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Sustainable Nanotechnology

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Yazgan I, Sadik et al, Journal of Membrane Science, 472, 2014, 261-271

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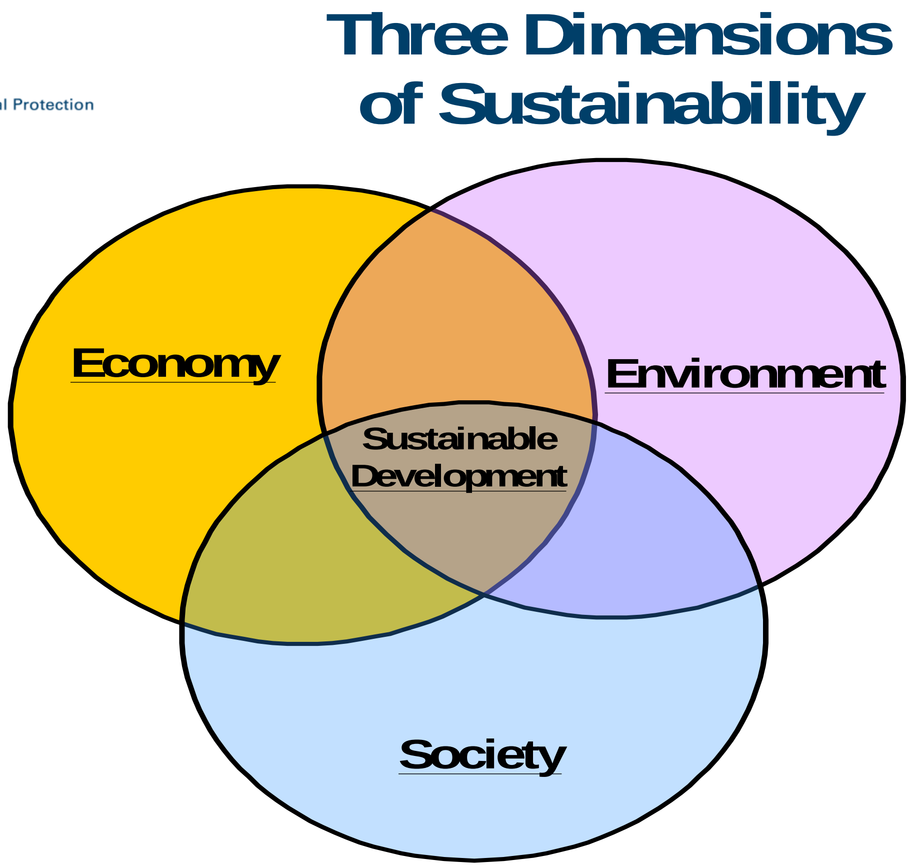
Sadik et al In:Chemical Processes for a Sustainable Future, eds. T. M. Letcher, J. L. Scott and D. Patterson, Royal Society of Chemistry, Cambridge, UK, **2014**, 27 chapters, pages, ISBN: 978-1-849739757

Sustainable Nanotechnology

EPA United States Environmental Protection Agency

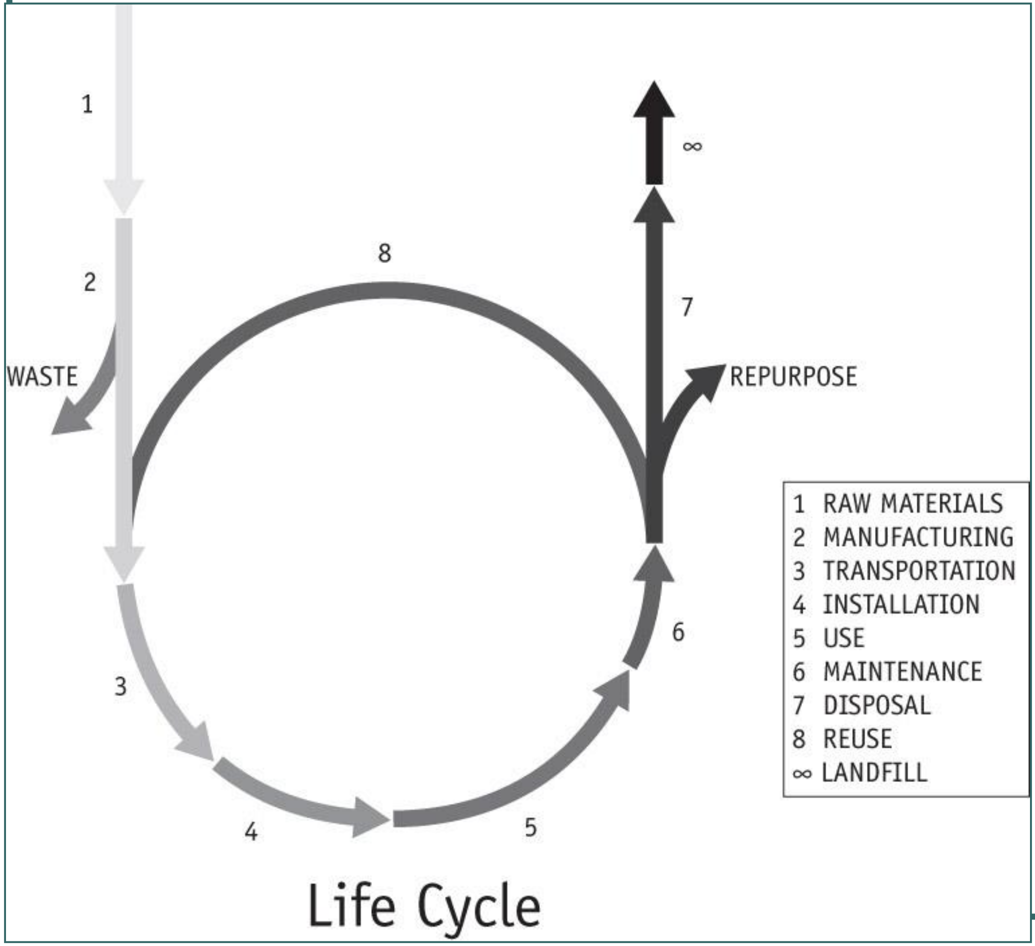


Development of nanotechnology with increasing economic and societal benefits and decreasing environmental impact

Five Axioms of Sustainability

- **Axiom 1**: Any society that continues to use critical resources unsustainably will collapse.
- **Axiom 2**: Population growth and/or growth in the rates of consumption of resources cannot be sustained.
- **Axiom 3**: To be sustainable, the use of renewable resources must proceed at a rate that is less than or equal to the rate of natural replenishment.
- **Axiom 4**: To be sustainable, the use of nonrenewable resources must proceed at a rate that is declining, and the rate of decline must be greater than or equal to the rate of depletion.
- **Axiom 5**: Sustainability requires that substances introduced into the environment from human activities be minimized and rendered harmless to biosphere functions.

