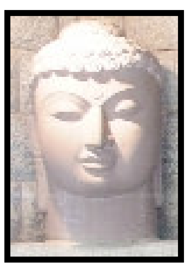
Noble metal nanoparticles for water purification: A critical review

Thin Solid Films



Professor Pradeep's Research Group

DST Unit on Nanoscience

IIT Madras

December 12, 2008

Content of the review article

Introduction – relationship of life and human civilization with water

- Water has been the most vital component of life during its existence on earth for last 3.5 billion years.

- The earliest form of life appeared in sea water (3.5 billion years ago) and transferred to land only 380 million years ago.

- Despite of this transfer to land, an ocean, in terms of fluidic composition, continues to exist within us. Similarly keeping a very high proportion of living organisms' body weight as water (~70%), Nature has iterated the vitality of water for life.

- Water is one of the purest signs of prosperity, health, serenity, beauty, artistry, purity and many other attributes. Leonardo Da Vinci had described water as "the vehicle of nature" ("*vetturale di natura*").

- The Nile was the lifeline of the Egyptian civilization. The Indus Valley civilization flourished on the banks of the Indus river.

Noble metals in human life

- Gold and silver belong to the family of "metals of antiquity", having their history with mankind dating back to 6,000 BC and 4,000 BC respectively. They have been associated with the gods, with immortality, and with wealth across the human civilizations.

- Use of noble metals in medicines is aplenty: swarna *bhasma*, tears of the sun, arthritis and anti-bacterial.

Drinking water purification – a historical perspective

Year	Milestone
1804	Setup of world's first city-wide municipal water treatment plant (Scotland, sand-filter technology)
1810	Discovery of chlorine as a disinfectant (Humphrey Davy)
1852	Formulation of Metropolis Water Act (England)
1879	Formulation of Germ Theory (Louis Pasteur)
1902	Use of Chlorine as disinfectant in drinking water supply (calcium hypo chlorite, Belgium)
1906	Use of ozone as disinfectant (France)
1908	Use of Chlorine as disinfectant in municipal supply, New Jersey
1914	Federal regulation of drinking water quality (USPHS)
1916	Use of UV treatment in municipal supplies
1935	Discovery of synthetic ion exchange resin (Adams, Holmes)
1948	Nobel Prize to Paul Hermann Müller (insecticidal properties of DDT)
1959	Discovery of synthetic reverse osmosis membrane (Yuster, Loeb, Sourirajan)
1962	Publishing of *Silent Spring,* first report on harmful effects of DDT (Rachel Carson)
1965	World's first commercial RO plant launched
1974	Reports on carcinogenic by-products of disinfection with chlorine
	Formulation of Safe Drinking Water Act (USEPA)
1975	Development of carbon block for drinking water purification
1994	Report on use Zerovalent Iron for degradation of halogenated organics (Gillham, Hannesin)
1997	Report on use Zerovalent Iron nanoparticles for degradation of halogenated organics (Wang, Zhang)
1998	Drinking Water Directive applied in EU
2000	Adoption of Millennium Declaration during the UN Millennium Summit (UN Millennium Development Goals)
2003	Report on use Noble metal nanoparticles for degradation of pesticides (Nair, Tom, Pradeep)
2004	Stockholm Convention, banning the use of persistent organic pollutants
2007	Launch of world's first nanotechnology based domestic water purifier (Pradeep, Eureka Forbes Limited)

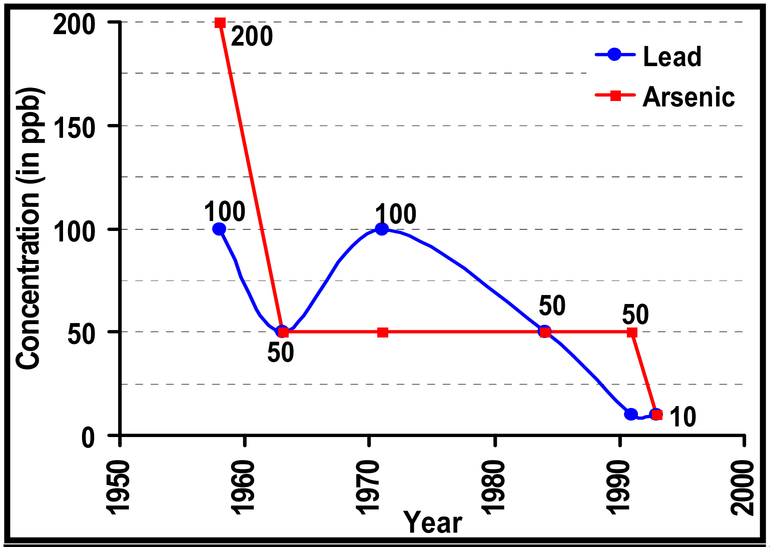
Important milestones in the history of water purification (1800-2007) multiple sources from internet

Review of major contaminants in drinking water

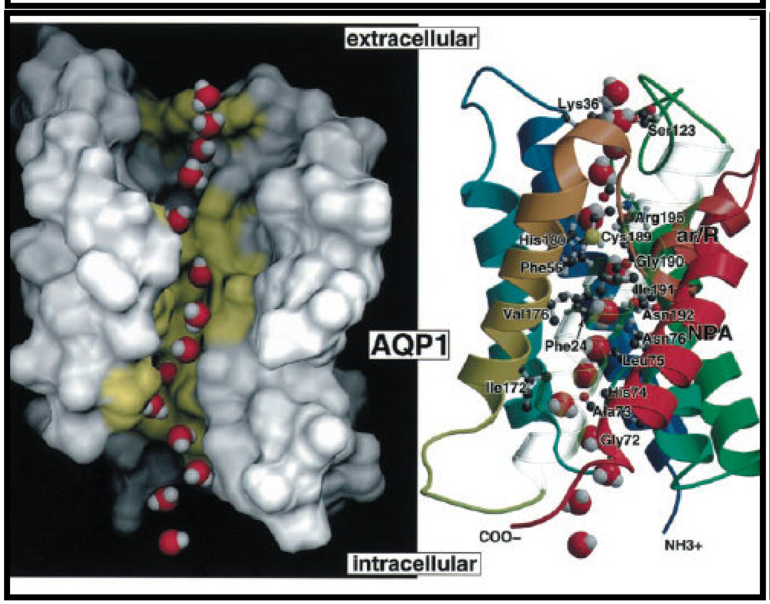
Major pollutant	Origin	Permissible limits	Affected countries	Population at risk	Health effects	Remarks
Pesticides	- Farming, effluents, home use	DDT: 1 ppb Carbofuran: 40 ppb Simazine: 4 ppb	US, Kenya, Egypt, India, European Union, Africa, China, Australia	Poisoning: 28 million agricultural workers in the developing countries. ~18,000 deaths.	Cancer, cardiovascular/ reproductive/ neurological disorders, Liver/kidney problems	Pesticide contamination in soft drinks, the Union Carbide Bhopal tragedy (India)
Halogenated organics	Chlorination, effluents, home insecticide	CCl_4: 5 ppb TCE: 5 ppb TTHMs: 80 ppb	Japan, Central Asia, Arabian Peninsula, Sweden, Poland, Germany, USA, Egypt, China	- ~180 million people in US consume chloraminated water	CCl_4: High toxicity to liver and kidney, carcinogenic. TCE: Lung/liver tumor	- 25 million pounds of TCE were released into the U.S. environment by manufacturing plants in 1995
Fluoride	- Geological origin, mineral weathering, coal mining	- 2 ppm	Asia, Mexico, Australia, Argentina, Africa, New Zealand	62 million (India)	- Dental and skeletal fluorosis, Muscle fibre regeneration, nervous system malfunction	- In 1999, a union of 1,200 scientists, doctors and lawyers announced their opposition to water fluoridation (USA)
Arsenic	- Geological origin	10 ppb	Bangladesh, India, China, Pakistan, Nepal, Myanmar, Vietnam	65 million (Asia)	High blood pressure, glucosuria, hyperpigmentation, keratoses, cancer	- 1 in 100 people (Conc: 0.05 mg/l) and 10 in 100 people (Conc: 0.5 mg/l) die due to cancer in long-term
Mercury	- Industrial pollution, dental filling, Food (fish)	- 2 ppb	Indonesia, China, Africa, Philippines, Japan, Kazakhstan, USA, Brazil, Australia, Taiwan, EU	~630,000 infants are born with high Hg content in the blood every year (EPA)	Neurotoxicant, tremors, respiratory failure, gastrointestinal failures, and kidney damage	- ~30% of the mercury in US comes from abroad e.g. China - Unilever plant, Kodaikanal (India). Minamata, Niigata (Japan), River Nura (Kazakhstan).
Lead	- Old piping lines, mineral weathering, paint	15 ppb	Egypt, EU, USA, Thailand, China, Cambodia	>300,000 US children and 65% of Shanghai children have high lead concentration	Delays in physical/ mental development, Kidney problem, high blood pressure	- Incidence of Gout due to leaded wine and rum - Use of lead in paints and discharge in environment

