Noble metal nanomaterials for water purification

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New materials


Faraday’s gold preserved in Royal Institution. From the site, http://www.rigb.org/rimain/heritage/faradaypage.jsp
Fluorescent superlattices

For several of our concerns on water, such materials offer solutions.

There is indeed a need.
Market is ripe.
Solutions exist.

What is the problem then?
One can look at India in many ways
Let's take a look at India from the perspective of (a) Groundwater availability (b) Water quality (c) Population and (d) water contamination due to fluoride.

We have a problem; can nanotechnology help?
India has a long tradition in clean water

Mohenjodaro - well

Mohenjodaro – the great bath
Gas hydrates to ozone chemistry
Regulatory coverage of USEPA for safe drinking water has increased over 4 times since its inception, with revisions in regulations of many old contaminants.
Future of water purification: An enigma with some pointers

Continued focus of USEPA regulatory activities on various other halogenated organics found in drinking water. The allowed concentration limits for a number of species may shift to sub-ppb range.

Source: [www.epa.org](http://www.epa.org) and [www.who.int](http://www.who.int)
Future of water purification: Shrinking limits for allowed concentration of contaminants in water

Changes in maximum allowable concentration for lead and arsenic in drinking water, based on WHO advisory
Nanotechnology holds the future for effectively removing many drinking water contaminants

- Number of contaminants present in extremely low concentration range (< $10^{15}$ molecules per glass of water) are quite significant
- Many of those contaminants contain C-Cl bond or are metallic in nature
Permissible contamination reaches limits of detection

$10^{12}$ molecules
### Important milestones in the history of water purification (1800-2007)

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

**Last globally big invention in water purification**

**There is a gap and technology is waiting**

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**Credits to several governments, organizations and individuals, we have moved ahead. The journey of “pure water for all” calls for next big innovation.**

*Source: Multiple sources from internet*
Nanotechnology Applications for Clean Water

This landmark reference details nanotechnology breakthroughs, cutting-edge technologies, and future trends that point to widespread applications for nanotechnologies employed in water remediation and pollution prevention.

A full range of treatment and remediation topics using nanotechnologies are covered, including a case study in detecting and extracting pesticides from drinking water. The U.S./Israel Workshop on Nanotechnology for Water Purification is outlined. Societal implications that may threaten the adoption of these new technologies are also addressed.

KEY FEATURES

- Covers drinking water purification, treatment, and desalination; microbial disinfection; nanofiltration applications; and commercialization of nanotechnology for the removal of heavy metals
- Balanced analysis of nanotechnology-enabled disinfection and microbial control; the principles and applications behind Dendrimer-enhanced filtration; and possible applications of fullerene nanomaterials and the ion exchange process in treatment and reuse
- Explains biosensors for pesticide and explosive detection, nanosensors for environmental monitoring, and colorimetric / fluorescent sensors
- Exhaustive coverage of remediation topics: contaminated site clean up; physicochemistry to increase stability, mobility, and contaminant specificity of nanoparticles; heterogeneous catalytic approaches in purification; stabilization / destruction of chlorine; reducing leachability; synthesis of particles; etc.

ABOUT THE EDITORS

Nora Savage is an Environmental Engineer with the US Environmental Protection Agency in Washington, DC. She is the agency lead for developing nanotechnology research strategy, with a primary emphasis in environmentally benign chemistry/engineering and nanotechnology.

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Illustration of metal adsorption on nanoparticle surface (ZVI surface)


All inclusive affordable water purifier using nanomaterials

Microbes
Organics
Heavy metals
Anions

Not purification alone
Sensing
End of life indicators
Visual inspection
Salinity

Affordable ? < 5 paise per litre at point of use

Green – Water based synthesis, maximum temperature ~ 65 °C, scalable locally, back to nature after use
Noble metal nanoparticles: removal of pesticides from water

Variation of the UV-visible absorption spectrum of silver nanoparticles upon the addition of CCl₄

Gas chromatogram of chlorpyrifos solution (L) and after treatment with silver nanoparticles (R)

(L) Silver nanoparticles coated on activated alumina (R) Photograph of a pesticide filter device using supported nanoparticles (WQA certified)
A pesticide filter debuted in India

28 April 2007

Kumagai Giken is marketing now a domestic water filter that uses silver nanoparticles to remove dissolved pesticide residues, a step towards improving water quality.

The filter is made by the Indian Institute of Technology (IIT) in Chennai. According to the company, silver nanoparticles are known to be effective in removing bacteria and viruses from water.

The filter consists of a cartridge that can be easily replaced. The company claims that the filter can remove up to 99.9% of harmful substances from water.

A pesticide test kit has been developed to detect residues above 25 ppb, making it easier to monitor the effectiveness of the filter.

The product is being showcased at the 12th International Water Quality and Treatment Conference in India, where it has generated significant interest among water treatment experts and stakeholders.

The filter is expected to be available in the market soon, and the company has plans to expand its reach to other countries.

