CHAPTER 3

SYNTHESIS OF METALS AND METAL OXIDE NANOSTRUCTURES AND THEIR PROPERTIES

3.1 Introduction

Development of reliable protocols for the synthesis of materials at nanoscale is an important aspect of nanotechnology. The progress in nanotechnology is largely governed by the availability of perfect nanoscale structures. Nanomaterials possess unique chemical, physical, mechanical, thermal, optical, magnetic, electrical and biological properties [1]. These properties of nanomaterials are tunable and depend on their physical size [2], size distribution [3], surface features [4], functionalization [5], and dispersion stability [6]. These features of nanomaterials can be controlled to desired limit by choosing an appropriate technique for nanomaterials synthesis and fine tuning variables of synthesis protocols. This chapter describes the development of appropriate protocols for the synthesis of metals (silver and copper) and metal oxide (titanium dioxide) nanoparticles with desired physical, chemical, structural, optical and surface properties.

Synthesis of silver nanoparticles (SNPs) by chemical reduction method in the presence of mild reducing agent is a promising approach to achieve high yield SNPs without deteriorating their physical and surface properties [7]. This method has an advantage of yielding nanoparticles with no or little aggregation. In the present study, synthesis of uniform, monodisperse SNPs is carried out by simple one-pot method using oleylamine as reducing and capping agent [8]. It is a two-step process. In the first step, oleylamine capped hydrophobic SNPs are prepared by reducing AgNO₃ with oleylamine. Effect of concentration of reducing cum capping agent and growth kinetic parameters i.e. nucleation temperature, growth temperature, nucleation time and growth time on the product quantity and quality is evaluated in terms of colloidal yield, physical size, morphology and dispersity. In the second step, hydrophobic SNPs are phase transferred into water by ligand exchange reaction using block co-polymer, pluronic F-127 [9]. From the detailed investigation of as-synthesized nanoparticles by various characterization techniques, optimized conditions are being laid down for high yield, monodisperse; water dispersible SNPs that can be directly used as antimicrobial agents in nanomedicine.
Plasmonic nanostructures are gaining increasing attention due to their wide range of applications ranging from plasmonic photovoltaic to photothermal therapy [10-12]. Amongst the plasmonic nanostructures, copper nanoparticles (CNPs) could be a potential alternative to silver and gold but it is largely undermined because of the difficulties in synthesizing high quality, stable, ultra-small CNPs as they are prone to oxidation [13]. The second important aspect dealt-with in this chapter is the development of protocols for the synthesis of ultra-small, plasmonic copper nanostructures, which are resistant to oxidation and stable in ambient environment. In the present study, CNPs are synthesized by chemical reduction of copper chloride under mild reaction conditions by using a unique combination of reducing (sodium borohydride and L-ascorbic acid) and capping (Polyvinylpyrrolidone and L-ascorbic acid) agents. Synthesized CNPs are stable in its native metallic phase (Cu\(^0\)) under the dynamic equilibrium established between the surface of CNPs and the capping agents. Synthesized product is stable against both the oxidation and the aggregation and suitable for biomedical applications.

Titanium dioxide nanoparticles (TNPs) are another important system, which are widely researched for their photocatalytic and disinfectant properties [14-16]. The major limitation with TNPs is their photo-response, which lies in the ultraviolet region. Improved photo response in the visible region is the chief target for researchers. This chapter also deals with the development of synthesis protocols for sol-gel synthesis of pristine and Co-doped TNPs. Effect of dopant concentration has been studied on the optical band edge of the TNPs, and the processing parameters and dopant concentration have been optimized for the synthesis of visible light responsive TNPs with uniform size and shape. Subsequent sections of this chapter describe detailed protocols followed for the synthesis of SNPs, CNPs and TNPs and their subsequent characterizations to find their suitability as biocidal agents, which is the subject matter of chapter - 4.

