REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
12/13/00

3. REPORT TYPE AND DATES COVERED
Final Report 12/1/97 - 11/30/99

4. TITLE AND SUBTITLE
"Revolutionary Smart Self Assembling Crystalline Colloidal Array Materials for Controlling IR Light Propagation

5. FUNDING NUMBERS
Grant#:
"DAAG-55-98-1-0025

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park,, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
ARO Proposal #:
ARO
38355.1 - PH

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
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12 b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

To develop new syntheses for monodisperse polystyrene colloids.

20010222 034

14. SUBJECT TERMS
C

15. NUMBER IF PAGES
20

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

Enclosure 1

REVOLUTIONARY SMART SELF ASSEMBLING CRYSTALLINE COLLOIDAL ARRAY MATERIALS FOR CONTROLLING IR LIGHT PROPAGATION

FINAL PROGRESS REPORT

PROFESSOR SANFORD A. ASHER

DECEMBER 13, 2000

U.S. ARMY RESEARCH OFFICE

GRANT NUMBER DAAG-55-98-1-0025

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PA 15260

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TECHNICAL PROGRESS REPORT

A. STATEMENT OF PROBLEM

The work here developed new materials and fabrication methodologies to control IR light propagation.

1. We were to develop new syntheses for monodisperse polystyrene, silica, and PMMA colloids
2. Develop synthetic methods to produce colloidal particles containing quantum dots of CdS, CdTe, etc
3. Develop IR diffracting polymerized crystalline colloidal arrays (PCCA)
4. Develop methods to fabricate PCCA which diffract light in defined wavelengths and bandwidths
5. Fabricate PCCA which are thermally and chemically tunable in the 1-10 μm spectral region
6. Demonstrate thermal tuning and electronic control of PCCA diffraction
7. Develop synthesis of highly charged, monodisperse titania dioxide colloids
8. Fabricate and characterize photonic bandgap crystals

B. SUMMARY OF IMPORTANT RESULTS

1. We developed new methods to synthesize highly charged, monodisperse large polystyrene colloidal particles as reported in enclosed publication 1.

2. We developed novel methods to synthesize monodisperse silica colloids in microemulsions as shown in the synthetic scheme of Fig. 1, and the TEM showing examples of these colloidal particles in Fig. 2. We also developed synthetic methods to form silica particles which contain Ag, or Au quantum dots as shown in Figs. 3 and 4. We functionalized these silica composite particles to make them highly charged, such they self assembled into CCA as shown in Figs. 5 and 6. In addition, we developed methods to form polystyrene colloids which contained Ag quantum dots which also self assembled into CCA (Fig. 7 and 8).

We also developed methods using microemulsions to synthesize large silica particles containing CdS quantum dots (Fig. 9).

3. We developed a number methods to produce PCCA which diffract in the IR. In one method we hydrolyzed the acrylamide PCCA to form carboxylates. At neutral pH the charged carboxylates caused the PCCA to swell due to formation of a Donnan potential. Fig. 10 shows the resultant diffraction shift of a PCCA into the IR as the time for hydrolysis increases. This hydrolysis also creates a PCCA, which operates as a pH and ionic strength sensor. Our publication 2 is a careful study of the physics of the pH and ionic strength swelling, and its utility for sensing pH and ionic strength.

We also developed a chemically reversible disulfide cross linking approach (Fig. 11) and a hydrolysable crosslinking approach (Fig. 12 – 15) to swell PCCA into the IR.

4. The methods discussed above allow us to sensitively control the wavelength of diffraction of the PCCA by carefully adjusting the pH or ionic strength or by decreasing the PCCA crosslinking. We developed methods to control the diffraction bandwidth by altering the scattering power of the colloidal particles by changing their size or refractive index. We also attempted to swell colloidal particles already polymerized into the PCCA. Preliminary attempts to swell polystyrene particles by adding styrene to the PCCA solution indicates success. Further work will be necessary to speed up this process in order to make it practical.

5. We demonstrated that we could achieve thermal tuning by utilizing PCCA synthesized by using hydrogels of N-isopropyl acrylamide.

We began working on electronic control of the PCCA diffraction by utilizing a PCCA which contains an 18-crown-6 crown ether group. This molecular recognition agent binds Pb^{2+}, which causes the PCCA to swell and red shifts the diffraction. We attempted electronic control of the PCCA diffraction by utilizing the electrochemical oxidization of lead metal to Pb^{2+} which would then swell the PCCA into the IR. Preliminary data suggests that this method is viable for the control of PCCA diffraction wavelengths.

6. The most challenging part of the research program involved synthesis of highly charged, monodisperse titania spheres. Although the literature reports synthesis of large, relatively monodisperse titania spheres, we found that none of these recipes were reproducible and did not yield monodisperse colloidal particles. We developed a number of new approaches for synthesizing titania spheres of relatively uniform size, but when we tried to add surface charge the titania colloids suffered, what we think, was a Coulomb explosion where the particles disintegrated into their small primary particles. Only just recently, with funding from other grant support, have we finally succeeded in fabricating monodisperse titania colloidal particles which self assemble into CCA that Bragg diffract light. Fig. 16 shows TEM micrographs of these particles.

7. We reported earlier that colloidal arrays made from polystyrene colloids with a lattice spacing that diffracts ~1200 nm light from the fcc 111 planes diffracts essentially all light of all polarizations at wavelengths below 500 nm. Clearly the refractive index contrast, and the fact that it is an fcc crystal will not allow this sample to be a 3-D photonic bandgap crystal. We have been carefully characterizing the crystal structure and diffraction properties and writing up these results for publication. We expect to submit this work by the end of December, 2000.

C. PUBLICATIONS

1. C. Reese, C. Guerrero, J. Weissman, K. Lee and S. A. Asher, "Synthesis of Highly Charged, Monodisperse Polystyrene Colloidal Particles for the Fabrication of Photonic Crystals", Journal of Colloid and Interface Science, **232**, 76-80 (2000)
2. K. Lee and S. A. Asher, "Photonic Crystal Chemical Sensors: pH and Ionic Strength", Journal of American Chemical Society, **122**, 9534-9537 (2000)

