Gold/Polymer Nanocomposites by Dispersed Phase Polymerisation

Ultrasonic Initiation and Agitation

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Outline

- Background
  - photonic and biological applications
  - ultrasonics and free radicals
  - miniemulsion polymerisation
- Combining these:
  - gold particles
  - polymer particles
    - » miniemulsion or not?
  - Au/pMMA nanocomposite synthesis

Inorganic Core, Polymer Shell

- Polymer particles
  - cheaply produced, easily functionalised
  - variety of mechanical and chemical properties
  - dispersible in water
- Inorganic cores (Au, CdSe, ...)
  - novel optical and biolabelling properties
  - aggregate in water

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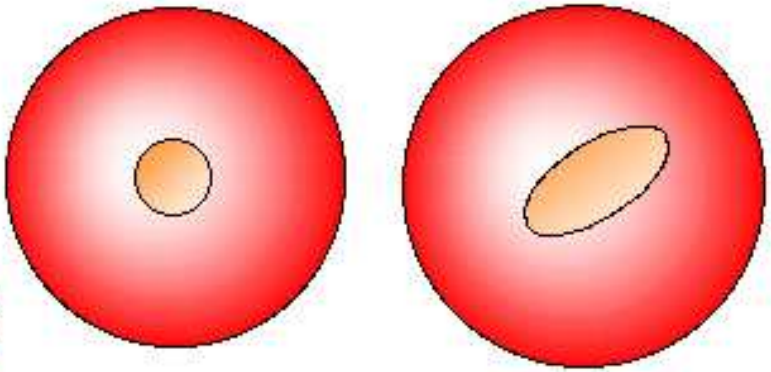
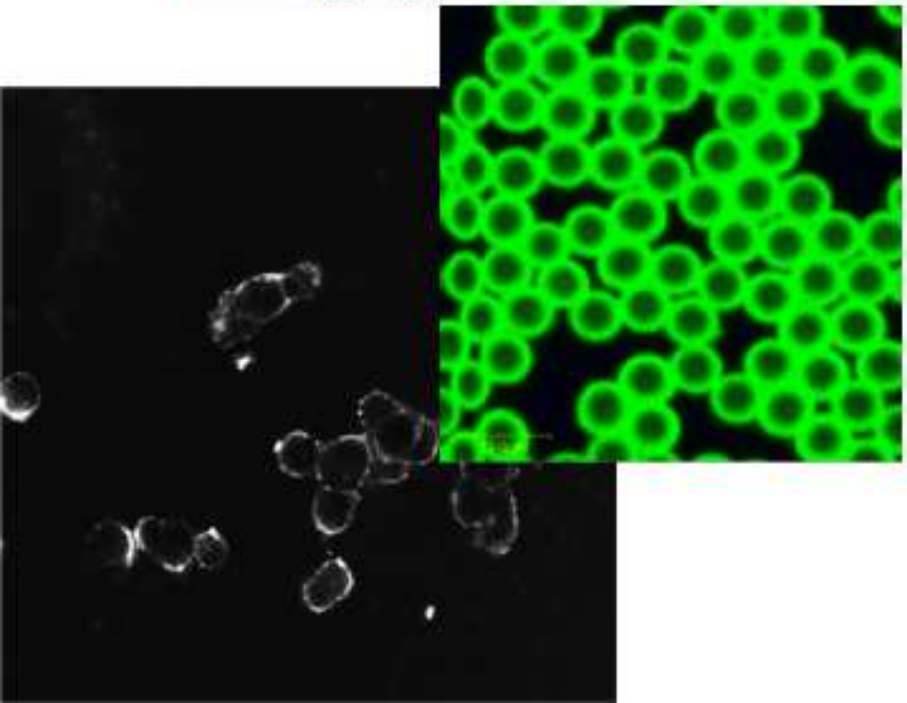
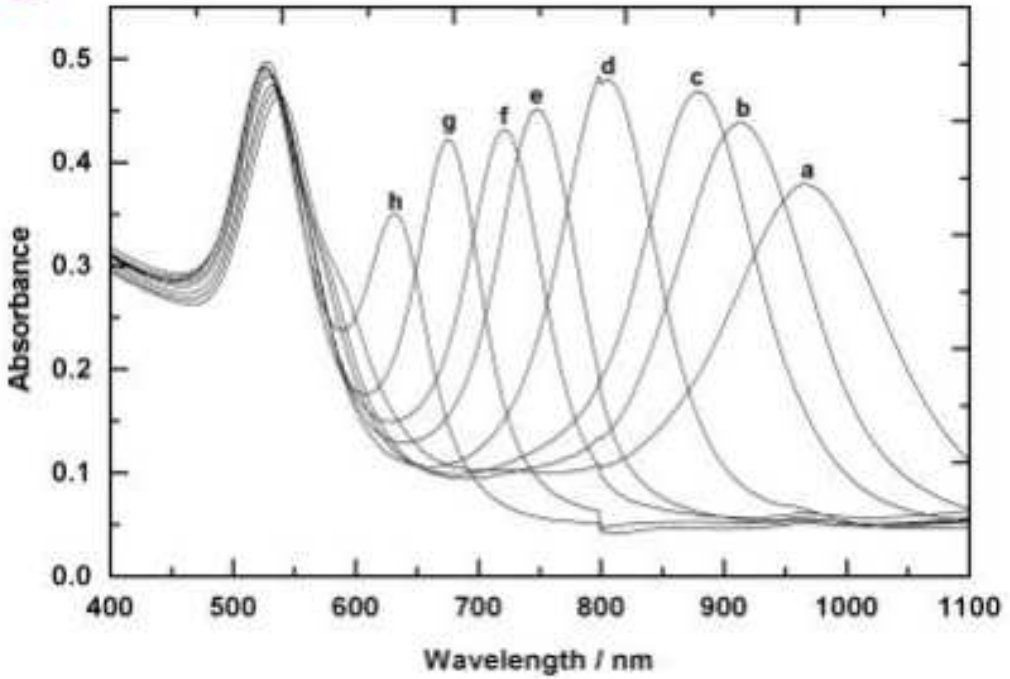




