Nanosphere Reactive Oxides for Environmental Remediation

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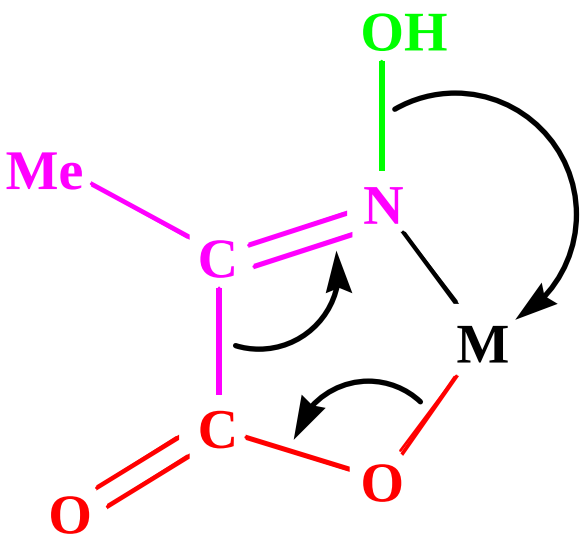
Low Temperature Precursors for Preparation of Nanoparticulate Metal Oxides

Low temperature synthesis prevents sintering

Allows synthesis of metastable phases

Can be used for coating of heat-sensitive substrates

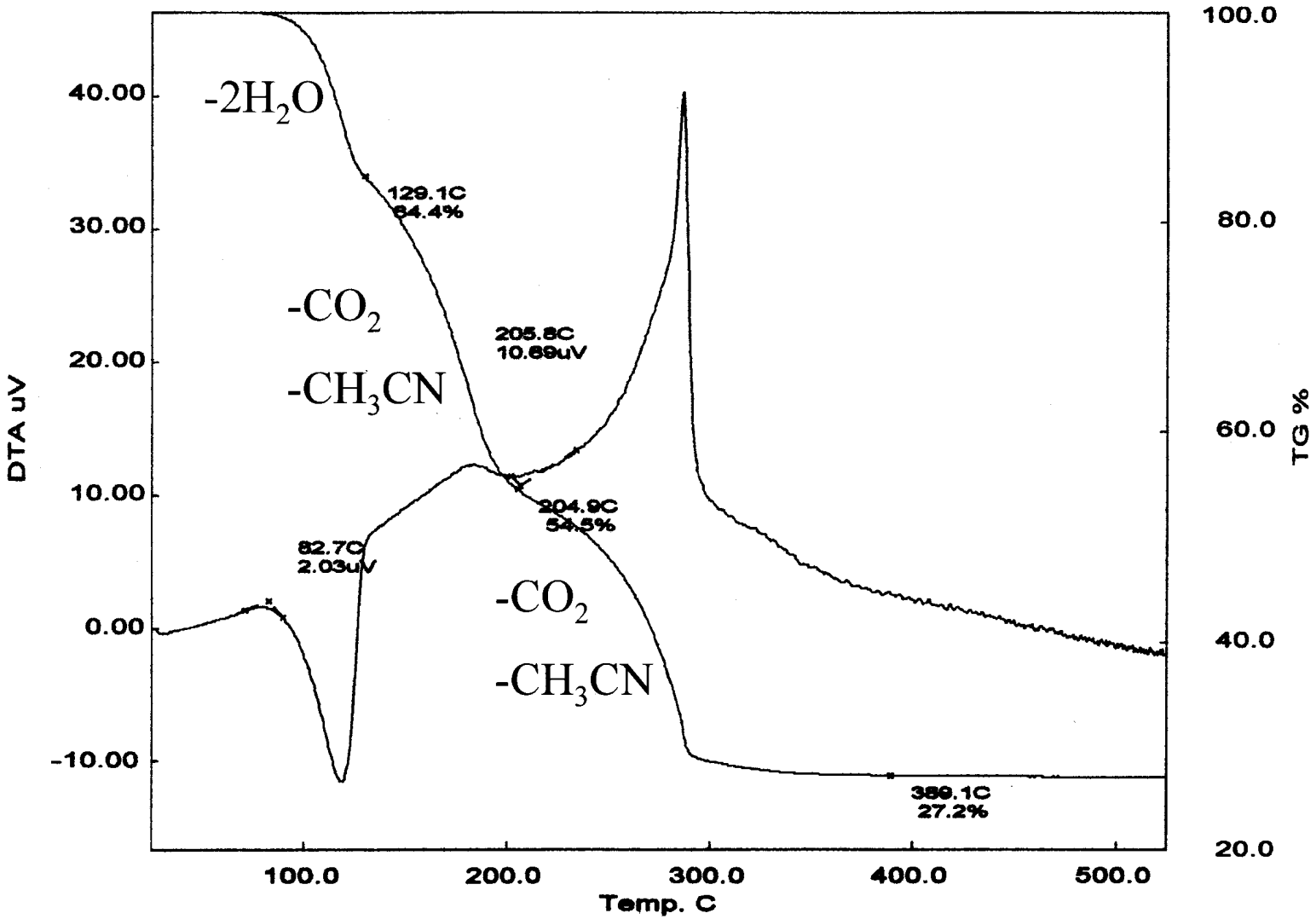
Amorphous phases can also be synthesizd



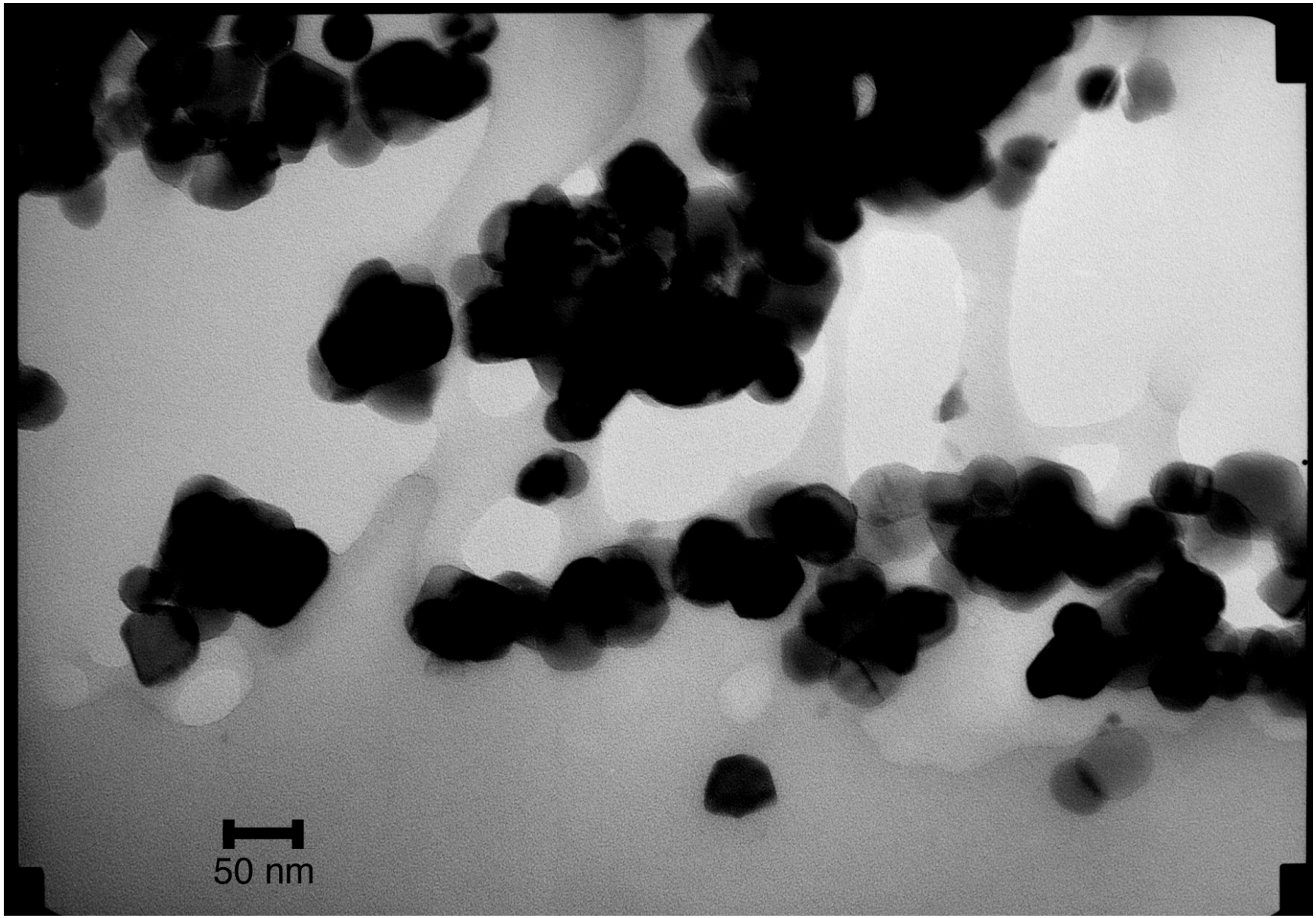
MOH + CO_2 + MeCN

Metal Salts of pyruvic acid oxime (PAO)

