

Surface Chemistry and Stability of Nanostructured Materials in Natural Aquatic Environments

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List of nanostructures and the related materials

Nanostructure	Chemical Composition	Potential Application	Structural Parameter
Mesoporous structure	SiO ₂ , Al ₂ O ₃ , ZrO ₂ , CeO ₂ , Zr-phosphate, etc	Photon/electron devices, catalysts & catalyst supporters, sensing materials, adsorbents, etc.	Pore geometry, pore size
Nanotubes	TiO ₂ , carbon, etc	Photon/electron devices, catalysts, sensing materials, etc.	Pore size, wall thickness, tube length
Core-shell structure	Iron oxides (especially magnetite), metallic particles, etc	Chemical separation, Photon/electron devices, catalysts, medical treatments, etc.	Particle size, shell thickness and coverage
Nanoparticle & nano-rods	TiO ₂ , iron oxides, metallic iron, metallic Pd, etc	Catalysts, photon/electron devices, environmental remediation, cosmetics	Particle size, morphology

Nanotechnology is anticipated to be a trillion dollar industry by 2015.

Environmental & Health Concerns of Nanomaterials

NEWS & VIEWS

NANOECOTOXICOLOGY

Nanoparticles at large

Environmental toxicologists, chemists and social scientists have identified three priorities for research into the impact of engineered nanoparticles on the environment.

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LETTERS

Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study

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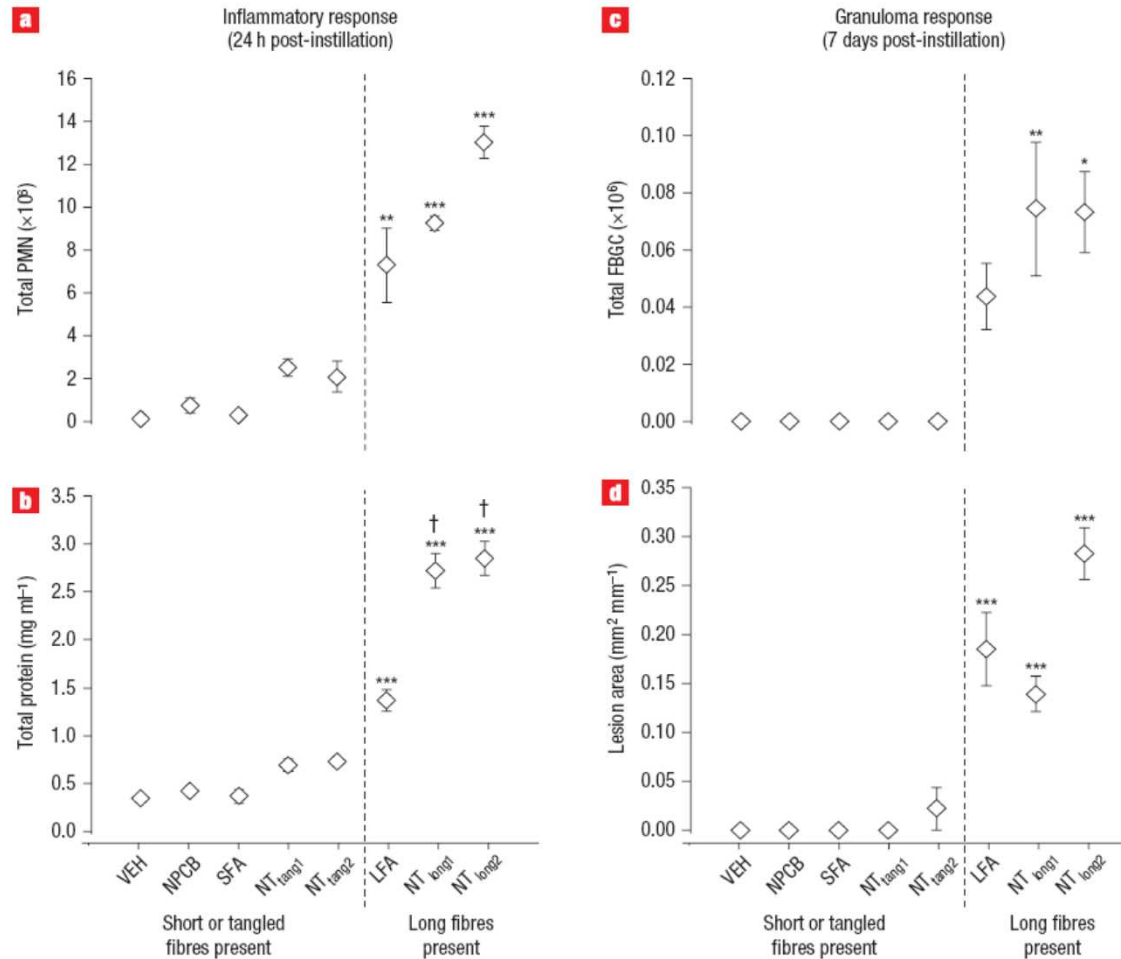
³Woodrow Wilson International Center for Scholars, 1300 Pennsylvania Avenue, NW, Washington DC 20004-3027, USA

