Raman Probe of Particle Size Effects in Aftertreatment Catalysts

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Raman Probe of Microcrystalline of Silicon

Raman has been used to determine whether a Si-film is crystalline or amorphous

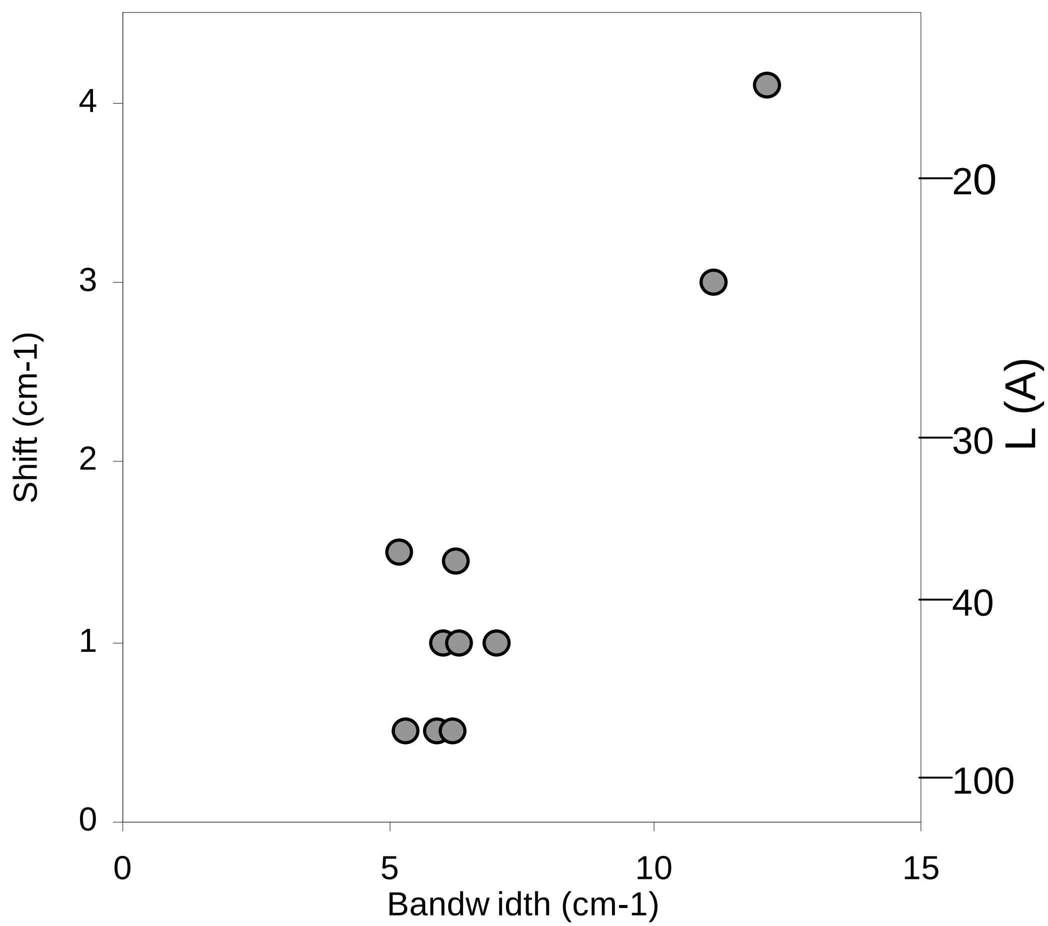
crystalline Si: sharp band at 522 cm^{-1} ($\Delta\omega_{1/2}$ = 3.5 cm^{-1})

amorphous Si: hump ~480 cm^{-1} (very broad due to a loss of long range ordering)

laser annealed Si: 515 cm^{-1} ($\Delta\omega_{1/2}$ = 8 cm^{-1}) *Morhange et. al. Solid State Comm. 31, 805 (1979)*

plasma deposited Si: 476~512 cm^{-1} ($\Delta\omega_{1/2}$ increases with decreasing energy)

Tsu et. al. Solid State Comm. 36, 817 (1980)



$\Psi(k, r) = A\exp[-2(r/L)^2]\ \phi(k, r)$

L: crystalline size

Crystallite size can be related to Raman bandwidth of Si-band

H. Richter et. al. Solid State Comm. 39, 625 (1981)

Raman Probe of Carbonaceous Materials

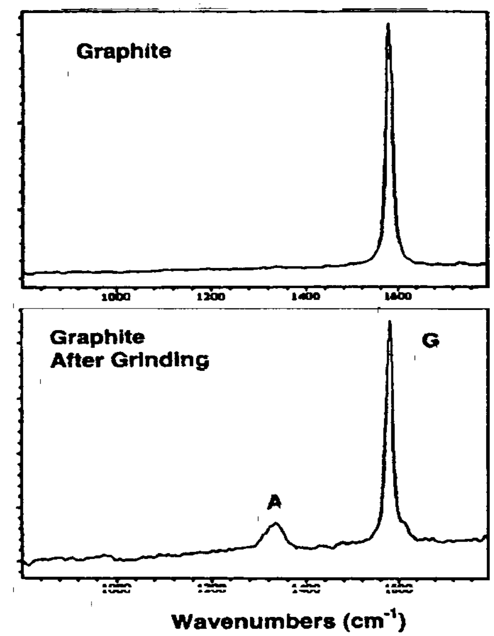
Pure graphite: a sharp *graphitic* band at 1578 cm^{-1} ($\Delta\omega_{1/2}$ = 16 cm^{-1})

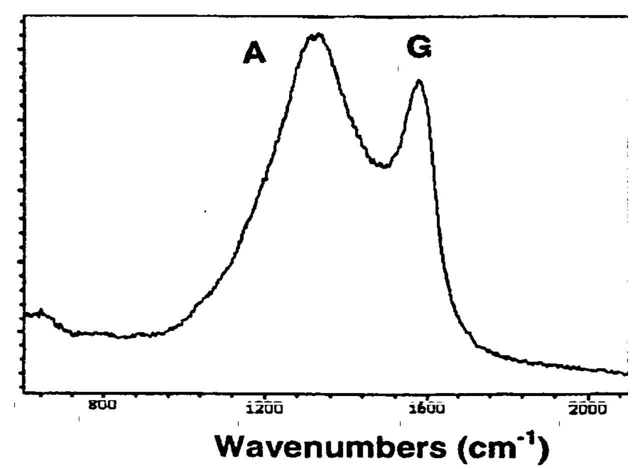
Ground graphite: a second *amorphous* band at 1335 cm^{-1} ($\Delta\omega_{1/2}$ ~ 40 cm^{-1})