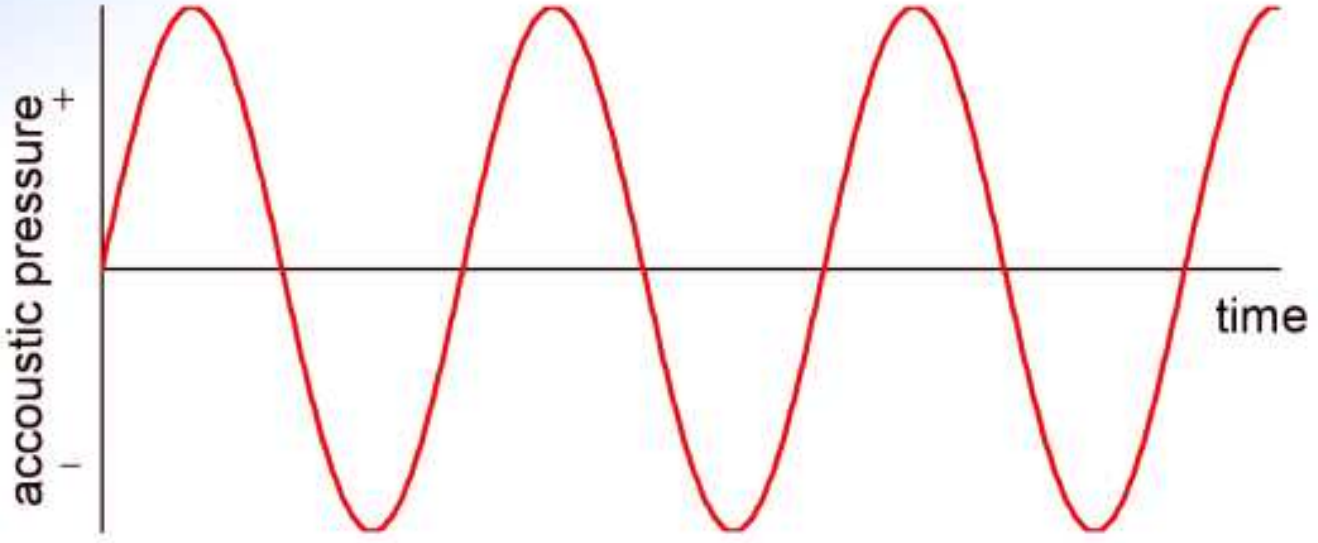


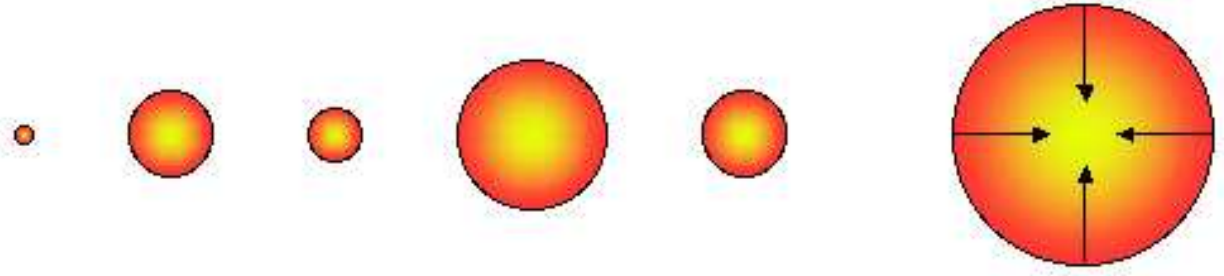
Ultrasonics

- clean source of radicals
  - for reduction
  - for polymerisation
- high shear environment
  - miniemulsion without added hydrophobe
- potential to make a one-pot synthesis of nanocomposite particles
  - core can be later removed $\Rightarrow$ hollow particle