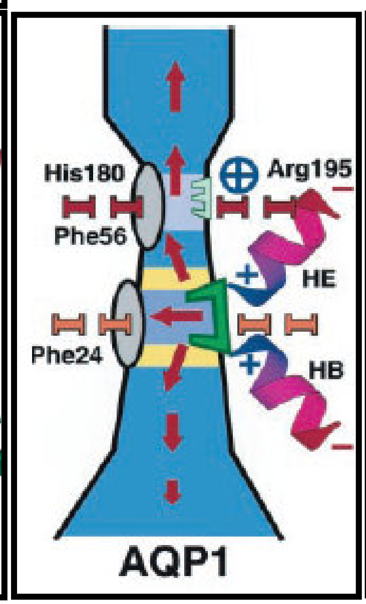
Review of major drinking water contaminants, their health impacts and a few associated events multiple sources from internet

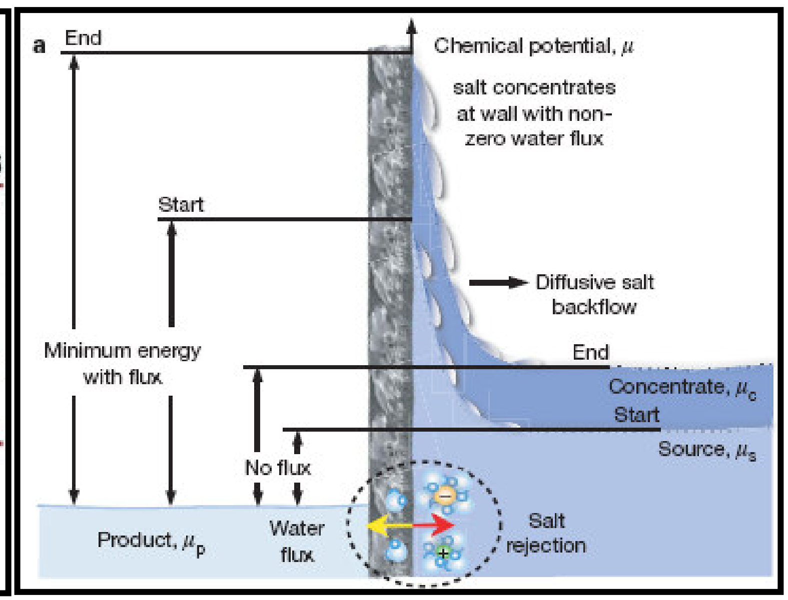
Important reasons for use of nanotechnology in drinking water purification



	Permeability coefficient (cm.s^{-1})	
Membrane preparation	D-Glucose	D-Mannitol
Synthetic lipid bilayer	2.4 X 10^{-10}	4.4 X 10^{-11}
Calculated non-mediated diffusion	4 X 10^{-9}	3 X 10^{-9}
Intact human erythrocyte	2 X 10^{-4}	5 X 10^{-9}





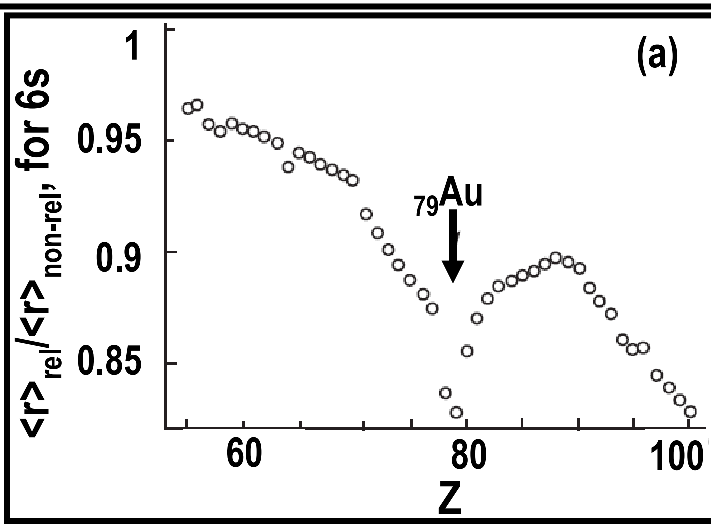


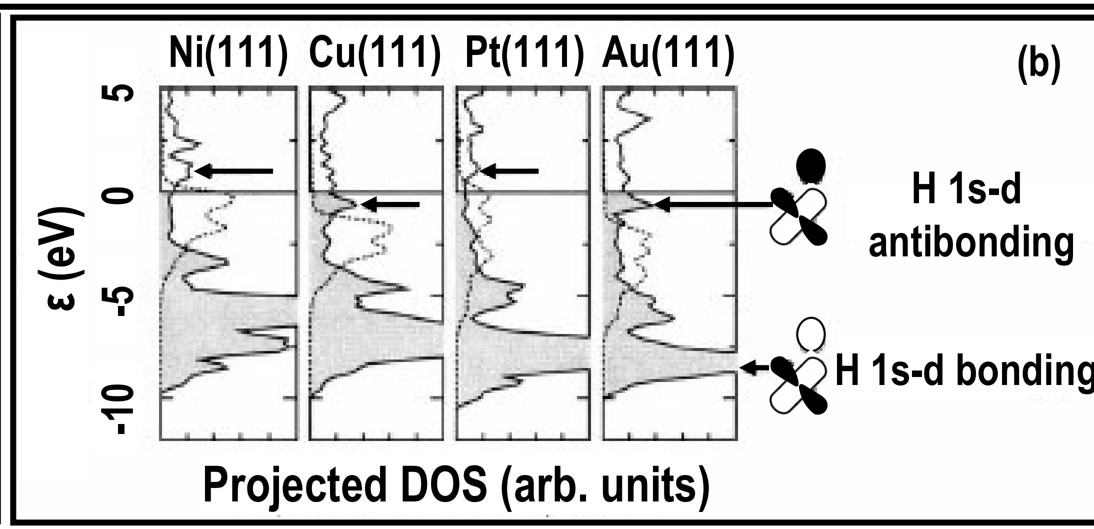
Science, 2001, 2353-57

Nature, 2008, 301-10

Origin of nobility at bulk scale

Noble metal	Atomic Number and Mass	Lattice Structure	Melting point (K)	Boiling point (K)	Electronegativity	Electron Affinity (kJ/mol)	Ionization energy (kJ/mol)	Radius (pm)	Hardness (MPa)	Density (kg/m^3)	Electrical conductivity (mho/cm)	Thermal conductivity (W/mK)
Copper	29/63.5	FCC	1,090	887	2.2	78	947	114	1,440	5,727	596	50
Gold	79/197	FCC	1,337	3,129	2.5	223	890	174	2,450	19,300	446	320
Silver	47/107.8	FCC	1,235	2,435	1.9	126	731	165	25	10,490	631	430
Platinum	78/195	FCC	2,041	4,098	2.3	205	870	177	392	21,090	94	72
Palladium	46/106.4	FCC	1,828	3,236	2.2	54	804	169	37	12,023	95	72
Mercury	80/200.6	Rhombohedral	234	630	2.0	0	1,007	171	-	13,534	10	8
Ruthenium	44/101	HCP	2,607	4,423	2.2	101	710	178	2,160	12,370	132	120
Rhodium	45/102.9	CCP	2,237	3,968	2.3	110	720	173	1,100	12,450	222	150
Rhenium	75/186.2	HCP	3,459	5,869	1.9	15	760	188	1,320	21,020	52	48
Osmium	76/190.2	HCP	3,306	5,285	2.2	106	840	185	3,920	22,610	105	88
Iridium	77/192.2	CCP	2,739	4,701	2.2	151	880	180	1,670	22,650	189	150
Average value: Noble metals	-	-	2,010	3,515	2	106	833	170	1,451	15,751	234	137
Average value: Transition metals	-	-	2,277	4,021	1.7	45	690	182	865	9,027	77	61

