MELTING OF NANOPARTICLES

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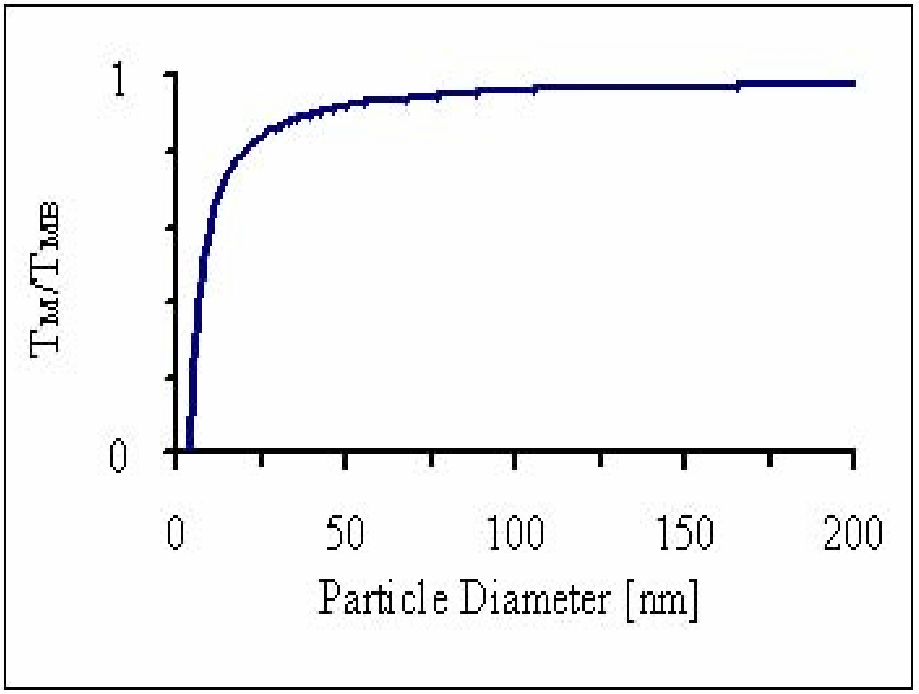
INTRODUCTION

The bulk melting temperature is independent on its size.
However nanoparticle melting temperature depends on its dimension, due to higher value of surface by volume ratio. The deviation can be ten to hundred kelvin.



A normalized melting curve for gold as a function of nanoparticle diameter.

STUDY OF ZINC NANOPARTICLE

The experiment was done taking 99.9+% zinc nanoparticle.

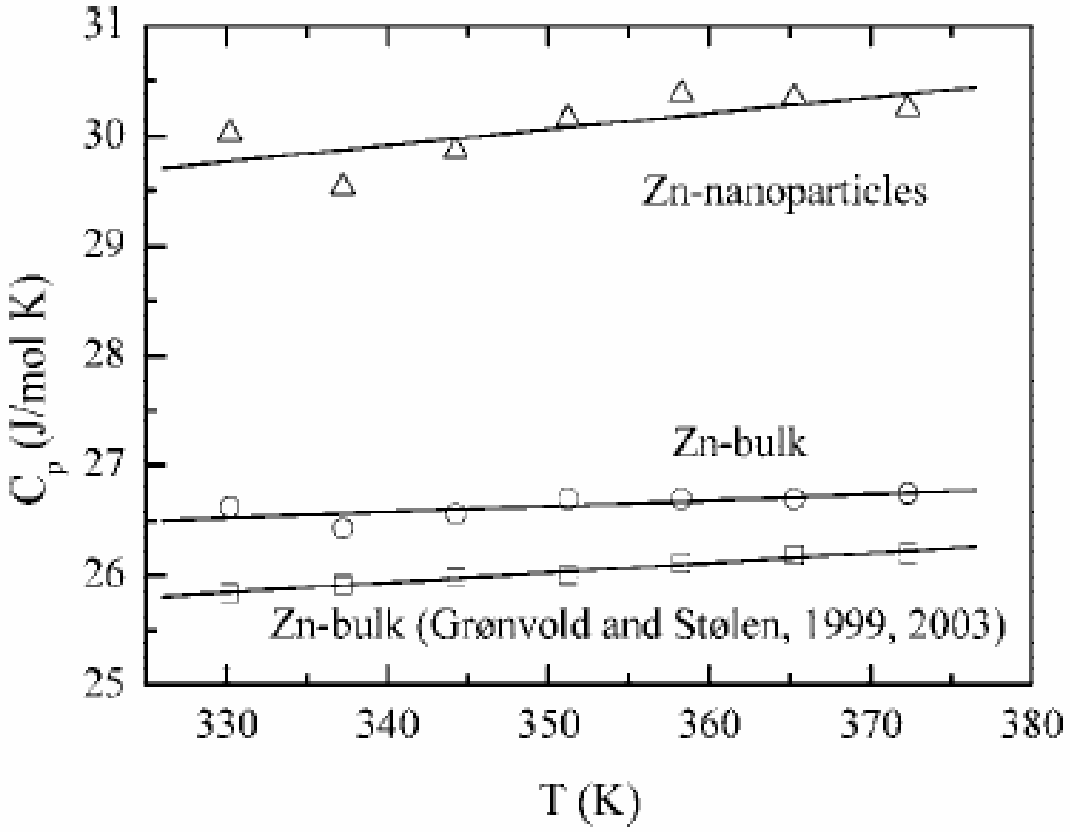
The average particle size was 35-80 nm range.

The container of the particle was opened in high purity Argon atmosphere.
These particles were stored in several sealed glass vials.