Ultrasonic Cavitation

- adiabatic bubble collapse ➔ 5000 K



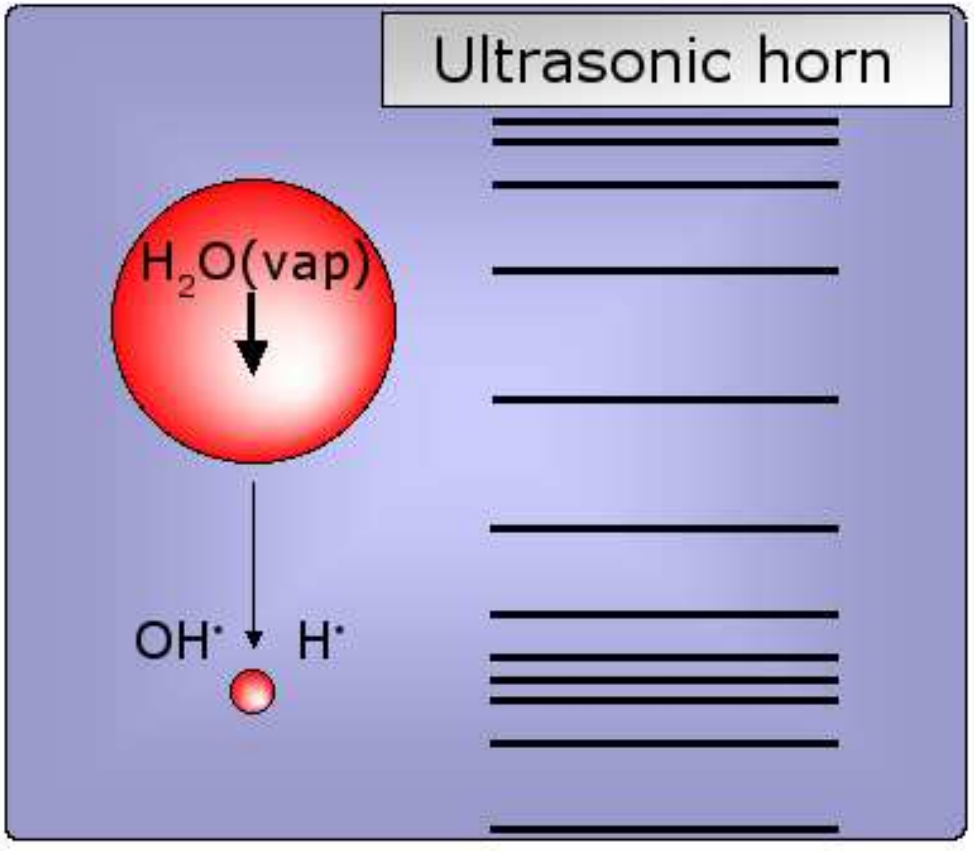


initial bubble

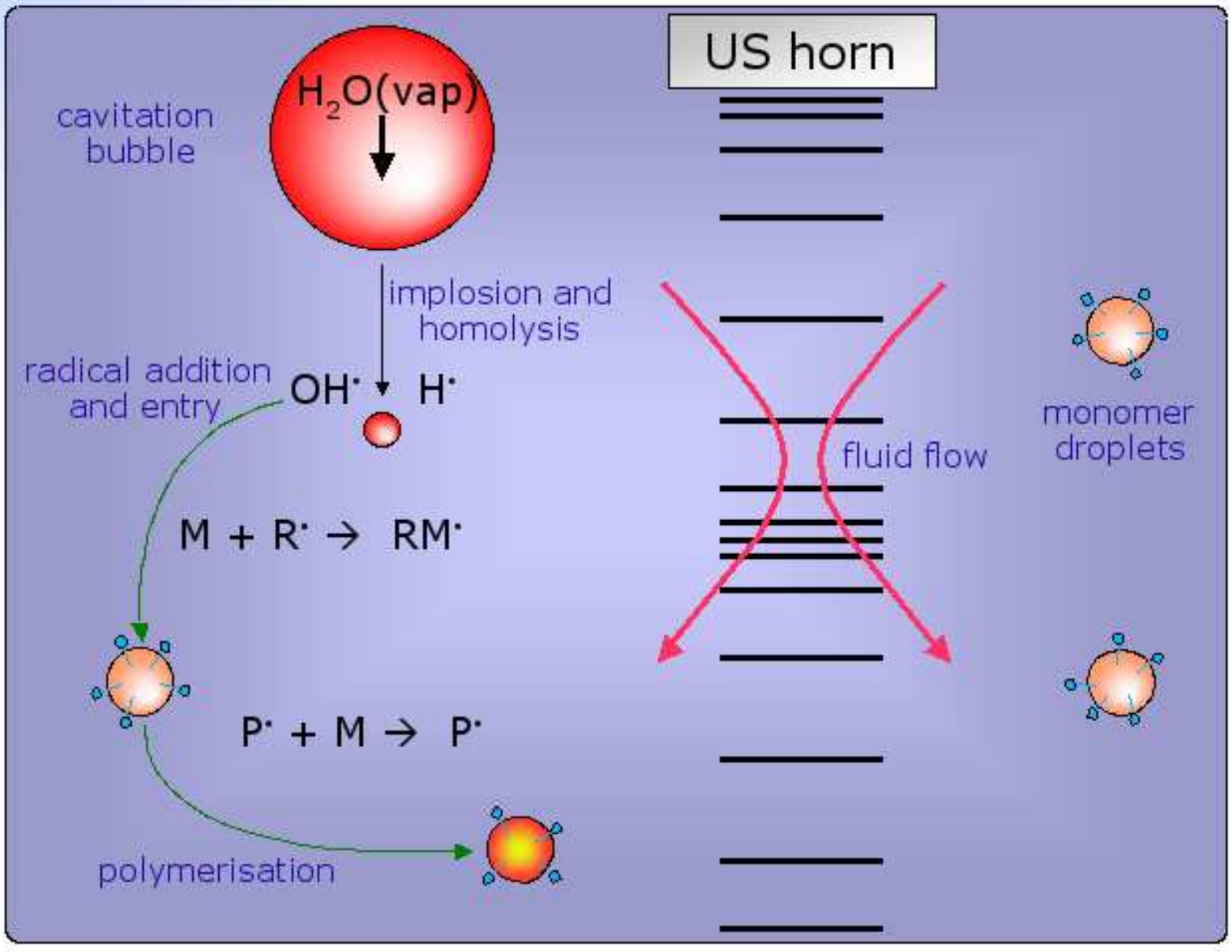
bubble collapse

Ultrasonic Cavitation

- cavitation + implosion creates radicals:
  - $OH^{\bullet}$ and $H^{\bullet}$
  - both can initiate polymerisation
- high shear
  - agitation
  - fine droplets, ~80 nm diameter
- 20kHz field, ~26W