TGA Trace for $Zn(PAO)_2 \cdot 2H_2O$



TEM Image of ZnO Particles

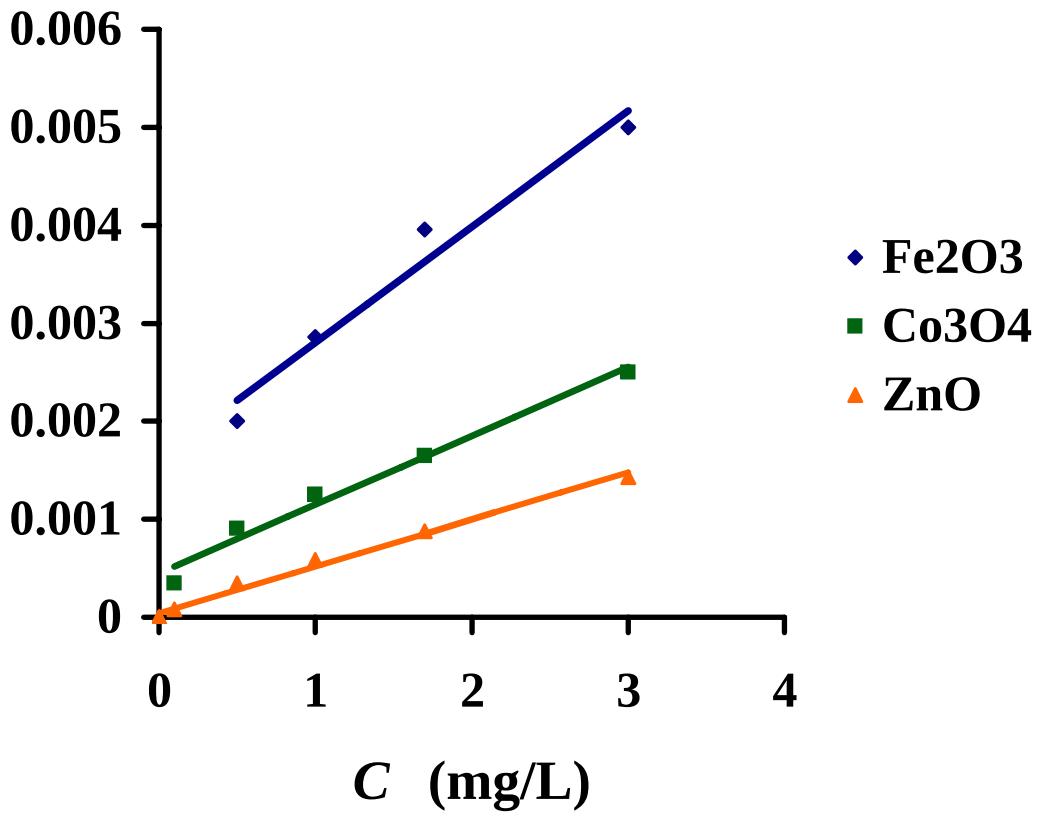


Textural and Surface Acid-Base Properties of Transition Metal Oxides

Transition Metal Oxide	Surface Area (m^2/g)	Acidity (μmol/g)	Basicity (μmol/g)	Average Crystallite Size (nm)
Fe_2O_3	140	32.56	130.2	30.0
Co_3O_4	58.76	162.6	22.43	6.4
ZnO	37.37	147.82	57.04	24.6

Determination of Arsenate Uptake

The arsenic adsorption capacities were determined using Langmuir adsorption isotherms: $C/X = C/M + 1/KM$.