3.2 Synthesis of Silver Nanoparticles (SNPs)

3.2.1 Materials

Silver nitrate (AgNO\(_3\)) (99.8%) and diphenyl ether were procured from S.D. Fine-Chem. Ltd. Oleylamine (70%) and pluronic F-127 were obtained from Sigma-Aldrich. Absolute ethanol, n-hexane (95%) and HPLC grade water were purchased from Merck. All the
chemicals were used as received without any further purification. For all experiments, aqueous solutions are prepared in Millipore ultrapure water ($\rho = 18.2 \, \text{M}\Omega$).

### 3.2.2 Synthesis Process

SNPs were prepared by reducing AgNO$_3$ with oleylamine (OA) in a simple one pot method. It was reported by Chen et al. [17] that for homogeneous nucleation of silver from AgNO$_3$ by OA, nucleation temperature should be $\geq 150$ °C. For fast and homogenous nucleation, AgNO$_3$ was added into the oleylamine - diphenylether mixture, which was preheated at 160-240 °C. Ripening of nanoparticles at a lower temperature is critical for homogeneous growth [18]. To achieve better control on the growth of individual crystallites, the reaction temperature was lowered to 150-200 °C [19]. Synthesis protocols followed for the preparation of SNPs are summarized as a flow chart in Fig. 3.1. Effect of following process variables has been evaluated on the quality and quantity of SNPs.

1) Concentration of surfactant cum reducing agent (oleylamine)
2) Nucleation temperature
3) Nucleation time
4) Growth temperature
5) Growth time

#### 3.2.2.1 Effect of Oleylamine (OA) Concentration

To investigate the effect of OA concentration on the quality and quantity of SNPs, the concentration of OA was varied from 0.5 mM - 30 mM. In brief, 20 mL diphenyl ether was mixed with desired volume of OA in a three neck 250 mL round bottom flask, equipped with a magnetic stirrer, condenser and a thermometer. The mixture was heated to 200 °C at a rate of 3 °C min$^{-1}$. 3 mM AgNO$_3$ was added into this preheated mixture under continuous magnetic stirring. Upon addition of AgNO$_3$, the colour of the mixture immediately turned blue. Strong surface plasmon resonance (SPR) was observed, indicating the nucleation of SNPs. The mixture was refluxed for 30 min and then rapidly cooled down to 150 °C. It was then ripened at 150 °C for another 4 h and subsequently cooled to 25 °C.
Fig. 3.1 Flowchart of synthesis protocols followed for the preparation of colloidal SNPs. Image (at the end of the flow chart) shows strong surface plasmon resonance in the colloid confirming the formation of SNPs.
The product was purified by the precipitation-redispersion. Equal volume of absolute ethanol was added into the mixture. Alcohol addition precipitates the SNPs which were isolated from the suspension by centrifugation at a relative centrifugal force (RCF) of 10744 x g (10000 rpm) for 10 min. Nanoparticles were then dispersed in 20 mL n-hexane. The dispersion was again centrifuged at 3868 x g (6000 rpm) for 10 min and undispersed residues, if any, were removed. 5 mL SNPs suspension in n-hexane was preserved at 4 °C and rest of the solution was again precipitated with absolute ethanol. The precipitates were collected by centrifugation at 10744 x g (10000 rpm) for 10 min and preserved at room temperature.

Effect of concentration of reducing agent on the quality and quantity of nanostructures has been evaluated in terms of product yield, size and size distribution, crystal phase and morphology. It was observed that irrespective of OA concentration, it always reduces AgNO₃ into SNPs with spherical morphology. To understand the effect of concentration of reducing agent on the quantity, % yield of SNPs obtained after precipitation-redispersion was determined. Fig. 3.2 shows the plot of % yield of SNPs obtained at different OA concentration.

![Graph](image.png)

**Fig. 3.2** Variation in % yield of SNPs with oleylamine concentration. % yield is measured for the product obtained after the precipitation-redispersion.
SNPs’ yield is 0% until OA concentration is > 4.5 mM. This is because no SNPs could be collected from the n-hexane phase after the precipitation - redispersion until the OA concentration is > 4.5 mM. These might be due to coagulation of nanoparticles in the absence of sufficient quantity of OA, which is also acting as capping agent. When the OA concentration is > 4.5 mM, % yield of SNPs increases following an exponential behaviour and saturates at 21 mM of OA. At this concentration, approximately 60% of the initial mass of Ag gets converted into SNPs. Low yield of SNPs might be because of incomplete reduction of AgNO$_3$ and partial losses during the purification.