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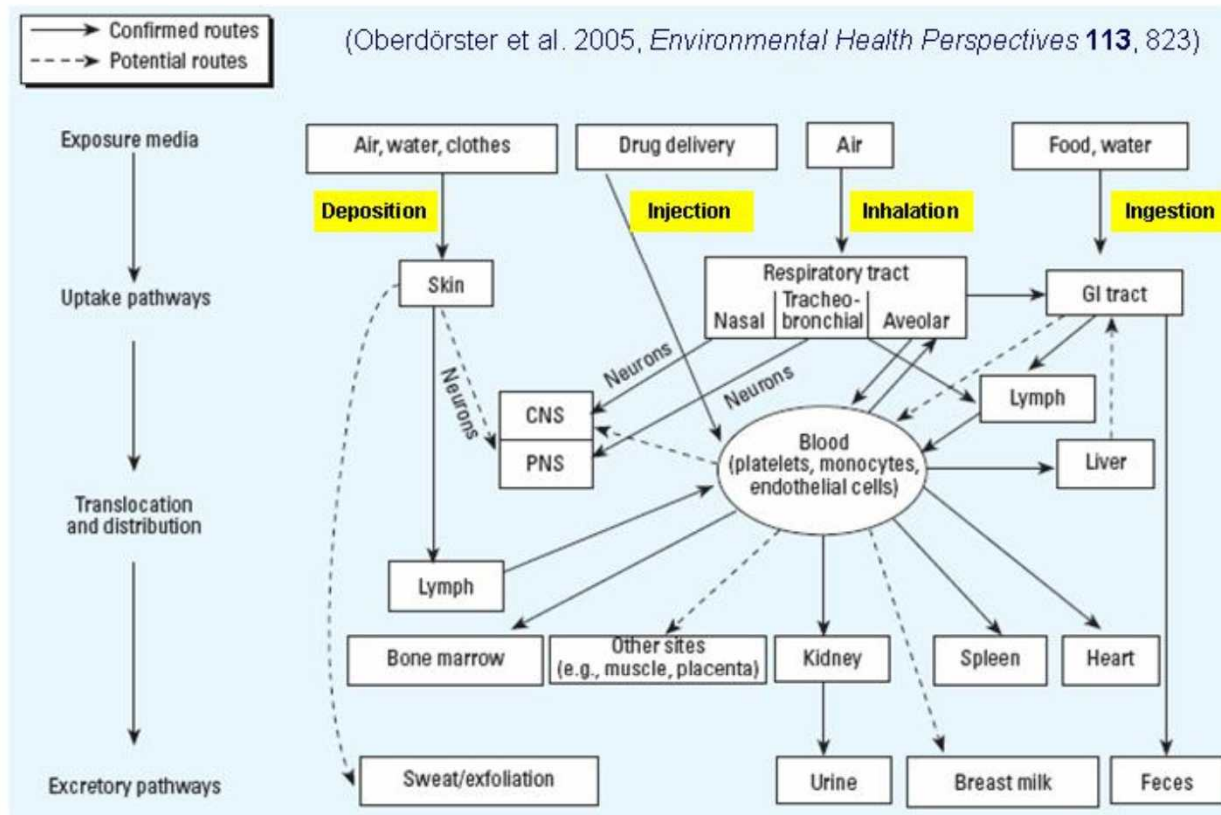
*e-mail: ken.donaldson@ed.ac.uk

Biological Effect of Carbon Nanotubes



Poland et al., 2008, Nature Nanotechnology

Nanotechnology and Human Health Impact



Acute - Contact with a substance that occurs once or for only a short time (up to 14 days)

Intermediate - Contact with a substance that occurs for more than 14 days and less than a year