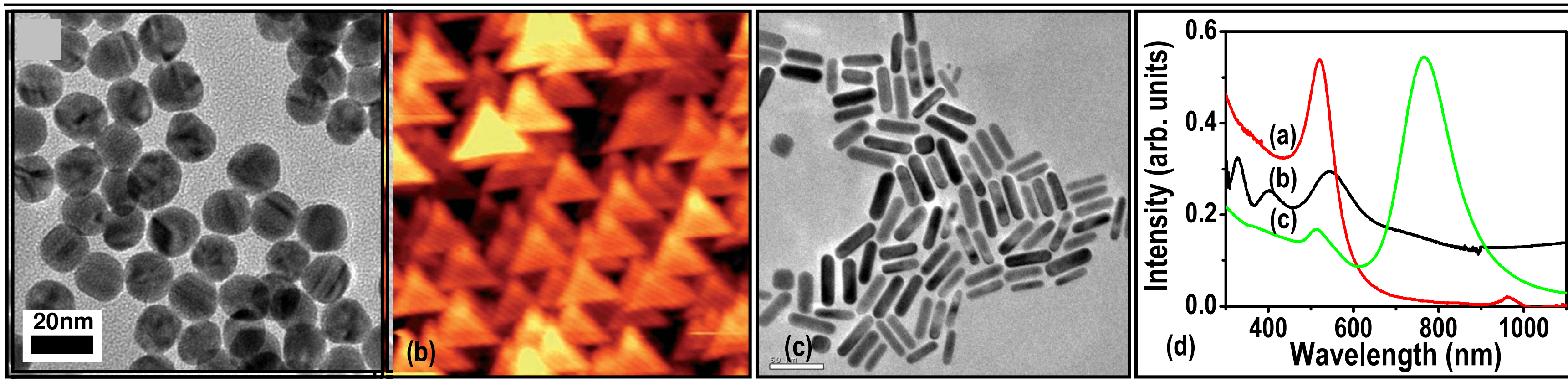




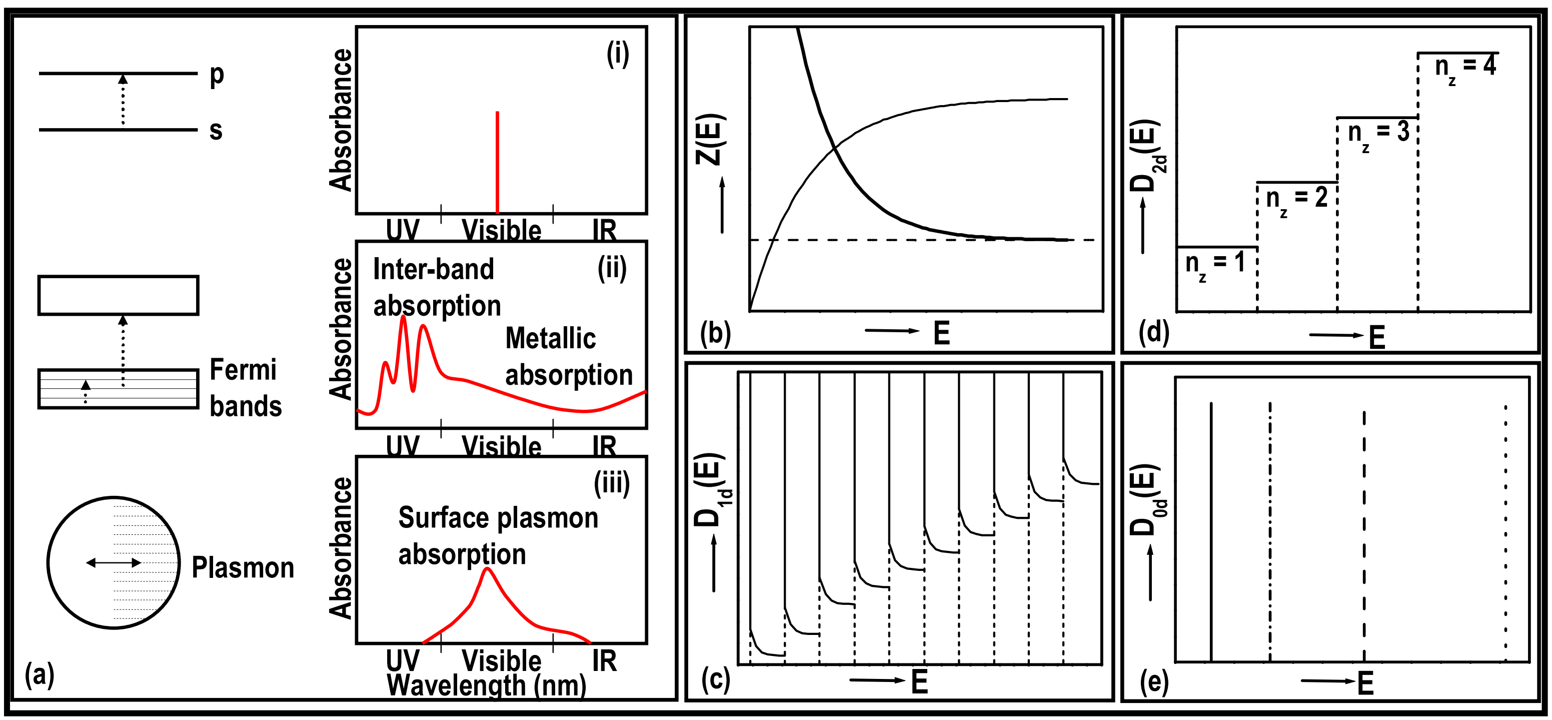
Acc. Chem. Res., 1979, 276-81

Nature, 1995, 238-40

Origin of reactivity at nanoscale

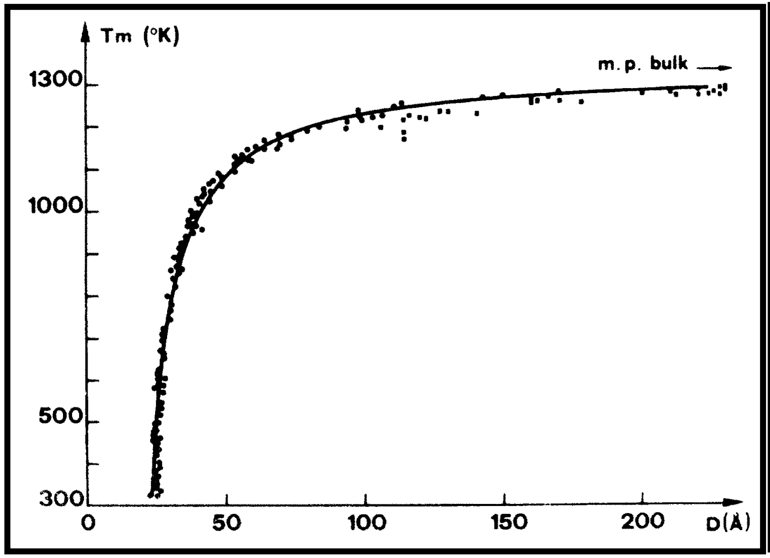


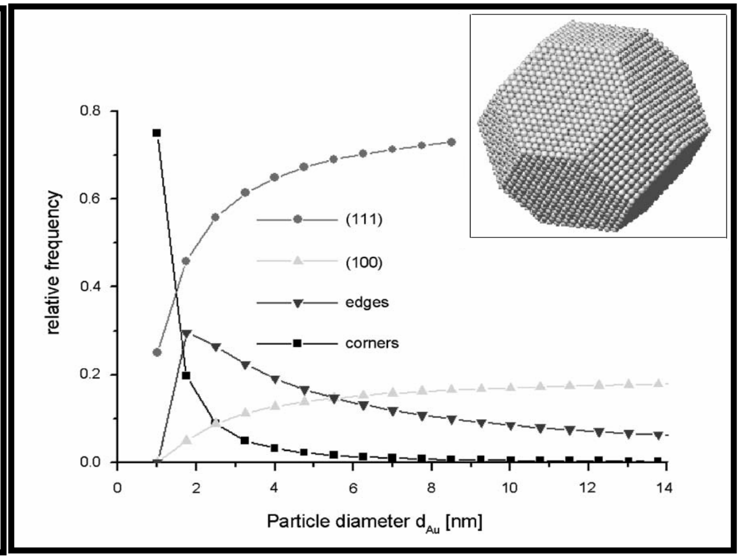
Gold Bullet. (submitted) *Adv. Mat.,2008, 980-83* *Langmuir 2008, 4589-99*



Origin of reactivity at nanoscale (continued)