Other carbonaceous materials:

	graphitic *(cm^{-1})*	*amorphous* *(cm^{-1})*
Engine soot	1570	1330
Carbon black	1585	1330
	varies with carbonization temperature	
Coal/Kerogens		
	~1580	~1330
	varies with sample maturation	

H. Fang & S. Kelemen, Energy & Fuels 15, 653 (2001)





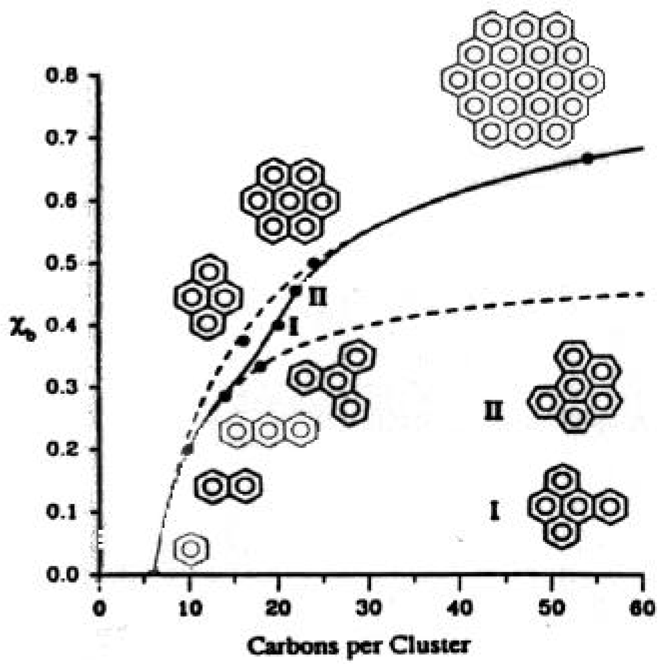
Raman Probe of Aromatic Ring Domain in Carbonaceous Materials

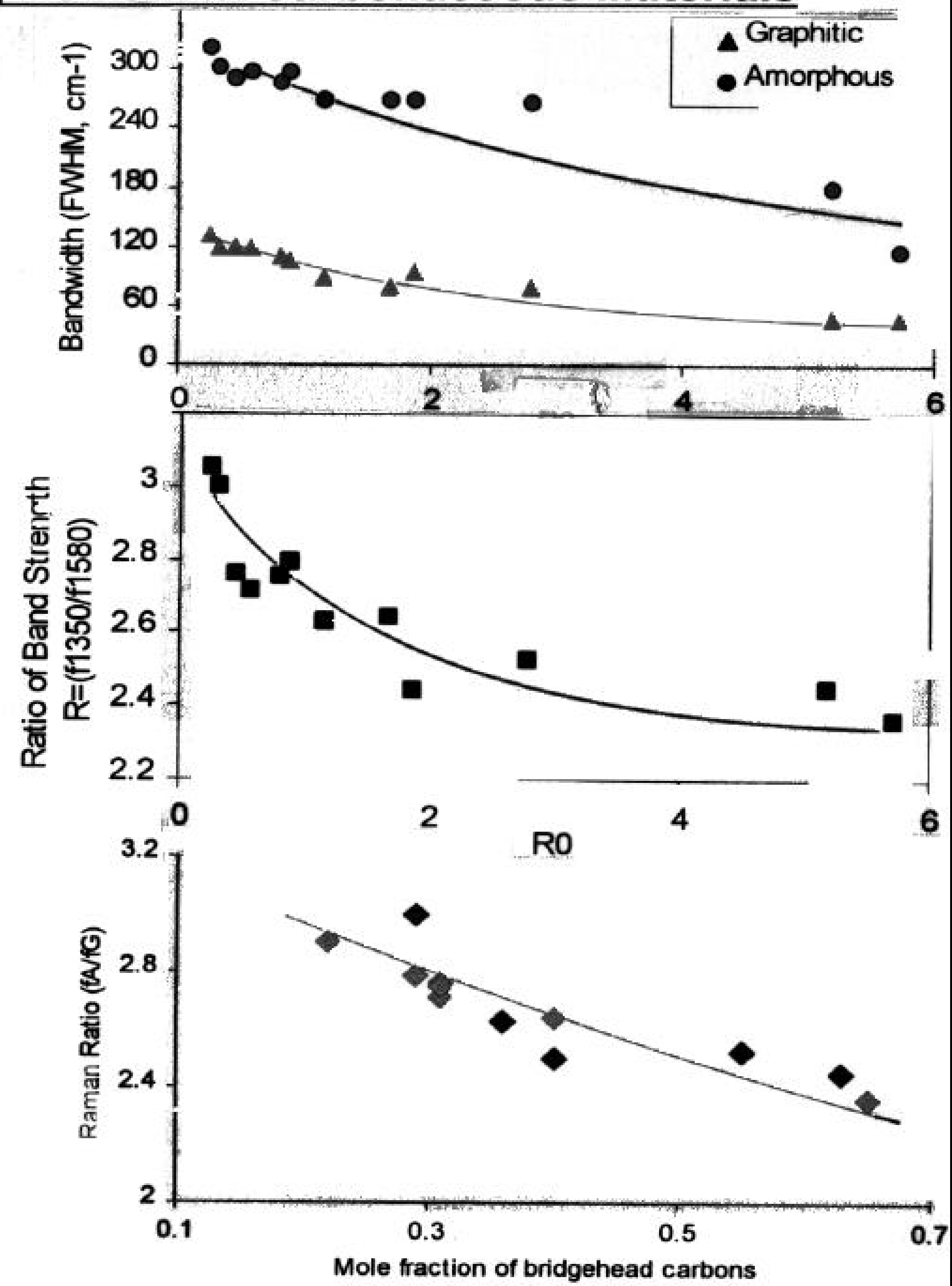
Samples: Argonne Premium Coal &
Penn State Coal
(with R0 0.25 ~ 5.7)