Life-Cycle Thinking



The elements of a product’s life cycle

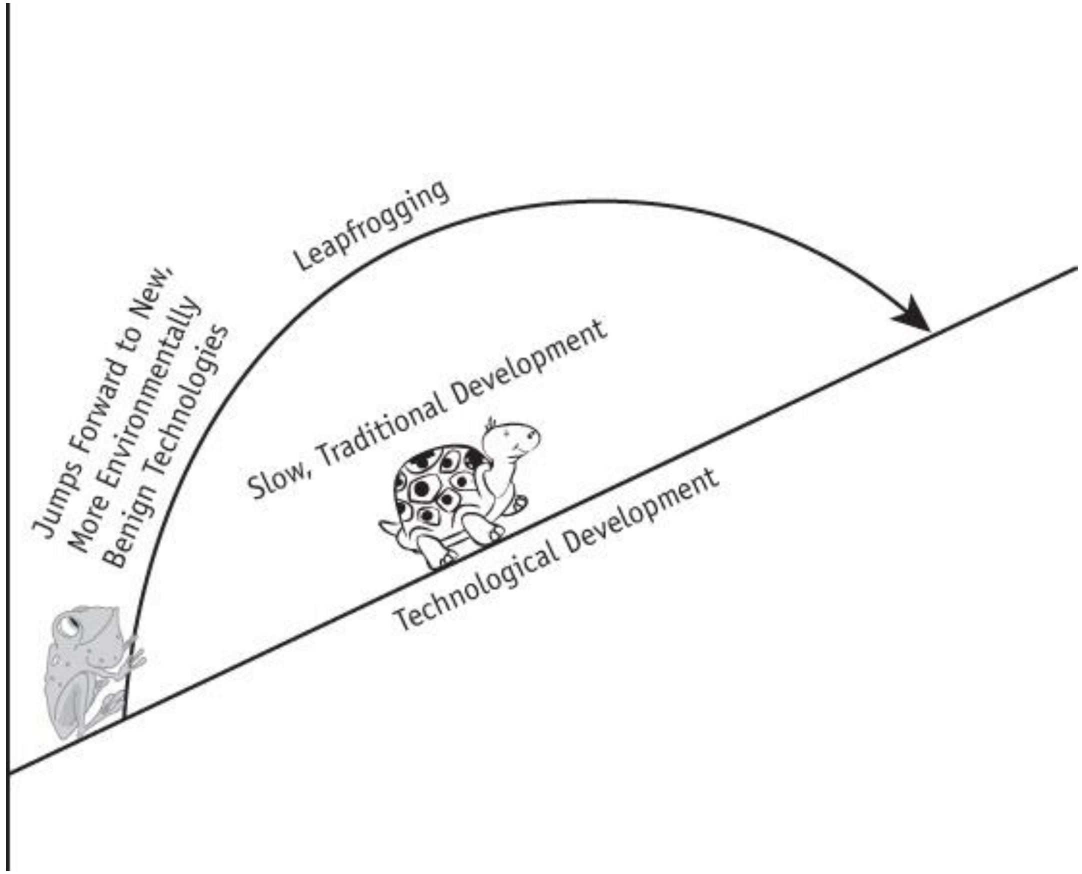
How can nanotechnology be sustainable?

- A complete set of synthetic protocols are needed to support the development of sustainable nanomaterials.
- Scientific excellence
- Economic benefits
- Ethical considerations
- Societal benefits/legal considerations
- Learn from conventional green chemistry

Current Challenges

- Synthesis of many of the existing nanomaterials is not sustainable because
  - Dependence on high temperature
  - High pressures
  - Use of large quantities of hazardous reagents and /or solvents
  - insufficient understanding of their environmental health and safety
  - Existing nanomanufacturing processes rely on non-renewable materials

Leapfrog Technology



Leapfrogging means abandoning traditional development steps to get to advanced technology faster

Learning from Green Chemistry Examples

- Replacing toxic metals
  - Yttrium in automotive paint
  - Removing arsenic and chromium from pressure-treated lumber
- Environmentally benign pesticides
  - Sentricon termite system
  - Harpin
  - Insect Molting Hormone
  - Caterpillar Control and Mosquito Larvicide
- Atom Economy
  - Ibuprofen
  - Click Chemistry

Green Chemistry Examples in Nano

- Greener solvents
  - Water as reagents
  - mild reducing agents with cheap cationic surfactants to facilitate crystal growth
  - gent
- Replacement, substitution and/or functionalization of various types of nanomaterials with biological or naturally-occurring macromolecules such as carbohydrates, proteins or polypeptides

Examples of Sustainable Nano Technologies

- Minimally Toxic Quantum Dots
- Green Gold, Green Silver
- Polysaccharide Method
- Tollen's Method
- Green Graphene Nanosheets
- Biomass Extracts as Precursor for the Synthesis of Nanomaterials
- Safer-by-Design (S^bD) Concept
- Microwave-mediated Synthesis of Nanomaterials
- Life Cycle Assessment

Green Gold

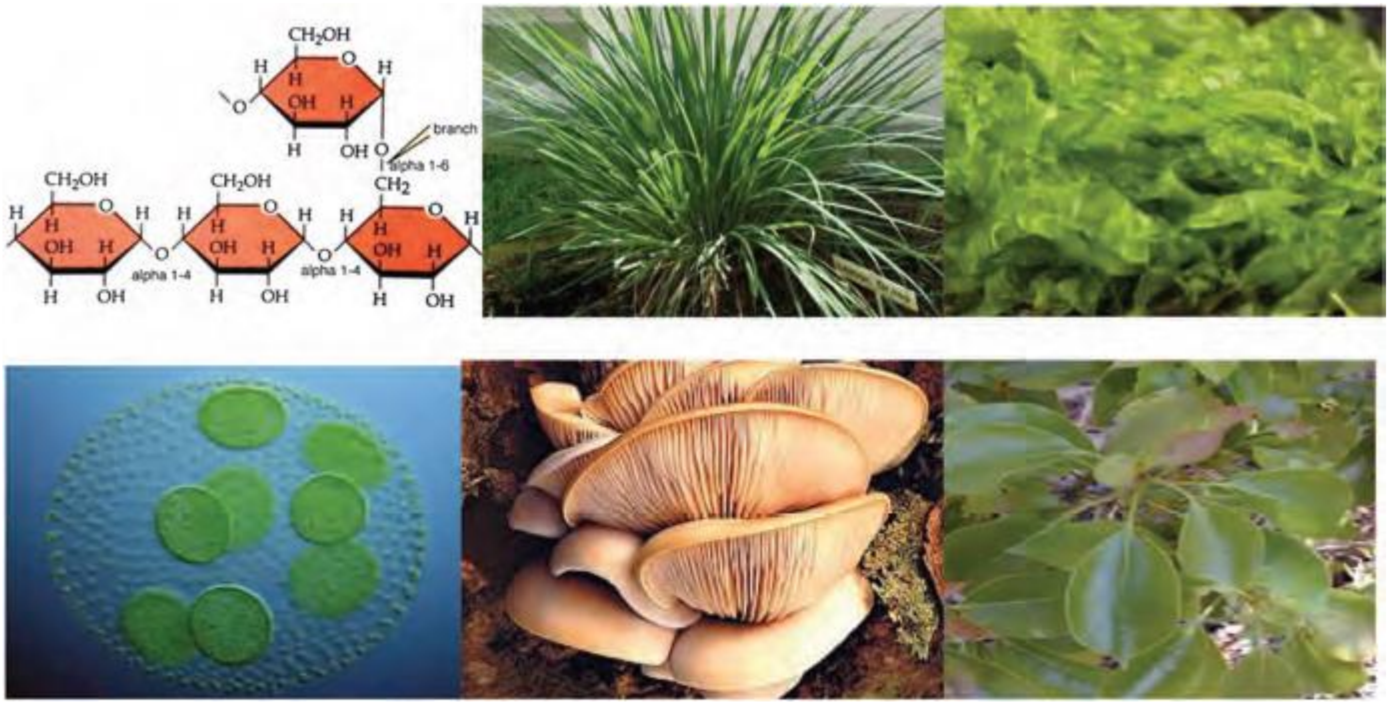
- The original preparation of gold nanoparticles (NPs) uses benzene as a solvent and gaseous diborane as a reducing agent. Researchers such as Hutchison et al, have developed greener method to make ultra-small (1.5 nm) gold NPs.
  - The authors replaced diborane with sodium borohydride and benzene with toluene. They considered these reagents ‘greener’ benzene vs toluene.