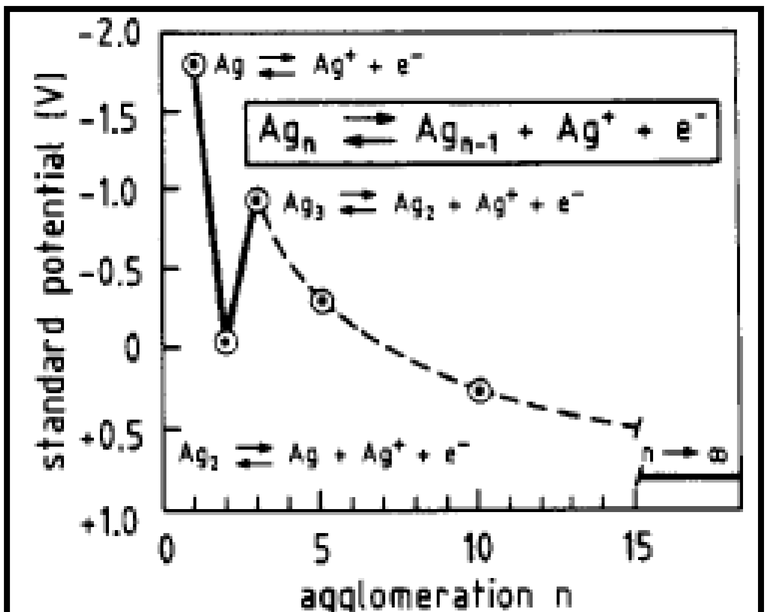
Phys. Rev. A, 1976, 2287-98

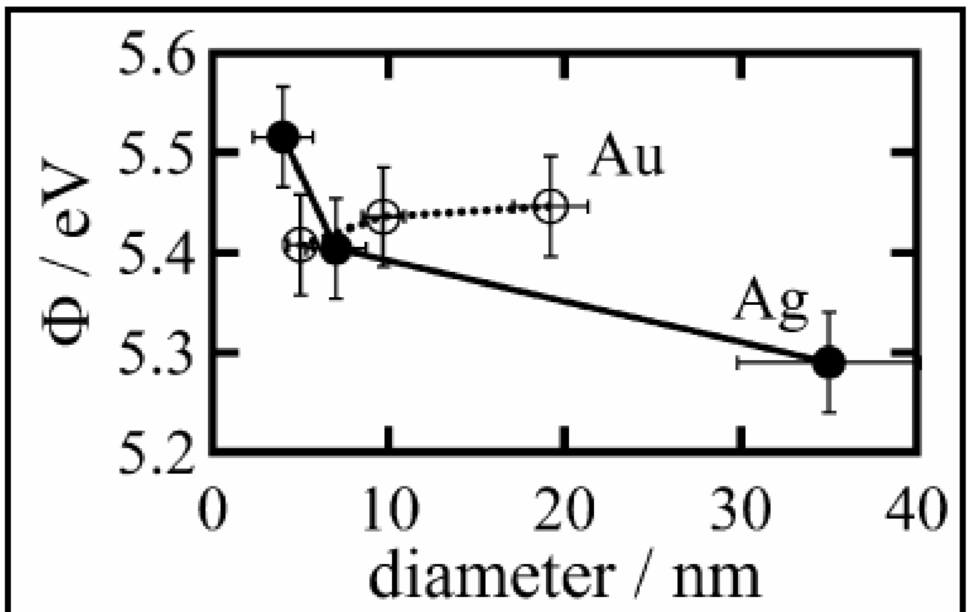




Catal. Today, 2002, 63–78

J. Phys. Chem., 1993, 5457-71





Nature, 1998, 396, 444–446
Phys. Chem. Chem. Phys., 2007, 725–30

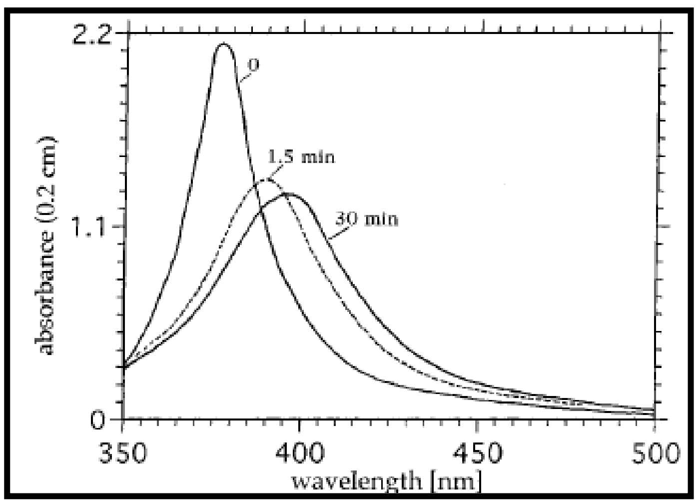
Drinking water purification: Novel reactions at the nano-scale

Chemistry of organic compounds with noble metal nanoparticles

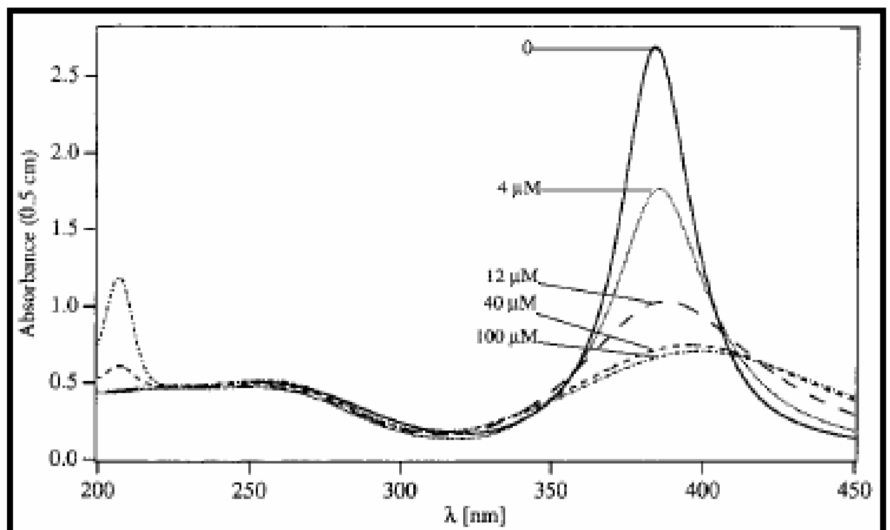
reaction[a]	products found
CCl_4 + Mg (ribbon) + H_2O	$Mg(OH)_2$; H_2; $CHCl_3$ trace
CCl_4 + Sn (mossy) + H_2O	$CHCl_3$; CO_2; HCl; SnO_2 (cassiterite)
CCl_4 + Sn (granular) + H_2O	the same; CO trace
CCl_4 + Sn (cryo) + H_2O	the same; CH_2Cl_2; $ClH_2C\text{-}CH_2Cl$ trace
CCl_4 + Zn (dust) + H_2O	$CHCl_3$; CH_2Cl_2; CH_3Cl; CH_4; $ZnCl_2$; $Zn(OH)_2$; CO trace
CCl_4 + Zn (cryo, 360 Å) + H_2O	the same; $ClH_2C\text{-}CH_2Cl$
$CHCl_3$ + Zn (dust) + H_2O	CH_2Cl_2; CH_3Cl; CH_4; $ZnCl_2$; $Zn(OH)_2$; CO trace
CH_2Cl_2 + Zn (dust) + H_2O	CH_3Cl; CH_4; $ZnCl_2$; $Zn(OH)_2$

Environ. Sci. Techno. 1995, 1511-17

$$Cl_2C{=}CCl_2 + H^+ + 2e^- \rightarrow Cl_2C{=}CClH + Cl^-$$
$$Cl_2C{=}CCl_2 + 2e^- \rightarrow ClC{\equiv}CCl + 2Cl^-$$
$$CCl_3H \rightarrow {:}CCl_2 + HCl \rightarrow \text{variety of products}$$
$$RCl_2C\text{-}CClHR' \rightarrow RClC{=}CClR' + H^+ + Cl^-$$
$$RClC{=}CClR + H_2 \rightarrow RHClC\text{-}CClHR$$