Raman : 633 nm excitation

NMR: ^{13}C CP/MAS

M. Solum et. al. Energy & Fuels 3, 187 (1989)

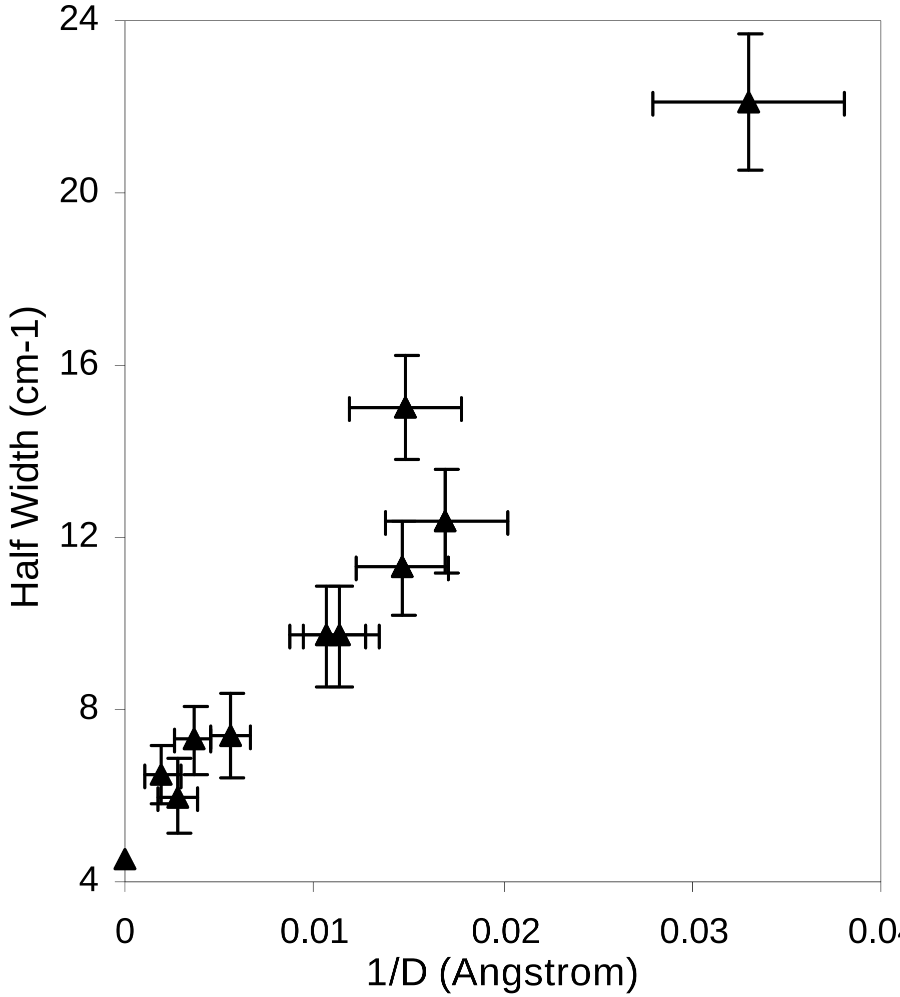


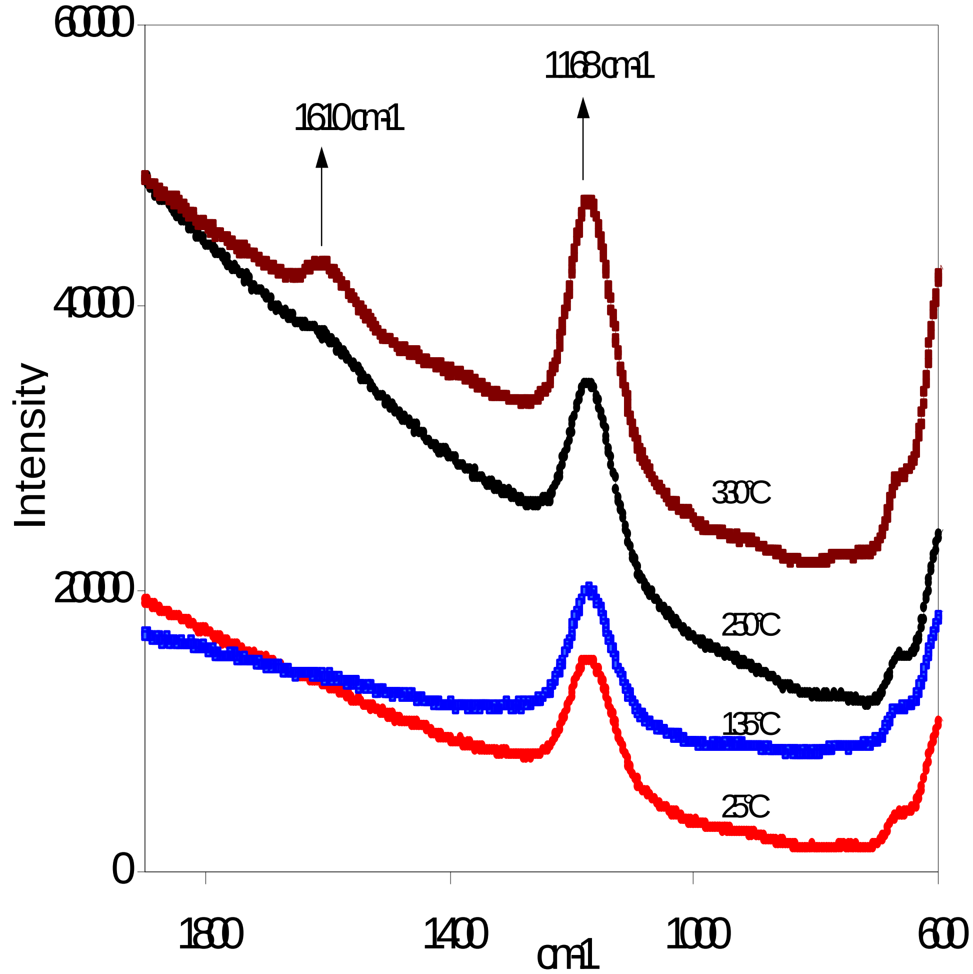


Raman Probe of Particle Size of CeO_2

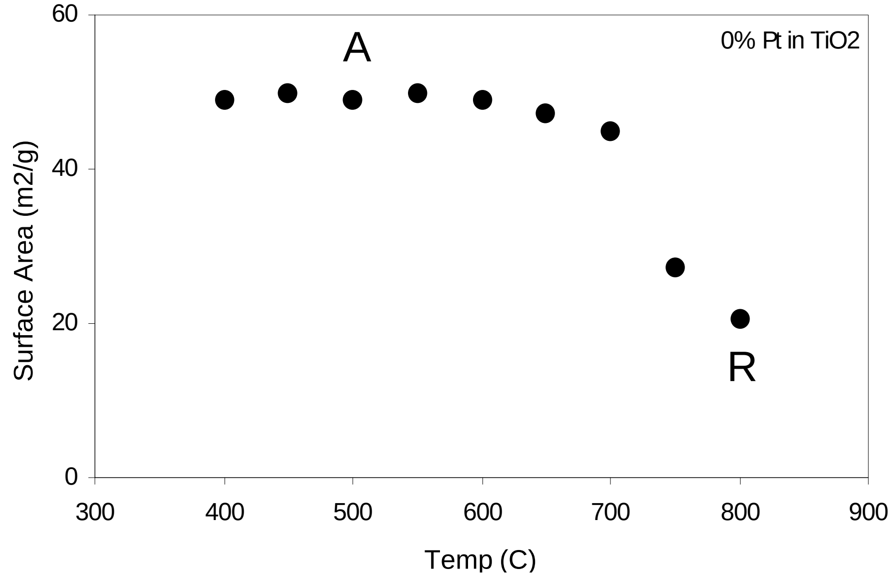