Benefit?

- The purification step, which involves liters of organic solvent, can now be achieved using filtration membranes.
- This has led to a drastic reduction in the cost of preparing gold NPs from $300 000 per gram of product to $500.
- Such examples should be studied for other NPs.

S.F Sweeney, G.H. Woehrle, and J.E. Hutchison, Journal of the American Chemical Society, 2006. 128(10): p. 3190-3197.
J., Weng, et al., Green Chemistry, 2006. 8(1): p. 96-99.

Biomass Precursors for Ag, Ag, Co, Ni, and Ni-Co Alloy NPs



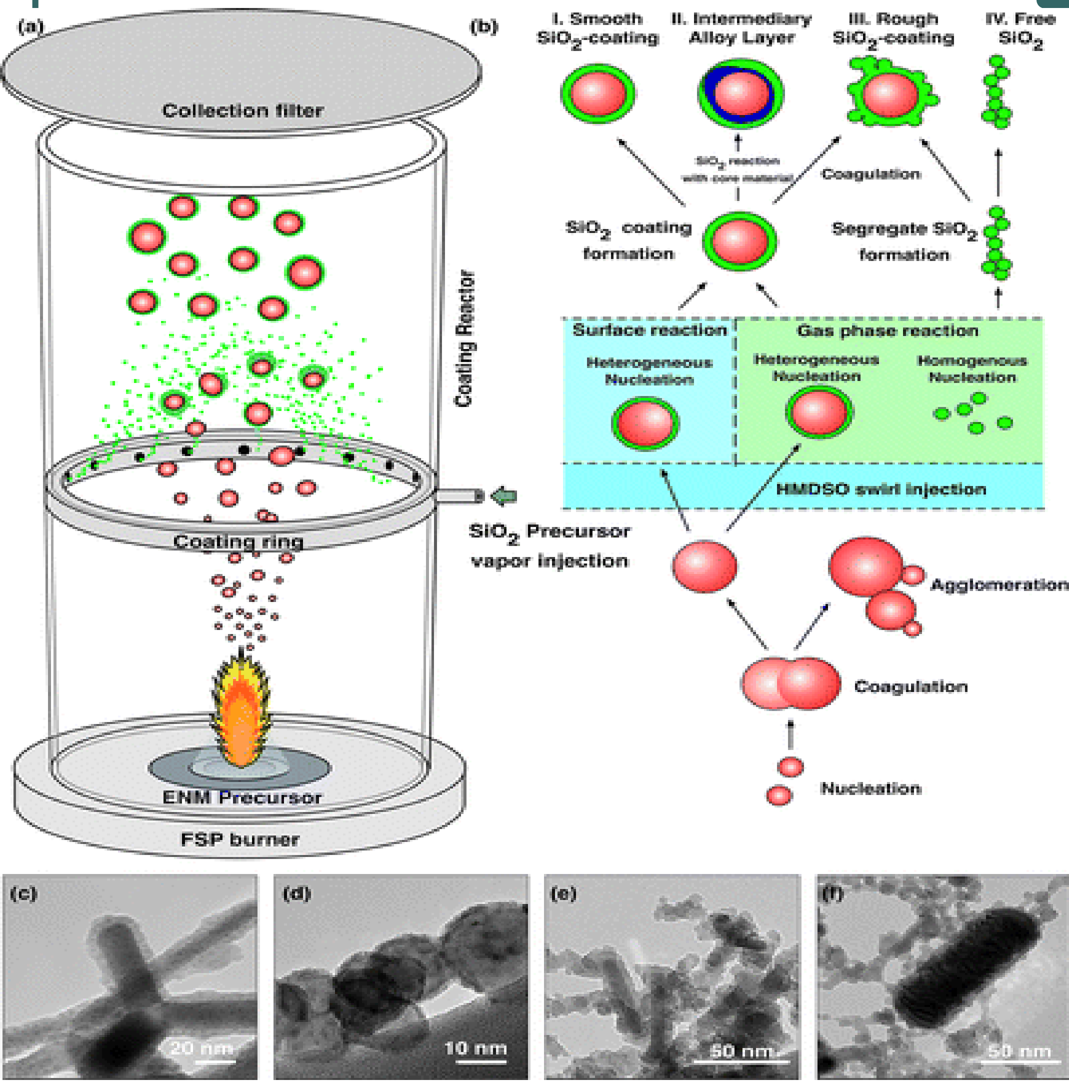
Examples of biomass-based reducing agents include starch, [31]extracts from lemon-grass, [41,42] seaweed, [43] algae , [44]and mushroom. [45]

This brings about an advantage in recycling of food wastes for chemical production from a sustainability point of view

Safer-by-Design (S^bD) Concept

- Conceptually, it is relatively easy to eliminate known hazards from a synthesis or a process; but it is much more difficult to ensure that the alternative is benign.

Synthesis of engineered nanomaterials using SiO_2 coating



- Potentially toxic nanomaterials are coated with a biologically inert layer of amorphous SiO_2.