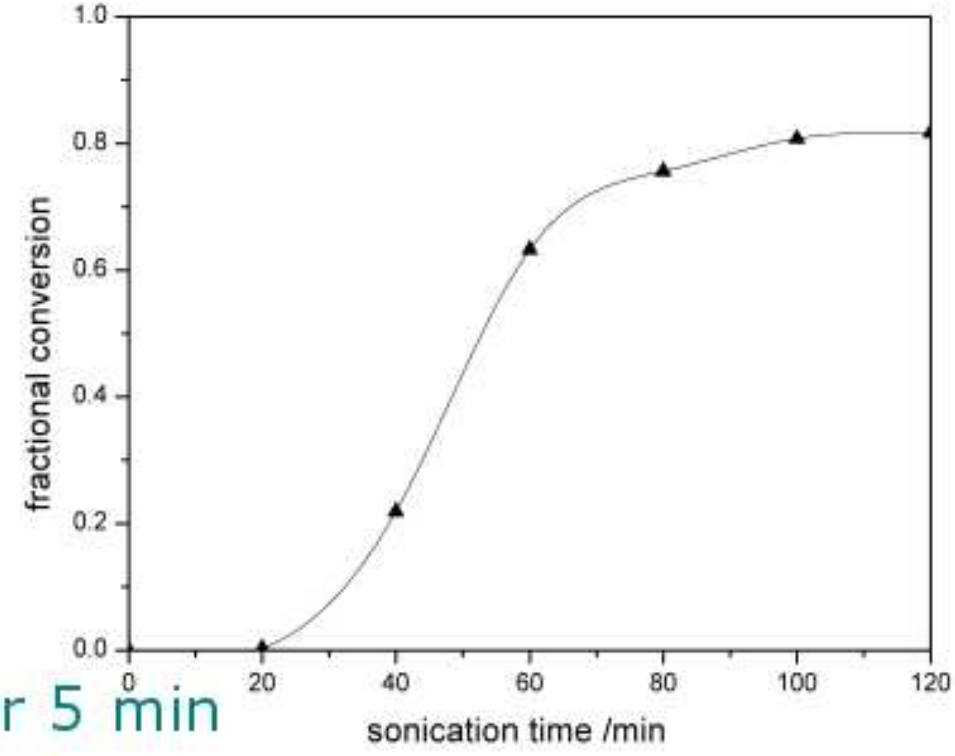


Miniemulsion Polymerisation



Synthesis of pMMA particles

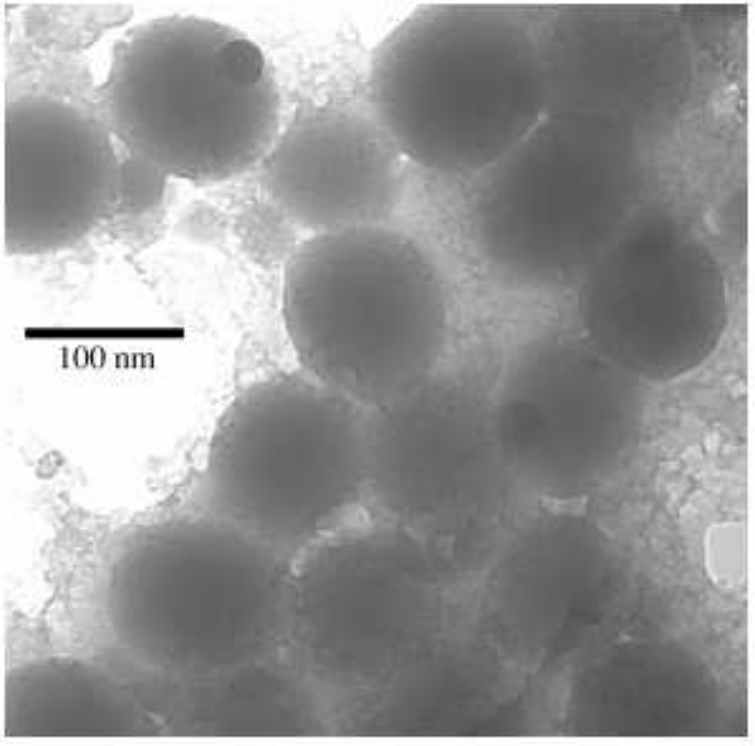
- Typical recipe:
  - 6.4 g MMA
  - 0.45 g SDS
  - 36 g H_2O
  - Ar purge
  - sonication:
    - » on for 10 min, off for 5 min
  - water jacket: 25±2°C
- 80% conversion in 60 min sonication



e.g. Bradley, Ashokkumar, & Grieser, JACS 2003, 125, 525.