To evaluate the effect of OA concentration on particle size, X-ray diffraction, transmission electron microscopy and photon correlation spectroscopy techniques were employed. The X-ray diffraction patterns of as-synthesized SNPs show four diffraction peaks (Fig. 3.3) corresponding to the FCC structure.

![XRD diffractograms of SNPs prepared at different oleylamine concentration.](image)

Fig. 3.3 XRD diffractograms of SNPs prepared at different oleylamine concentration. (a) 1.5 mM, (b) 3 mM, (c) 4.5 mM, (d) 6 mM, (e) 9 mM, (f) 12 mM, (g) 15 mM, (h) 18 mM, (i) 21 mM, (j) 24 mM, (k) 27 mM and (l) 30 mM. Samples corresponding to 1.5 - 4.5 mM oleylamine are the undispersed residues obtained during precipitation-redispersion. No dispersed particles could be extracted due to heavy clustering in these samples. The broadening of diffraction peaks increases with oleylamine concentration till 12 mM and is constant above this concentration.
The peaks matched well with the standard PCPDF database (card no. 040783) of silver. Diffraction peaks are quite broad indicating that the particle size of SNPs is very small. A slight variation in the Bragg positions of various reflections has also been observed. This variation might be due to the change in the lattice strain of the nanoparticles. To understand the effect of crystallite size and lattice strain on the size broadening of SNPs, Williamson-Hall analysis was used [20].

Experimentally observed peak broadening (β) is related to crystallite size, t and lattice strain, η by following expression:

$$\beta \cos \theta = \frac{k\lambda}{t} + \eta \sin \theta$$  

where β is experimentally observed integral breadth of X-ray diffraction peak, θ is diffraction angle, λ is the wavelength of X-ray source (λ = 1.5406 Å), t is crystallite size, η is lattice strain and k (= 0.9) is geometrical constant. By plotting βcosθ vs sinθ, crystallite size and lattice strain has been determined. The plot of crystallite size as a function of OA concentration is shown in Fig. 3.4.

![Graph](image)

**Fig. 3.4** Variation in the crystallite, physical and hydrodynamic particle size of SNPs with oleylamine concentration. Trend lines are drawn for the sake of clear viewing.

The crystallite size decreases exponentially with increasing OA concentration and saturates at ≈ 5.5 nm for 15 mM of OA. This result indicates that the OA traditionally
known as a reducing and capping agent also acts as grain growth inhibitor. 15 mM OA is sufficient to produce uniform grains in SNPs. Further increase in OA concentration does not alter the crystallite size but increases the product yield until the OA concentration is 21 mM (Fig. 3.2).

The variation of lattice strain of SNPs as a function of OA concentration is shown in Fig. 3.5(a). When OA concentration increases, the lattice strain also increases till the OA concentration is 12 mM. This increase in lattice strain could be due to the corresponding decrease in the crystallite size of SNPs. The lattice strain is independent of OA concentration beyond 12 mM of OA, which is in direct correlation with the crystallite size trend observed in Fig. 3.4.

![Graphs showing variation in lattice strain with different parameters](image)

**Fig. 3.5** Variation in the lattice strain of SNPs with (a) oleylamine concentration, (b) nucleation temperature, (c) nucleation time, (d) growth temperature and (e) growth time.
To further understand the effect of OA on the physical size and morphology of SNPs, transmission electron microscopy was employed. **Fig. 3.6** shows the representative TEM images of SNPs prepared with different OA concentrations. Each silver nanoparticle has a spherical morphology. Nanocrystals of silver self-assembled into hexagonal closed pack lattice. No agglomeration was observed when OA concentration is $\geq 15$ mM.