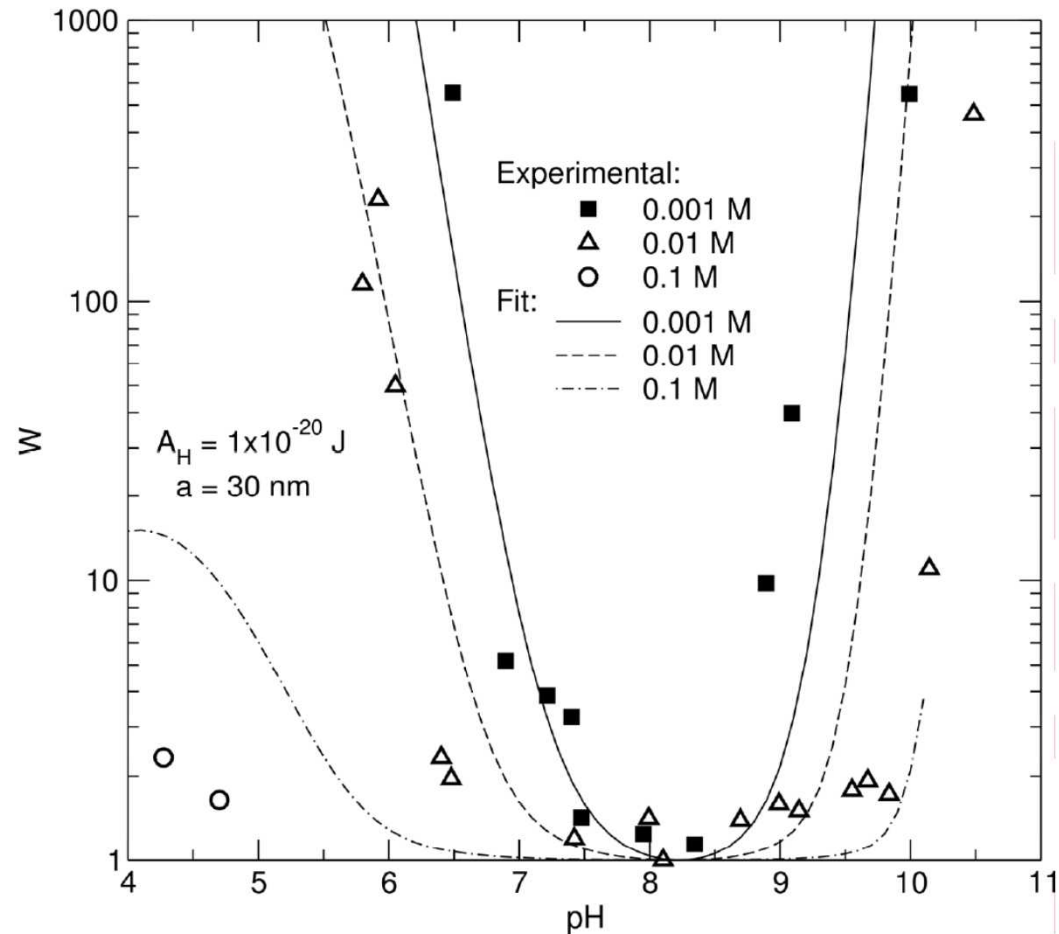
Chronic - Contact with a substance that occurs over a long time (more than 1 year)