- Amorphous SiO_2 is used since it is considered a biologically and environmentally inert material. [46]
- Demokritou et al have formulated a concept for flame generated ENMs based on a one step, in-flight SiO_2 encapsulation process.
- This process is versatile and they have utilized similar procedure to coat four engineered nanomaterials: **CeO_2, ZnO, Fe_2O_3, and Ag**. [46]

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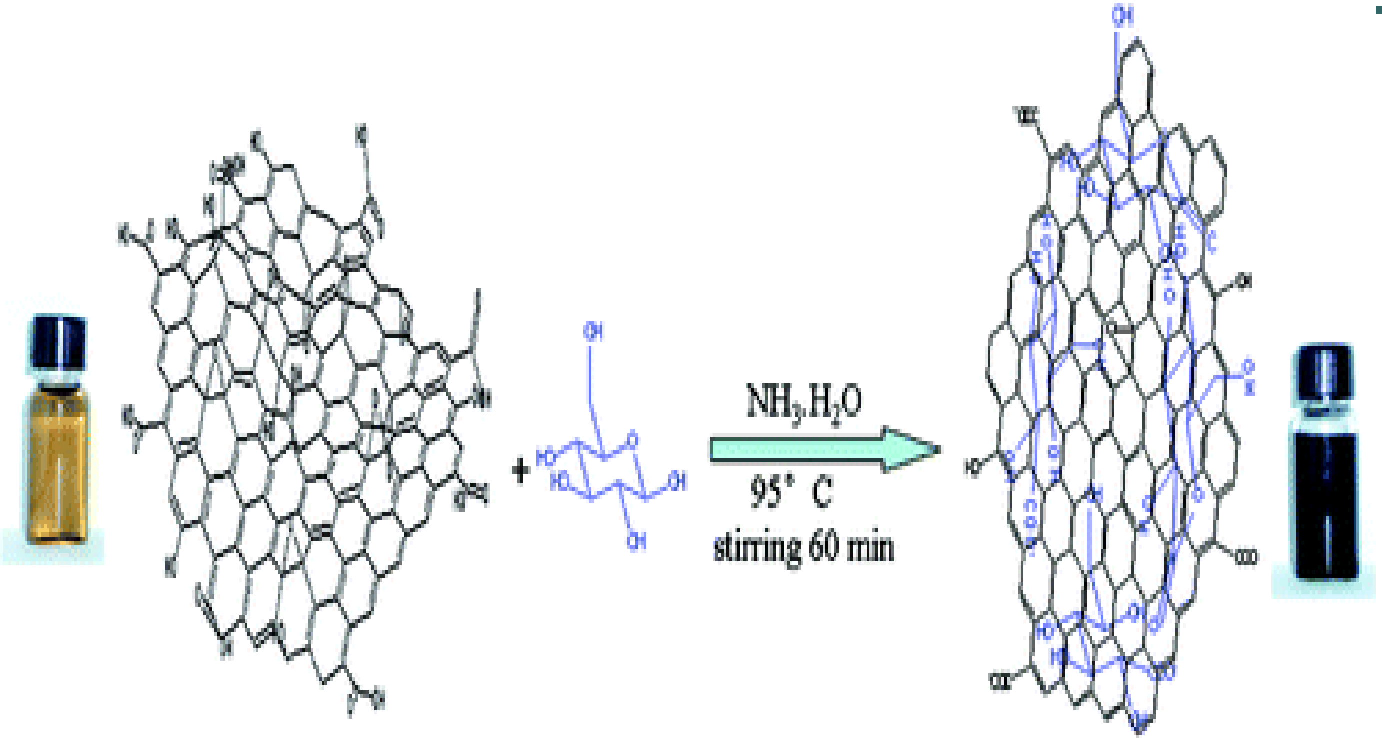
Green Graphene Nanosheets



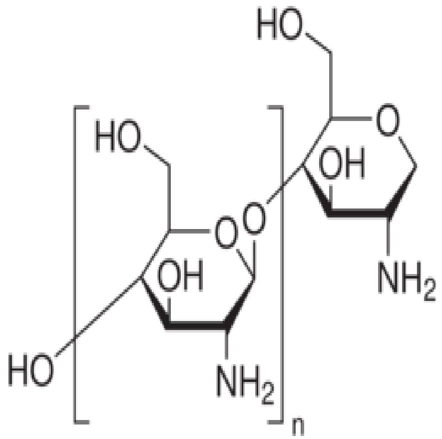
Chengzhou Zhu et al have developed a green approach to the synthesis of chemically converted graphene nanosheets (GNS) based on reducing sugars, such as glucose, fructose and sucrose using exfoliated graphite oxide (GO) as precursor.

Nanotechnology for Water Purification-Challenges

- Membrane permeability/exclusion characteristics
  - Preserve fundamental smoothness/hydrophobicity
- Materials capable of collecting and pre-concentrating contaminants per unit volume
- Insufficient selectivity for test species
- Many expensive nanoparticles cannot be added to water as with commodity chemicals
- Some nanoparticles present new hazards

Biological Building Blocks

- Chitosan:
  - *Natural and soluble polymer*
  - *Can be used in many formats as membrane*
  - *Can be chemically modified*
  - *Possesses anti-microbial property*
  - *Pre-filtration membrane*



Polymer 50 (2009) 3661–3669
Separation and Purification Technology 75 (2010) 358–365