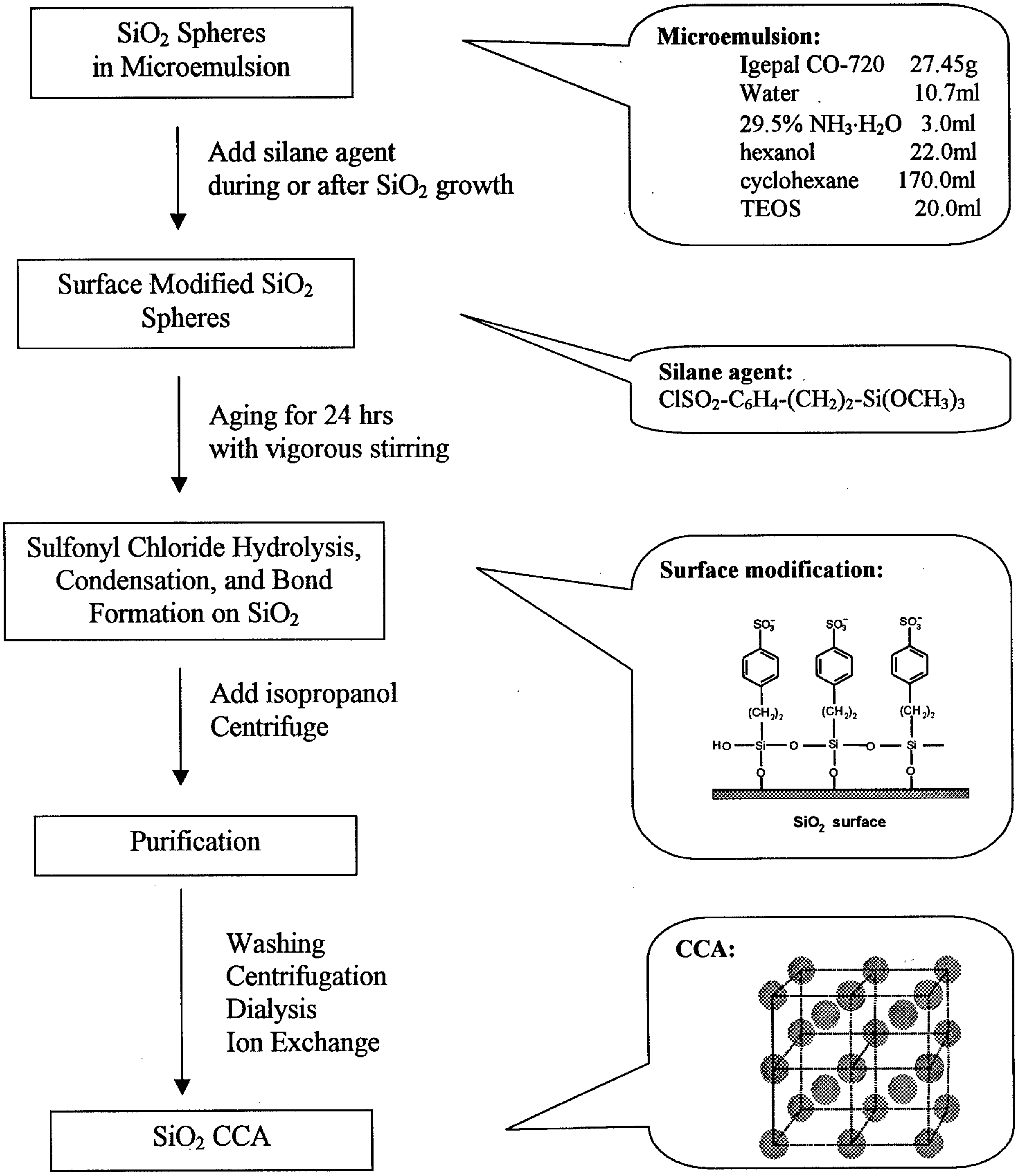
D. LIST OF SCIENTIFIC PERSONNEL EMPLOYED ON PROJECT

Sanford Asher	PI	12%
We Wang	Res. Associate	50%
Igor Lednev	Res. Associate	50%
Jeff Sicher	Machinist	4%
Douglas Hackworth	Graduate Student	75%
Jonathan Keim	Graduate Student	25%
Aleksandr Mikhonin	Graduate Student	25%
Vasil Pajcini	Graduate Student	25% Received PhD
Hua Zhang	Graduate Student	75% Received MS

E. REPORT ON INVENTIONS

None, as yet.

Figure 1. **Synthesis of Highly Charged, Monodisperse SiO_2 Particles**



Microemulsion:

Igepal CO-720	27.45g
Water	10.7ml
29.5% $NH_3{\cdot}H_2O$	3.0ml
hexanol	22.0ml
cyclohexane	170.0ml
TEOS	20.0ml

Silane agent: $ClSO_2\text{-}C_6H_4\text{-}(CH_2)_2\text{-}Si(OCH_3)_3$

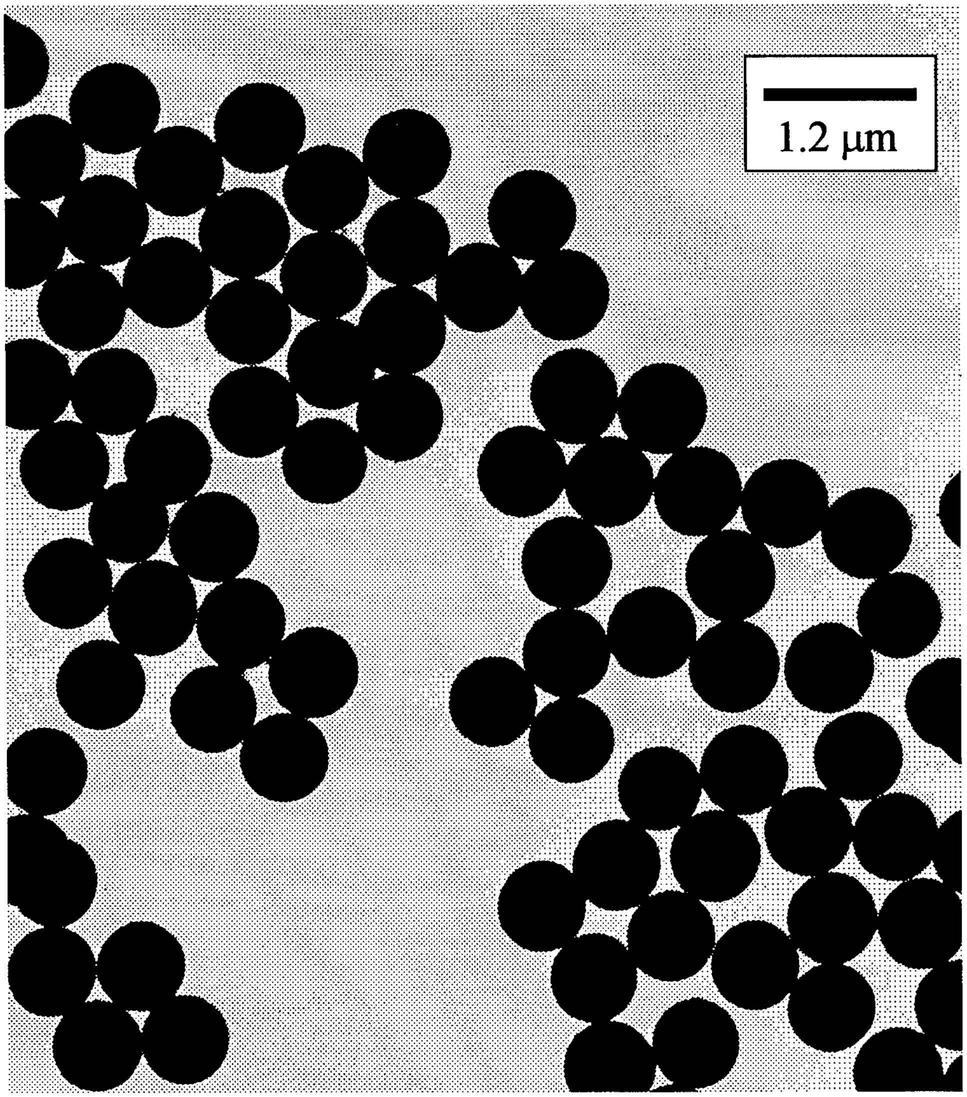


Figure 2. **TEM Picture of Surface Modified SiO_2 Particles**

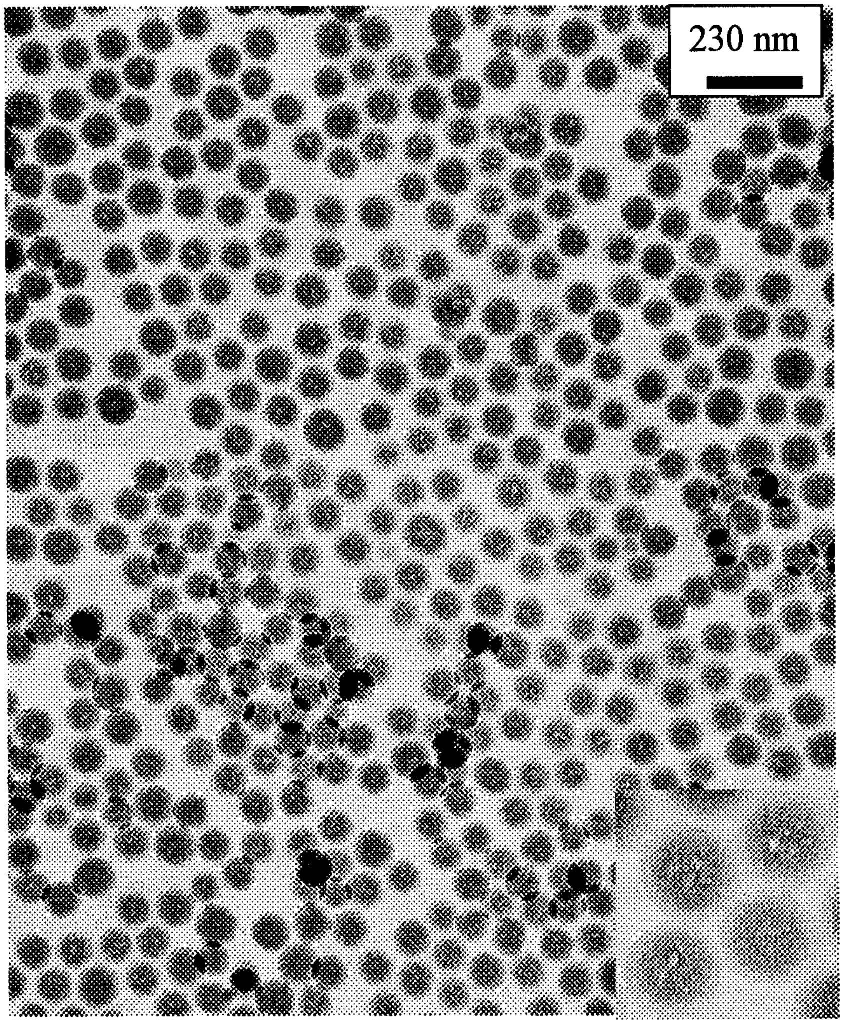


Figure 3. TEM picture of SiO_2-Ag composite particles (Ag homogeneously distribution in SiO_2 spheres)