Stability of Colloid Suspension

$$V_T = V_A + V_R$$

$$V_R = 2\pi\epsilon d_p \zeta^2 e^{-\kappa h}$$

$$W = 2 \int_0^\infty \frac{\exp(V_T / kT)}{a(h/a + 2)^2} dh$$

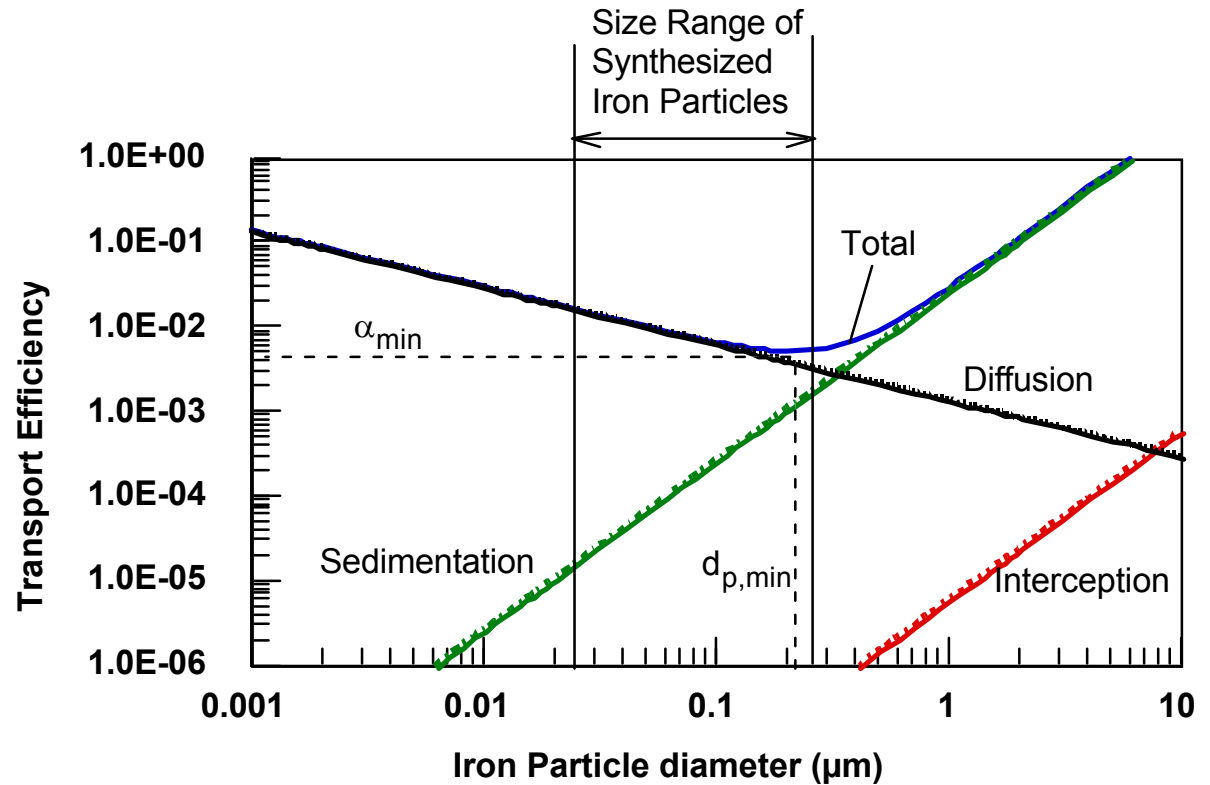


SNL, 2007

Colloid Transport & Filtration

$$\frac{dN}{dL} = -\frac{3}{2}\alpha\eta\frac{(1-\varepsilon)}{d_c}N$$

$$\alpha = f(pK_a, pH, \sigma \dots)$$



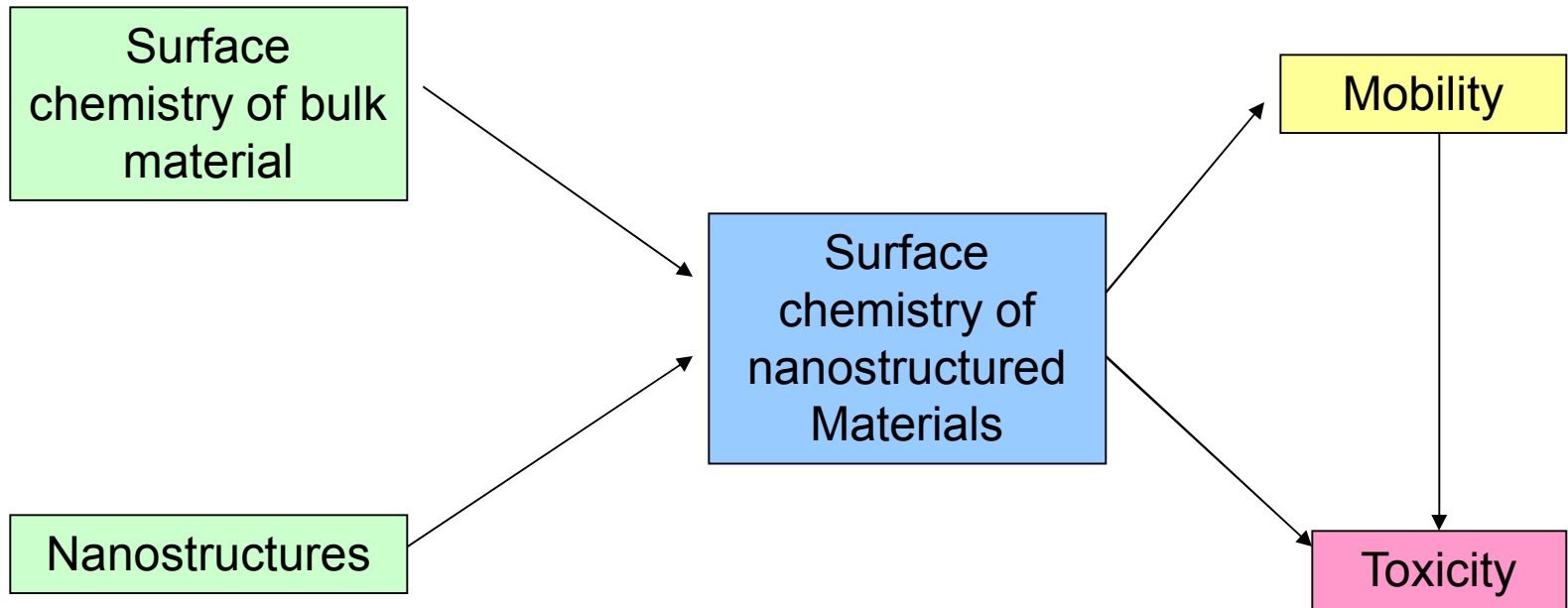
$$\eta = \eta_D + \eta_I + \eta_G = 0.9 \left(\frac{kT}{\mu d_p d_c v} \right)^{\frac{2}{3}} + 1.5 \left(\frac{d_p}{d_c} \right)^2 + \frac{(\rho_p - \rho) g d_p^2}{18 \mu v}$$