Transition Metal Oxide	Arsenic Capacity (μmol/g)
Fe_2O_3	11.29
Co_3O_4	19.01
ZnO	27.77

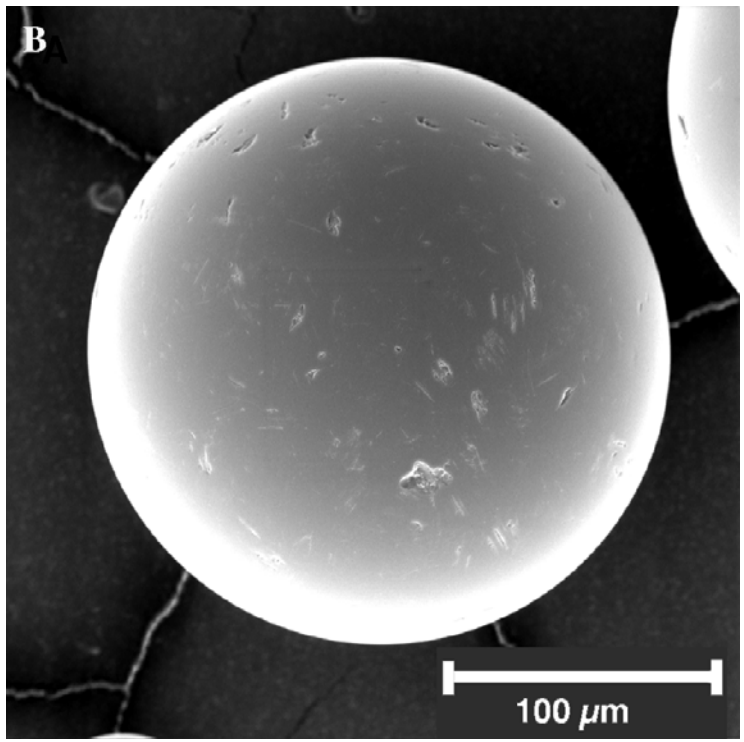
Problem: Keeping Nanoparticles in Place

Small particles escape with air or water flow.