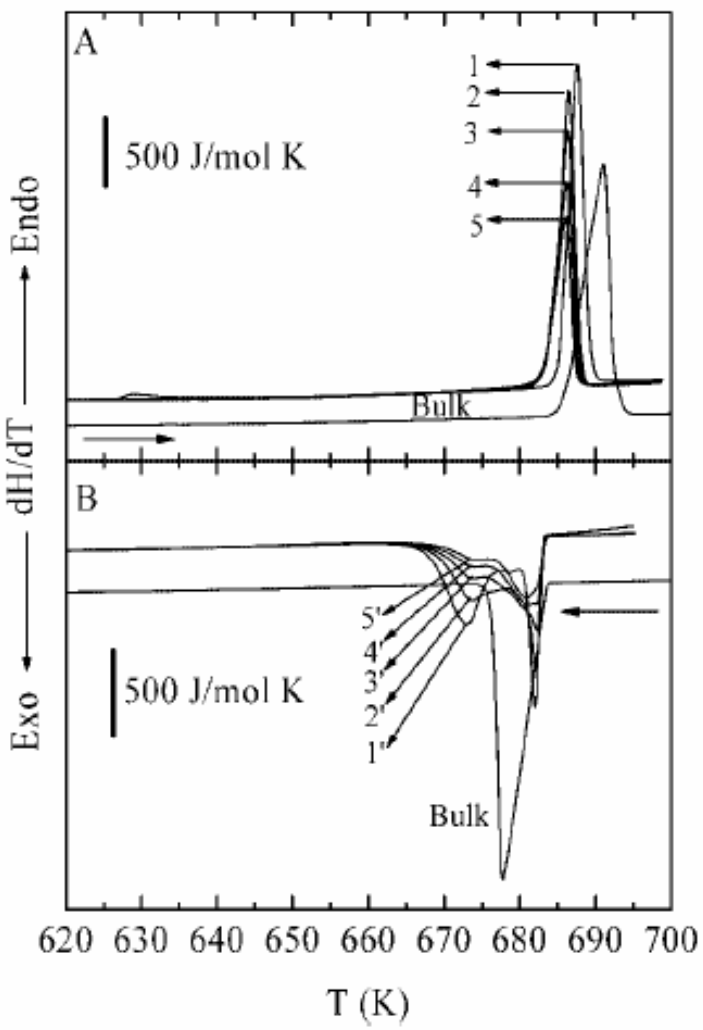
The experiment was done using
DSC.
Two calorimeter was used:- Perkin-Elmer Pyris Diamond DSC and
Thermal analysis Q-100 assembly.

The purged gas used high purity Ar in the first case and in the second case h
Purity Nitrogen gas.The instrument was calibrated against the melting of Indi

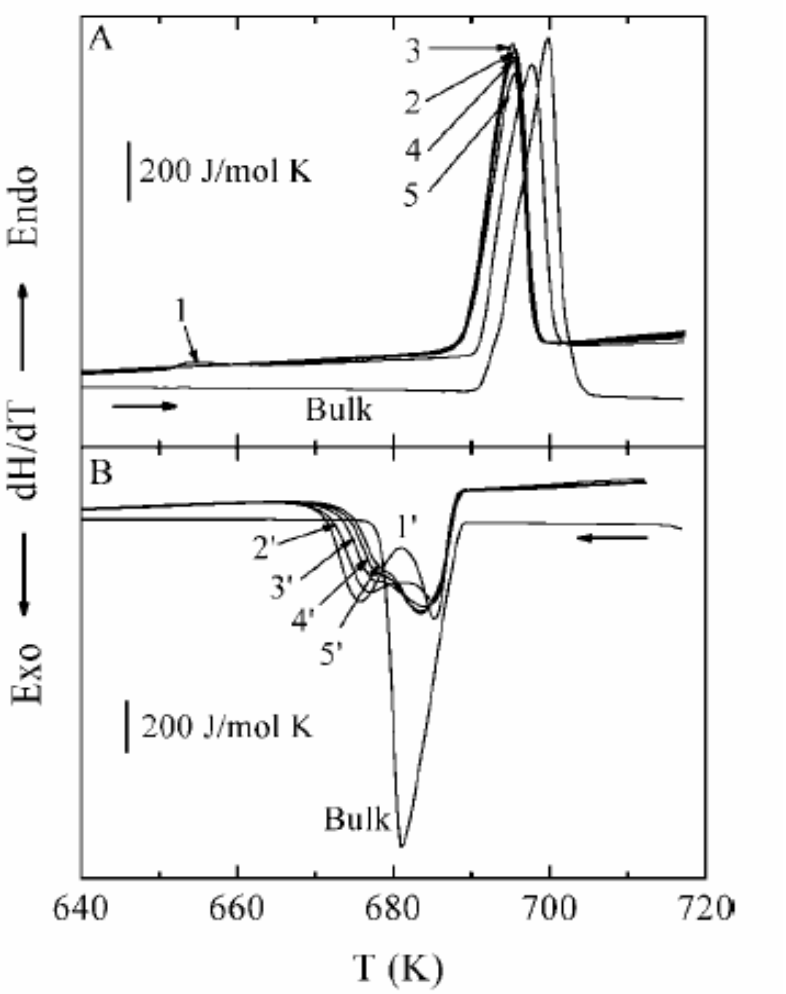
- The specific heat of Zinc nanoparticles was measured over the 623-703K range.
- A base line was obtained by averaging several heating scans at 20K/min of two aluminium DSC pans. Which differ in weight by 0.5 mg.
- One of the empty pans was then used as sample (sapphire, bulk Zinc, Zinc nanoparticle) container. The base line were subtracted from measured heat flow curve. Thus the error of weight difference between two pans eliminated .