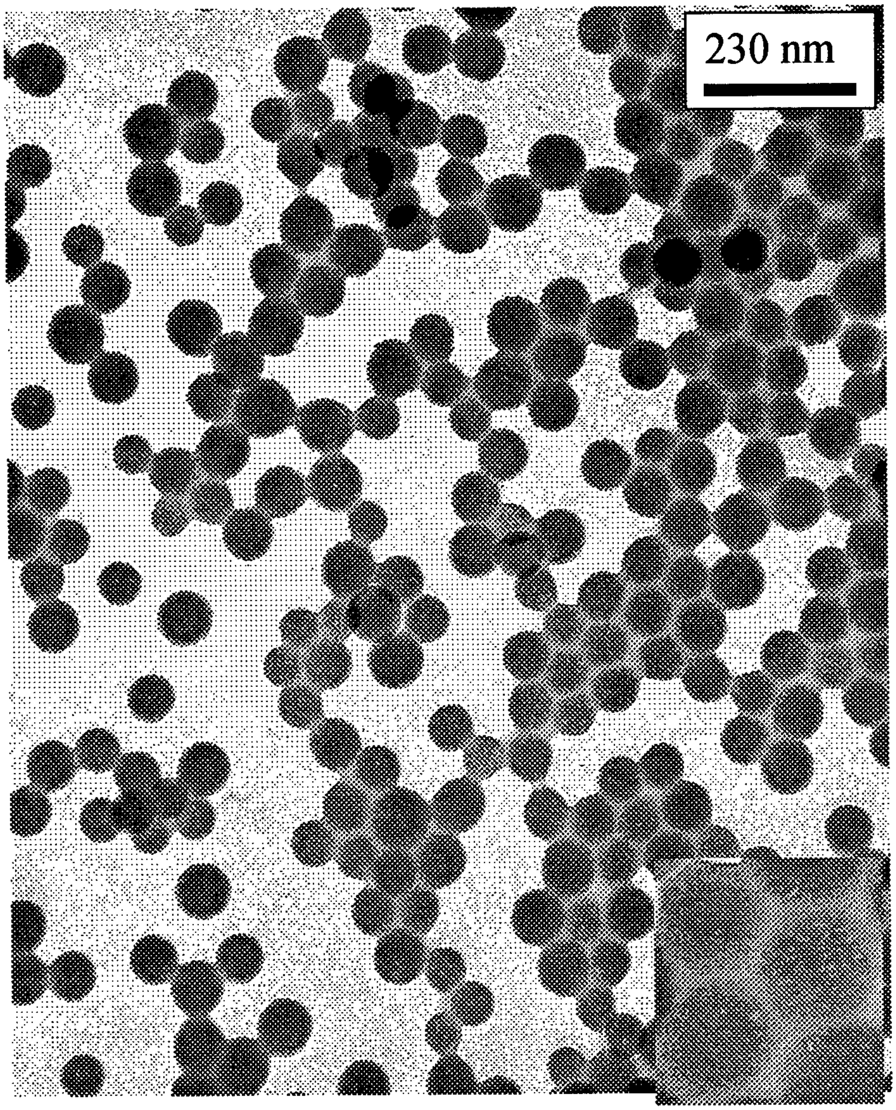


Figure 4. TEM picture of SiO_2-Au composite spheres. The Au nanoparticles homogeneously distribute in the SiO_2 spheres.

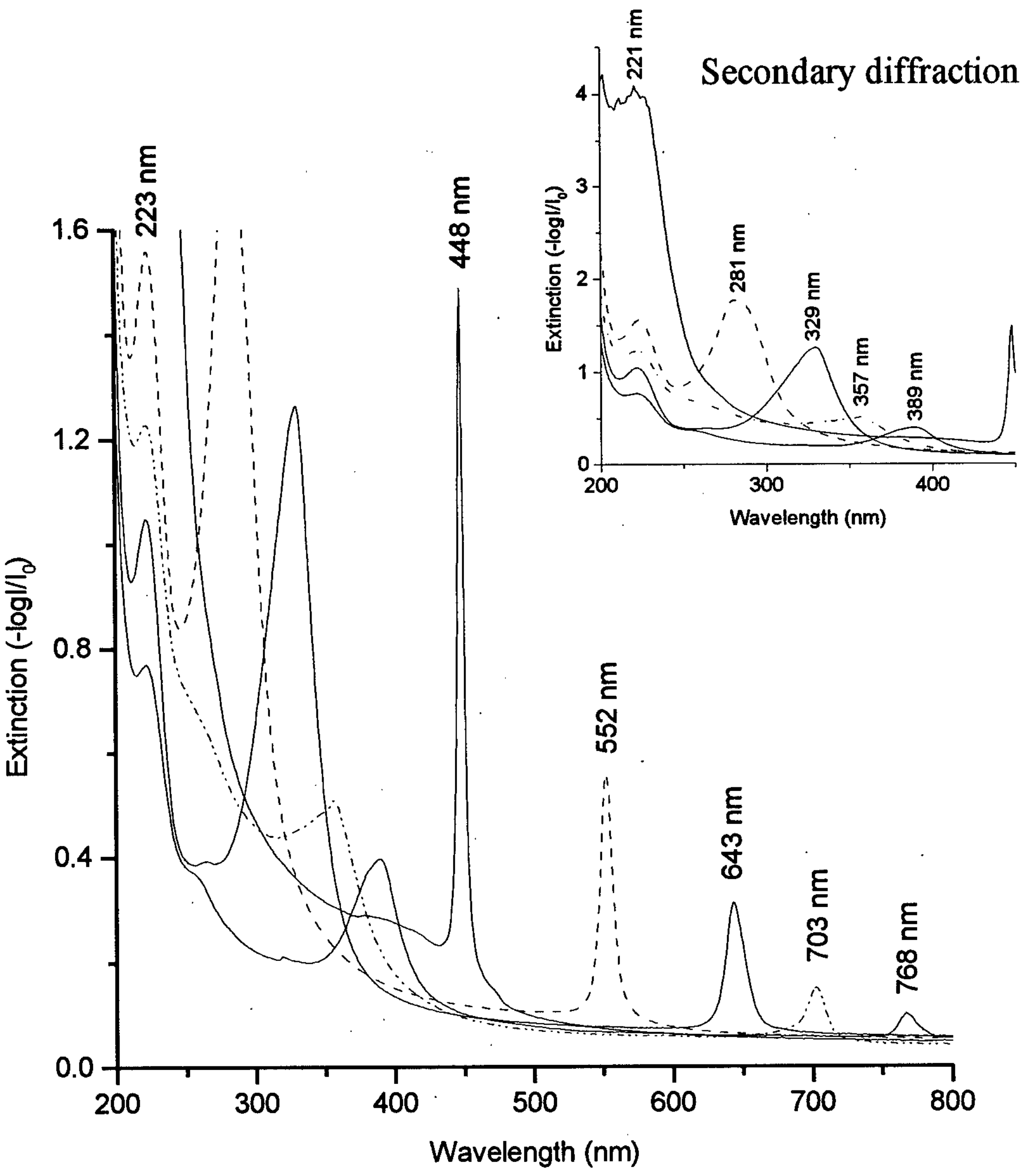


Figure 5. Extinction spectra of $Ag@SiO_2$ composite sphere CCA at different colloidal concentrations. The $Ag@SiO_2$ sphere diameter is 98±8 nm.