If trapped with a frit backpressure can be phenomenal

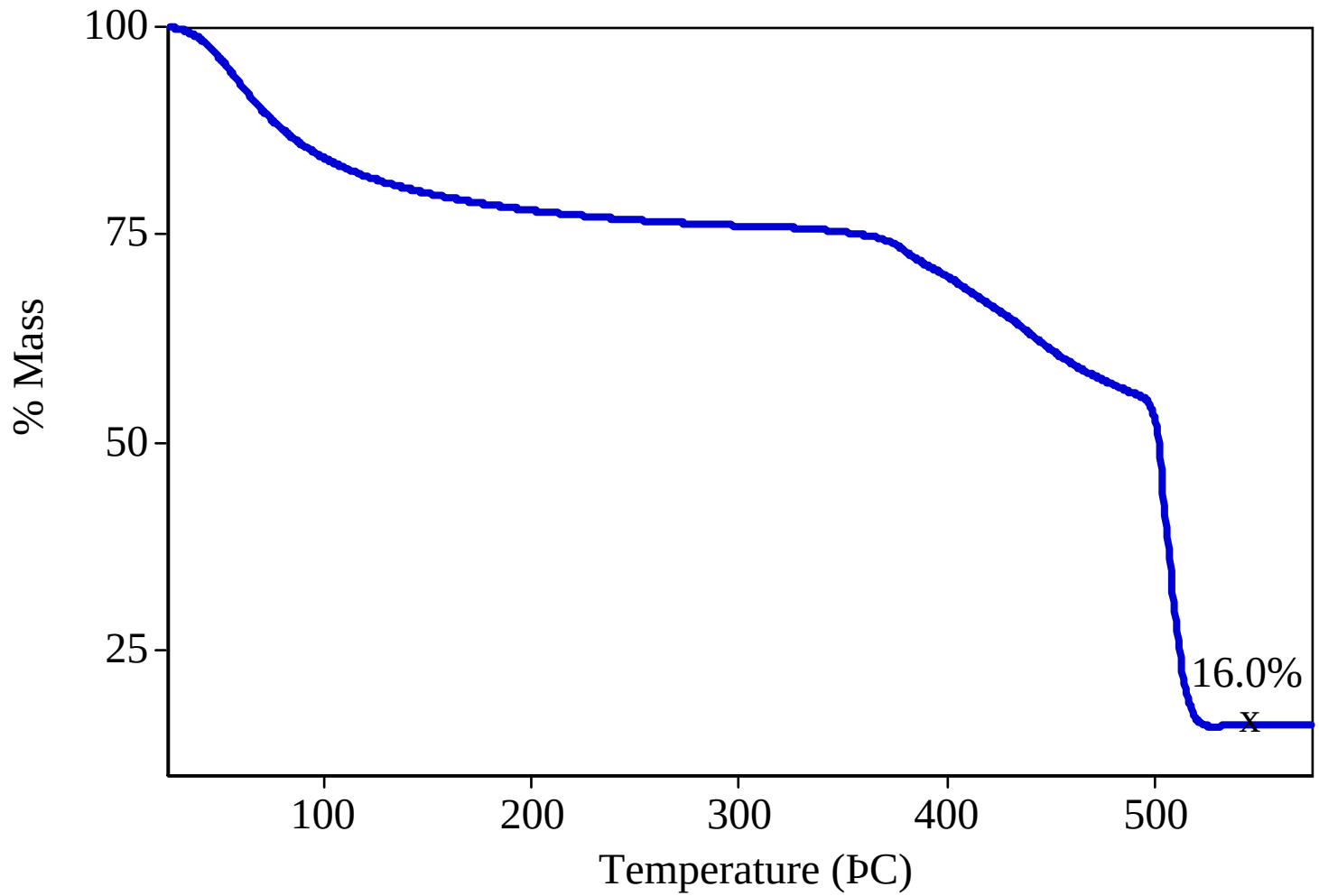
SPHERICAL NANOPARTICLE AGGLOMERATES

- **Discrete nanoparticles are unsuitable for use in columns for water treatment or for fluidized beds**
- **Larger,monodisperse, spherical agglomerates are preferred**
- **Ion-exchange resins can be obtained that meet the size requirements**
- **Can they be converted to nanoparticulate ceramic replicas?**



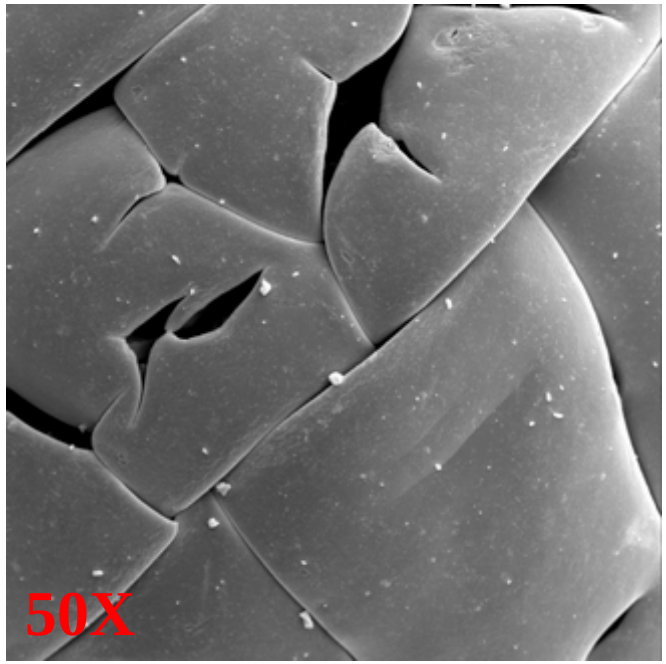
SEM Image of Dowex 650C Resin Bead

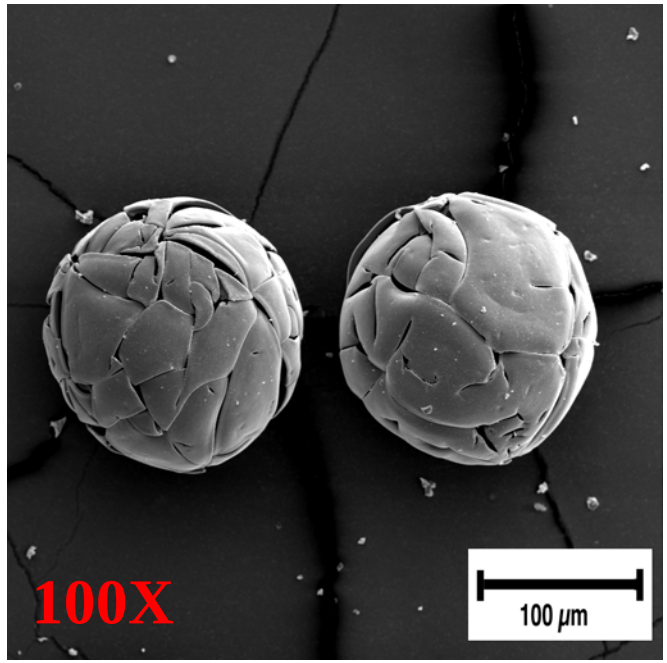
Thermal gravimetric analysis trace for zinc-loaded Dowex 650C cation exchange resin