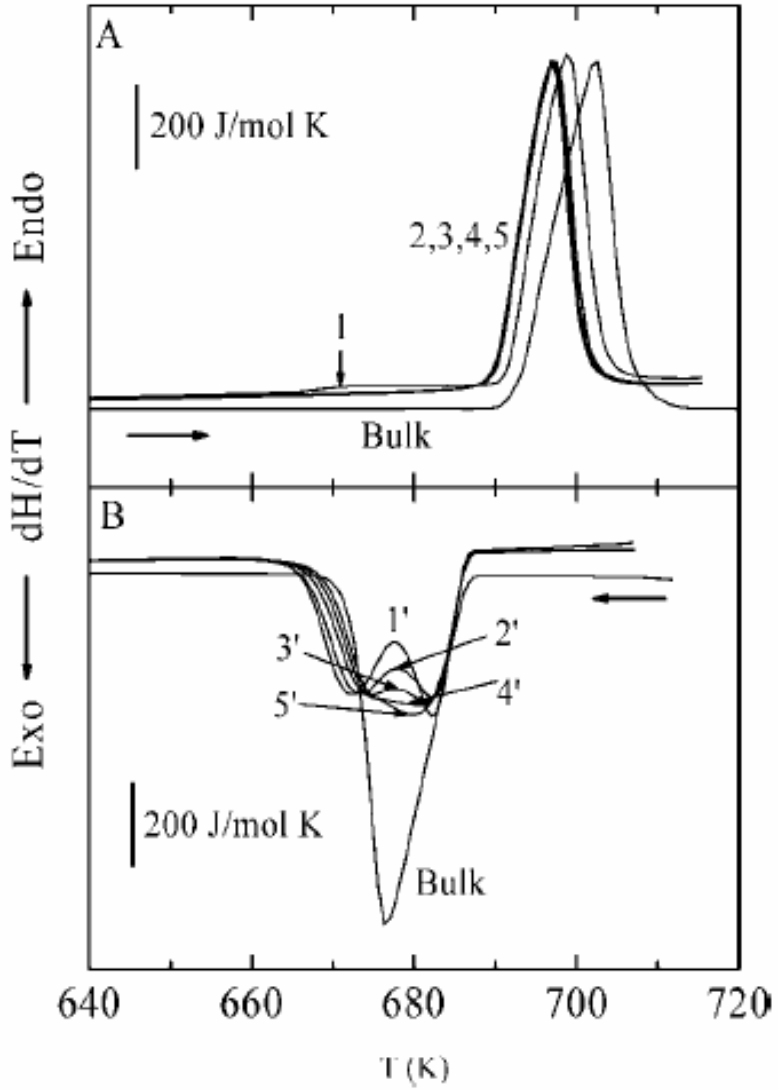
CALORIMETRIC STUDIES



10K/min



20K/min

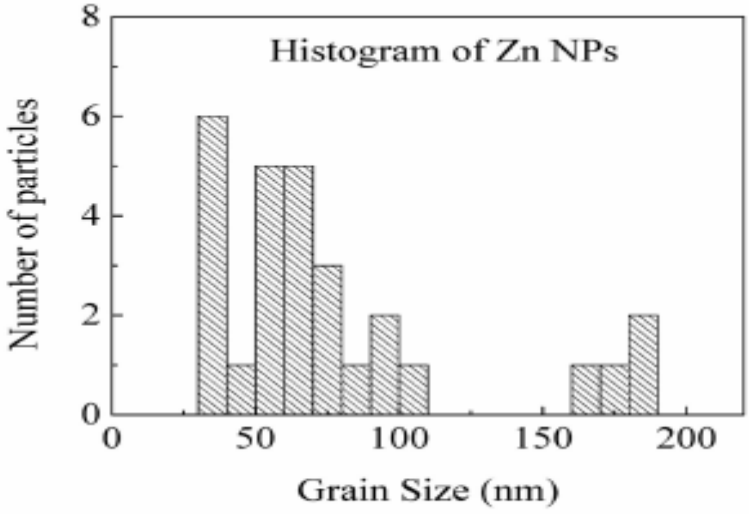


(A) Plots of d*H/dT of zinc nanoparticles and bulk Zn against* the temperature during heating. The curves are numbered in the sequence in which they were obtained. (B) Plots of d*H/dT of Zn* nanodroplets and bulk Zn against the temperature during cooling. In this figure and Figures 2-5, Curve 1′ was obtained during cooling of the molten (nm size droplets) from 573 K after heating to 713 K in curve 1 in panel A, curve 2 ′ after the sample had been heated to 723 K in curve 2 in panel A, and so on.

