



Gold/Polymer Nanocomposites by Dispersed Phase Polymerisation

Ultrasonic Initiation and Agitation

Jasmina Zukan, Stuart W. Prescott,
Franz Grieser, Muthupandian Ashokkumar





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

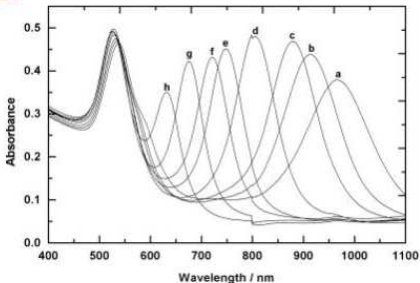
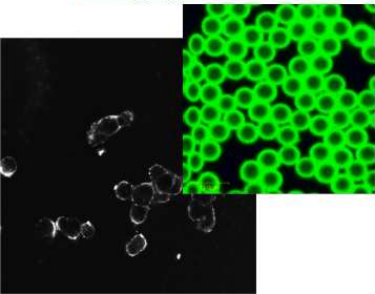
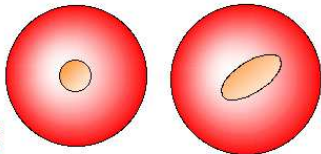


Inorganic Core, Polymer Shell

- ▶ 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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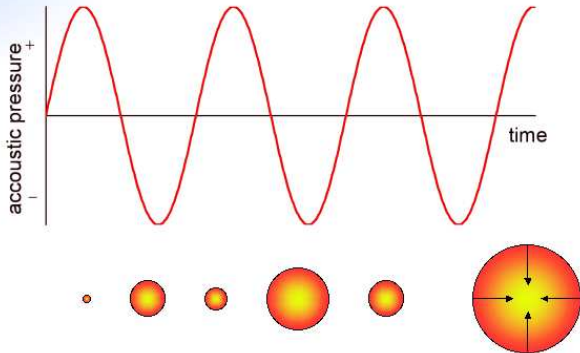


Ultrasonics

- ▶ 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

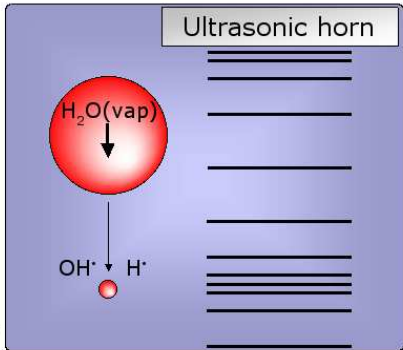


initial bubble

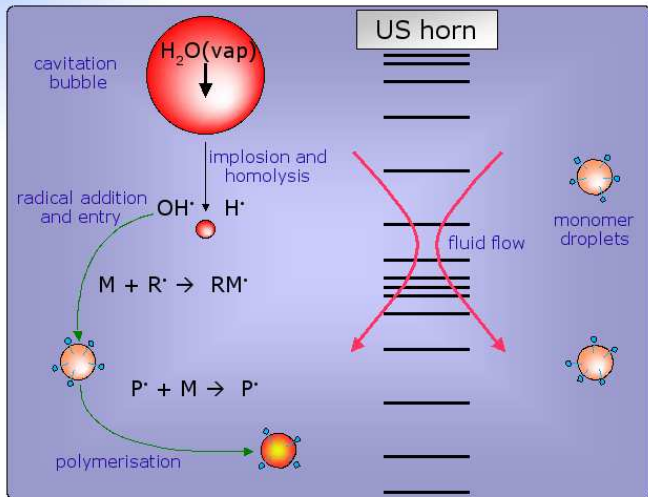
bubble collapse

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, $\sim 26\text{W}$



Miniemulsion Polymerisation



Synthesis of pMMA particles

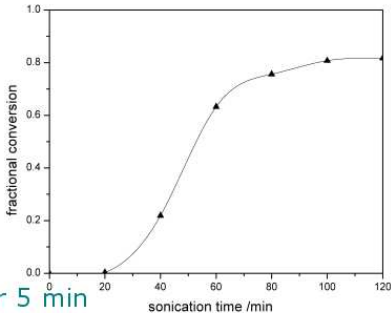
► Typical recipe:

- ◇ 6.4 g MMA
- ◇ 0.45 g SDS
- ◇ 36 g H₂O
- ◇ Ar purge
- ◇ sonication:

» on for 10 min, off for 5 min

◇ water jacket: 25±2°C

► 80% conversion in 60 min sonication

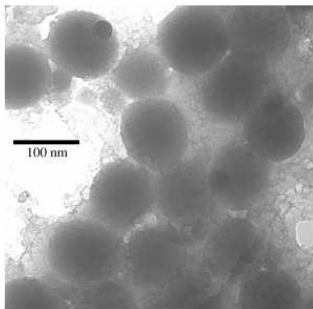


e.g. Bradley, Ashokkumar, & Griesor, JACS 2003, 125, 525.



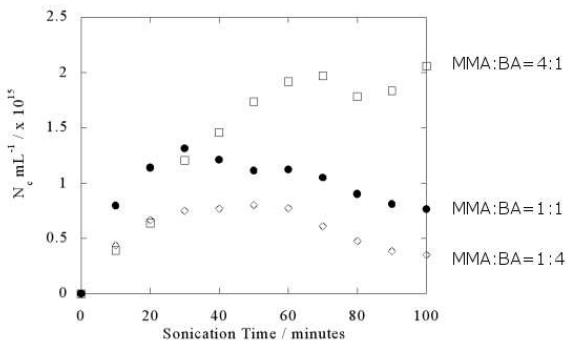
Synthesis of pMMA particles

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



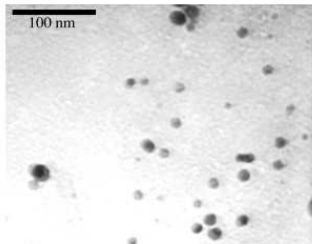
Droplets to particles

- ◇ 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



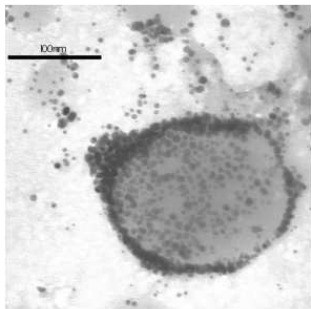
5–15 nm diameter particles

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



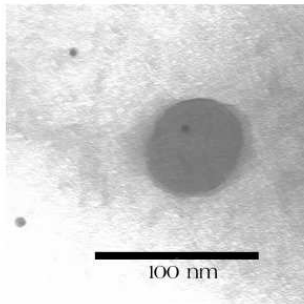
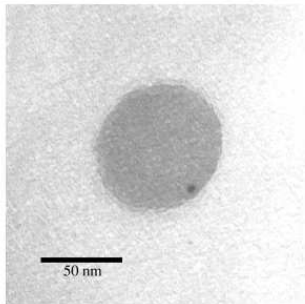
5–15 nm diameter particles

▶ Emulsify then polymerise

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

Au/pMMA particles

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





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





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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