![Fig. 3.6 TEM micrographs of as-synthesized SNPs obtained at different oleylamine concentration. Self-assembled hexagonal closed pack structure of SNPs could be observed.](image)

To further understand the effect of OA concentration on the physical size and its distribution, the size distribution histograms were prepared by measuring the diameter of at least 100 particles for each sample. Histograms are fitted with lognormal particle size distribution function [21].

$$P(D) = \frac{1}{(D\sigma\sqrt{2\pi})} \exp \left[ -\frac{\left( \ln \left( \frac{D}{D_o} \right) \right)^2}{2\sigma^2} \right]$$

(3.2)
where $\sigma$ is the standard deviation, $D$ the particle diameter and $\ln D_o$ is mean of $\ln D$. Histograms are shown in Fig. 3.7. The average physical size obtained from the fit are plotted as a function of OA (Fig. 3.4). For 15 mM OA, the polydispersity index is 0.17 and for 30 mM OA, it is 0.2. This confirms our belief that the as-synthesized SNPs are nearly monodisperse in size. SNPs prepared with 12 mM and 21 mM OA has higher polydispersity of 0.24 and 0.26, respectively. This might be because of few larger size particles (Fig. 3.6). The average inter-particle distance is 3.2 nm. Chain length of an OA molecule is 1.9 nm [22]. It means OA chains attached to the surface of two neighbouring SNPs are entangled by 0.3 nm. Ferrer et al. [22] have also made similar observation.

![Size distribution histograms fitted with lognormal particle size distribution of SNPs as a function of oleylamine concentration obtained from transmission electron microscopy.](image)

Fig. 3.7 Size distribution histograms fitted with lognormal particle size distribution of SNPs as a function of oleylamine concentration obtained from transmission electron microscopy.

UV-Visible absorption spectra of as-synthesized SNPs are shown in Fig. 3.8. Depending on the morphology of nanoparticles, two or more plasmon bands are expected for non-spherical SNPs [23]. In the present study, irrespective of the OA concentration, a single surface plasmon resonance (SPR) band is observed, indicating that the as-
synthesized nanostructures have spherical morphology [23]. This observation is also in agreement with the conclusions drawn from the TEM microscopy.

![UV-visible spectra of SNPs dispersed in n-hexane as a function of oleylamine concentration. A single SPR band is observed in each spectrum which is centred at 404 nm, confirming the spherical morphology of nanostructures.]

**Fig. 3.8** UV-visible spectra of SNPs dispersed in n-hexane as a function of oleylamine concentration. A single SPR band is observed in each spectrum which is centred at 404 nm, confirming the spherical morphology of nanostructures.

The hydrodynamic size distribution of SNPs dispersed in n-hexane was determined by photon correlation spectroscopy. Size distribution histograms were fitted with lognormal particle size distribution function [21] and the mean hydrodynamic size was determined. The hydrodynamic size as a function of OA concentration is also shown in **Fig. 3.4**. As can be seen, the hydrodynamic size of SNPs decreases exponentially as the OA concentration increases and levels off when the OA concentration is ≥15 mM. Lower OA concentration in the medium during the synthesis of SNPs was not able to control the agglomeration and hence resulted in the clusters of SNPs with larger size. As the OA concentration increases, it reduces the tendency of agglomeration of nanoparticles by increasing the electrostatic repulsion between the nanoparticles. The hydrodynamic size levels off at 10.2 nm for OA concentration ≥15 mM. At this concentration, each nanoparticle is coated with a monolayer of OA. This was also confirmed by thermogravimetric analysis. In TG thermogram (**Fig. 3.9**), 13% weight loss was observed, which is corresponding to a monolayer coating of oleylamine on the surface of SNPs.
The mean hydrodynamic size obtained for each concentration of OA is greater than that of crystallite size and physical size obtained from X-ray diffraction and transmission electron microscopy, respectively. This is quite obvious as hydrodynamic size also takes OA coating into the account while the other two methods only consider the bare nanoparticles. The difference between the physical size determined by TEM and the hydrodynamic size obtained from photon correlation spectroscopy gives an estimation of the organic shell around the nanoparticles, which is 2.1 nm when OA concentration is >15 mM. This also agrees well with the earlier observation of monolayer coating of OA on the surface of SNPs [22]. The same conclusion has also been drawn from the measurement of inter-particle distance in the self-assembly of SNPs in TEM micrographs and from the weight loss observed in TG thermogram.

