemental concentration	High sensitivity, efficient, no laborious digestion, low maintenance	Narrow linear range, one element each time, Complex sample preparation,	[13]

			and cost	speciation disability	
	X-ray absorption spectroscopy	Speciation and element distribution, geometry and oxidation states	Minimal sample preparation, little alteration of the physical and chemical original states of NPs	Low sensitivity, limited access and complicated data analysis	[14]
Electroanalytical techniques	Voltammetry of immobilized particles (VIP)	Chemical composition, oxidation state, size, mass concentration	Efficient, cost-effective	Unpractical for detecting trace levels of NPs in the environment due to the low sensitivity	[15,16]
	Particle collision coulometry (PCC)	Size, number concentration, mass concentration	High sensitivity, portability	Problematic to detect NPs in mixtures with their ionic species	[13]

[a] EDS: energy dispersive X-ray spectroscopy. [b] SAED: selected-area electron diffraction.

Table S2. Summary of potential nanomaterial analytes by SERS.

Category	**Nanomaterials**	**Potential indicators**	**Enhancement mechanisms**	**Ref**
Metal	Nickel nanowires	Crystal violet	Electromagnetic enhancement	[17]
	Copper nanoparticles	1,10-phenanthroline (phen), 4,4'-bipyridine (bipy)	ND[a]	[18]
	Copper nanoparticles	4-mercaptopyridine (4-Mpy)	ND	[19]
	Palladium	4-Mpy	Electromagnetic	[20]

	nanoplates		enhancement	
	Pt, Ru, Rh, Pd, Fe, Co, Ni, and their nanoalloys	Pyridine	Electromagnetic enhancement and charge transfer	21
Metal oxide	Cu_2O nanocrystals	4-Mpy	ND	22
	Cu_2O porous nanostructures	4- aminothiophenol (4-ATP) and dimercaptoazobenzene (DMAB)	Charge transfer and electromagnetic enhancement	23
	Cu_2O porous nanowires	4-aminobenzenethiol	ND	24
	Cu_2O nanospheres	4-mercaptobenzoic acid (4-MBA) and 4-Mpy	Charge transfer and electromagnetic enhancement	25
	One-dimensional ZnO nanostructures, nanowires and nanocones	4-Mpy	Cavity-like structural resonance of the electric field	26
	Porous ZnO nanosheets	4-MBA	Charge transfer	27
	ZnO nanorods	4-Mpy, 4-aminothiophenol (PATP), $(Bu_4N)_2[Ru(dcbpyH)_2-(NCS)_2]$ (N719) and acetaminophen	Charge transfer	28
	ZnO nanorods	Methyl orange (MO)	Charge transfer	29
	ZnO nanorods	4-Aminobenzenthiol	Charge transfer	30
	ZnO nanoparticles	4-Mpy and 4-MBA	Charge transfer	31

ZnO nanocrystals	4-Mpy	Charge transfer	32
Magnetite (Fe_3O_4) nanoparticles	Oxalate, pyrocatechol, cysteine	Electromagnetic enhancement	33
α-Fe_2O_3 colloids	Pyridine, 1,4-dioxane and 1-ethyl-3′-methyl-2-thiacyanine iodide	Electromagnetic enhancement for pyridine and 1-ethyl-3’-methyl-2-thiacyanine iodide; electromagnetic enhancement and surface-induced molecular resonance enhancement for 1,4-dioxane	34
α-Fe_2O_3 nanospheres	4-Mpy	ND	35
α-Fe_2O_3 nanoparticles	4-Mpy and 2-mercaptobenzothiazole (2-MBT)	Charge transfer	36
α-Fe_2O_3 nanocrystals (sphere, spindle, cube)	4-Mpy	Charge transfer	37
TiO_2 nanoparticles	4-MBA	Charge transfer	38,39
Anatase, TiO_2 nanoparticles	Polymethoxyflavones	Charge transfer	40
Anatase, rutile and mixed TiO_2 nanoparticles	4-MBA	Charge transfer and the mixed crystal effect	41
TiO_2 nanoparticles	Nitrothiophenol isomers	Charge transfer	42
Rutile, TiO_2	L-DOPA	Charge transfer	43

	nanoparticles			
	TiO_2 nanoparticles	Enediol	Charge transfer	[44]
	TiO_2, Fe_2O_3, ZrO_2, and CeO_2 nanoparticles	Catechol	Charge transfer	[45]
	TiO_2, SnO_2 and α-Fe_2O_3 nanoparticles	Catechol and dopamine	Charge transfer	[46]
Graphene family	Graphene	Phthalocyanine (Pc), rhodamine 6G (R6G), protoporphyin IX (PPP), and crystal violet (CV)	Charge transfer	[47]
	Graphene	Copper phthalocyanine (CuPc)	Charge transfer	[48–50]
	Graphene	Metal phthalocyanine (M-Pc) molecules (M = Mn, Fe, Co, Ni, Cu, Zn)	Charge transfer	[51]
	Graphene oxide nanosheets	Rhodamine B (RhB)	Charge transfer	[52]
	Graphene	R6G, melamine, and cephalexin	Charge transfer	[53]
	Graphene, oxidized graphene	R6G	Charge transfer	[54]
Composite	Silver-deposited TiO_2 (Ag-TiO_2) nanoparticles	4-MBA	Charge transfer; Ag-induced additional electron injection into the molecules adsorbed on the TiO_2 surface through the conduction band of TiO_2 NPs	[55]
	Zn doped TiO_2	4-MBA	Charge transfer	[56]

	nanoparticles			
	Au-ZnO NP hybrids	PATP molecules	Charge transfer	57
	InAs/GaAs quantum dots	pyridine	Charge transfer	58
Others	ZnS nanocrystals	4-Mpy	ND	59
	PbS quantum dots	4-Mpy	Charge transfer	60
	CdTe quantum dots	4-Mpy	Charge transfer	61

[a] ND: not determined.

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