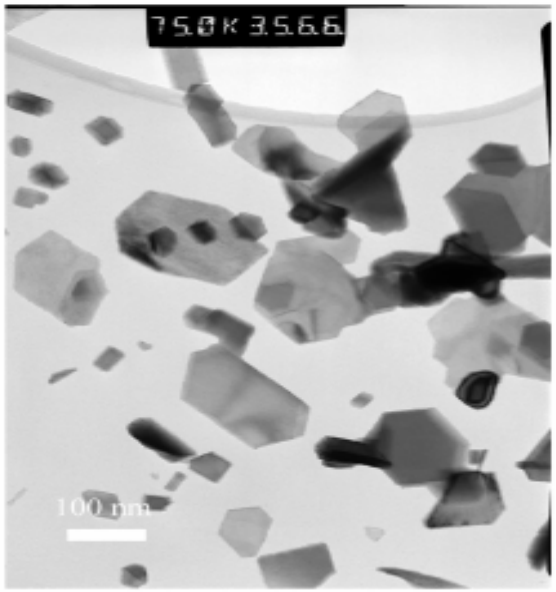
40K/min

ELECTRON MICROSCOPE STUDIES

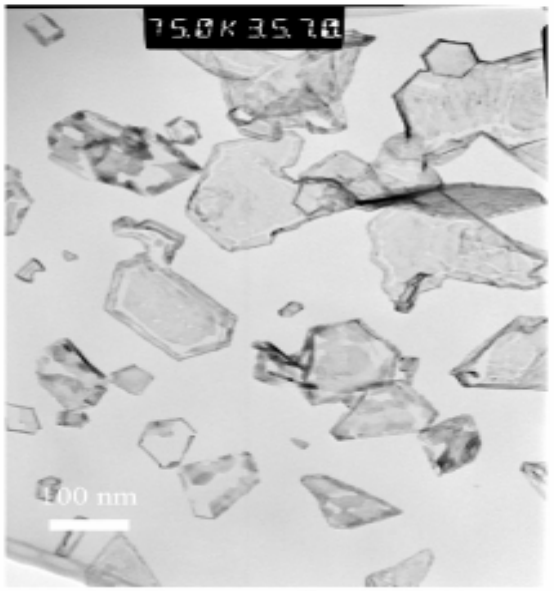
- For microstructural observations and chemical analysis, two transmission electron microscopes were used, namely JEOL 2010F TEM/STEM and a Philips CM12 TEM.
- In this procedure, the nanoparticles were dispersed in toluene to reduce their reactivity.
- A drop of this very dilute dispersion was then placed on a holey (containing holes) carbon film supported by a Cu grid and left in open air to allow the solvent to evaporate.



A



B



C

(A) Size distribution of zinc nanoparticles. (B) The TEM bright field image of zinc nanoparticles at 298 K before heating to 20 K above its *Tm (= 693.2 K) and (C) after heating to 20 K above its Tm.*

MELTING STUDY

the Gibbs-Thomson equation:- $$\frac{T_m^R}{T_m^{bulk}} = \exp\left[-\left(\frac{2\gamma_{s,l}V_s}{\Delta H_m^R}\right)\frac{1}{R}\right]$$

Also written as, $$T_m^R = T_m^{bulk}\left[1 - \left(\frac{2\gamma_{s,l}V_s}{\Delta H_m^{bulk}}\right)\frac{1}{R}\right]$$

Thus for 35-80 nm size (spherical) nanoparticles (R =17.5-40 nm), *Tm R* is in the range 598-650 K and lower for smaller nanocore of zinc. In contrast, the result obtained here shows that the minimum *Tm* is 687.2 K, which is 37-89 K higher than the value calculated.

The large deviation due ZnO shell.

We now consider the effect of thermal cycling on *Tm*

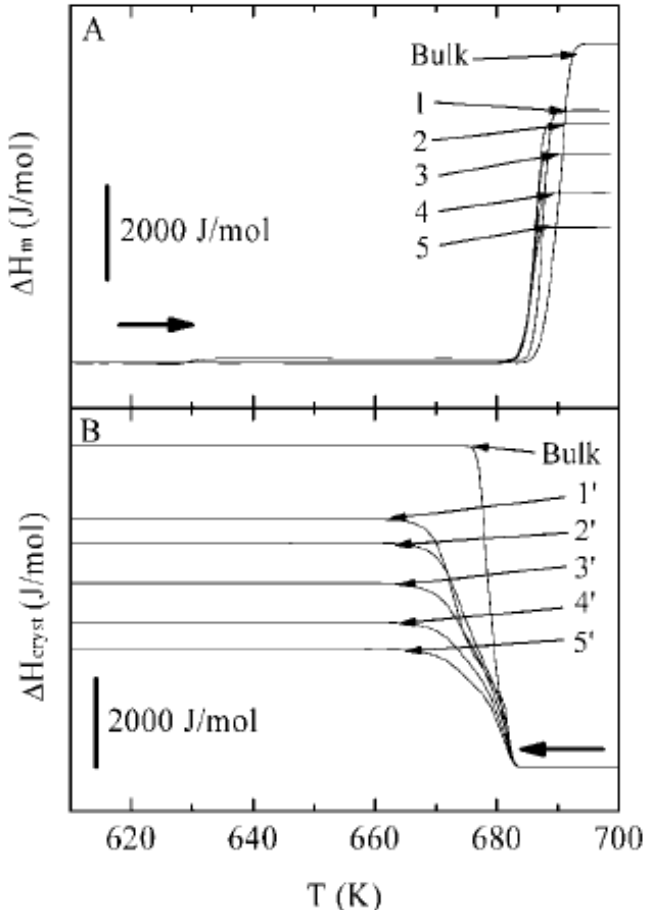
- For the 10 K/min rate, it decreases from 690.9 to 689.6 K from first to the second cycle and finally to 688.6 K in the fifth cycle.

- For the 20 K/min rate from 691.4 to 689.7 K and thereafter remains constant and for the 40 K/min rate from 691.7 to 690.3K and finally to 690.1 K.