![TG thermogram of as-synthesized SNPs prepared with 15 mM oleylamine concentration. 13% weight loss is observed in a two-step process corresponding to the decomposition and carburization of oleylamine.](image)

**Fig. 3.9** TG thermogram of as-synthesized SNPs prepared with 15 mM oleylamine concentration. 13% weight loss is observed in a two-step process corresponding to the decomposition and carburization of oleylamine.

### 3.2.2.2 Effect of Nucleation Temperature (N\textsubscript{T})

To understand the effect of nucleation temperature on the quality and quantity of SNPs, the nucleation temperature (N\textsubscript{T}) was varied from 160 °C to 240 °C in the regular intervals of 20 °C, while keeping the OA concentration constant at 15 mM. Rest of the parameters i.e. nucleation time (30 min), growth temperature (150 °C) and growth time (4 h) were same as used in the experiments of section 3.2.2.1. Both dispersion and precipitates of SNPs were obtained by following the identical protocols as explained in section 3.2.2.1 and purified samples were preserved at 4 °C for subsequent studies.
SNPs synthesis is a two-step process. In the first step, homogenous nucleation is achieved by minimizing the free energy of the system and in the second step; growth of these nuclei is realized by providing favourable conditions for growth. High activation energy is involved in nucleation, while the growth requires low energy. In the crystal growth, nucleation and growth mechanisms overlap and it is impossible to suppress the two. The final size and the shape of the nanoparticles also depend on the relative rates of these two competitive processes that could be controlled by reaction parameters like concentration, temperature, pH, reducing ability, etc. [24]. It is observed that for homogeneous nucleation of SNPs from AgNO₃ by OA, it is necessary to have Nₜ between 160 °C-240 °C.

Fig. 3.10 shows the effect of variation of Nₜ on the yield of SNPs. With increase in Nₜ, SNPs yield increases. When Nₜ = 200 °C, the yield is maximum at 46%. Further increase in Nₜ decreases the yield of SNPs. This observation suggests that Nₜ has major effect on the yield of SNPs. It is expected that nanoparticles’ yield should increase with Nₜ because of the high reduction rate of AgNO₃ at elevated temperatures. It should saturate at a temperature where the rate of reduction is maximum. Instead the yield picks at 200 °C followed by a sharp decrease. This can be understood if we consider controlled aggregation of nanoparticles followed by ripening at lower temperatures.

![Graph showing variation in % Yield of SNPs with nucleation temperature. Trend line is drawn for the sake of clear viewing.](image)
During the growth of nanoparticles, two competitive processes affect the yield of nanoparticles: (i) $N_T$ and (ii) $\Delta T = N_T - G_T$. When $N_T$ is 160 °C i.e. just 10 °C above the $G_T (= 150 \, ^\circ C)$, the yield is very low. This is because of the poor reducibility of AgNO$_3$ by OA at this temperature. As $N_T$ increases, the yield also increases until $N_T = 200 \, ^\circ C$. At this temperature, the nanoparticle yield is maximum due to the highest rate of reduction at 200 °C. It is expected that further increases in $N_T$ should not affect the yield as the reduction rate is already in saturation, but contradictory to that the yield falls above 200 °C. This decrease in yield might be due to a large $\Delta T \geq 50 \, ^\circ C$. During the synthesis when the mixture was abruptly cooled to the $G_T (= 150 \, ^\circ C)$ from $N_T > 200 \, ^\circ C$, the embryo will start dissolving in the growth medium. When $\Delta T$ is large, only few nuclei could survive before the beginning of the growth stage. This would result in decrease in the yield of SNPs for $N_T > 200 \, ^\circ C$. Hence, the controlled aggregation followed by sintering is essential for homogeneous growth and the difference between nucleation and growth temperature should not exceed 50 °C to achieve a high yield of SNPs.