Anti-microbial action of PAA-GA and PAA-CS-GA

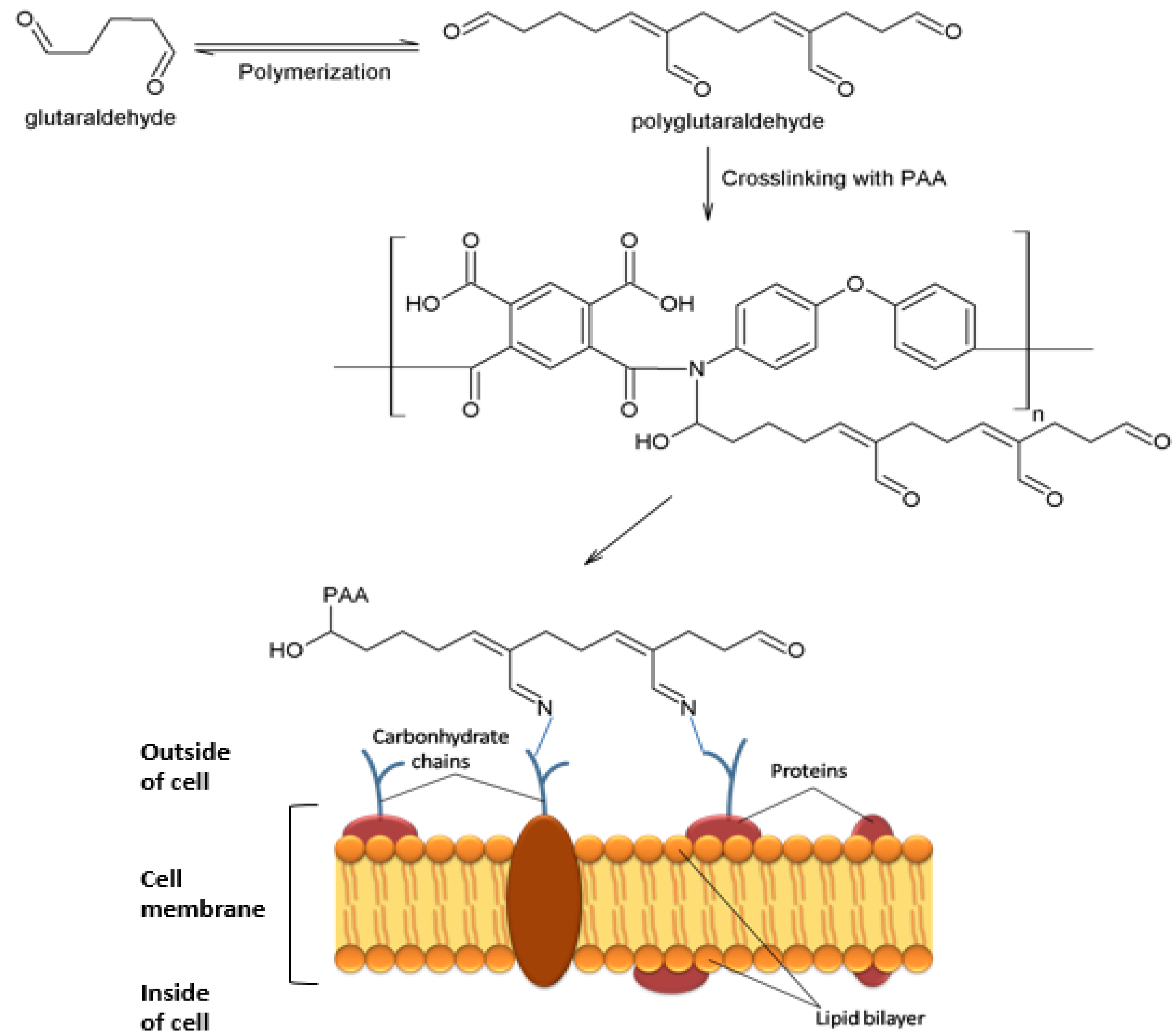
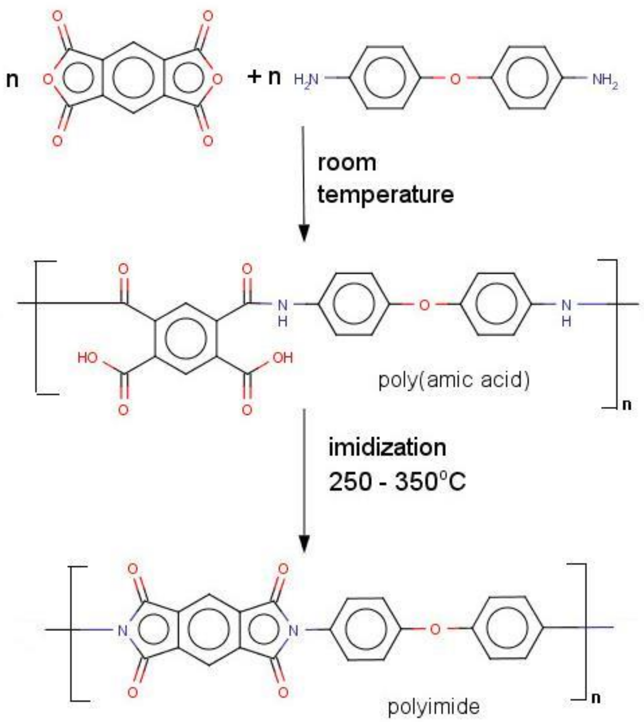


Plate-counting results showed that PAA-GA decreased viable microbial population at 2.8 log while that of PAA-CS-GA diminished by 2.3 log. However, PAA and PAA-CS showed less than 1.4 log microbial population.

Poly(amic acid) or PAA

- Poly(amic acid) (PAA) is the precursor of polyimide (PI).

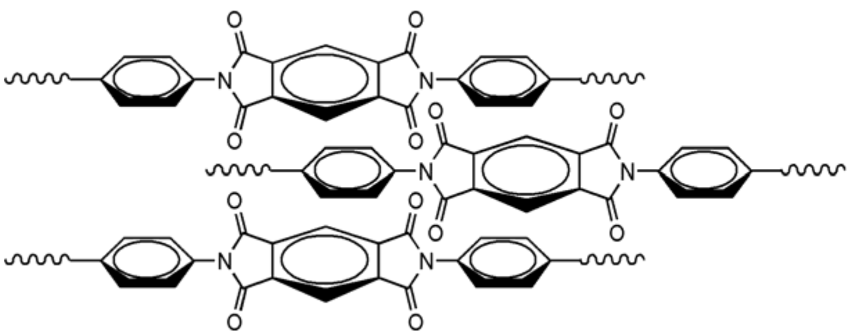


- PAA

  Powder or liquid, poor mechanical property.

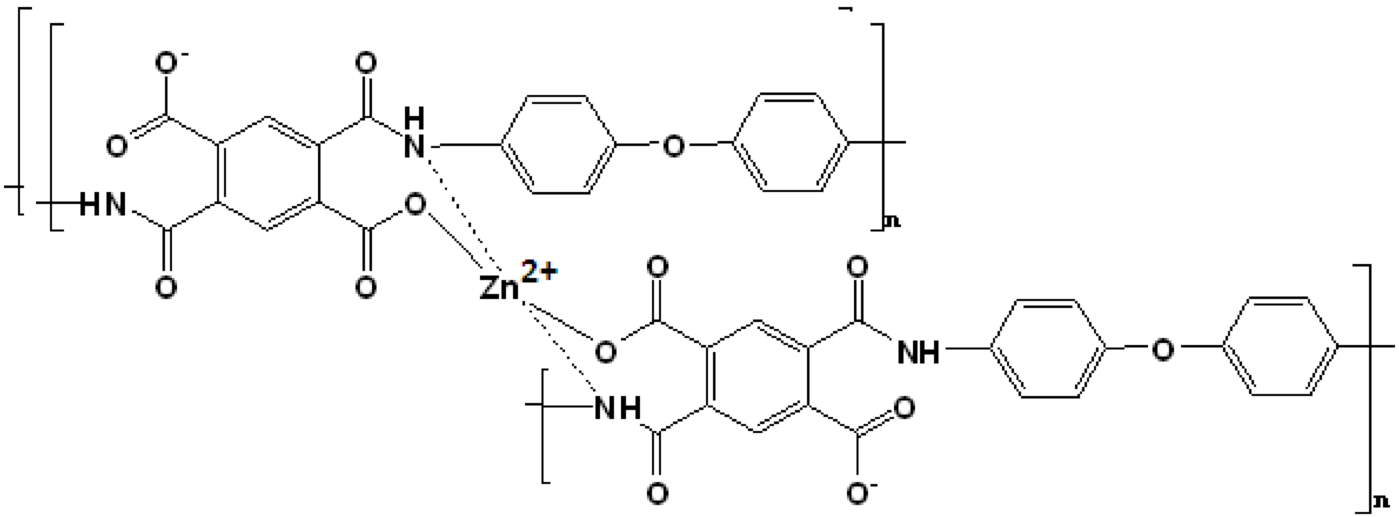
- PI

  Thin film, flexible, durable.