- The initial decrease in *Tm* indicates reduction in the zinc nanocore on oxidation and consequent thickening of the ZnO layer and ultimately sealing of the ZnO shell. After that has occurred, oxygen diffuses far too slowly through the ZnO shell to further oxidize significantly the zinc nanocore during the

The heat flow data are thus used to determine the enthalpy difference from the relation,

$$\Delta H(T) - \Delta H(T_{ref}) = \int_{T_{ref}}^{T} \left(\frac{\partial H}{\partial T}\right) \mathrm{d}T$$



The Δ*Hm* of nanoparticles would be lower than that of the bulk. This is ageneral feature of melting of all nanoparticles.

10K/min

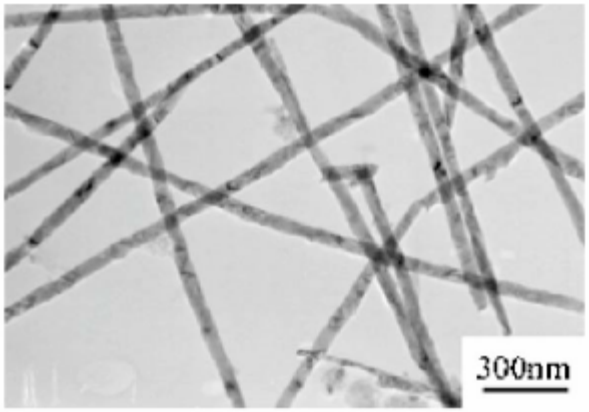
CONCLUSION

- The melting temperature of Zn nanoparticle is higher thanbulk melting temperature.
- But it’s higher than expected value according to Gibb;s-Thomson relation, due to supper heating effect for the presence of ZnO matrix.
- The oxidation process of Zn nanoparticle is very slow.
- The heat of melting of Zn nanoparticle is lower compare to bulk.

Melting behavior of Zn nanowire Arrays

A direct current electrodeposition method is employed to prepare the Zn nanowire arrays in the holes of the porous anodic alumina membrane (PAAM) with the diameter from 22 to 225 nm, respectively.

X-ray diffraction and transmission electron microscopy (TEM) were carried out to study the crystalline structure and morphology of nanowires.



It is clear from the Fig that nanowires have a high-aspect ratio and the diameter is uniform

Fig1 shows a typical TEM image of Zn Nanowire with diameter 45nm

The melting behavior of Zn nanowires was studied by using **Differential scanning calorimetry (DSC)** and the heat flow recorded at a scanning rate of 10 °C/min.

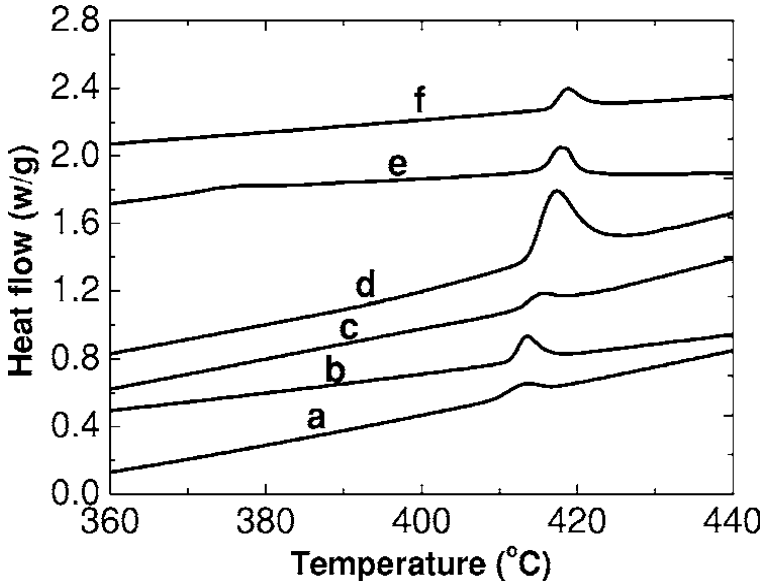


Fig 2. DSC trace of Zn nanowire arrays with diameters of 25 nm (curve a), 45 nm (curve b), 65 nm (curve c), 90 nm (curve d) 145 nm (curve e), and 225 nm (curve f).

The size-dependent endothermic peak of the nanowires is observed. It is clear that the onset point of the endothermic peak shifts to low temperature with the decrease of the diameter.

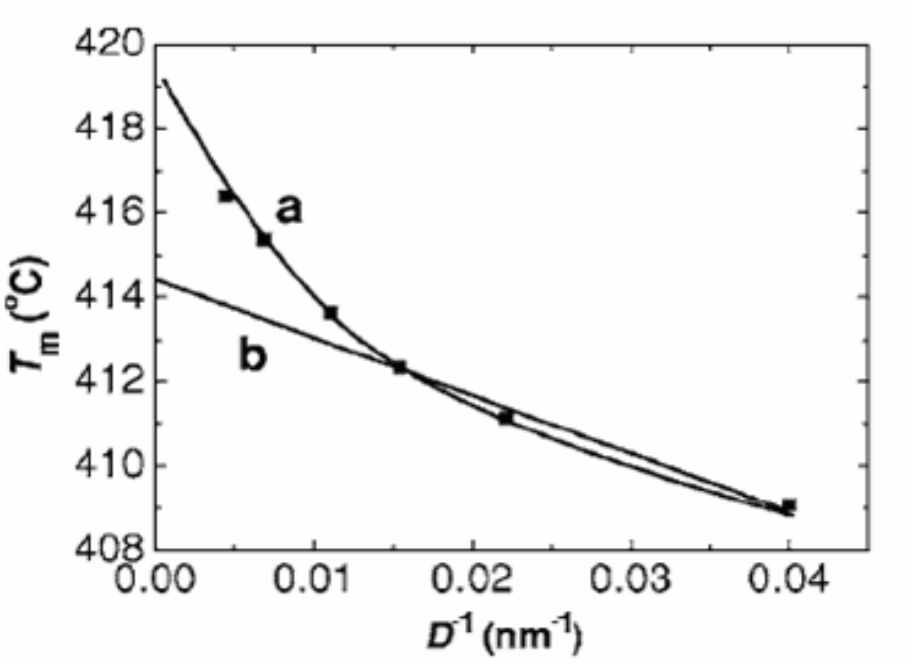


Fig 3 shows melting Temp T_m of Zn nanowire arrays as a fn of the reciprocal of diameters