Chem. Mater., 1998, 444-50



J. Phys. Chem. B, 1998, 8364-66

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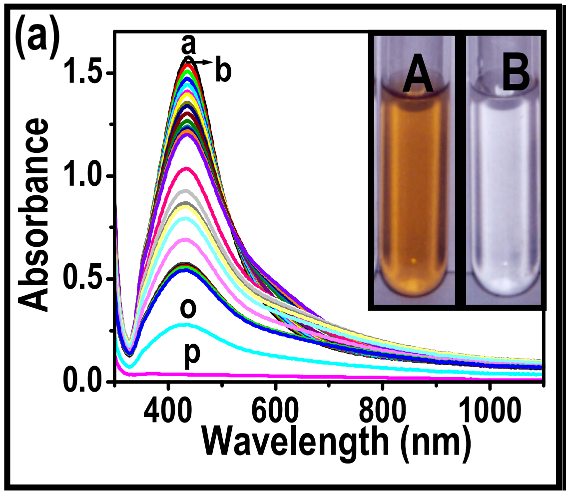
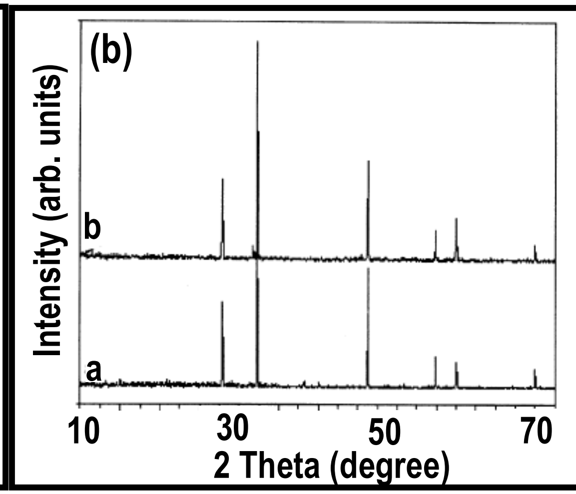
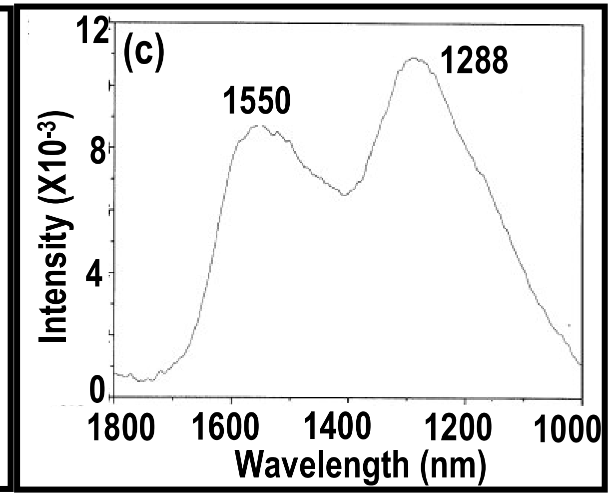
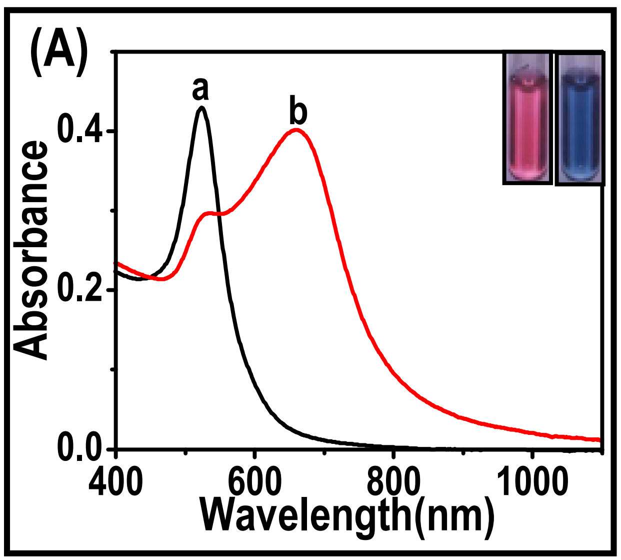
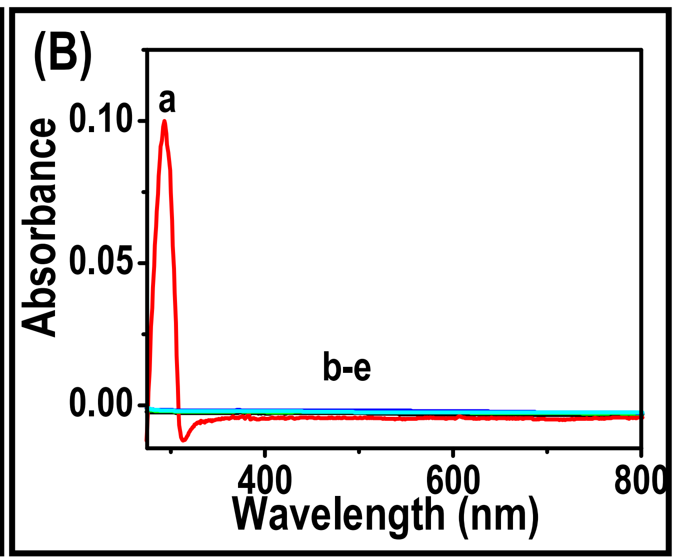