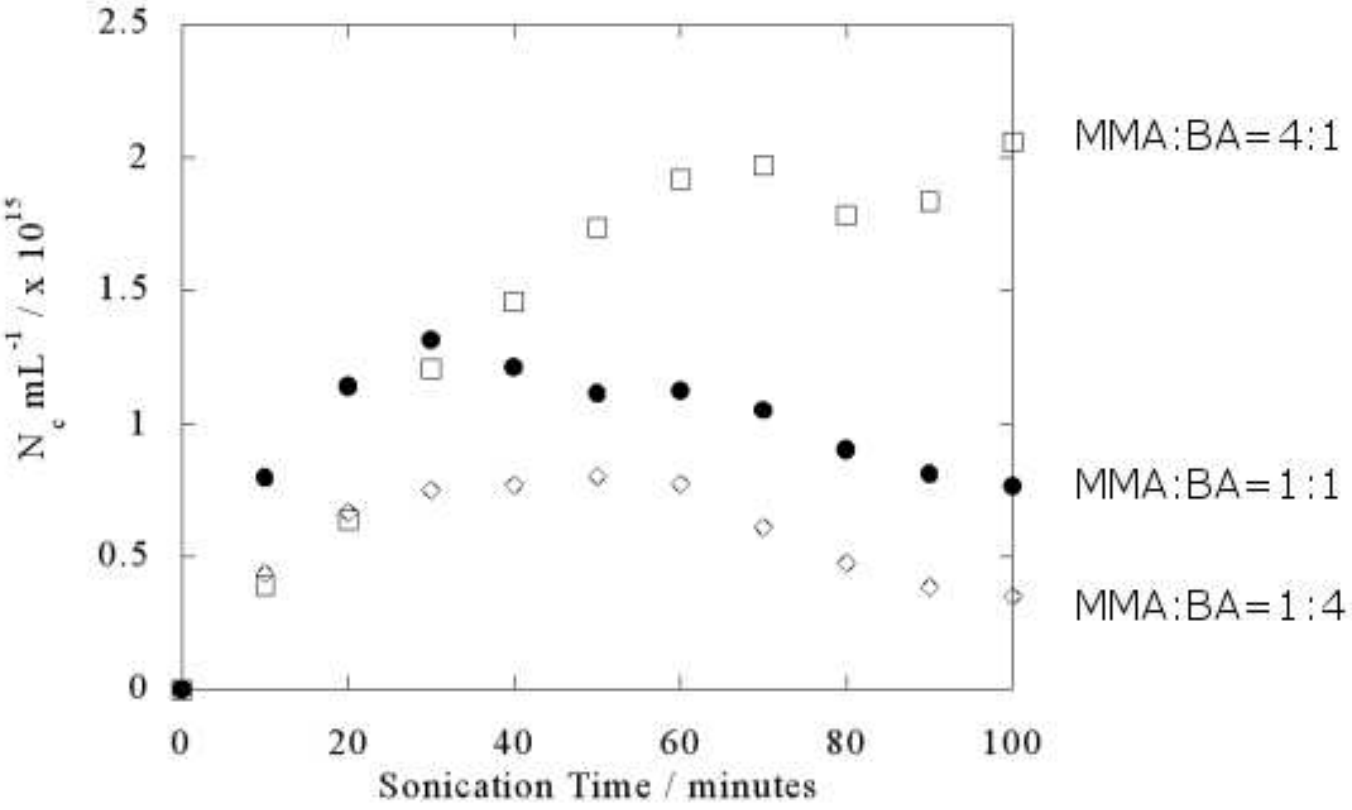
Synthesis of pMMA particles

- Stable dispersion of pMMA in water
  - reasonably monodisperse particle size
  - ~100nm diameter, 10^{18} particles dm^{-3}