Zhang, per. Comm.

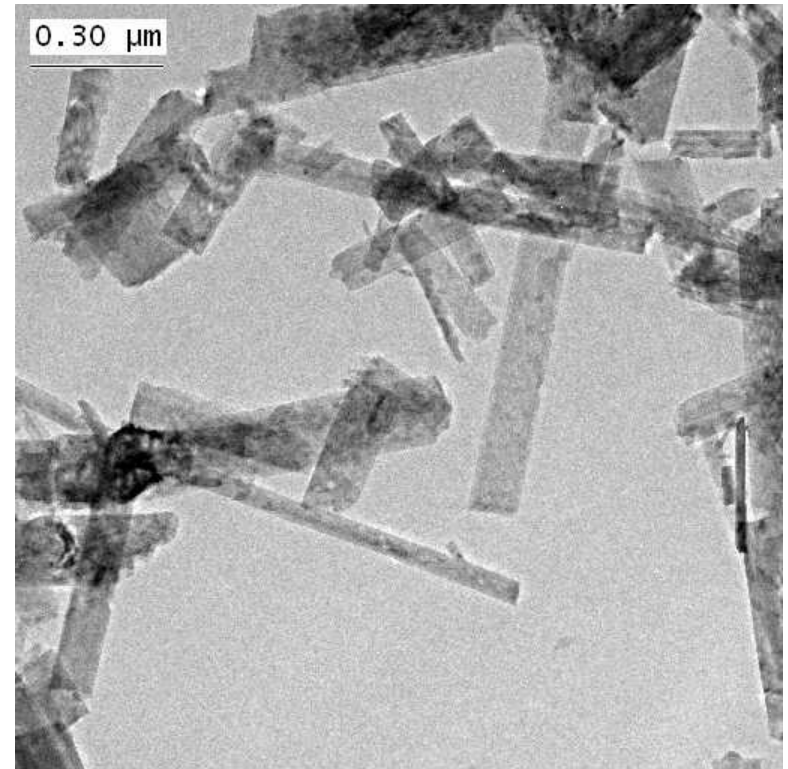
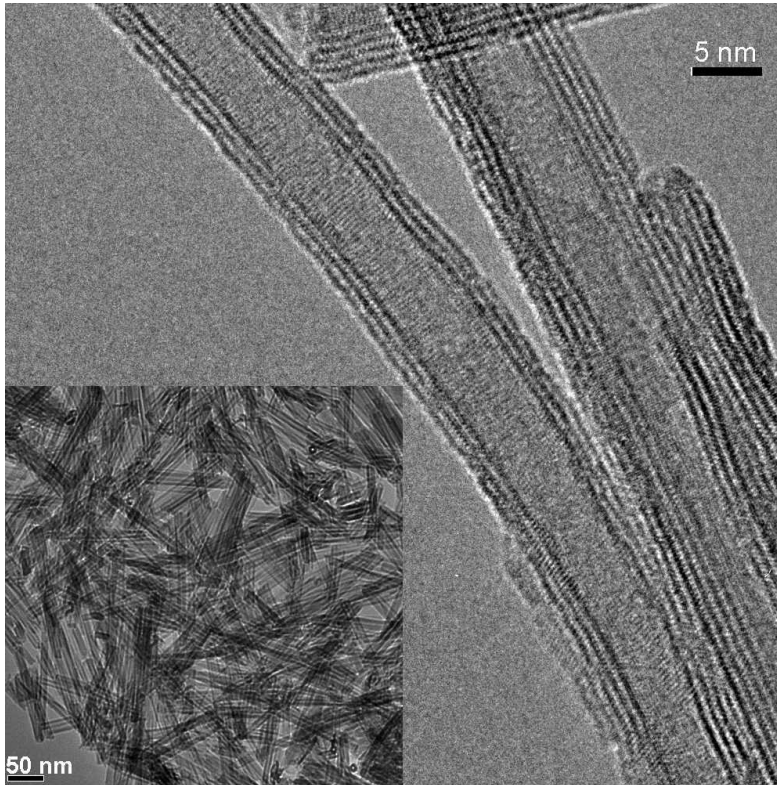
Technical Gaps for Evaluating the Impacts of Nanomaterials