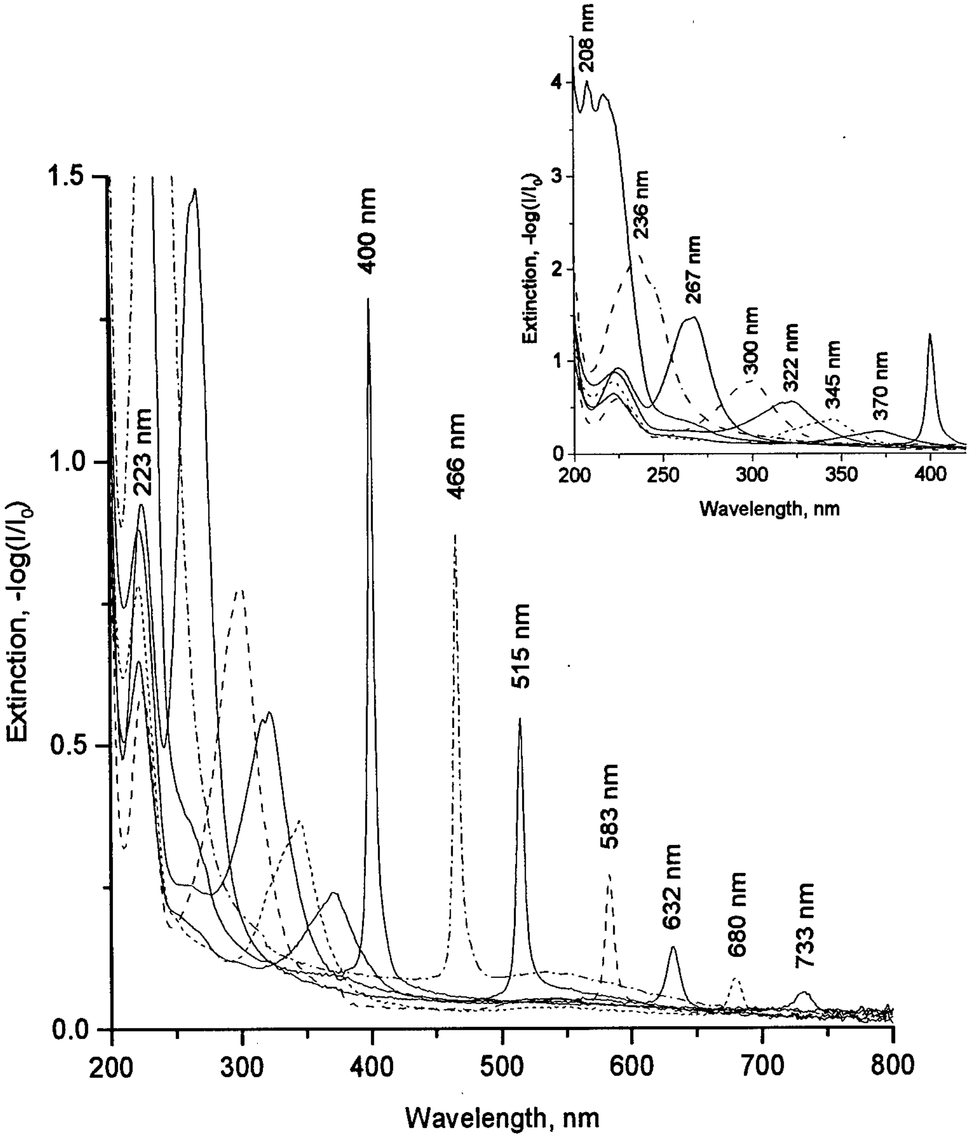


Figure 6. Extinction spectra of Au@SiO$_2$ composite sphere CCA at different sphere concentrations. The sphere diameter is 110±10 nm, and the thickness of the CCA is 0.125 mm.

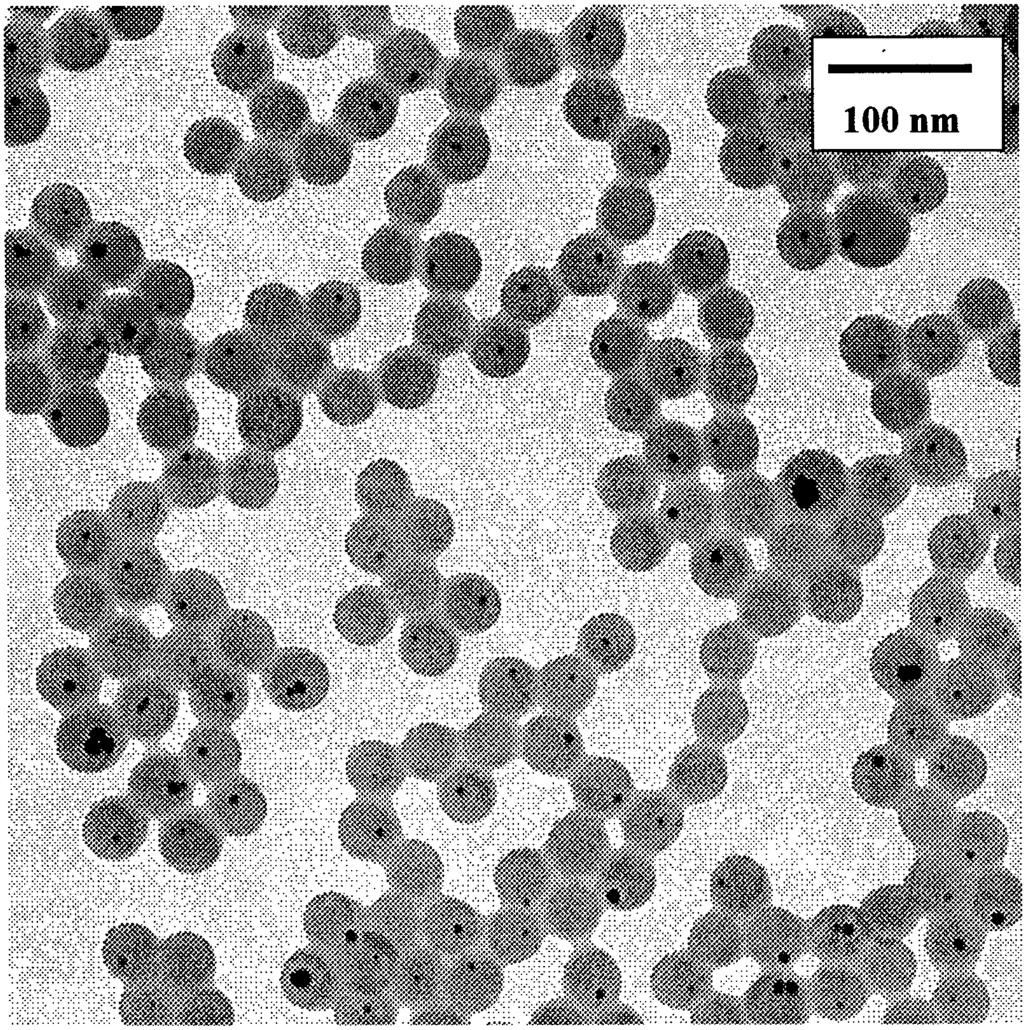


Figure 7. TEM picture of polystyrene-silver shell-core particles.

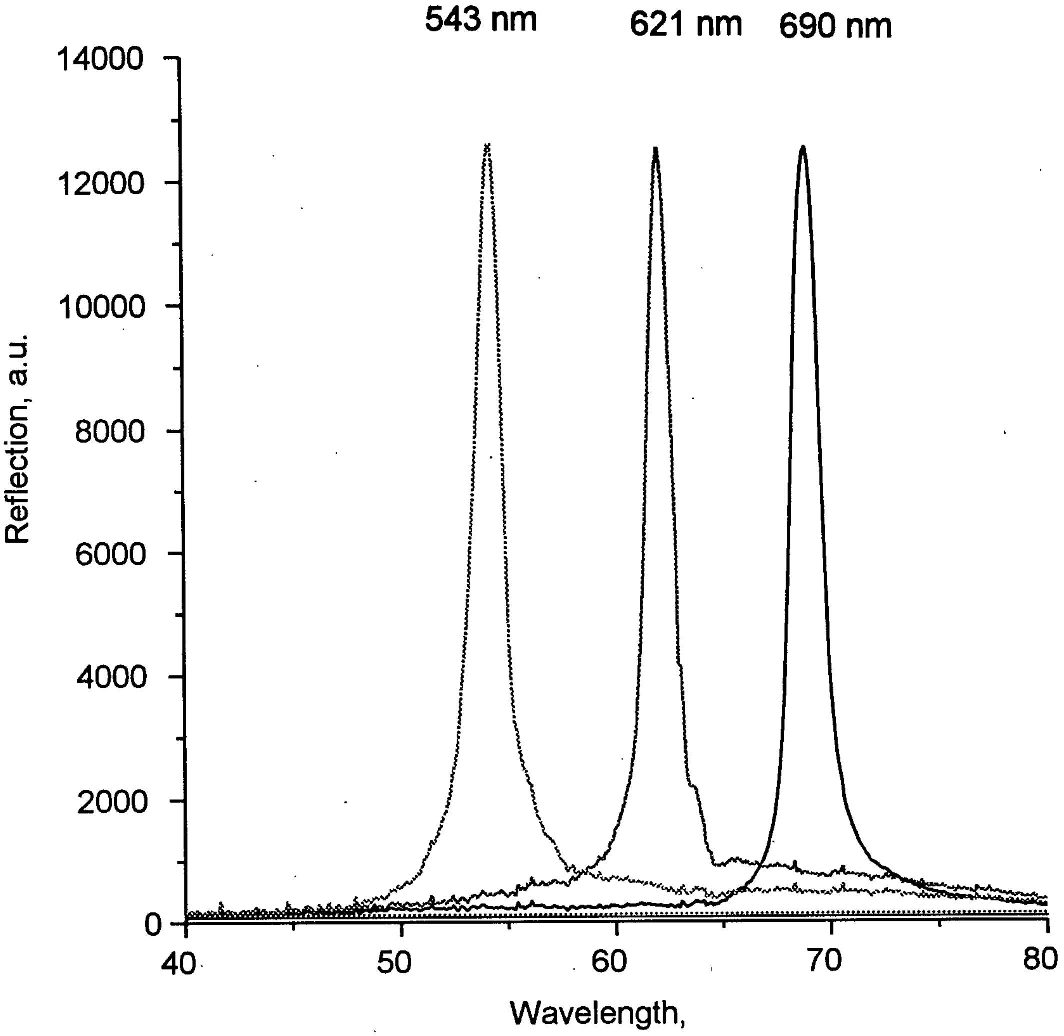


Figure 8. **Back-scattering diffraction spectra of polystyrene-silver shell-core composite CCA at different particle concentrations.**