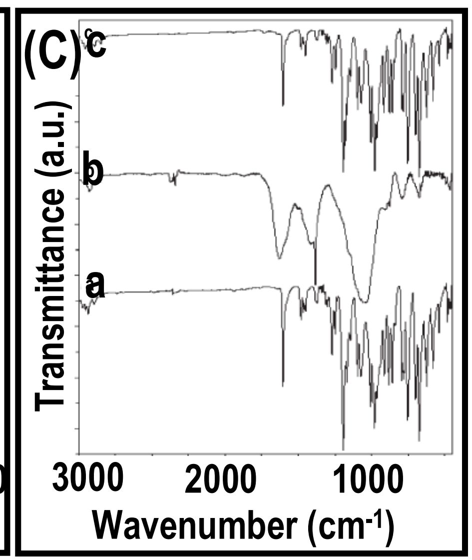




Curr. Sci., 2003, 1560-64





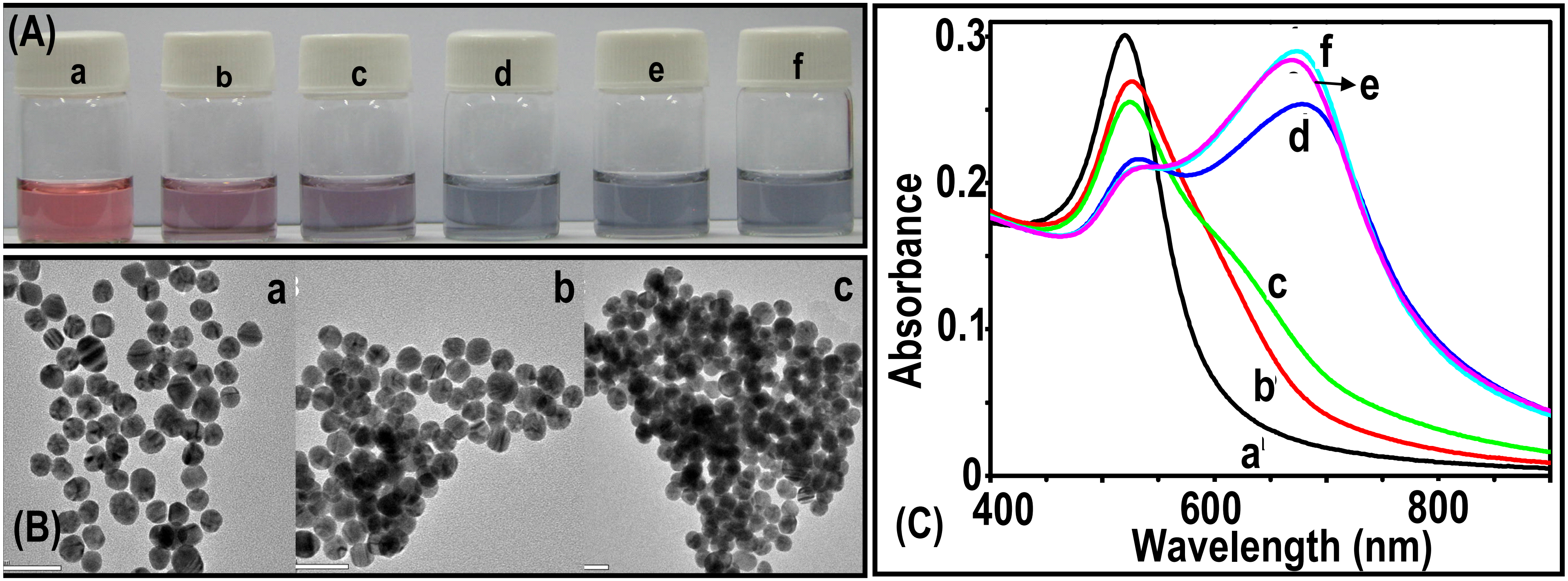


J. Environ. Monit., 2003, 363–65

J Nanosci Nanotechnol. 2007, 1871-7

Drinking water purification: Novel reactions at the nano-scale

Detection of pesticides in drinking water with noble metal nanoparticles



J. Environ. Health (submitted)

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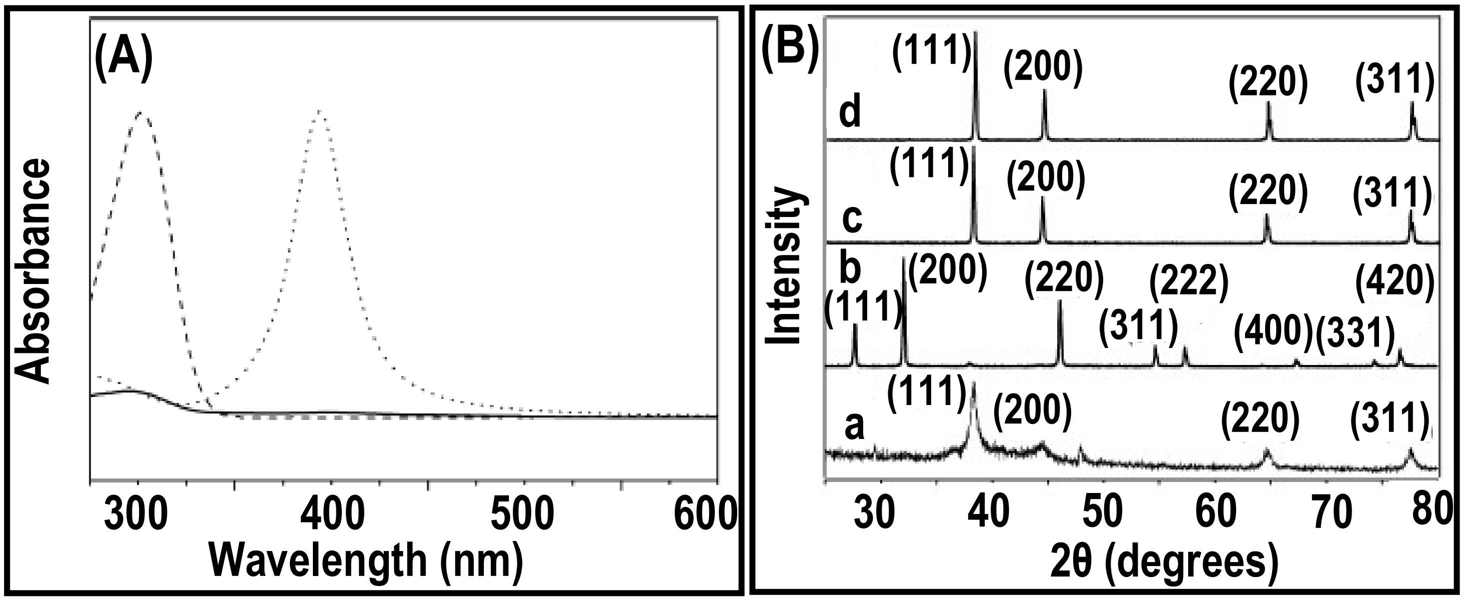
Chemistry of heavy metal ions with noble metal nanoparticles



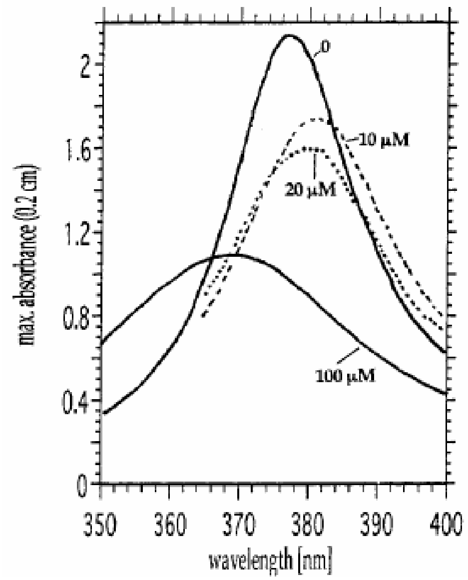
J. Colloid Interf. Sci. 2006, 415–18

Ag (s) + H^+ + Cl^- → AgCl (s) + H_2 E° = -0.22 V

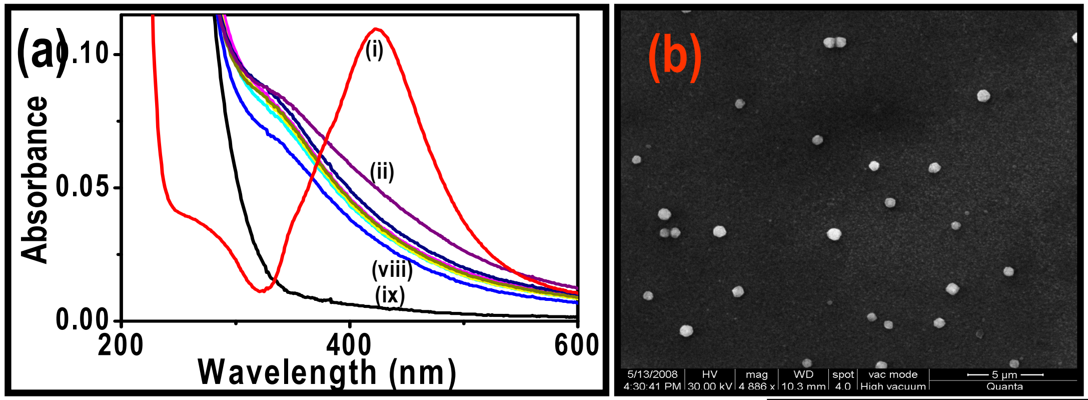
The non-reactivity of bulk silver can again be understood from the absence of driving force for the reaction. However, at the nano-scale, the feasibility of the reaction (i.e. E > 0) confirms the increasing reducing nature of the silver nanoparticle surface.

Drinking water purification: Novel reactions at the nano-scale

Chemistry of heavy metal ions with noble metal nanoparticles



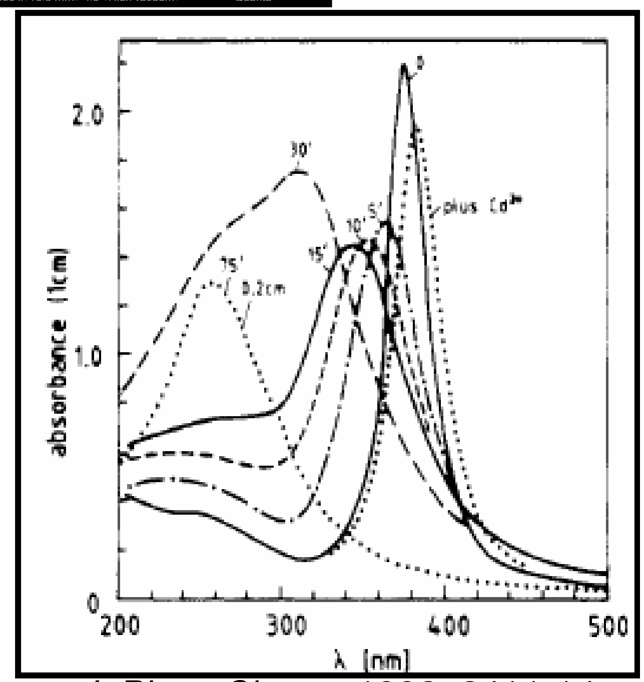
Chem. Mater., 1998, 444-50



$Ag \rightarrow Ag + e^-$ $E°_{oxidation} = -0.8$ V

$Hg^{2+} + 2e^- \rightarrow Hg$ $E°_{reduction} = 0.85$ V

$2Ag + Hg^{2+} \rightarrow Hg + 2Ag^+$ $E° = 0.05$ V



J. Phys. Chem., 1992, 2411-14

$Ag_n + Cu^{2+} \rightarrow Ag_{n-1} + Ag^+ + Cu^+$
followed by similar reaction of Ag_{n-1},
$Cu^+ + Ag_{n+m} \rightarrow Cu^{2+} + Ag^-_{n+m}$
$Ag^+ + Ag^-_{n+m} \rightarrow Ag_{n+m+1}$