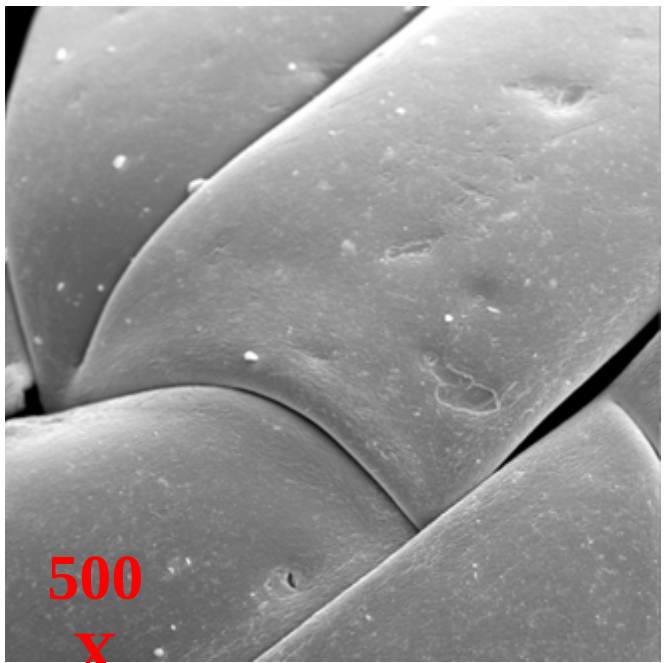


ZnO Spheres from Firing of Zinc Loaded Dowex Resin

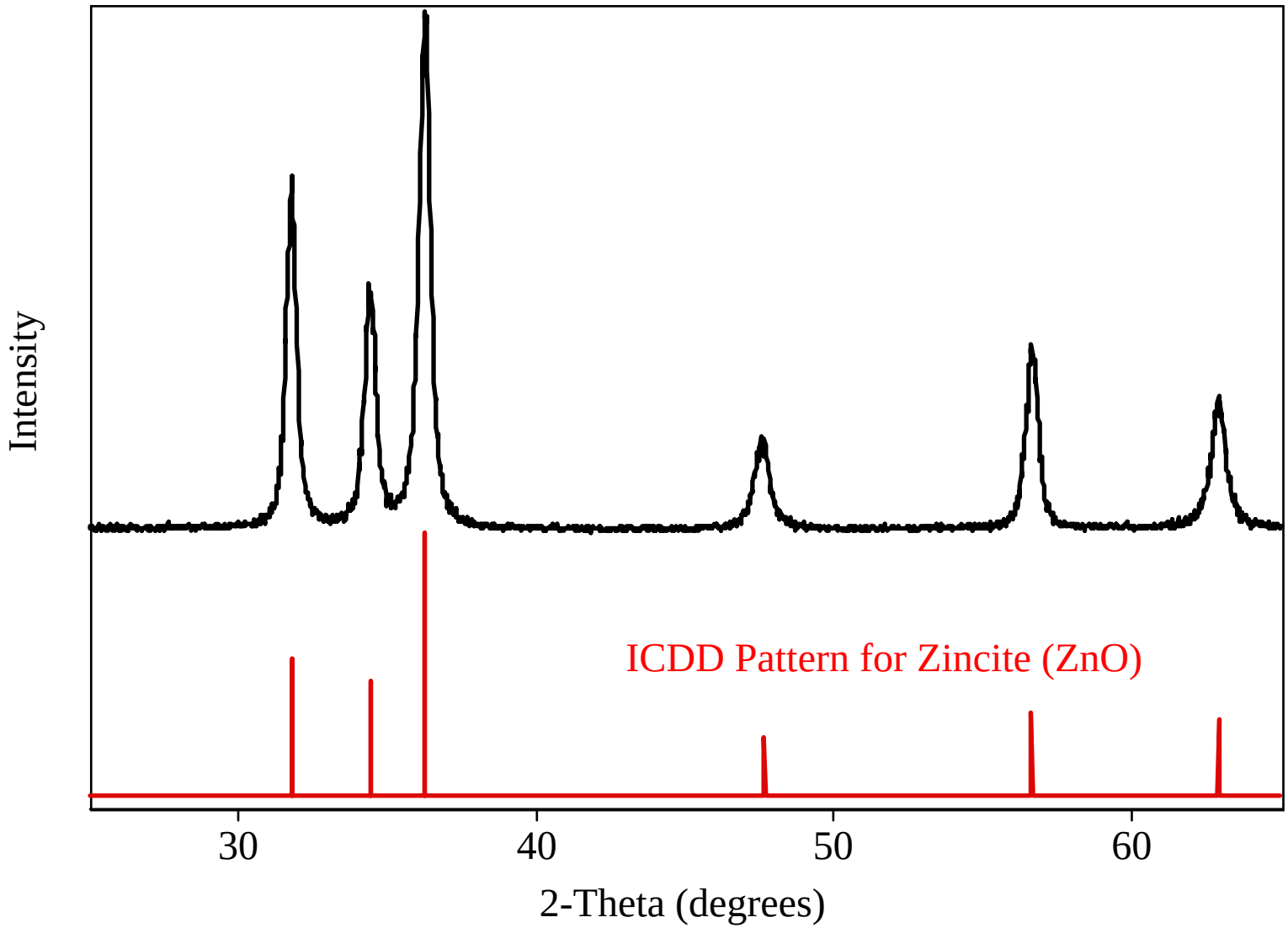
SEM Images Of ZnO Spheres From Firing Of Zinc-Loaded Dowex Resin