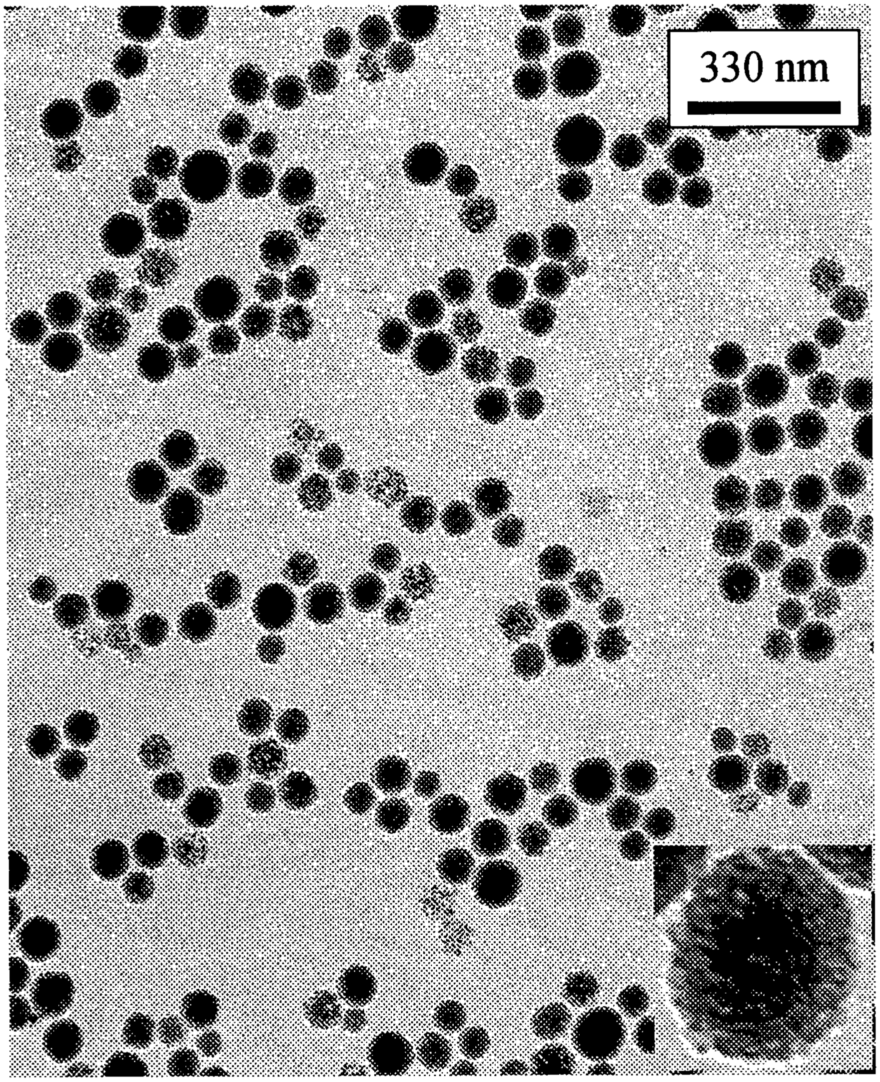


Figure 9. **TEM picture of SiO_2-CdS (surface) composite particles**

PCCA SWELLED INTO IR

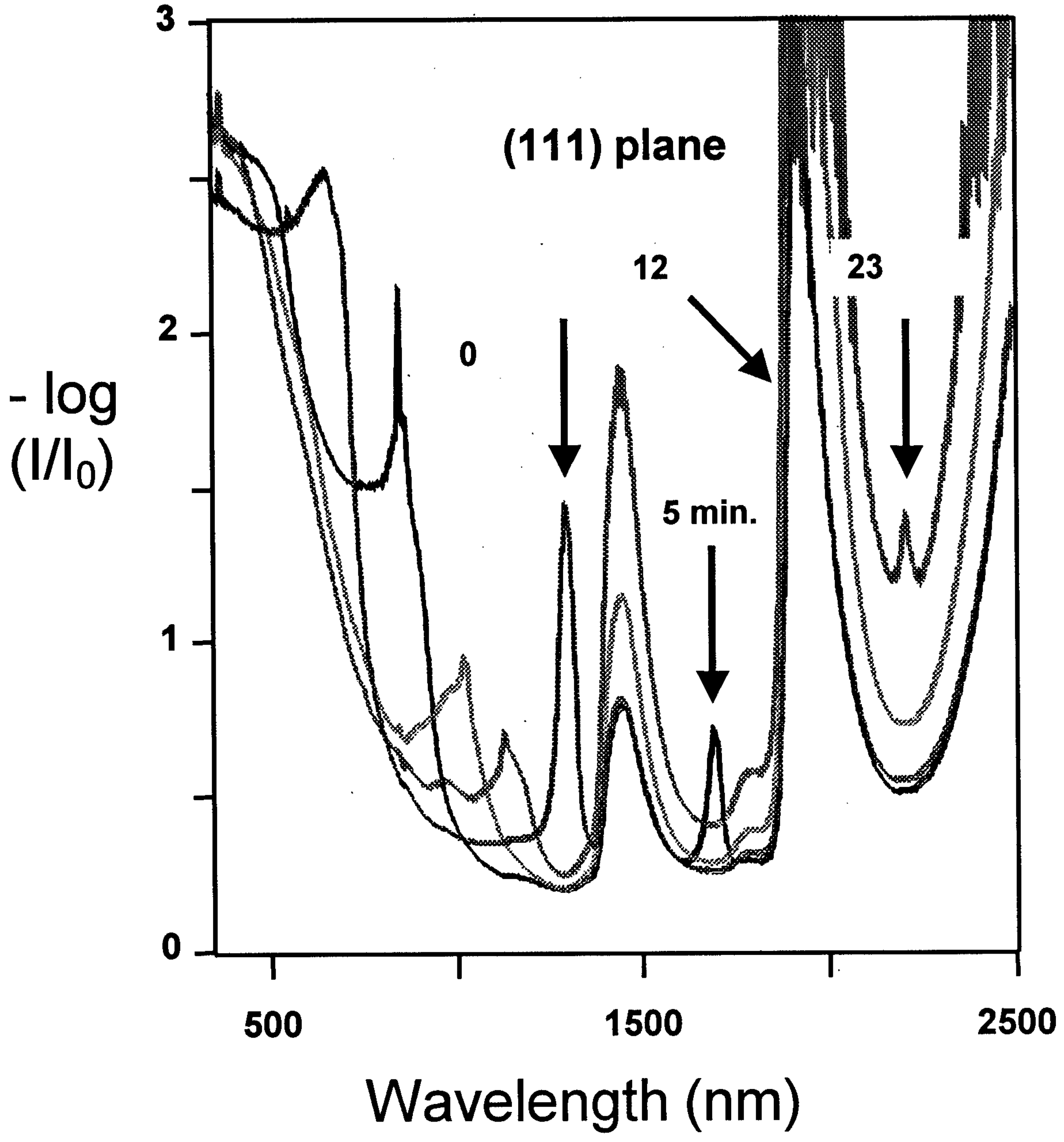