D. Andreescu, A. K. Wanekaya, O. A. Sadik, J. Wang, "Nanostructured polyamic acid membranes as novel electrode materials", Langmuir, 21(15), 6891-6899, **2005**

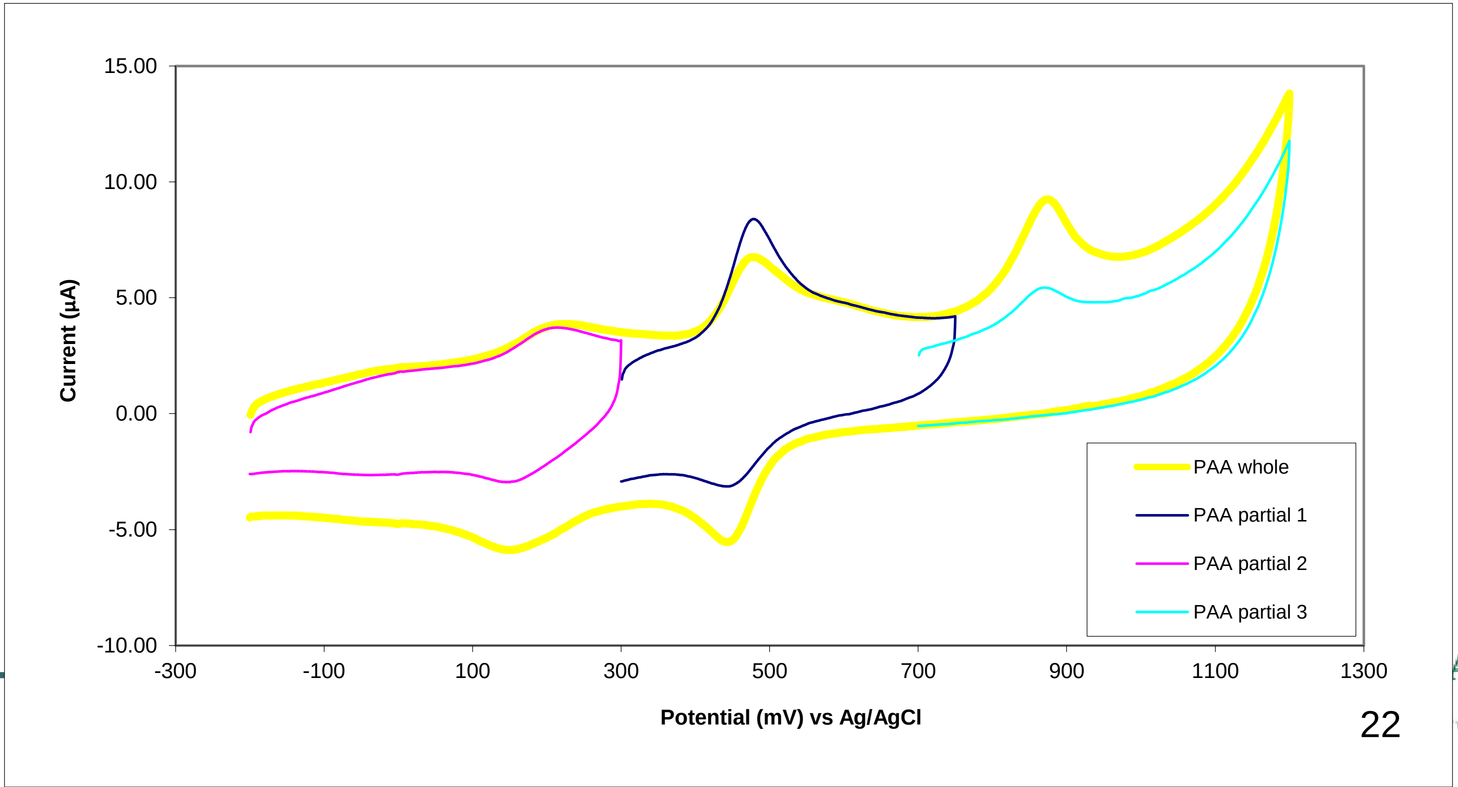
Improving Mechanical Strength



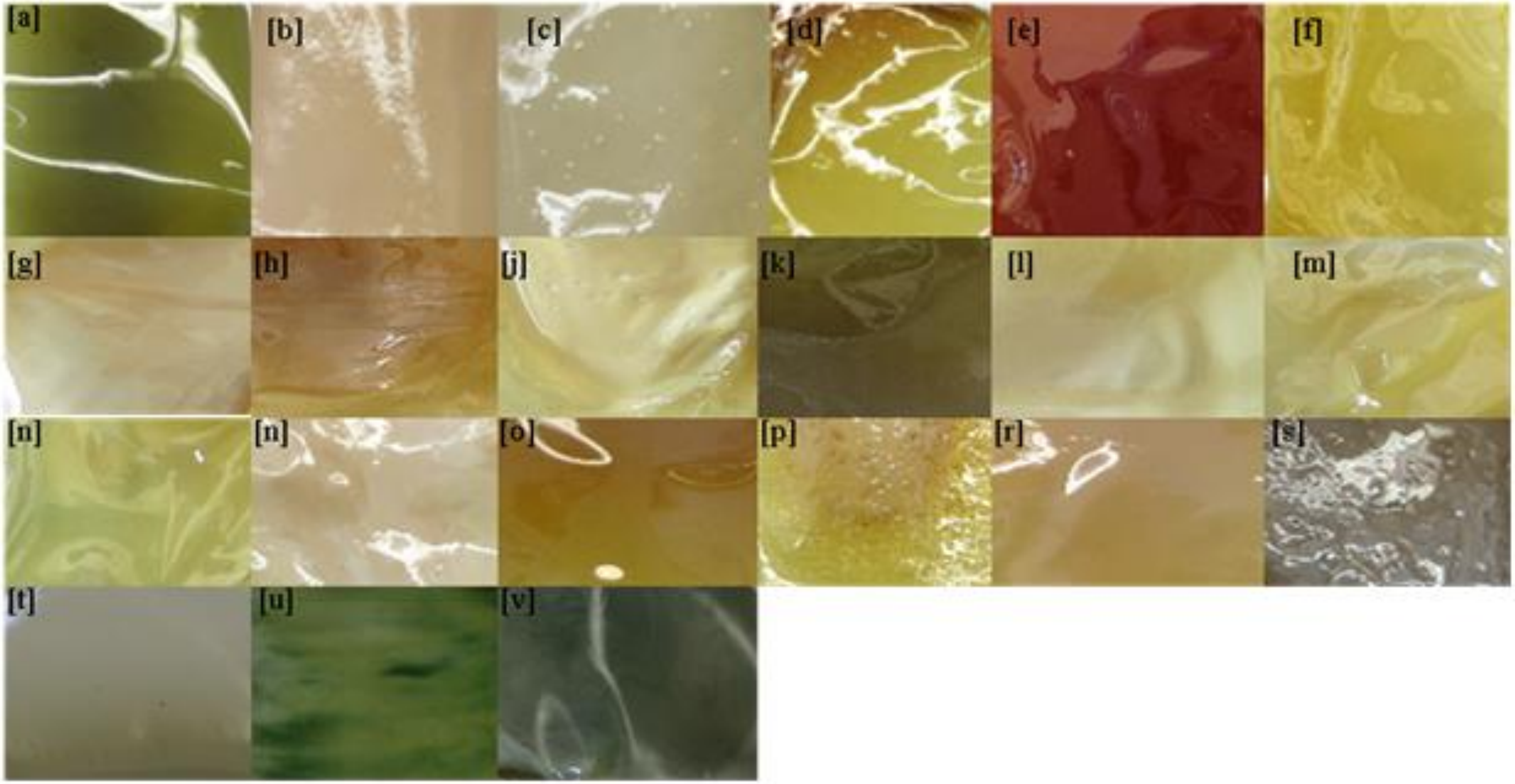
Addition of metal cation may improve mechanical properties by creating complexation networks:

Mechanical and electrochemical properties

- Flexible, minimum bend radius is 3mm
- Conductive and electroactive
- Biodegradable and non-toxic



AMTON
R S I T Y



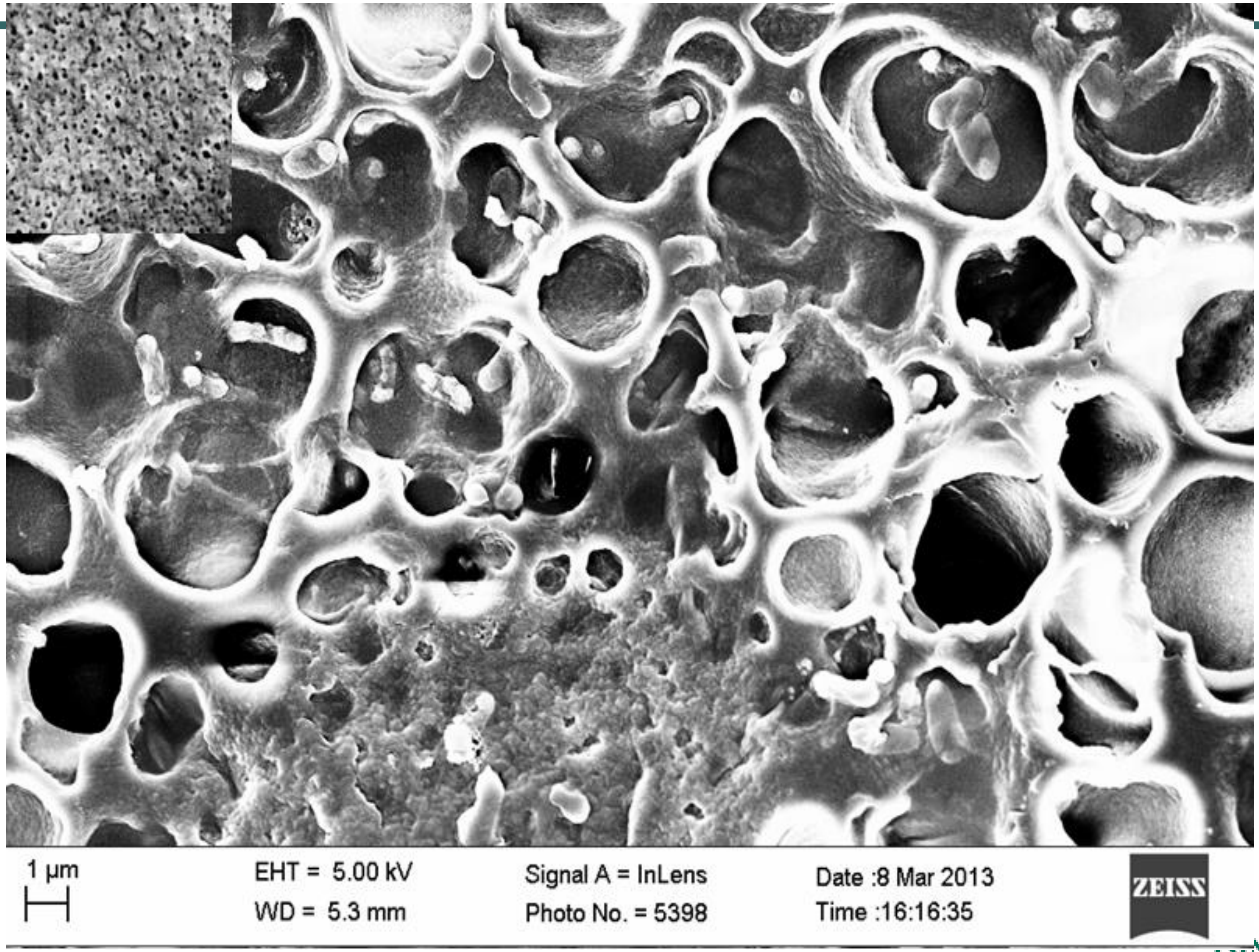
Pre-dissolving GA in dry DMAC affects the actions of GA, and the resulted membrane formation gives difference in terms of color and contact angle. For example, the membranes “n” and “s” were from PAA-DA. Even though, the membrane “n” is plastic-like transparent while the membrane “s” is opaque and dark-blue color with possessing higher contact angle;

Disinfection of drinking water

Sample volume (mL)	Amount spiked (cfu/mL)	Amount after filtration (cfu/mL)	% Disinfection	Membrane Type Employed
500	3×10^8	none	100	PAA-GA
700	3×10^8	none	100	PAA-CS-GA
1000	3×10^8	none	100	PAA-CS-GA

Yazgan I. Sadik et al, Journal of Membrane Science 2014 (In press)