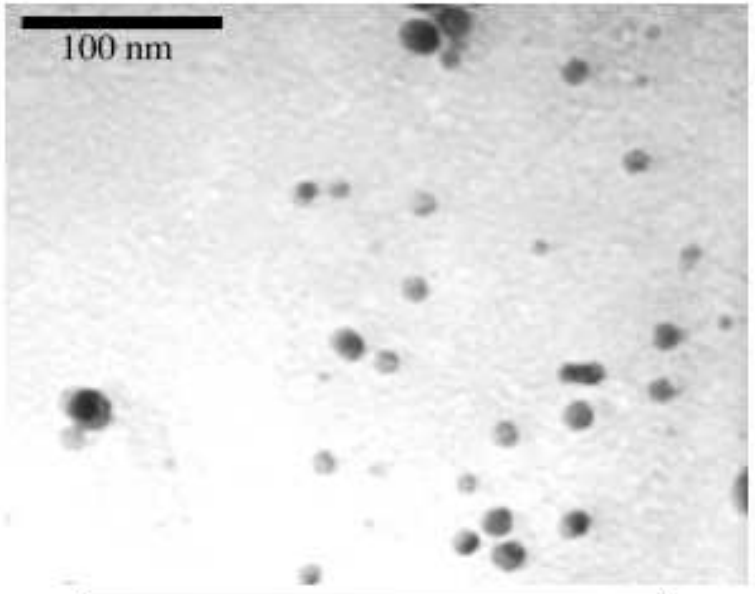
Droplets to particles

- Unswollen radius increases with conversion
- Particle number increases due to continuous droplet nucleation



Synthesis of Au nanoparticles

- Sonochemical reduction
  - particles in water phase
    - » propanol and SDS
  - only low concentration of particles possible
    - » limited by ultrasonic radical generation

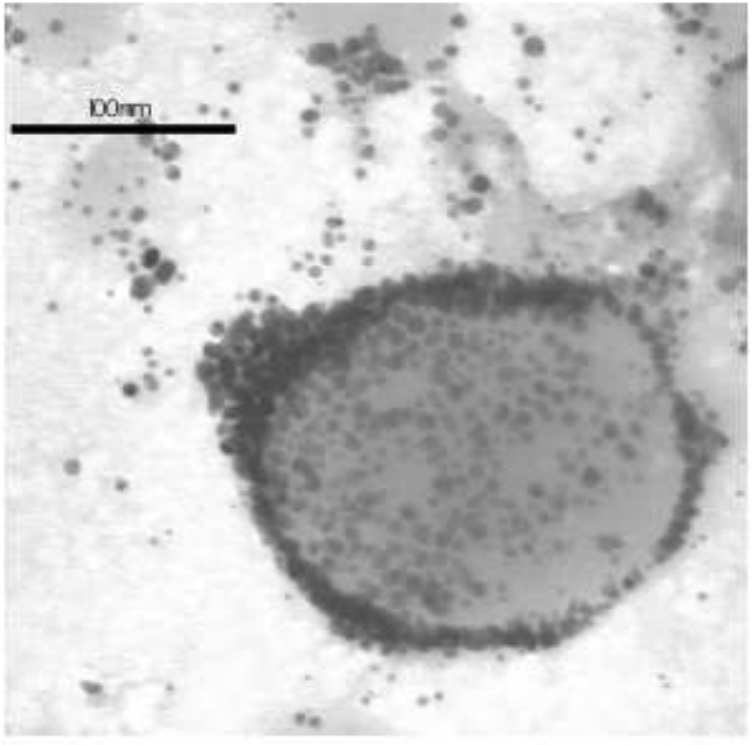


5–15 nm diameter particles

Caruso, Ashokkumar & Grieser, Langmuir 2002, 18, 7831.

Synthesis of Au nanoparticles

- Borohydride reduction
  - 2-phase system
  - synthesise Au particles in MMA
    - » tetraoctylammonium bromide stabiliser
    - » well dispersed particles, high concentration



5–15 nm diameter particles

- Emulsify then polymerise

Au synthesis based on: Gittins & Caruso, Angew. Chem. Int. Ed. 2001, 40, 3001.