Irrespective of $N_T$, SNPs crystallizes into FCC lattice. The X-ray diffraction pattern of SNPs presented at different nucleation temperature is shown in Fig. 3.11. It matches well with the X-ray diffraction pattern of bulk silver reported in PCPDF no. 040783. The variation in crystallite size as a function of $N_T$ obtained from the Williamson-Hall analysis of X-ray diffractograms (Fig. 3.11) is shown in Fig. 3.12. The crystallite size of SNPs ranges between 5.5-7.15 nm. This means that nucleation temperature does not affect the crystallite size much. The variation of lattice strain as a function of $N_T$ is shown in Fig. 3.5(b). Lattice strain gradually increases from $31 \times 10^{-3}$ to $50 \times 10^{-3}$ when $N_T$ was raised from 160 °C to 200 °C. Beyond this temperature, lattice strain is independent of $N_T$. This observation is in agreement with very small change observed for crystallite size of SNPs in Fig. 3.12.

The representative TEM micrographs of SNPs prepared at different $N_T$ is shown in Fig. 3.13. When the $N_T$ is 160 °C, non-spherical SNPs were obtained whose mean size is 10.14 ± 0.04 nm. When the $N_T$ is 200 or 240 °C, self-assembly of spherical SNPs were obtained. The average physical size of SNPs is 8.07 ± 0.02 nm for $N_T = 200 \, ^\circ C$ and 9.65 ± 0.05 nm for $N_T = 240 \, ^\circ C$. The mean sizes are obtained from the best fit of the size distribution histograms with lognormal size distribution function [21]. The
random morphology of SNPs in case of $N_T = 160 \, ^\circ C$ may be due to the poor control over aggregation during ripening. Both particle size and polydispersity index were minimum for $N_T = 200 \, ^\circ C$. This might be due to optimum conditions for controlled aggregation and sintering at this temperature. A similar trend was also observed for yield data (Fig. 3.10).

![Fig. 3.11 XRD diffractograms of SNPs prepared at different nucleation temperatures.](image)

![Fig. 3.12 Variation in the crystallite, physical and hydrodynamic particle size of SNPs as a function of nucleation temperature. Trend lines are drawn for the sake of clear viewing.](image)
**Fig. 3.13** TEM micrographs of as-synthesized SNPs prepared at different nucleation temperatures.

**Fig. 3.12** shows the variation in the hydrodynamic size of SNPs as a function of $N_T$. The same trend as observed in physical size measured by TEM microscopy is followed here. The earlier explanation for the physical size variation as a function of nucleation temperature is applicable for hydrodynamic size too, as the $N_T$ does not affect...
the interaction of surfactant molecules with nanoparticles. The hydrodynamic size is constant at 9.7 ± 0.4 nm for $N_T = 180$-$220 \degree C$ while it increases to 15 nm when $N_T$ is either 160 \degree C or 240 \degree C. This might be due to very small and very large difference between $N_T$ and $G_T$ at these temperatures.

UV-visible spectra of SNPs prepared at different nucleation temperatures are shown in Fig. 3.14. Irrespective of nucleation temperature, a single SPR band is observed. It is centred at 404 nm. No change in the position and shape of SPR band shows that the morphology of the SNPs did not depend on the nucleation temperature.

![UV-visible spectra of SNPs dispersed in n-hexane as a function of nucleation temperature.](image)

**Fig. 3.14** UV-visible spectra of SNPs dispersed in n-hexane as a function of nucleation temperature. A single SPR band is observed in each spectrum which is centred at 404 nm, confirming the spherical morphology of nanostructures.