Post-filtration SEM image of PAA-CS



10 mL tap water containing 1 e8 E.coli filtrated via dead-end filtration

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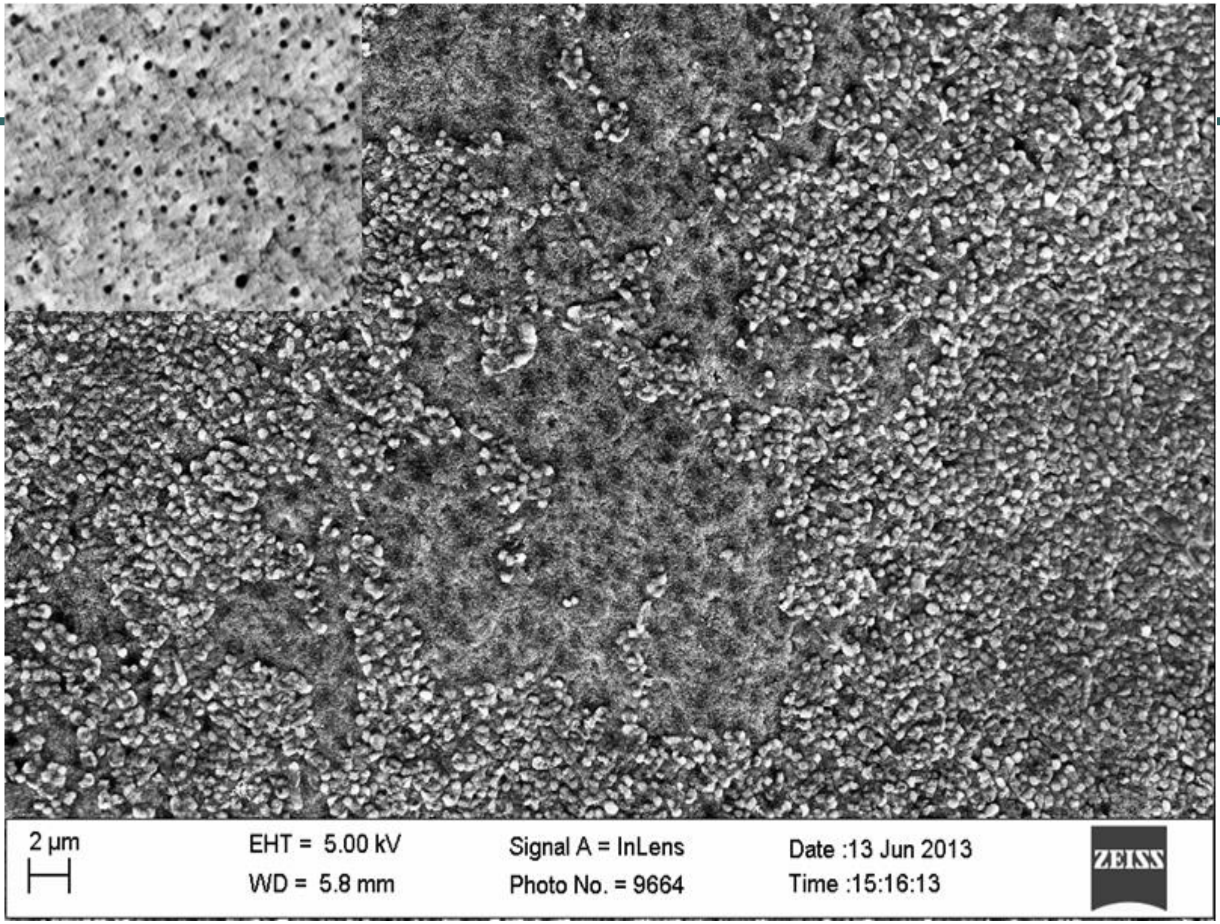
Post-filtration SEM image of PAA-CS-GA



GA treated PAA-CS and PAA did not lose their surface integrity and pore-size distribution for disinfection of 1000 mL tap water containing 3 e8 Staphylococcus epidermidis, *Escherichia coli* and *Citrobacter frenduii*

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Elements of Sustainable Nanotechnology

- Green synthesis
- green energy
- sustainable manufacturing, nanomedicine
- environmental applications
- toxicology of nanomaterials
- fate/transports of nanomaterials,
- Nanotools
- legal aspects, and societal/policy considerations

Objectives

- Develop green poly(amic) acid membranes using biological building blocks, metal ions, and known disinfectants
- Utilize PAA membranes for water disinfection
  - Capture - applied potential
  - Isolate - size-controlled selective removal
  - Disinfect- incorporate biological building block
    - Especially useful for small communities, home-based systems, remote areas etc

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U.S. EPA - Science To Achieve Results (STAR) Program
Grant #

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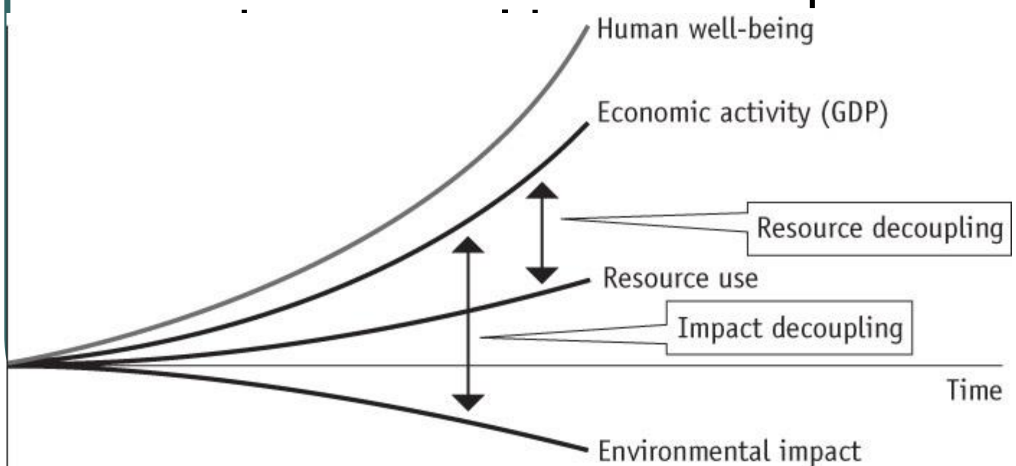
Green Chemistry

- Prevention
- Atom economy
- Less hazardous chemical syntheses
- Design of safer chemicals
- Safer solvents and auxiliaries
- Design for energy efficiency
- Use of renewable feed stocks
- Reduced use of derivatives
- Catalysis
- Design for degradation
- Real-time analysis for pollution prevention
- Inherently safer chemistry for accident prevention

United Nations Commission on Sustainable Development

- **Marrakesh process**
  - Assist countries in efforts to “green” their economies
  - Help corporations develop greener business models
  - Encourage consumers to adopt more sustainable lifestyles
- **Resource decoupling** means reducing the rate of use of primary resources for each unit of economic activity
- **Impact decoupling**, by contrast, requires an economy to increase its economic output while reducing its negative



Decoupling seeks to improve human and economic well-being while slowing resource use and decreasing environmental impact.

UNEP (2011) Decoupling natural resource use and environmental impacts from economic growth, A Report of the Working Group on Decoupling to the International Resource Panel. Fischer-Kowalski, M., Swilling, M., et al.