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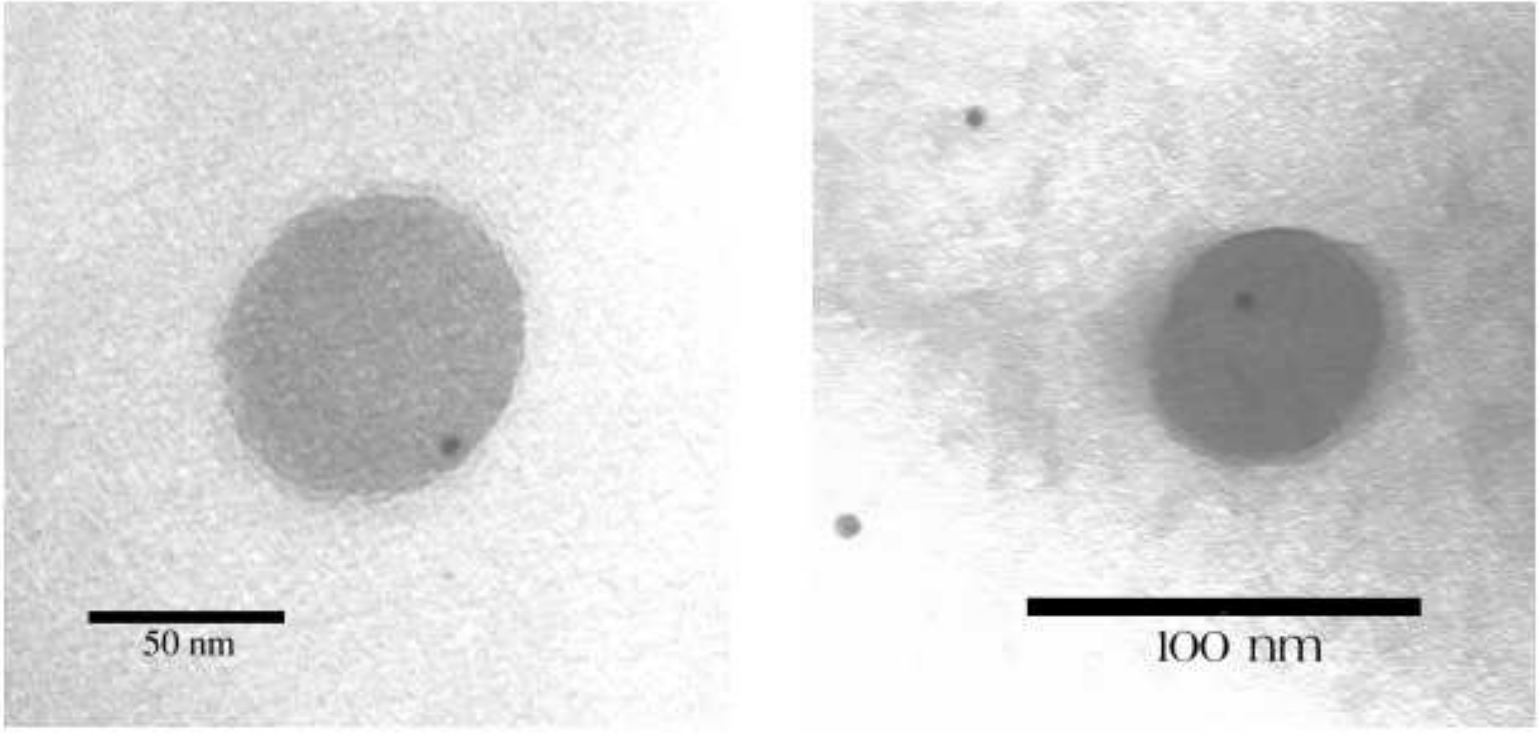
Au/pMMA particles

1. Dispersion of Au sol in MMA
2. Emulsify using ultrasound
3. Polymerise using ultrasound



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Further work

- Investigate optical properties
  - Au/pMMA dispersion
  - films made from Au/pMMA
- Use of phase transfer catalyst
  - sonochemically synthesised Au sols
    - » transfer particles to monomer phase
- Other inorganic cores
  - CdSe quantum dots

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Conclusions

- Successful incorporation of gold particles into polymer particle
  - » can synthesise Au/pMMA particles

- Evidence that ultrasonic dispersed phase polymerisation proceeds by miniemulsion mechanism
  - » incorporation of pigments such as Au particles cannot be done via conventional emulsion polymerisation approaches

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