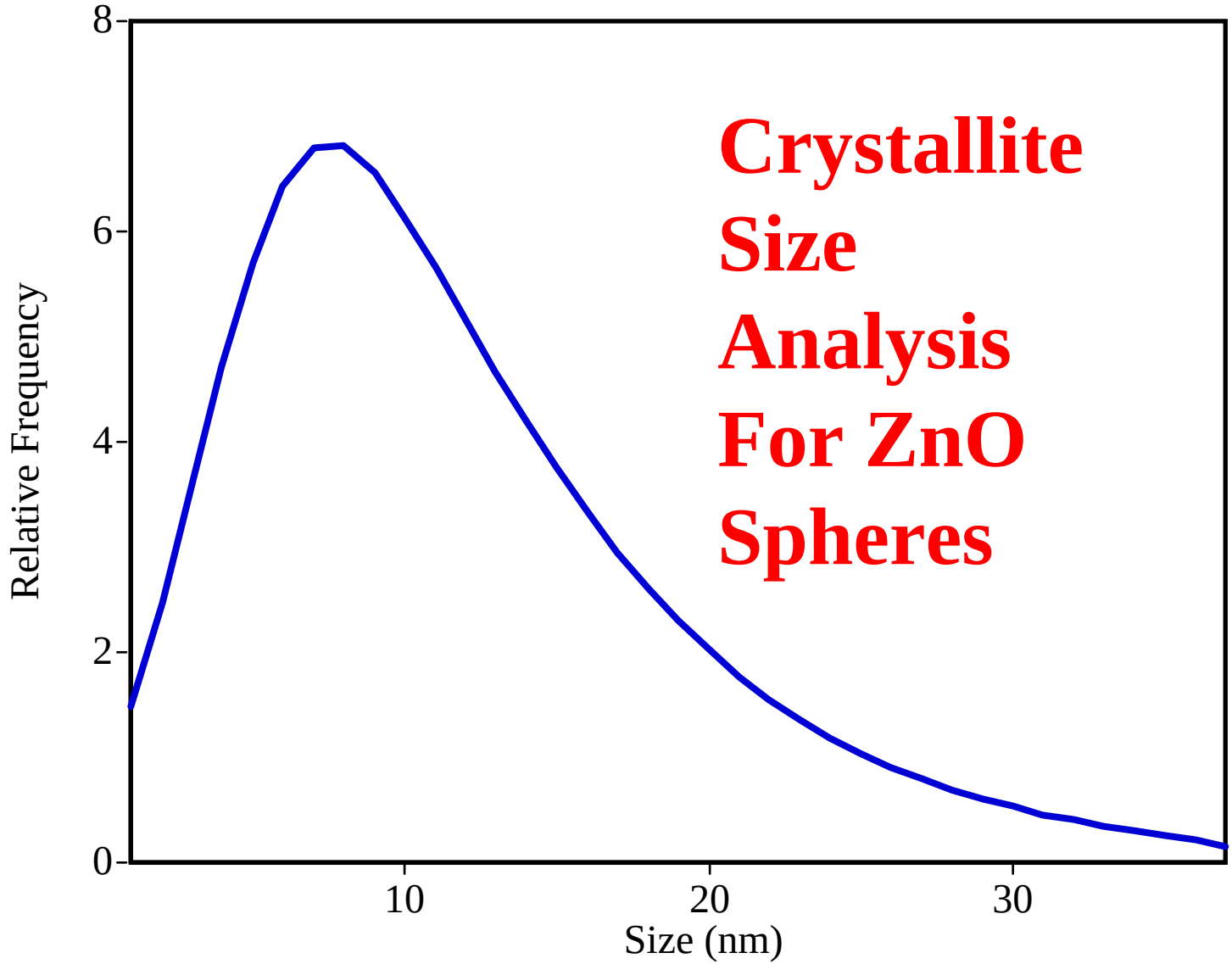






XRD Pattern for Spherical Zinc Oxide





Average Size: **12.3 nm** **Maximum of Rel. Frequency**: **7.6 nm**

FWHM of Size distribution: **12.9 nm**

Adsorption of Arsenic (Sodium Dihydrogen Arsenate) By ZnO

ZnO Sample	Surface Area (m^2/g)	Initial [As] (ppb)	Final [As] (ppb)
Commercial	0.13	300	300
Spheres	30.7	300	10
Spheres	30.7	3,000	40
Spheres	30.7	10,000	150

Capacity for Arsenic Adsorption is 985 µg/g. Only nanoparticles are reactive towards Arsenic

Removal of Lead and Other Heavy Metals from Water

Pb^{2+} in water →  → Pure water

Useful reagents:

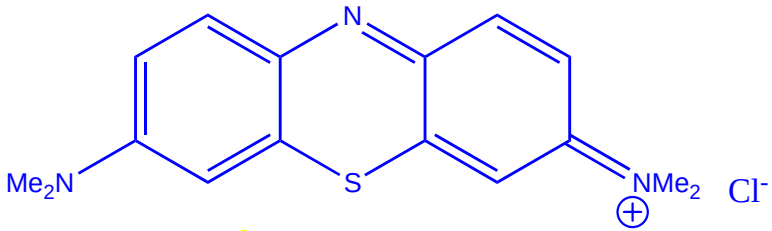
MnO_2 Nanospheres (shown above) adsorb lead on the surface (1 mg Pb/g)

FeS Nanospheres prepared by pyrolysis of iron-loaded ion-exchange resin under nitrogen react to form PbS and release Fe^{2+} -very high capacity

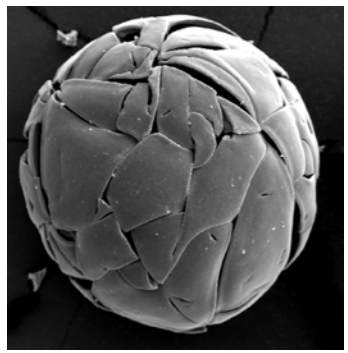
Photocatalytic Oxidation

"Sense and shoot" approach for photocatalytic degradation of organic contaminants in water. When ZnO nanoparticles are exposed to UV radiation, they fluoresce. In the presence of organic pollutants, the ZnO oxidizes the pollutant, and its fluorescent signal is reduced.

Methylene blue



365 nm



ZnO

CO_2 + H_2O + NH_3 + SO_2