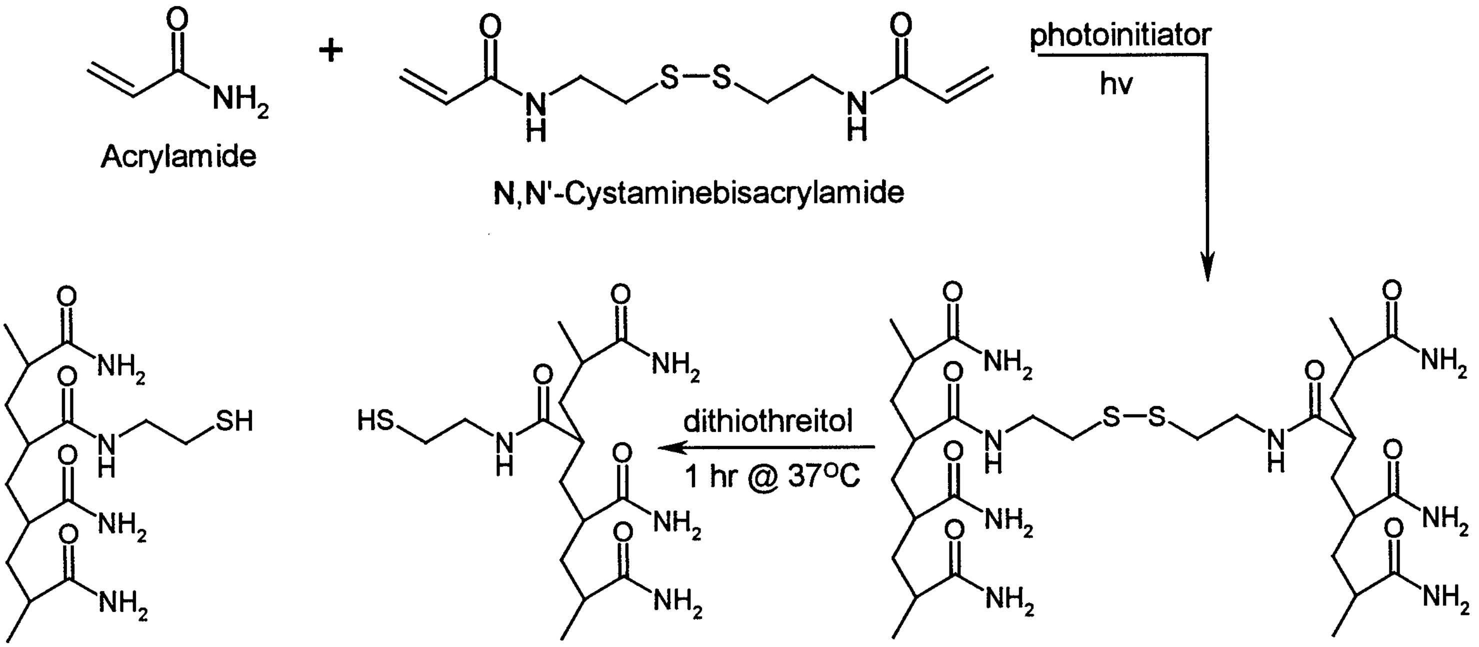
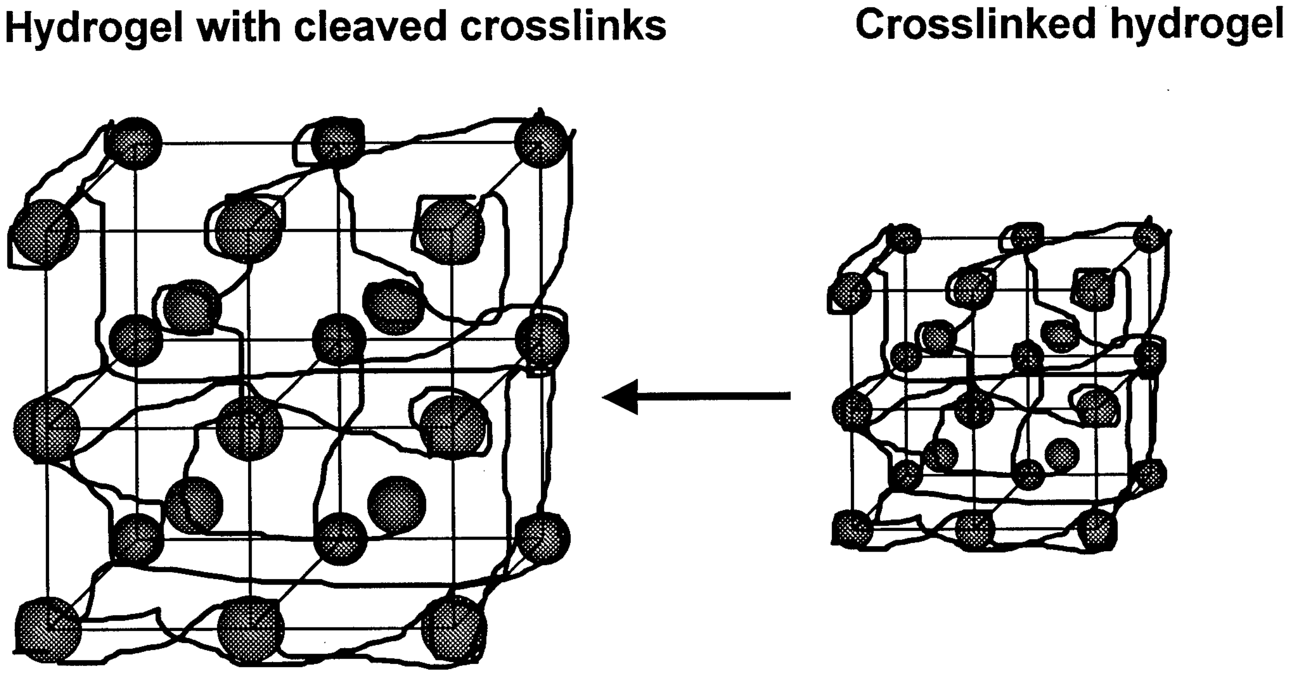


Figure 10. PS Colloid 270 nm diameter, Acrylamide PCCA Hydrolyzed for **0**, **5**, **12**, **23** minutes.