Chem. Phys. Lett., 1989, 473-76

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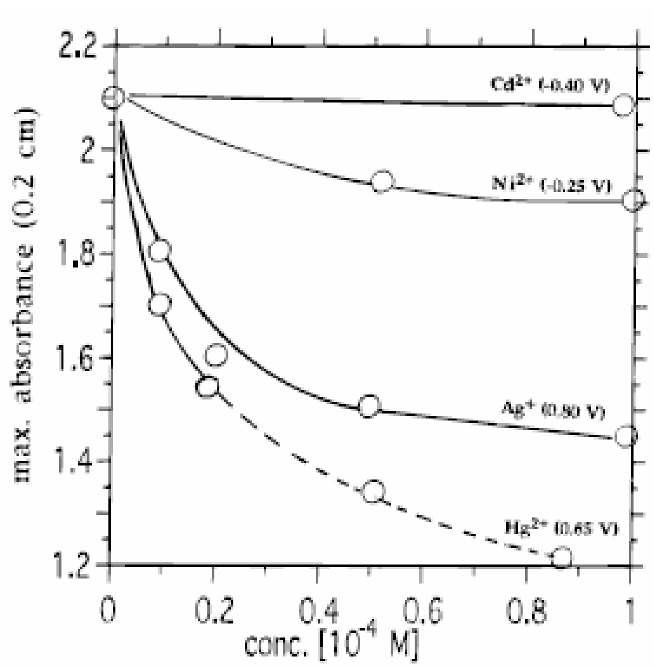
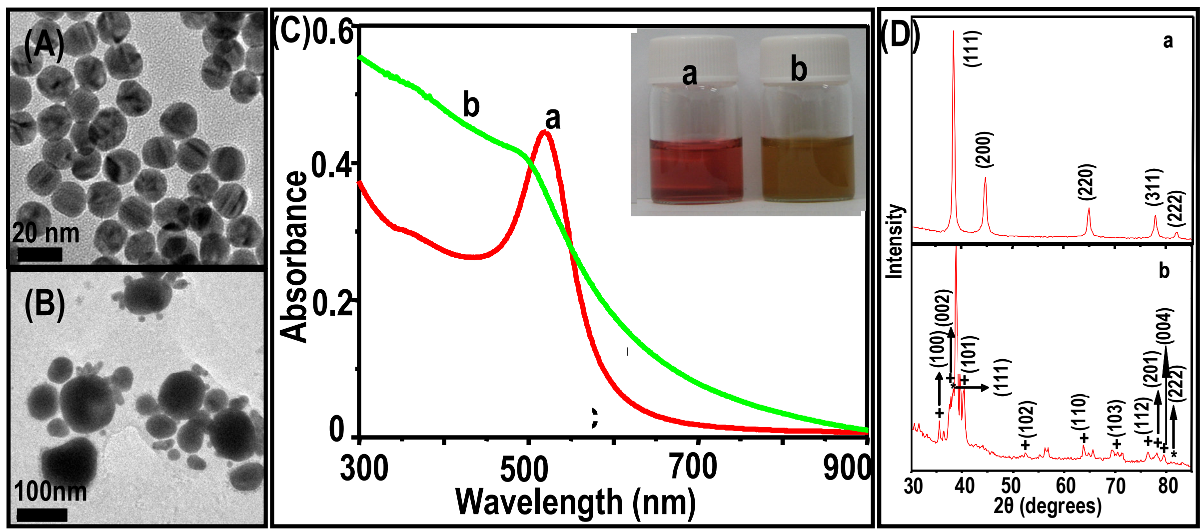
Chemistry of heavy metal ions with noble metal nanoparticles



Chem. Mater., 1998, 444-50



Gold Bullet. (submitted)

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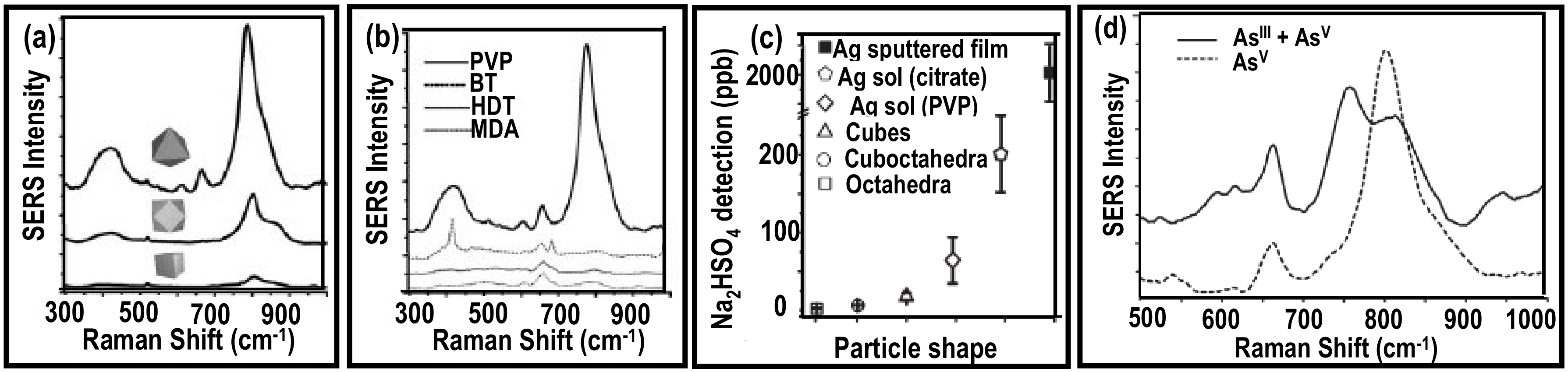
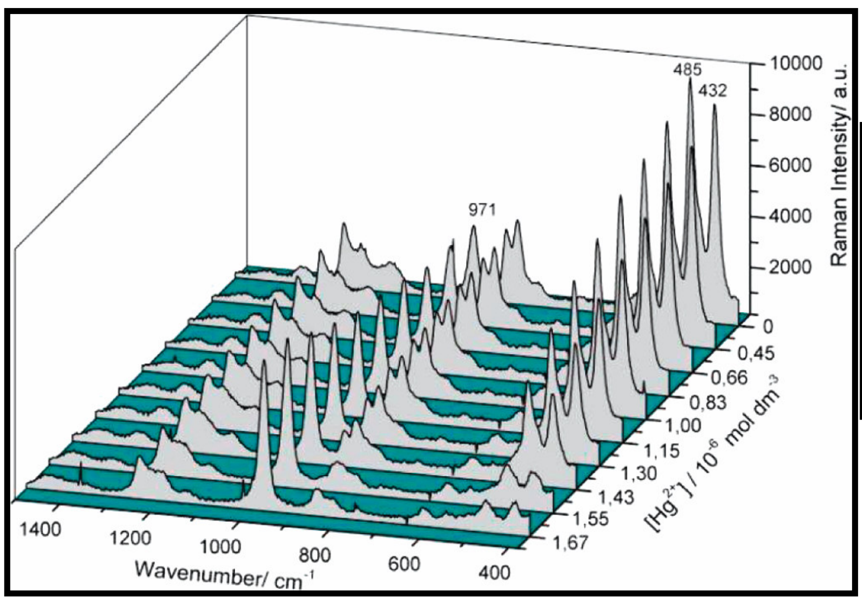
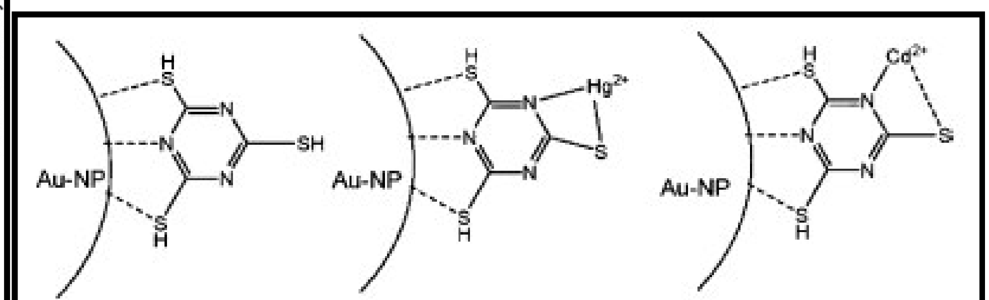
Detection of heavy metal ions with noble metal nanoparticles