- The key factors controlling the mobility of nanomaterials are the chemical properties of particle surfaces including the point of zero charge (PZC), acidity constant, and sorption capability.
- These properties are also important for mechanistic understanding of the uptake, persistence, and biological toxicity of nanoparticles inside living cells.
- Given the number of new nanomaterials daily emerging, to determine their surface chemical properties individually is a formidable task, if not impossible.

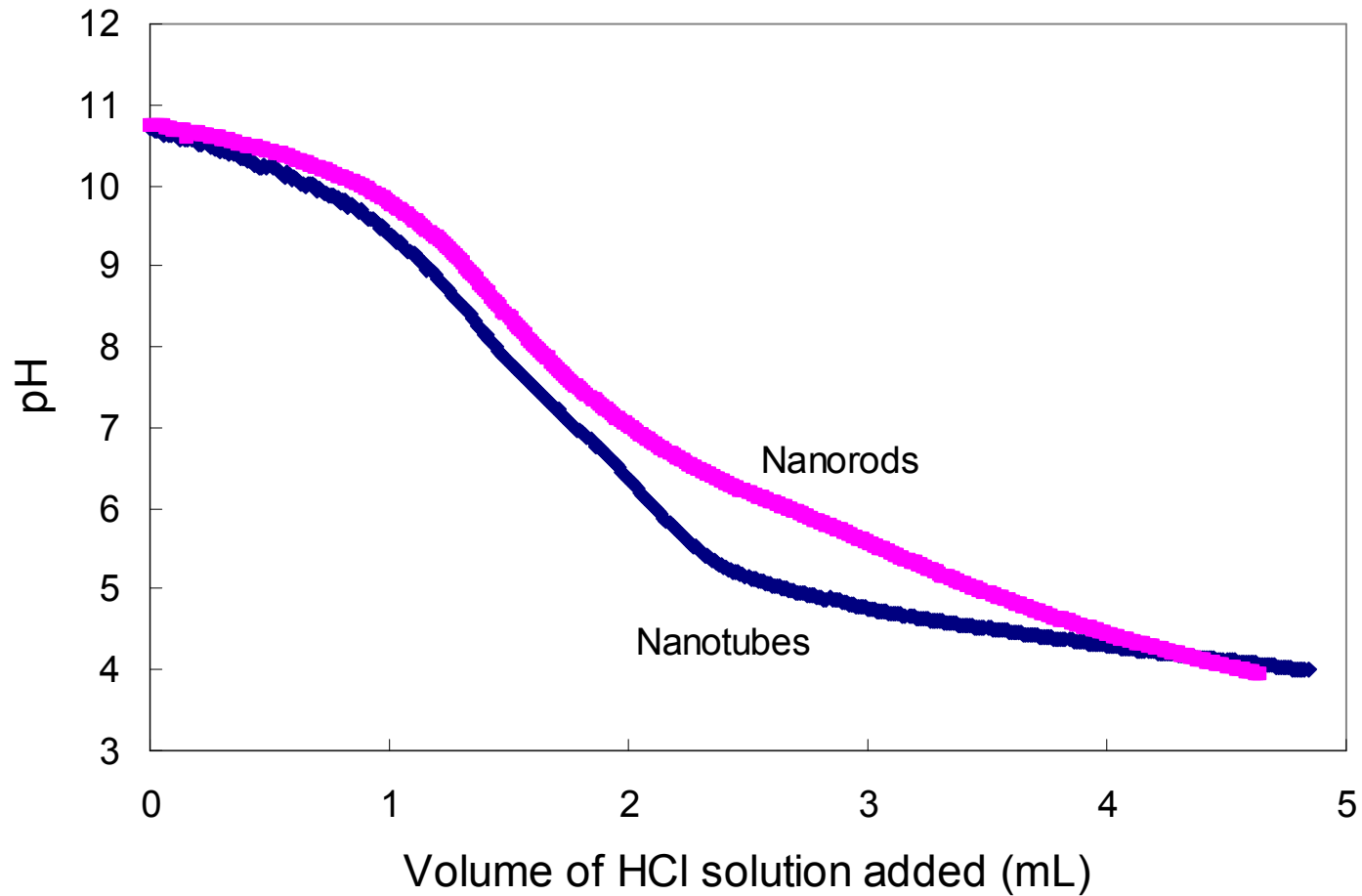
Structure-Function Relationships



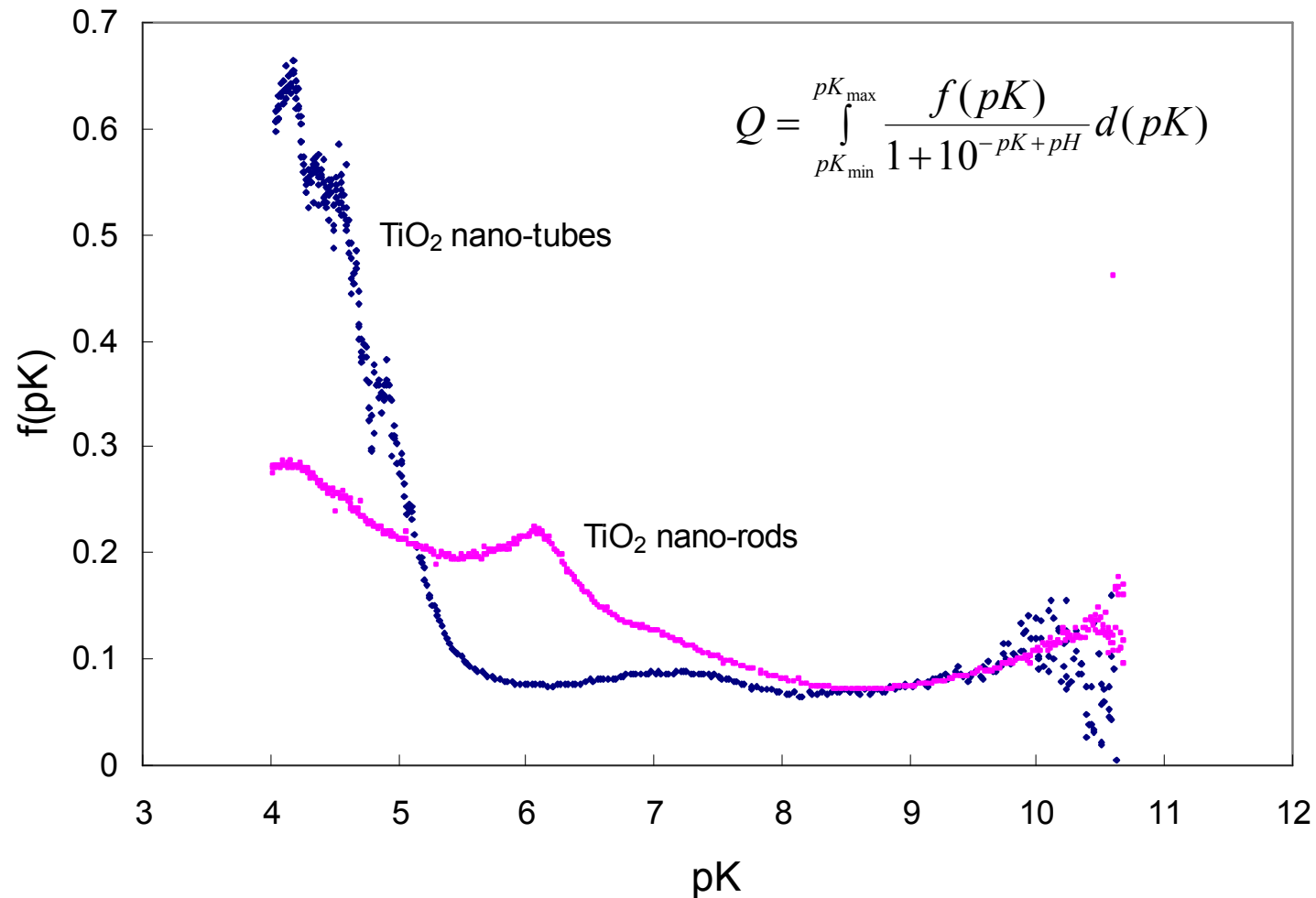
Synthesis of TiO_2 Nanotubes and nanorods