### 3.2.2.3 Effect of Nucleation Time ($N_t$)

To investigate the effect of nucleation time on the product quality and quantity, oleylamine - diphenylether mixture was refluxed at 200 \degree C for desired nucleation time to promote uniform nucleation. $N_t$ was varied from 0-60 min by keeping rest of the growth variables identical to that used in section 3.2.2.1. OA concentration was constant at 15 mM. Four samples were prepared with $N_t$ of 0, 30, 45 and 60 min. SNPs are purified and preserved by following the same protocols as explained in section 3.2.2.1.
Variation in the % yield of SNPs as a function of $N_t$ is shown in **Fig. 3.15**. The highest yield ($\approx 46\%$) is obtained when $N_t$ is 30 min. When $N_t$ is $> 30$ min, the yield abruptly decreases to below 20%. This is unusual, generally an increase in $N_t$ should increase the product yield followed by saturation. The contradictory trend observed here might be due to the smaller size of nuclei, which might have nucleated during the last phase of the nucleation compared to those which were nucleated during the early stage of nucleation. These delayed nuclei are susceptible to dissolution during the rapid cooling. $N_t = 30$ min is optimum. Increasing $N_t$ beyond this decreases the yield of the SNPs.

![Graph showing % yield of SNPs vs nucleation time](image)

**Fig. 3.15** Variation in % Yield of SNPs with nucleation time. Trend line is drawn for the sake of clear viewing.

To further understand the effect of $N_t$ on the particle size and its distribution, X-ray diffraction, transmission electron microscopy and photon correlation spectroscopy were employed. The X-ray diffraction pattern of as-synthesized SNPs is presented in **Fig. 3.16**. In each diffractogram, four well resolved diffraction peaks corresponding to the standard FCC lattice of silver is observed. **Fig. 3.17** shows variation of crystallite size obtained from Williamson-Hall analysis of XRD, physical size obtained from TEM and hydrodynamic size from PCS measurements. The nature of particle size variation with $N_t$ is similar for all the three particle size types. The minimum size in each case was observed when $N_t$ is 30 min. On either side of this i.e. when $N_t$ is higher or lower than 30 min, the particle size is larger than obtained at 30 min.
Fig. 3.16 XRD diffractograms of SNPs prepared at different nucleation time.

Fig. 3.17 Variation in the crystallite, physical and hydrodynamic particle size of SNPs as a function of nucleation time. Trend lines are drawn for the sake of clear viewing.
When $N_t$ is small, i.e. 10 min, very few nuclei could nucleate. During the growth stage, these fewer nuclei would grow rapidly as the concentration of silver ions per nuclei in the growth medium is quite high. On the other hand, when the $N_t$ is high i.e. 45 min or 60 min, large number of nucleation took place initially that result in the decrease in the concentration of silver ions per nuclei available in the solution. Each nuclei would grow to a small size. $N_t = 30$ min is the optimum time to prepare smaller size, good quality SNPs with a moderately high yield (46%). This claim is also validated by TEM micrographs in the Fig. 3.18.

Fig. 3.18 TEM micrographs for SNPs prepared with different nucleation time.
SNPs prepared with $N_t = 10$ min have stronger tendency to agglomerate. These particles have irregular shape, larger size and broad size distribution. While SNPs prepared with $N_t = 30$ min are of uniform shape, smaller size and narrower size distribution. They self-assembled into HCP structure. The mean size of nanoparticles is $8.07 \pm 0.02$ nm. The TEM image of nanoparticles with $N_t = 60$ min also shows the high quality of the product. The only difference between the SNPs of two samples is their physical sizes. The mean size of SNPs for $N_t = 60$ min is $13.8 \pm 0.03$ nm. The hydrodynamic size also follows the same trend as observed for crystallite and physical sizes. The nucleation time does not affect the chemical interaction of OA with the surface of SNPs. Because of smaller size, strict size distribution and greater yield of SNPs obtained with $N_t = 30$ min, it is preferred over $N_t = 60$ min.

**Fig. 3.5(e)** shows variation of lattice strain as a function of $N_t$. The lattice strain is minimum when $N_t = 10$ min. As $N_t$ increases to 30 min, the lattice strain peaks at $50 \times 10^{-3}$. This might be because of corresponding decrease in crystallite size at this $N_t$. Further increase in $N_t$ marginally decreases the lattice strain. This observation is in consistent with gradual increase in crystallite size for $N_t > 30$ min. UV-visible absorption spectra of SNPs prepared at different $N_t$ are shown in **Fig. 3.19**. A single SPR band is observed which is centred at 404 nm. The presence of only SPR band in the UV-visible spectra means that irrespective of their nucleation time, nanoparticles grow with spherical morphology.