Major CeO_2 460 cm^{-1} band is sensitive to particle size (W.Weber, et. al. Phys. Review B48,178 (1993))

Sulfation generates additional bands at 1168 and 1610 cm^{-1} while the 1610 cm^{-1} band occurs at high temeprature





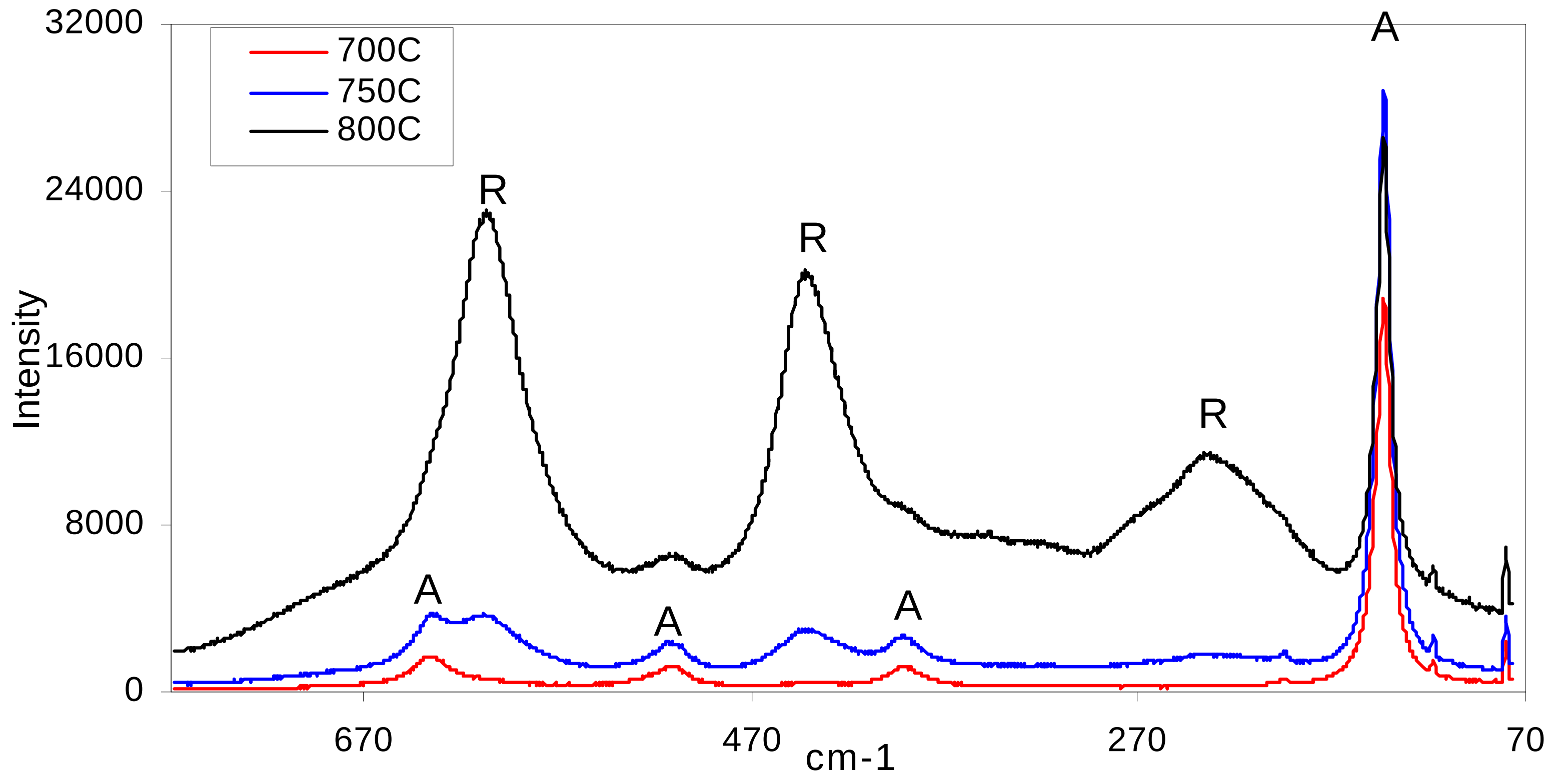
Raman Probe of Anatase/Rutile Phase Transition in TiO_2