Increasing PCCA Spacing and Decreasing Elastic Constant

Chemically Variable Crosslinking



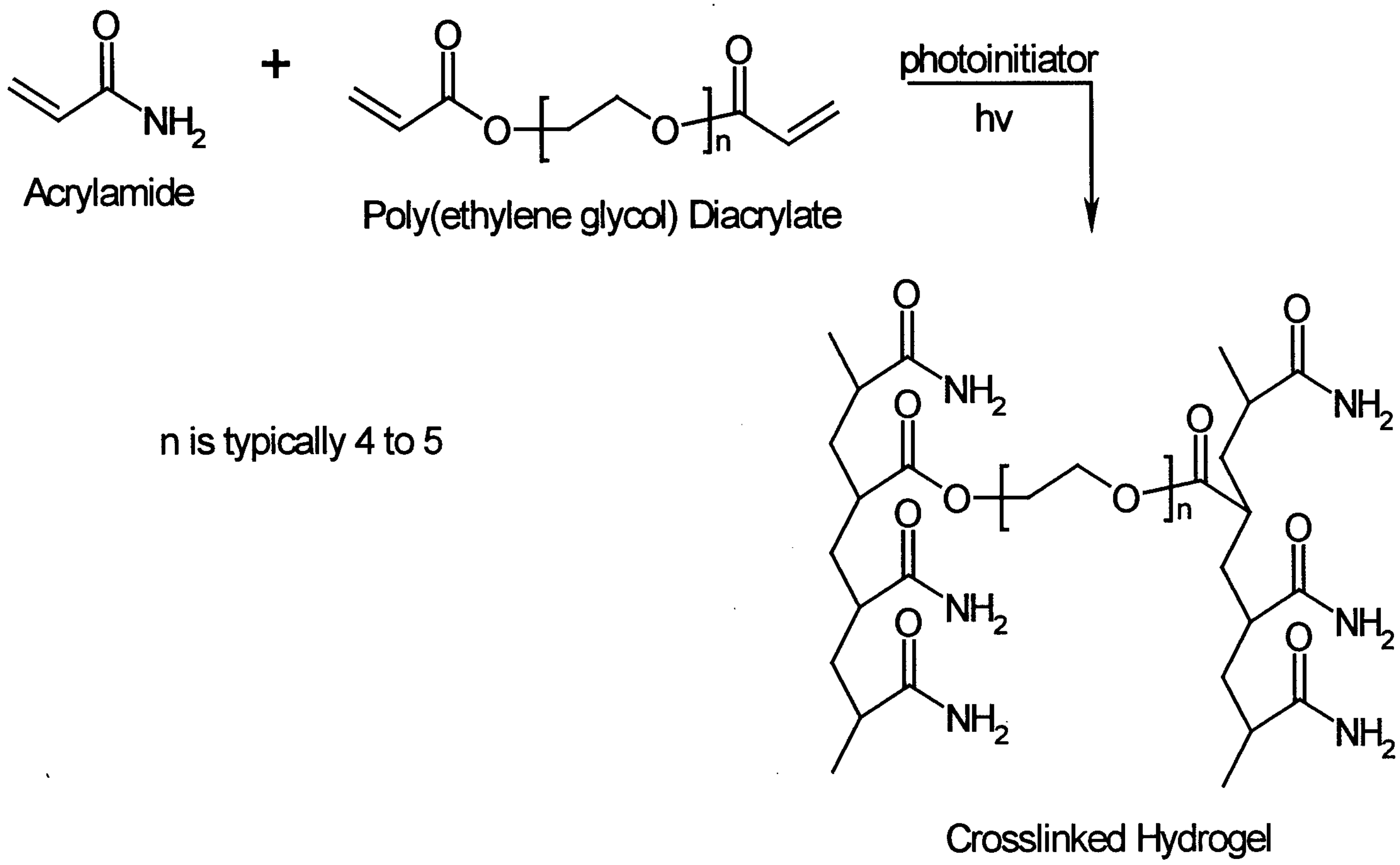

Hydrogel with cleaved crosslinks

Crosslinked hydrogel

Figure 11

Fabrication of IR Diffracting Hydrogels

Synthesis of PEG Crosslinked Hydrogels

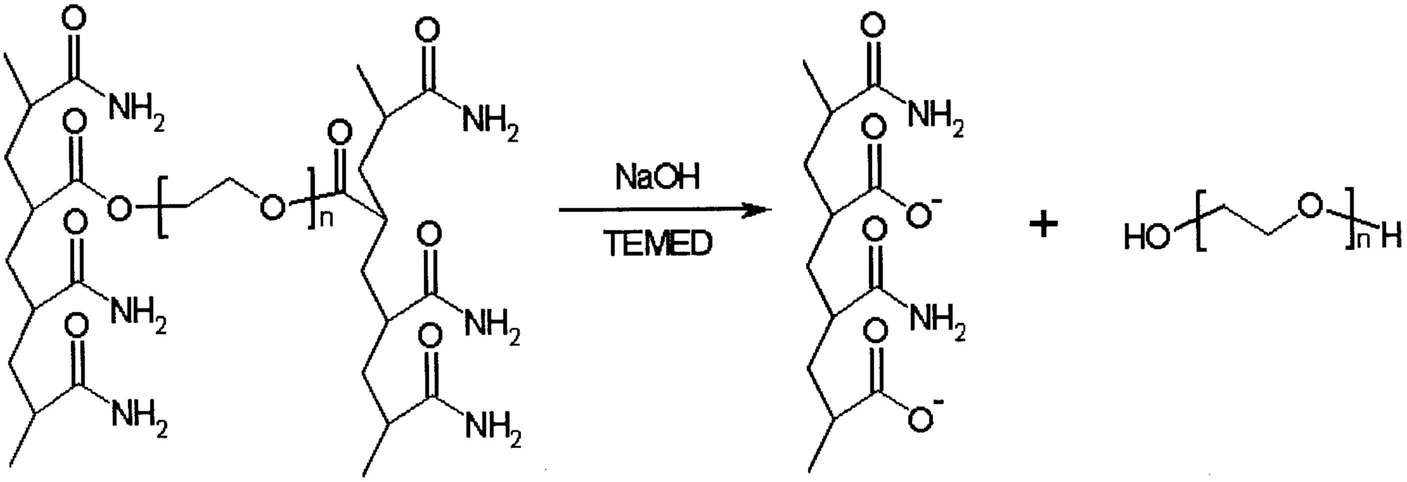


n is typically 4 to 5

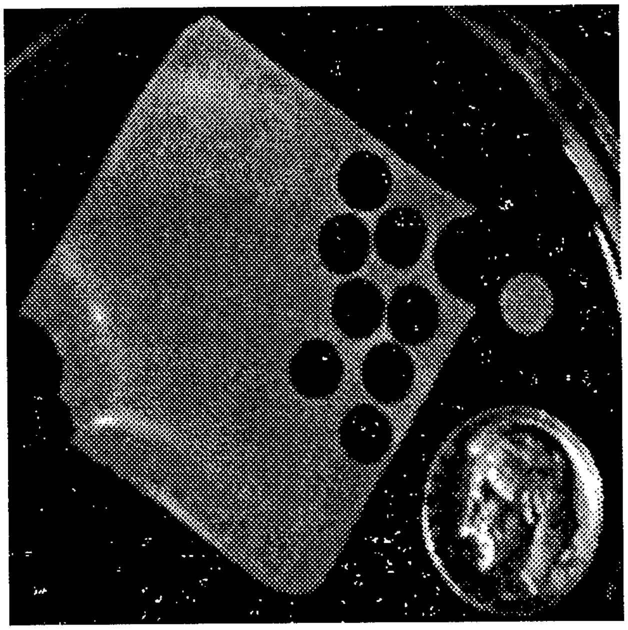
Figure 12

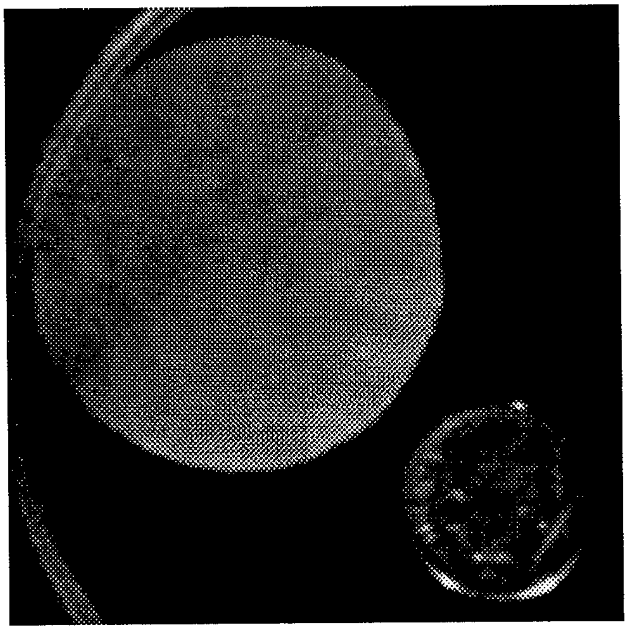
Fabrication of IR Diffracting Hydrogels

Hydrolysis of Crosslinks



Crosslinked Hydrogel





Typical Recipe:

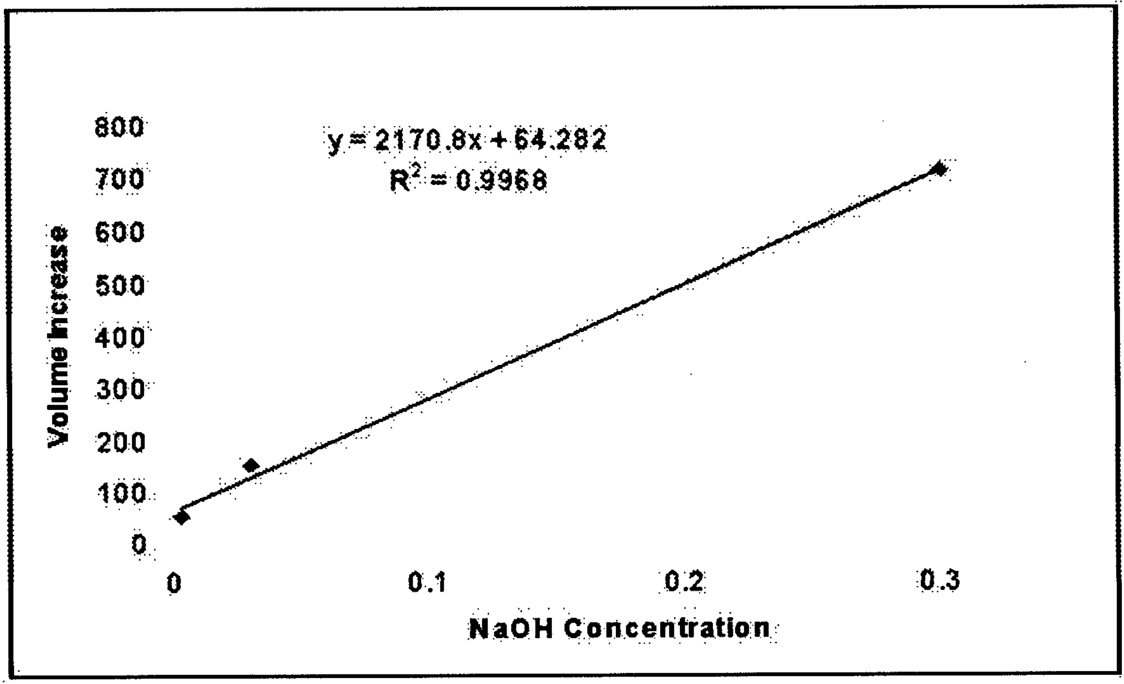
0.03 M NaOH

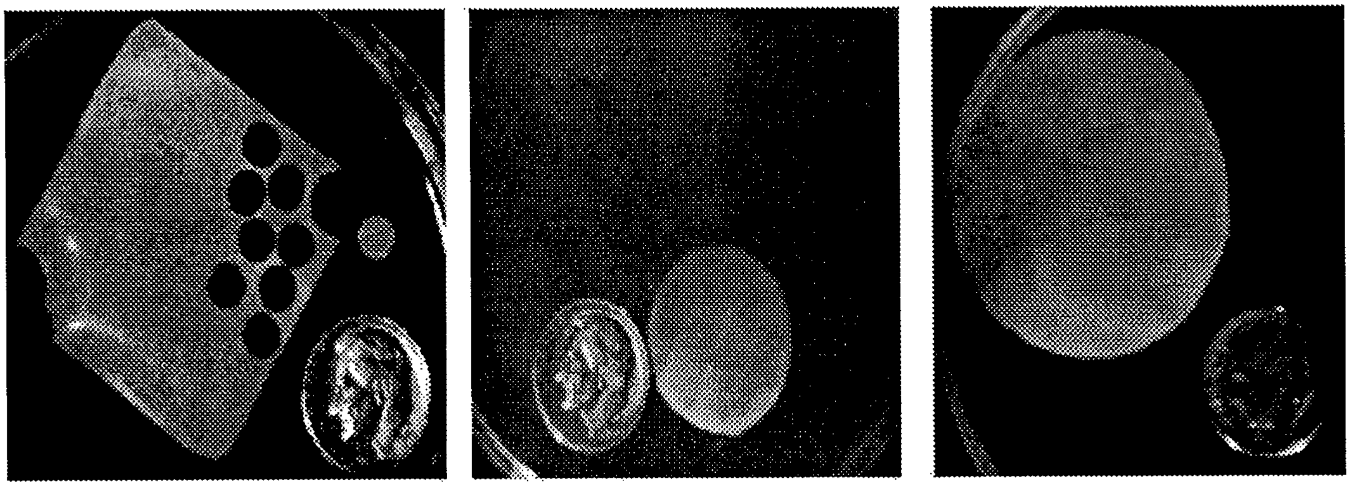
0.08% N,N,N′,N′-tetramethylethylenediamine (TEMED)

for 1 hour

Figure 13

Gel Volume Increase With Changing NaOH Concentration After 1 Hour Of Hydrolysis





Gel Before Hydrolysis

After Hydrolysis in 0.03 M NaOH

$$\frac{V_f}{V_i} = 150$$

After Hydrolysis in 0.3 M NaOH

$$\frac{V_f}{V_i} = 10^3$$

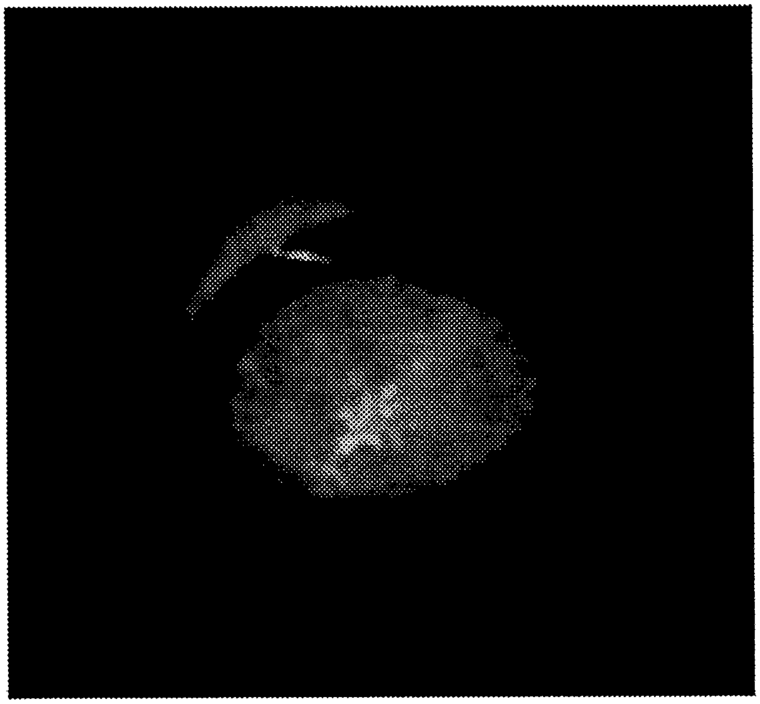
Figure 14

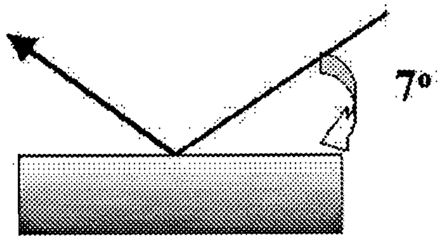
Diffraction Still Present After Swelling

$$\lambda^{i}_{111} = 950nm \quad d^{i}_{111} = 354\,nm$$

$$\frac{V_f}{V_i} = 150$$

$$\lambda^{f}_{111} = 5.035\,\mu m$$ **(Normal incidence)**





$$\lambda^{7^\circ}_{d} = 608nm$$

Figure 15

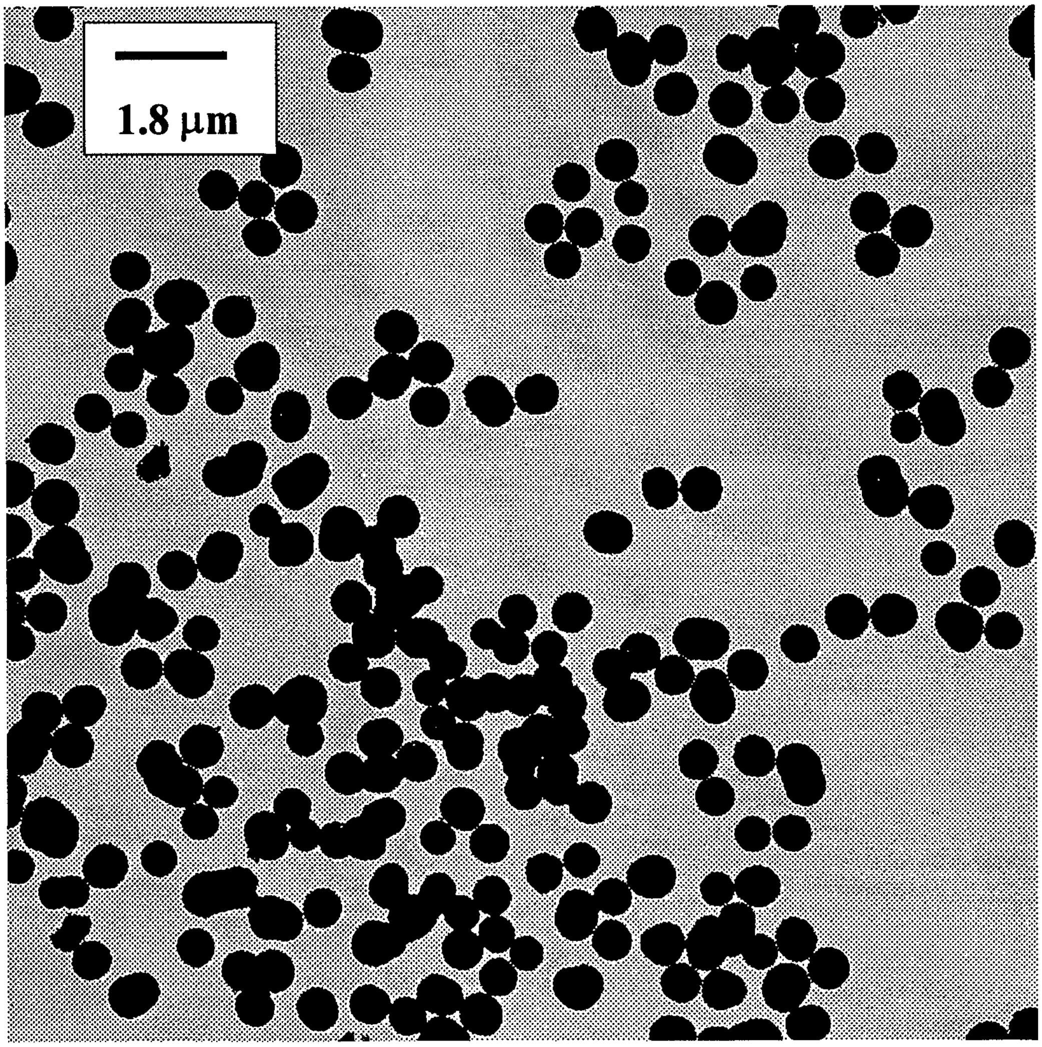


Figure 16. TEM picture of monodisperse TiO_2 spheres.