- It has been shown that the variation of the melting temperature of Zn nanowires is nonlinear .
- Moreover, the bulk melting temperature of nanowires or clusters cannot be extrapolated from the data in the intermediate size range since the extrapolated bulk melting temperature for them are remarkably lower than the experimental value for bulk .

By thermodynamic model, the melting temperature of a nanowire is given as

$$\Delta T = T_0 - T_m(D) = \frac{2vT_0}{\Delta H_f}\left[\gamma_{sv} - \left(\frac{\rho_s}{\rho_l}\right)\gamma_{lv}\right]\left(\frac{1}{D} + \frac{1}{l}\right) \qquad \text{---1}$$

It can be noted from above eq that $T_m(D)$ should show a linear dependence on 1/D in case of spherical nanoparticles which disagree with the experimental results.

According to the report of Lai et al. the heat of fusion ΔH_f depends on the diameter of the nanowire D by

$$\Delta H_f = \Delta H_0\left(1 - \frac{2t_0}{D}\right)^n \qquad \text{---2}$$

where H_0 is the heat of fusion for bulk materials
t_0 - critical thickness of liquid layer covering the solid core at the melting temperature T_m.
The exponent n is 3 for spherical nanoparticles and 2 for nanowires

This shows the relation between Tm(D) and 1/D should be curvilinear

CONCLUTION

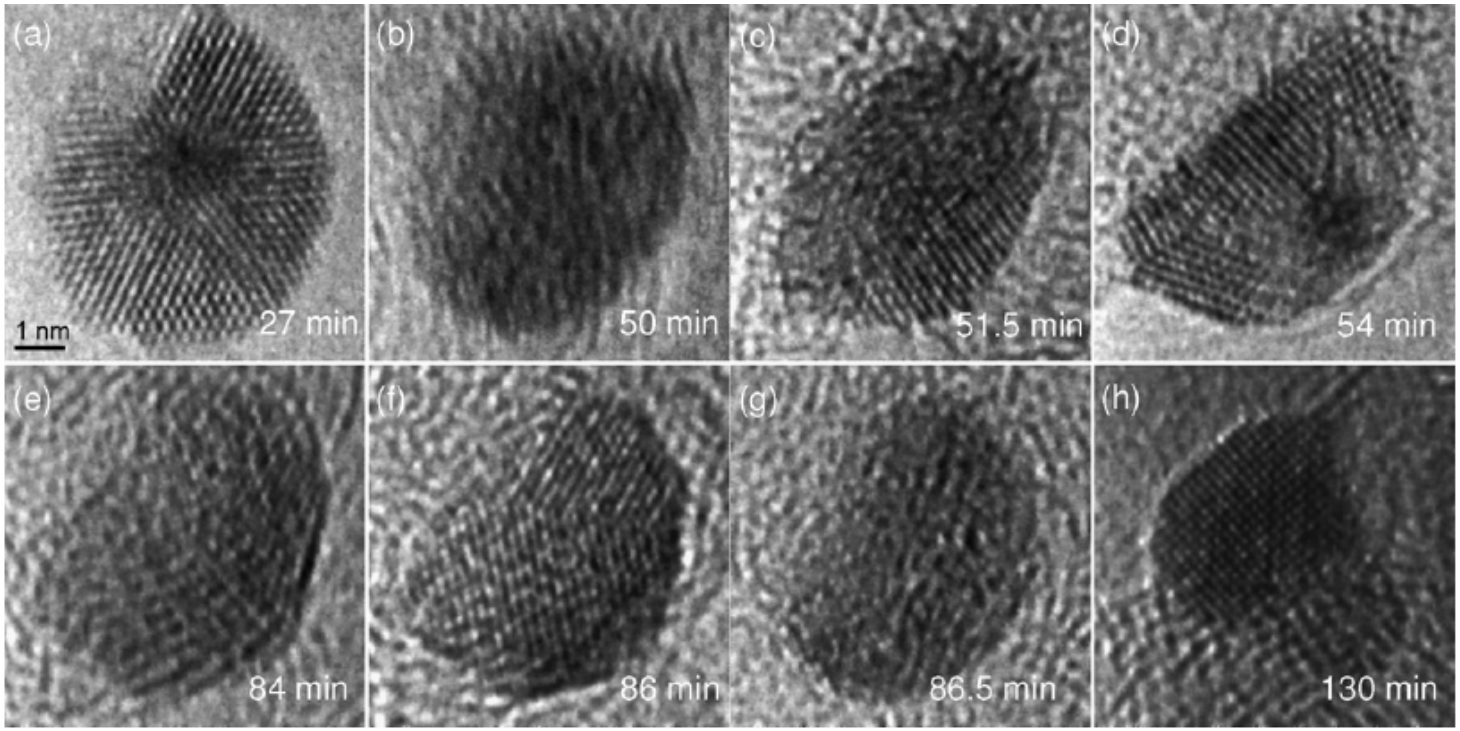
- The study of Zn nano wire shows non-linear dependence with respect to the dimension of the particle.