Anatase: 146, 399, 518 & 640 cm^{-1}, density~3.8 g/cc

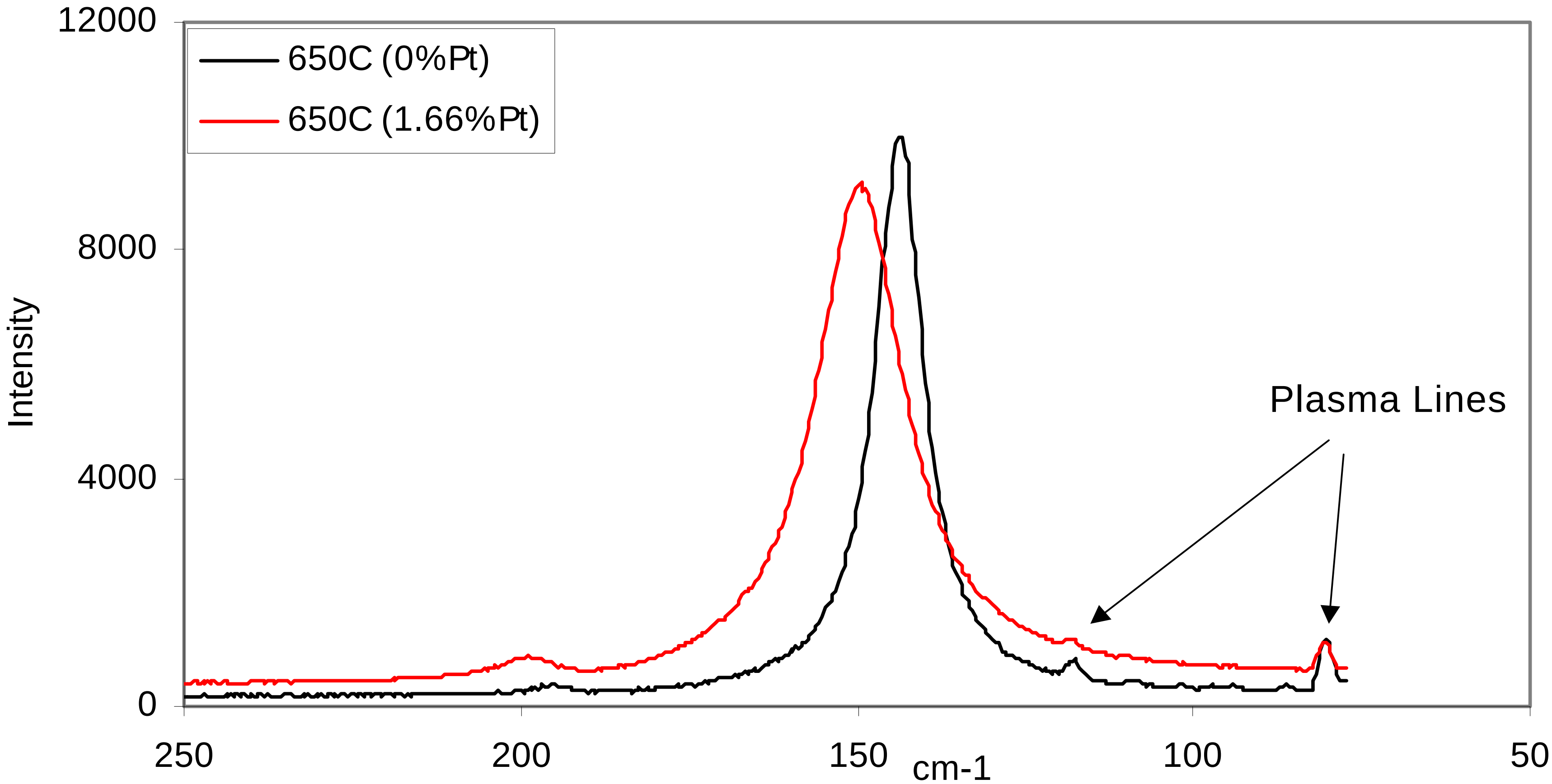
Rutile: 238, 450 & 613 cm^{-1}, density~4.3 g/cc

- Anatase dominates with T < 700°C while rutile begins to show at 750°C
- Transition frequencies and bandwidths of TiO_2 bands are invariant with temperature