Angew. Chem. Int. Ed. 2008, 6456 –60



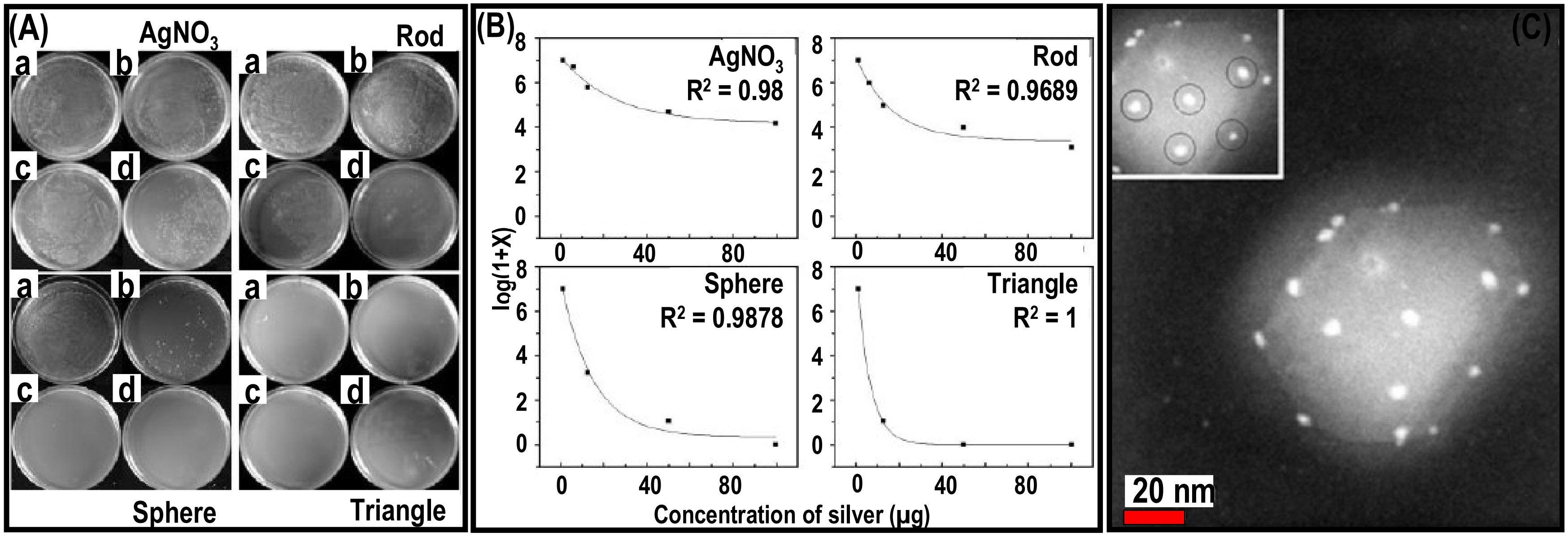
Inorg. Chem. 2008, 47, 2934-2936





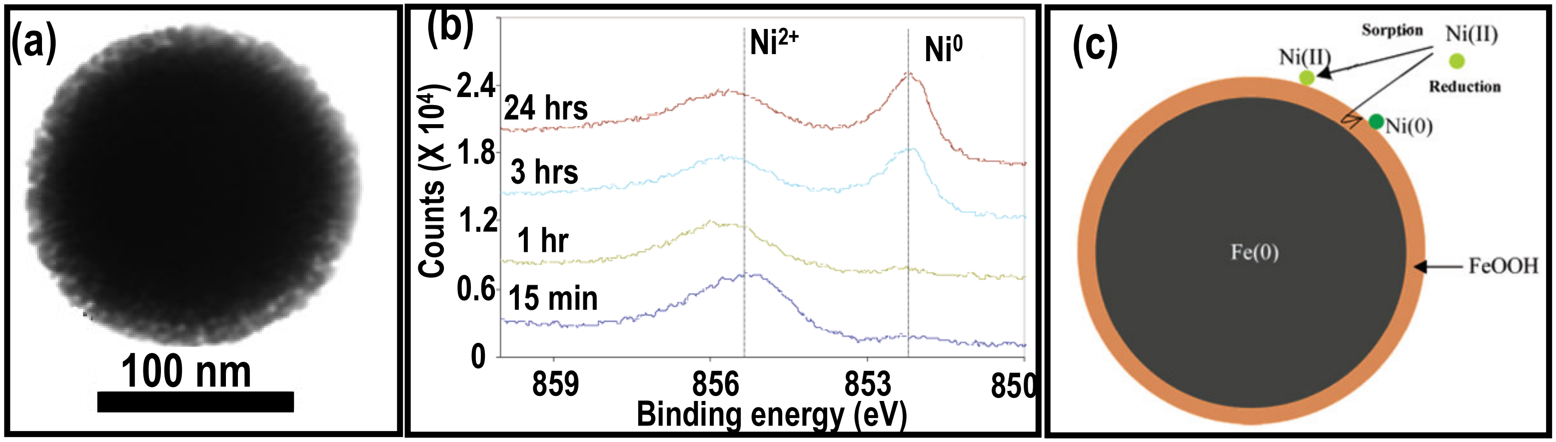
Drinking water purification: Novel reactions at the nano-scale

Chemistry of micro-organisms with noble metal nanoparticles

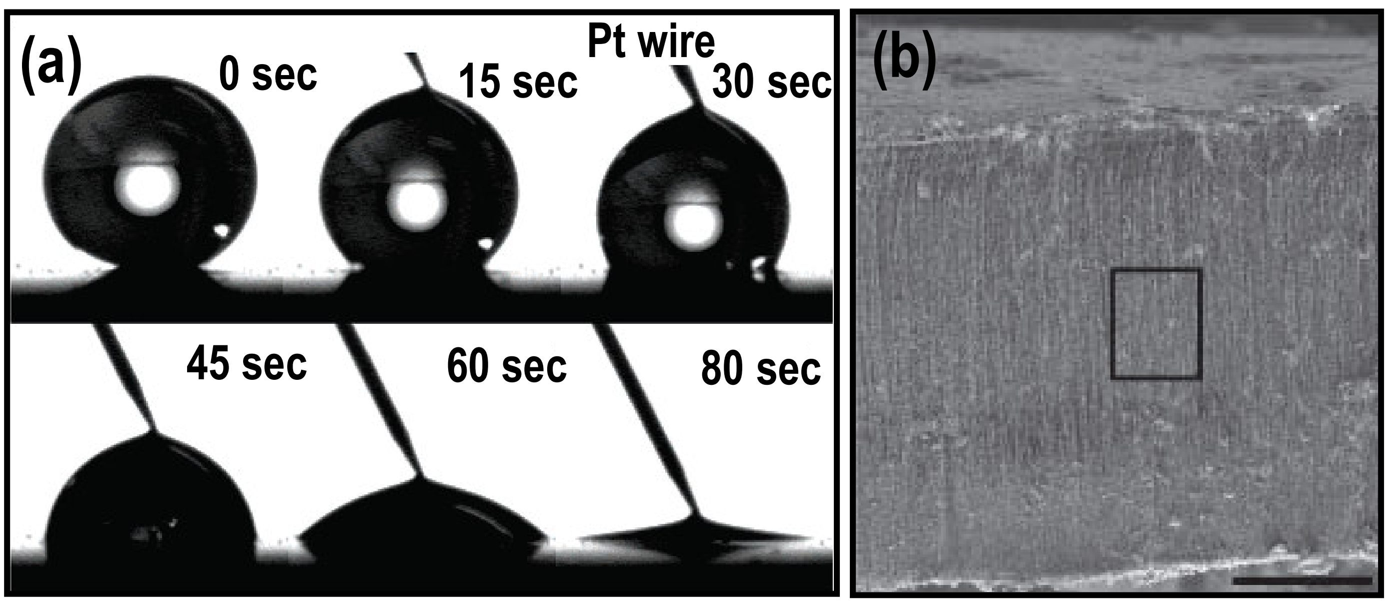


Other nanomaterial based approaches for water purification

Iron-based nanoparticles



Carbon nanotubes



Commercial interests in drinking water purification

Product Name	Nanomaterial utilized	Contaminants removal	Adsorption capacity	Product life	Product price
Aquaguard Gold Nova, Eureka Forbes Limited	Silver nanoparticles supported on alumina	Pesticides and halogenated organics	-	6000 liters	\$50
Adsorbia	Titania nanoparticles	Arsenic and disinfection	12-15 gm As(V) and 3-4 gm As(III) per kg of adsorbent	-	-
AD33, Adedge Technologies, Inc.	Iron oxide nanoparticles	Heavy metals including arsenic, lead, chromium, zinc, copper	-	3,800-11,400	\$50
Nanoceram, Argonide	Electropositive alumina nanofibers on a glass filter substrate	Disinfection, natural organic matter, turbidity, salt, radioactivity, heavy metals	-	-	\$3-10 per sq m^2, \$75 per filter
ArsenX, SolmeteX, Inc.	Hydrous iron oxide nanoparticles on polymer substrate	Arsenic, vanadium, chromium, uranium	38 mg of Arsenic per gm of adsorbent	-	\$0.07-0.20 per 1,000 liters (amortized due to reusability)
Nanopore, Nanovation AG	Membrane filters based on ceramic nanopowder supported on alumina	Disinfection	-	-	-