Product is marketed now
Cartridges are recovered after use

A pesticide test kit has been developed > 25 ppb
Noble metal nanoparticles: removal of heavy metals from water

(a) UV-vis absorption spectra of silver nanoparticles (i) before Hg\textsuperscript{2+} treatment (ii-ix) after Hg\textsuperscript{2+} treatment. (b) Large area SEM image of the Ag-Hg bimetallic nanoparticles

(a) SEM image of an Ag-Hg alloy nanoparticle, (b) elemental image of Ag and (c) elemental image of Hg overlaid on Si (Si is from ITO substrate).
Noble metal nanomaterials: detection of toxic species

SERS spectra of arsenate ion (1X10^-6 M) on (a) LB films of silver nanocrystals (b) LB arrays of silver octahedra coated with various organic species. BT: benzenethiol, HDT: hexadecanethiol, MDA: mercaptodecanoic acid. (c) SERS-based speciation of arsenate and arsenite ions (18 ppb)

Colorimetric detection of chlorpyrifos using the gold nanoparticle-Na2SO4 system

1. Bulk materials used for water purification can be made efficient – MnO₂

2. Nanomaterials have much larger capacity for scavenging

SEM images of mercury treated gold nanoparticles. (A) Large area image, (B) magnified image of few particles, (C) elemental map of Au, (D) elemental map of Hg and (E) EDAX spectrum of mercury treated gold nanoparticles. Inset is the composition table.

3. Monolayer makes a difference in metal ion removal

4. Size of core makes a difference

Sumesh *et al*. Submitted.
Sumesh et al. Submitted.
5. Graphene offers a number of possibilities
Figure: UV/Vis spectra of RGO upon the addition of metal ions. A) KMnO₄, B) Au³⁺, C) Ag⁺, and D) Pt²⁺. Absorption at 270 nm for RGO and the changes due to the formation of MnO₂, Au, Ag and Pt nanoparticles can be seen. Spectral changes are marked. Pt nanoparticles do not show a distinct Plasmon absorption.
Figure: TEM images of RGO-MnO$_2$ (0.05 mM) showing at various magnifications nanoparticles attached to RGO. Folded RGO sheets are marked with arrows in A.
Figure: TEM images of RGO-Ag (0.05 mM) showing well dispersed nanoparticles over a RGO sheet
Figure: Concentration dependent TEM images of RGO-MnO$_2$. A$_1$) 0.01 mM, A$_2$) 0.025 mM and A$_3$) 0.05 mM and RGO-Ag B$_1$) 0.01 mM, B$_2$) 0.025 mM and B$_3$) 0.05 mM. Insets in all figures show the lattice resolved images taken from the same sample. All scale bars in the inset correspond to 5 nm.

Sreeprasad et al. Submitted
Figure: Raman spectra of A) RGO-MnO$_2$ composite and B) RGO-Ag composite, at different loading of MnO$_2$ and Ag. Peak positions are marked.

Sreeprasad et al. Submitted
Figure: XPS spectra of samples containing 1) 0.025 mM, 2) 0.05 mM and 3) 0.1 mM KMnO₄. A) C 1s, B) O 1s, and C) Mn 2p regions.

Sreeprasad et al. Submitted
Figure: SEM Images of A) Ch-RGO-Ag@RS, B) Ch-RGO-MnO$_2$@RS; inset in A shows an SEM image of bare sand particles before coating. C) Raman spectrum of (a) RS, (b) Ch, C) Ch-RGO-MnO$_2$@RS and (d) Ch-RGO-Ag@RS. D) Photograph of RS, Ch-RGO-MnO$_2$@RS and Ch-RGO-Ag@RS showing the color change.
Figure: A) Comparison of Kd values obtained for the adsorption of Hg(II) of unsupported RGO composites with different materials examined. B) Comparison of Kd values obtained for the adsorption of Hg(II) of supported RGO composite with RS, Ch, Ch@RS. C) Kinetics of Hg(II) adsorption by various adsorbents (temperature = 30 °C; pH = 7 ± 0.2, initial Hg(II) conc. = 1 mg/L). D) Performance comparison of RGO composites for removing Hg(II) from distilled water and real water (initial Hg(II) conc. = ~ 1 mg/L.

Sreeprasad et al. Submitted
**Figure:** Pseudo-first-order kinetic plots with experimental data for adsorption of Hg(II) by GO, RGO and various RGO composites (E – experimental, P – predicted) A). unsupported and B) supported form.
6. Halogen and silver free antimicrobial media

(A) SEM and (B) TEM images at various magnifications of virus removal media, and (A (d) ] shows the UV-vis spectra of various virus removal compositions
350 nm

550 nm

550 nm

640 nm

TUB Rao and T Pradeep, Angew. Chem. Int. Ed. 2010

Current developments

Purifiers for specific areas – local issues
– seasonal problems
All inclusive solutions
Local manufacture
Sustainability
Nanomaterial toxicity
Community involvement – NGOs
Ongoing field trials

Ongoing field trials of fluoride treatment unit (domestic unit) at Kotlapalli, Anantapur, Andhra Pradesh

Date: August 07, 2010
Several new technologies
Nanotubes
Dendrimers
Magnetic particles
Membranes
Self organised structures
Capacitive deionization

Pure water can be affordable.....
A technology solution may appear to you in one of these forms.
Crystallographic structure of the aquaporin 1 (AQP1) channel.
On collaboration

New sensors for ultralow sensing in water
Visual displays
Sustainable purification technologies; combining solar, membrane and materials
Water harvesting
Aquaporins

On water nations can indeed come together!
Nano Mission, Department of Science and Technology
World Gold Council
Well-meaning individuals, Companies
IGCAR – Field trials

Thank you all