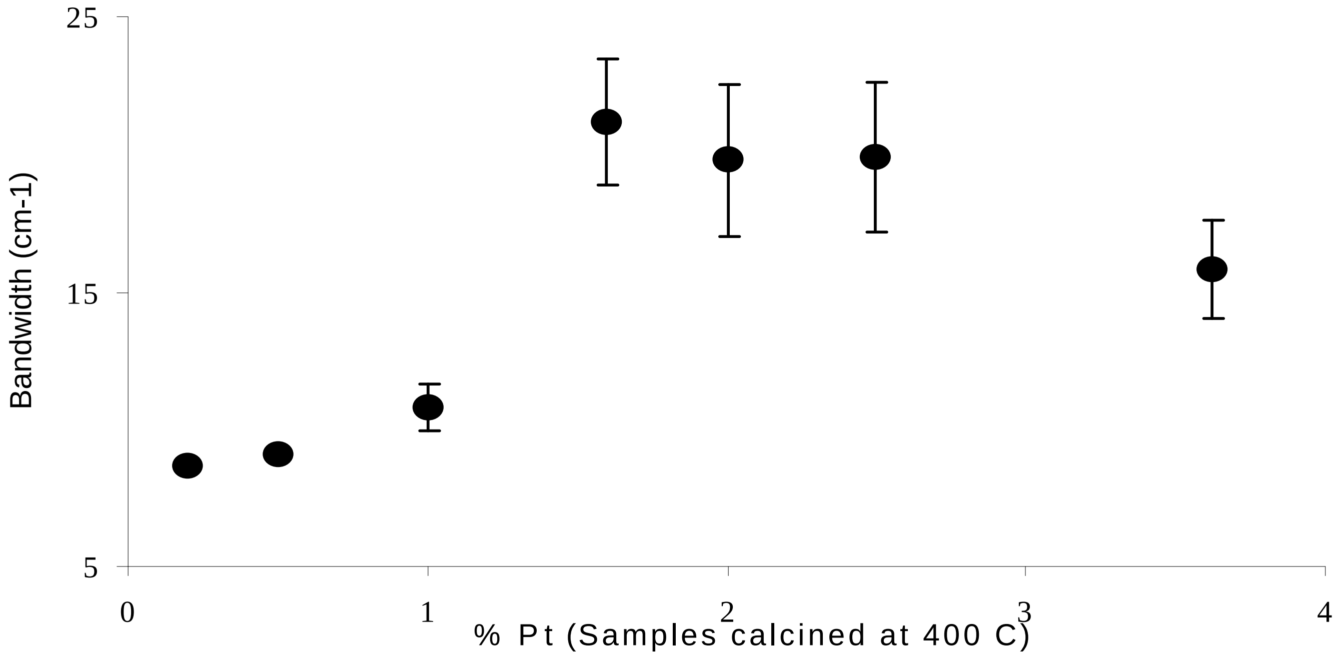


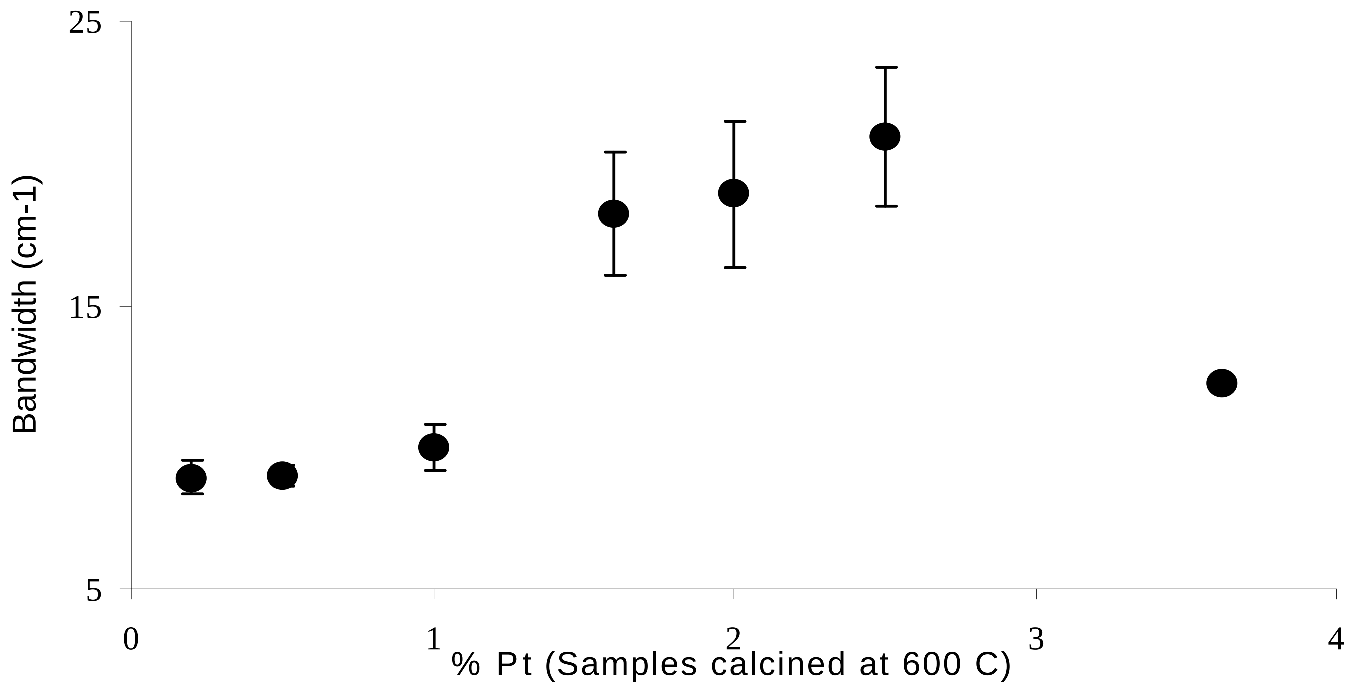
Raman is a sensitive probe of Pt dispersion

The 146.2 cm^{-1} Raman transition of TiO_2 shifts to 153.4 cm^{-1} while the bandwidth increases from 9 cm^{-1} to 18.3 cm^{-1} (almost 100% change)

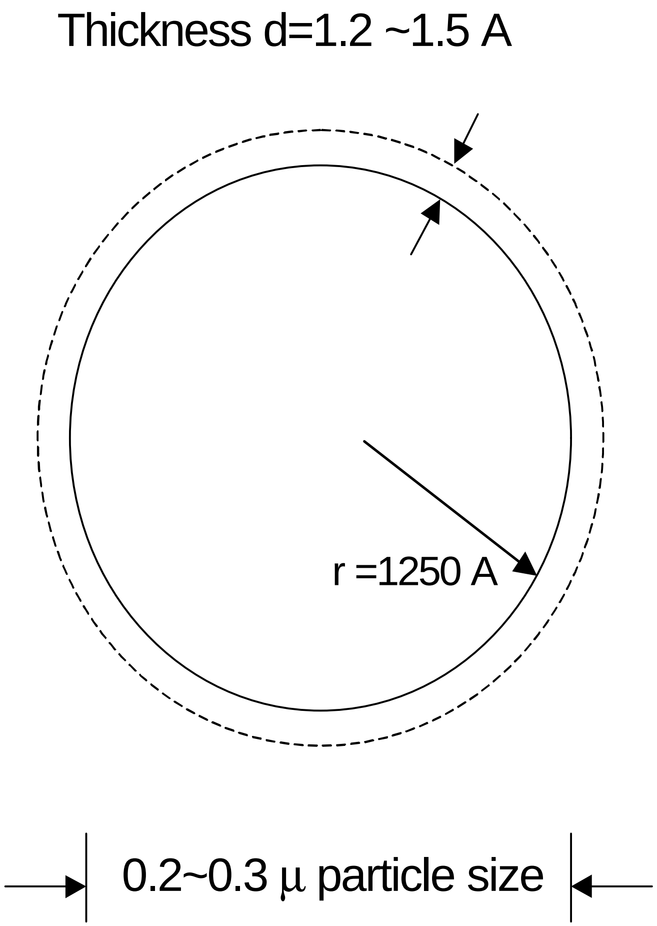