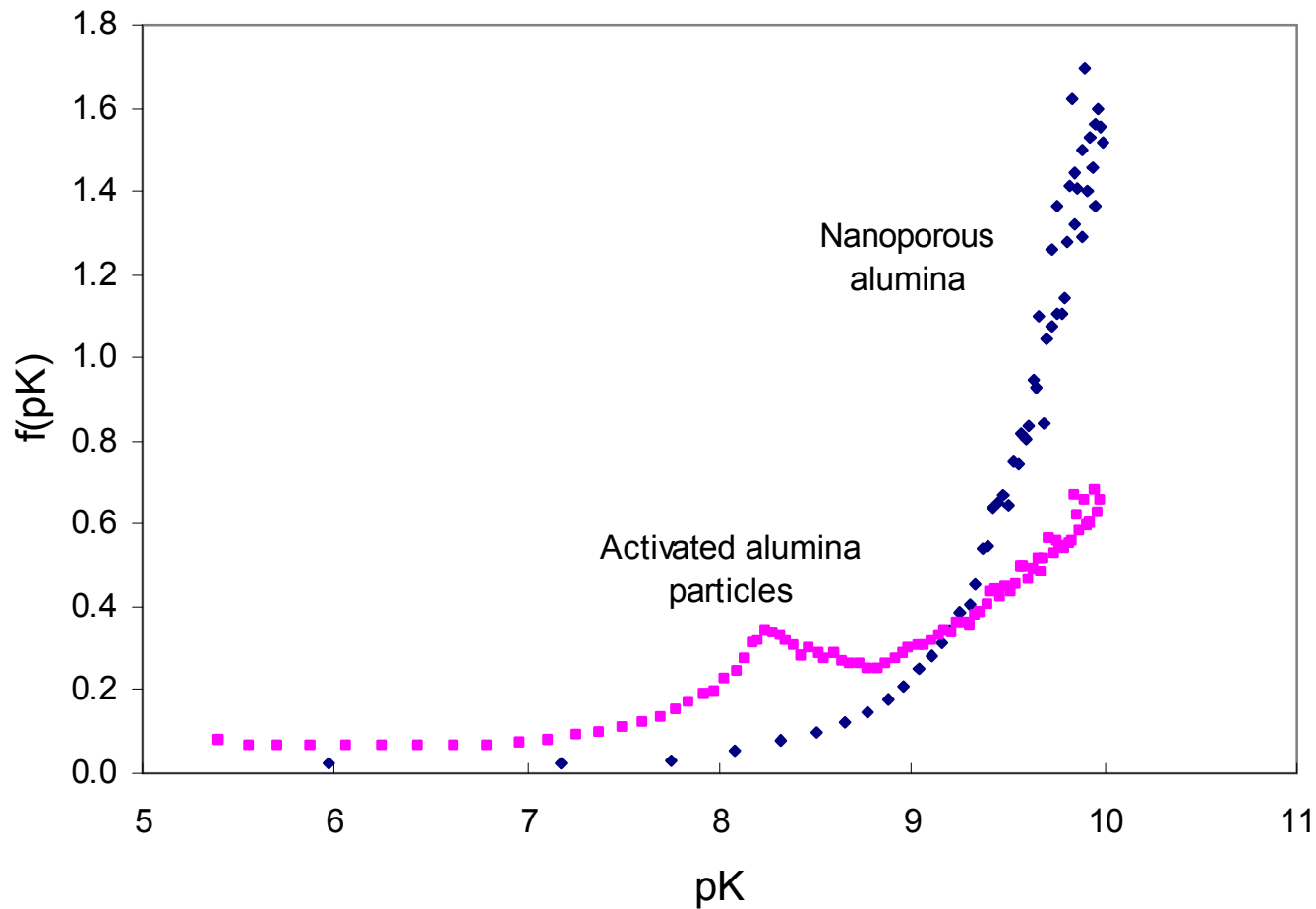
Titration Results



Distribution of Acidity Constant



Distribution of Acidity Constant



Concluding Remarks

- Like natural colloids, nanomaterials released into aquatic environments will experience a sequence of transformations including coagulation, settling, and filtration, which will ultimately control the bioavailability of these materials.
- The key factors controlling the mobility of these materials are chemical properties of particle surfaces including the point of zero charge (PZC), acidity constant, and sorption capability.
- It is possible to predict these properties based on the underlying nanostructures.