Structural Stability of Icosahedral FePt nanoparticles

- The structural stability of FePt nanoparticle of 5-6 nm diameter was investigated using dynamic high resolution TEM.

- With the electron beam of 200 A/cm^2 , the nanoparticle showed a typical behavoiur.

Various Stage during of melting



(a) Starting of melting; (b) melted state; (c) truncated icosahedron structure;
(d) Starting of melting of truncated structure; (e) melted; (f) unstable twin struct
(g) Again melting within 1 minute, (h) single crystal structure

Preparation and field emission of carbon nano tubes cold cathode using Ag nano particle

1.Carbon nanotubes are efficient electron emitters due to *high aspe ratio*, *high mechanical strength, high chemical stability.*

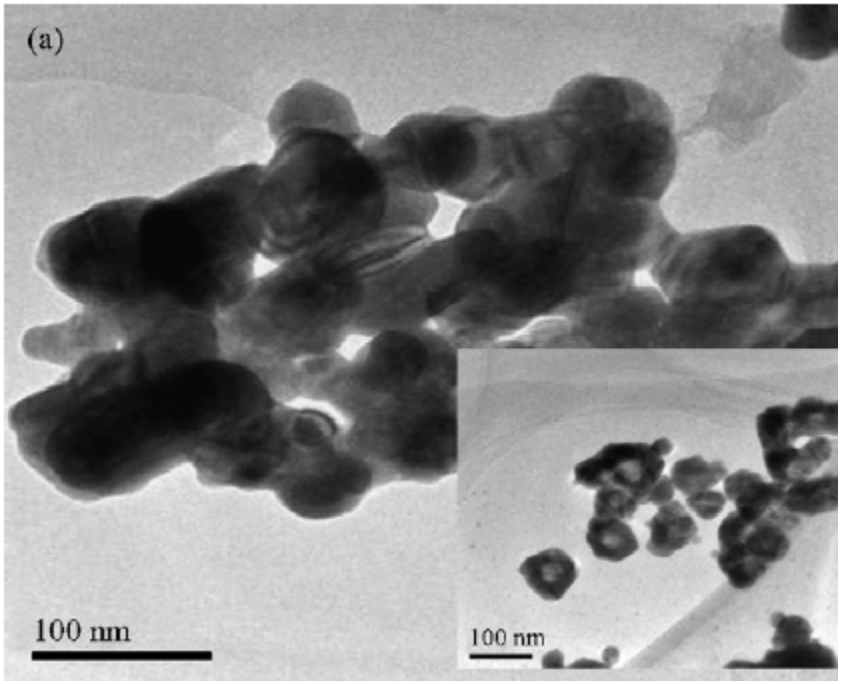
2.CNTs paste with organic and inorganic binder is well know but they have limitation due low electrical conductivity; where as Ag is highly conducting.

3. Ag nanoparticles can be melted below 200^0 C , though the meltin Point of the Ag bulk is 960.5^0C.

Preparation of CNTs cold cathode

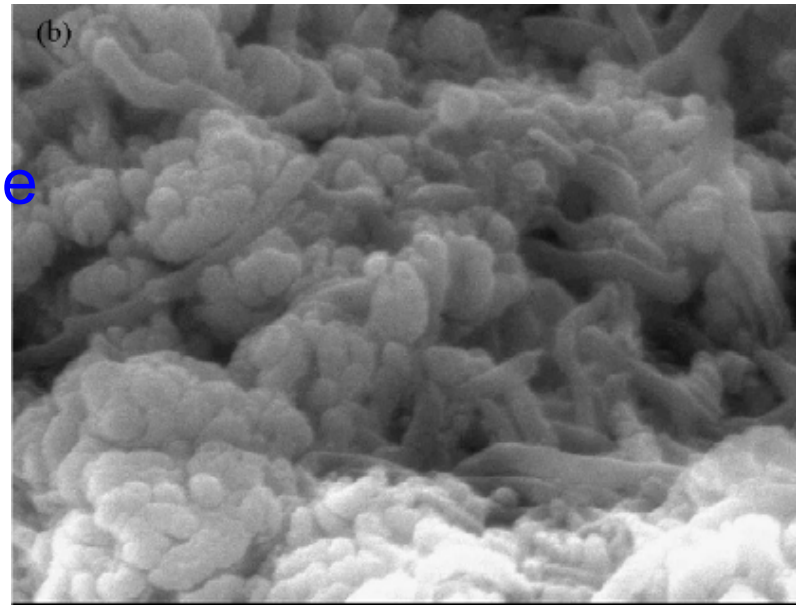
The multi walled CNTs and Ag nano particle was ultrasonically disp
in the 1:2 mass ratio. Suspension was filtered and wet powder mixe
terpineol and other organic materials with low boiling point