Concentration Dependence of [Pt] on Titania





Transition concentration corresponds to a monolayer coating of [Pt]



wt % of [Pt] on TiO_2

= (mass of the Pt layer)/(mass of the TiO_2 particle)

$$= (4\pi r^2 d \cdot \rho_{Pt})/(4/3\ \pi r^3 \cdot \rho_{TiO2})$$

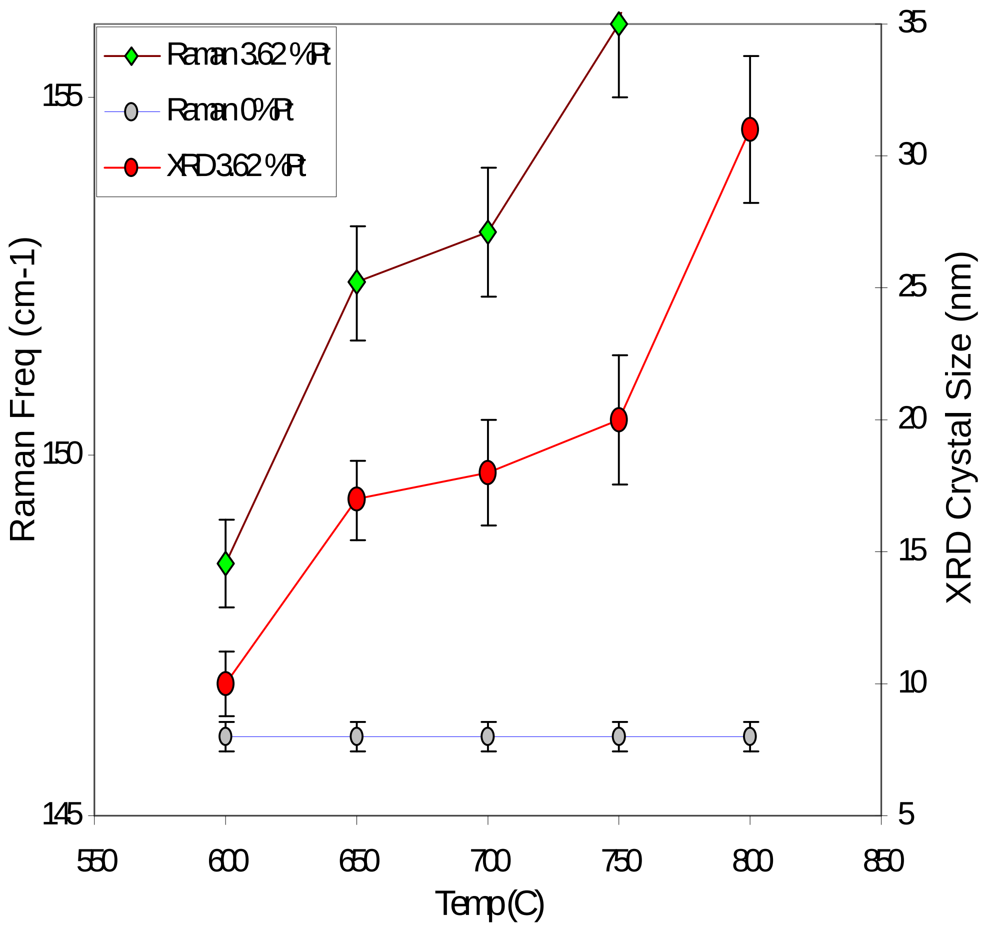
$$= 3d \cdot \rho_{Pt}/r \cdot \rho_{TiO2}$$