Anatase TiO_2 Nanospheres are also useful photocatalysts

TiO_2 Nanospheres

Produced by pyrolysis of ion exchange beads loaded with Ti^{3+} from hydrochloric acid solution of $TiCl_3$

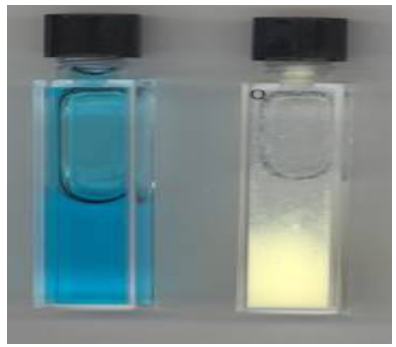
- 92% anatase, remaining rutile
    - good photocatalyst for oxidation reactions
        - oxidize chloride to chlorine

Practical application for water purification with a lasting disinfectant effect

Destruction of Halocarbon and Chemical Weapons

Chlorocarbons, e.g. CCl_4, chemical weapons, e.g. VX, undergo irreversible adsorption and hydrolysis. Reactivity comparable to Klabunde's MgO nanoparticulate powder

CCl_4



MgO Nanospheres

CO_2

MgO **MgO / I_2**

MgO/Halogen complexes can destroy bacteria, viruses and spores.

Conclusions & Acknowledgements

- Pyrolysis of ion-exchange resins provides a facile approach to porous spherical aggregates of nanoparticles
- Nanoparticulate zinc oxide is an excellent adsorbant for arsenate and photocatalyst for sense and shoot destruction of organics
- Other metal oxide and metal sulfide nanoparticles may also be excellent catalysts and adsorbants for various pollutants

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Catalysis

Solvent-free synthesis of chalcone, a chemical intermediate for perfume and pharmaceutical synthesis