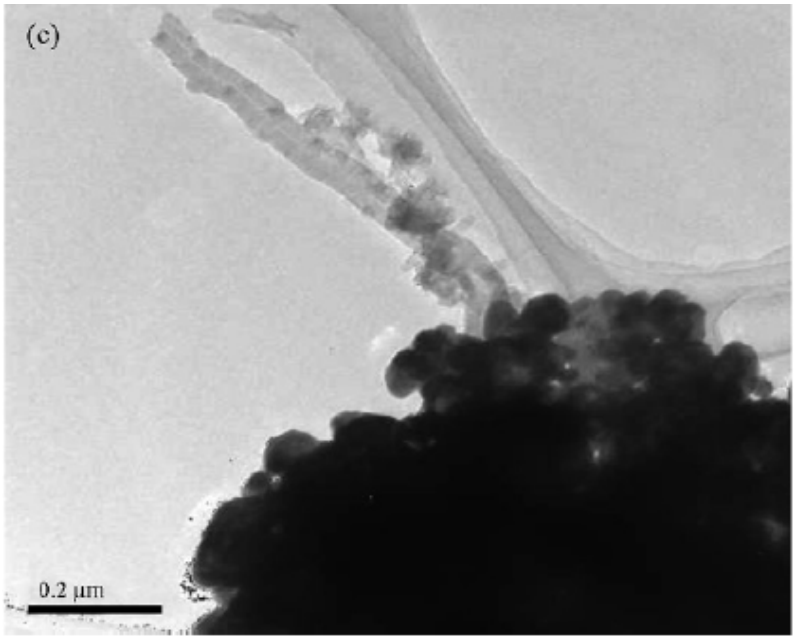
Then the CNTs paste was dispersed on the Si surface, which was p
cleaned Ultrasonically in acetone and ethanol , and then annealed f
30 min at 250 ^{0}C to remove organic materials and to melt Ag nano
particles.



HRTEM images of the Ag nano particle after Sintered at 150^0 C. In the inset the Ag nano paricle before sintered

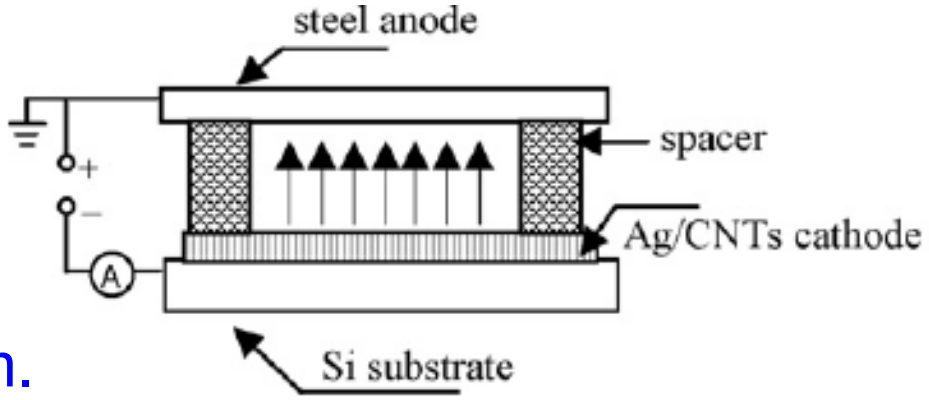
SEM images of the CNTs cathode by sintering CNTs and Ag nano paricle in 1:2 ratio





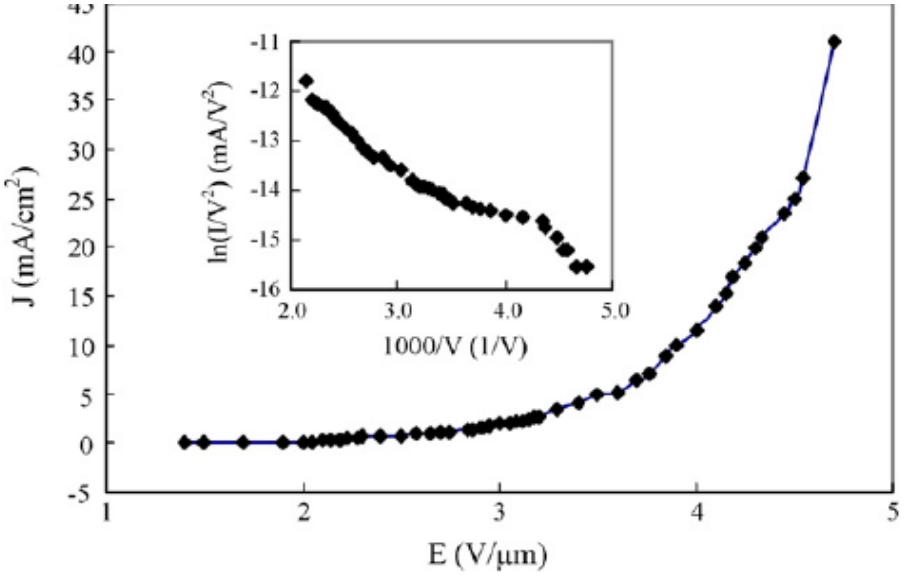
HRTEM images of the CNTs emitte
With the roots of CNTs embedded c
Ag nano film

Experimental setup for the measurement of the emission. cathode area was 2 nm x 2 nm and distance to anode was 100μm. the pressure was mentained at 2×10^{-4} Pa



Fowler-Nordheim Equation

$$I(E) = \frac{1.54x10^{6} A\ (\beta\ E)^{2}}{\Phi} Exp\left(-\frac{6.83x10^{3}\Phi^{3/2}}{\beta\ E}\right)$$



The turn on field and threshold field is 2.1 and 3.9 V/μm, and field emission current density is 41 mA/cm2 at an applied field 4.7 V/μm

CONCLUTION

- FePt nanoparticle with icosahedron shape shows typical behaviour of melting and recrystallisation in presence of elctron beam 200 A/cm^2
- CNTs paste using Ag nanoparticle as a binder turns out to be more efficient than the CNTs with conventional organic or inorganic binder.
- The low melting point of Ag nanoparticle makes the preparation easy.

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THANK YOU