$$= 3 \times 1.5 \times 19.7 / 1250 \times 3.8$$

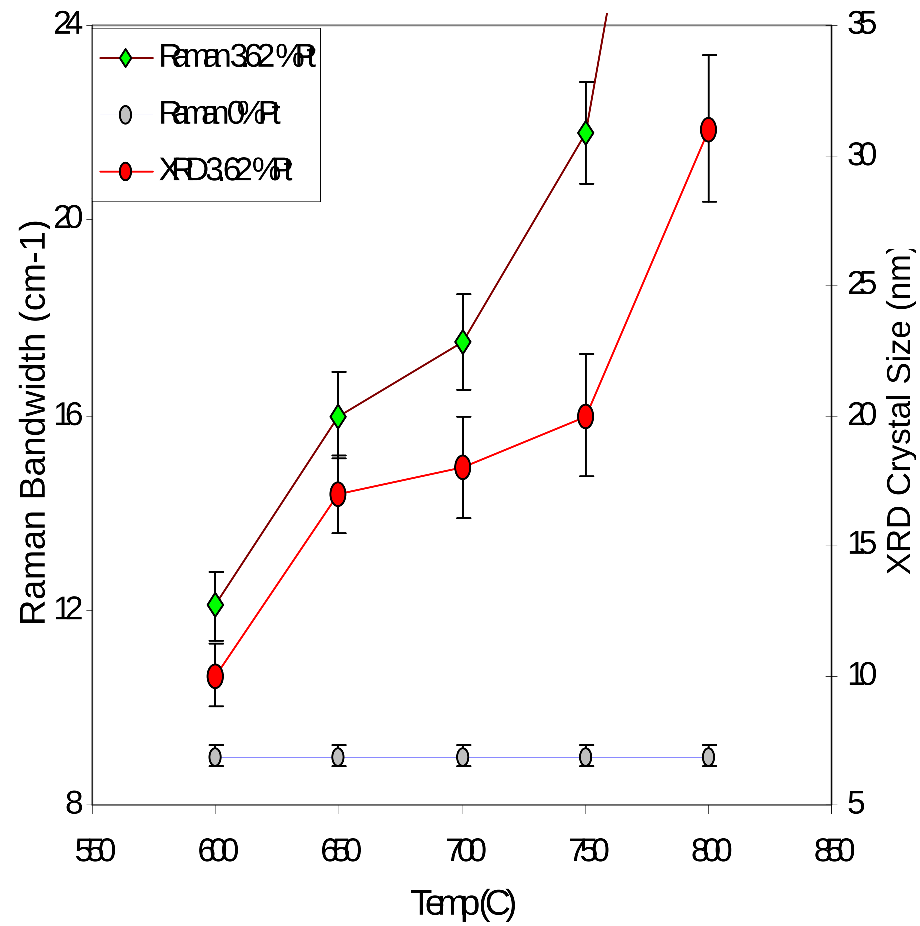
= 1.6 %

Particle Size Correlation between Raman and XRD Spectra

Raman transition frequency of TiO_2 band



Raman bandwidth of TiO_2 band

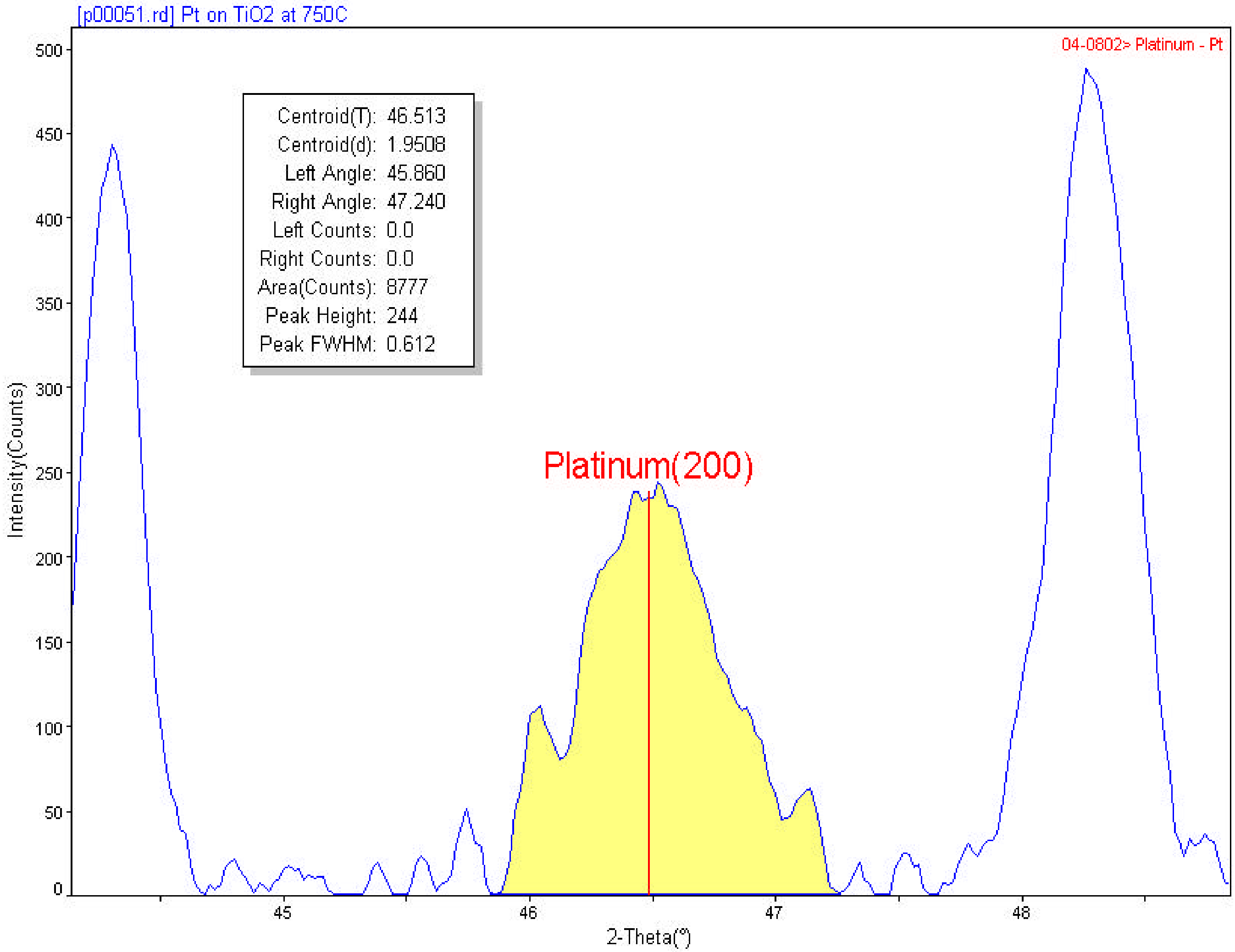


Particle Size Measurement by XRD

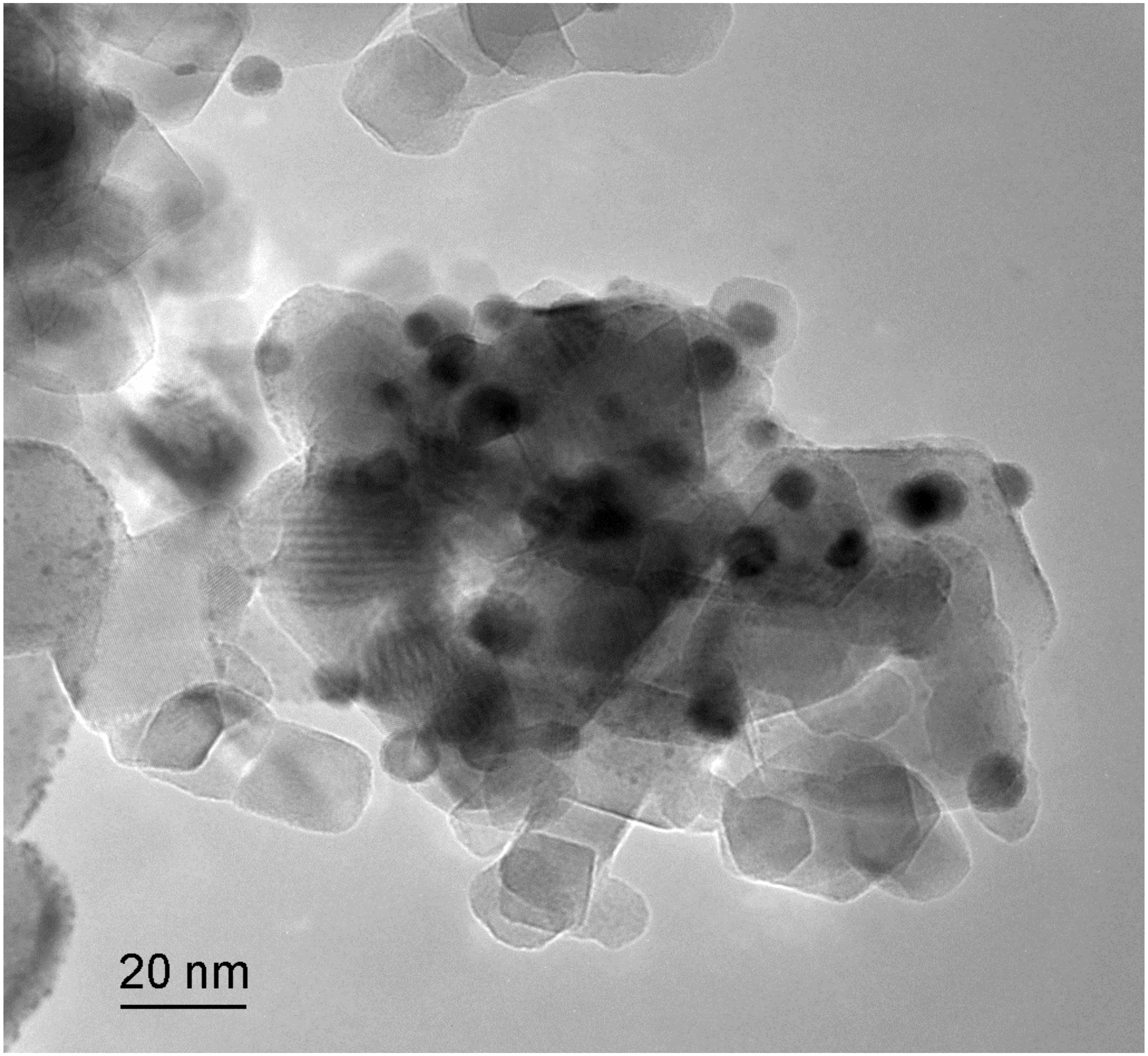
The mean crystal size can be calculated from Scherrer formula

$$\mathbf{t = 0.9\lambda/B\cos\theta_b}$$

where λ is the wavelength of incident radiation, θ_b is the Bragg angle and B is the peak breadth measured in radians



TEM Image of Typical Dispersion of Pt on Titania



CONCLUSIONS

- **Raman is a sensitive probe of Pt dispersion**

  -Raman response needs to be calibrated against a reference method such as XRD or TEM

- **The 146 cm^{-1} Raman band of TiO_2 shifts and broadens with [Pt] loading**

- **The bandwidth increases significantly at a critical concentration responsible for a monolayer coating on catalyst and finally collapses due to coalescence of particles into large agglomerates**