![Absorbance vs Wavelength](image)

**Fig. 3.19** UV-visible spectra of SNPs dispersed in n-hexane as a function of nucleation time. A single SPR band is observed in each spectrum which is centred at 404 nm, confirming the spherical morphology of nanostructures.
3.2.2.4 Effect of Growth Temperature ($G_T$)

To investigate the effect of $G_T$ on the quality and quantity of the SNPs, the $G_T$ was varied from 150 °C to 200 °C at intervals of 25 °C. Rest of the experimental conditions were kept unchanged as per section 3.2.2.1 with OA concentration fixed at 15 mM.

The correlation between the growth temperature and product quantity is established in terms of the % yield of SNPs. It is shown in Fig. 3.20. The yield of SNPs decreases with increase in $G_T$. The maximum yield (46%) was obtained when $G_T = 150$ °C. Increase in $G_T$ reduces the temperature difference between the nucleation and growth temperatures. As observed previously when $\Delta T = (N_T - G_T)$ decreases, the yield also decreases because of the obvious reasons as explained in section 3.2.2.3.

![Graph: Variation in % Yield of SNPs with growth temperature.](image)

**Fig. 3.20** Variation in % Yield of SNPs with growth temperature. % yield is measured from the product obtained after the precipitation-redispersion. Trend line is drawn for the sake of clear viewing.

Effect of $G_T$ on the particle size of SNPs was evaluated by measuring their crystallite, physical and hydrodynamic sizes. Variation of each of these sizes as a function of $G_T$ is shown in Fig. 3.21. The crystallite size calculated from X-ray diffractograms of SNPs (Fig. 3.22) is constant at 6 nm when $G_T$ is 150 °C and 175 °C, while it increases to 15 nm when the $G_T$ is same as $N_T$ i.e. 200 °C. The lattice strain gradually decreases when $G_T$ is raised from 150 °C to 175 °C (Fig. 3.5(d)). Further increase in $G_T$ to 200 °C sharply
decreases the lattice strain in SNPs. This might be because of sharp increase in the crystallite size at this $G_T$.

**Fig. 3.21** Variation in the crystallite, physical and hydrodynamic particle size of SNPs as a function of growth temperature. Trend lines are drawn for the sake of clear viewing.

**Fig. 3.22** XRD diffractograms of SNPs prepared at different growth temperature.
To further understand the effect of $G_T$ on physical size of nanoparticles, TEM was employed. TEM micrographs of SNPs prepared with different $G_T$ are shown in Fig. 3.23. SNPs self-assembled into HCP structure when prepared with $G_T = 150 \, ^\circ\text{C}$. Increase in $G_T$ deteriorated the morphology of SNPs. For $G_T = 175 \, ^\circ\text{C}$ and $200 \, ^\circ\text{C}$, polydispersed non-uniform nanoparticles were formed.

**Fig. 3.23** TEM micrographs of SNPs prepared at different growth temperatures.

Hydrodynamic size of SNPs as a function of $G_T$ is plotted in Fig. 3.21. It follows the similar trend as observed for crystallite and physical sizes. All the three particle sizes of SNPs i.e. crystallite, physical and hydrodynamic have their maximum values for $G_T =$
200 °C. This might be due to the copious agglomeration caused by the rapid growth of nanoparticles. The minimum for each of these sizes is observed at $G_T = 150$ °C. There is a little difference between the particle size obtained at 150 °C and 175 °C. But when considering the yield (Fig. 3.20) and quality of nanostructures (Fig. 3.23), $G_T = 150$ °C gives better result in comparison to $G_T = 175$ °C. Hence, $G_T = 150$ °C is the optimum growth temperature for the synthesis of good quality SNPs.

The UV-visible spectra of SNPs prepared with different growth temperatures (150-200 °C) are shown in Fig. 3.24. As expected, a single SPR band is again observed which is attributed to the spherical morphology of SNPs.

![UV-visible spectra of SNPs dispersed in n-hexane as a function of growth temperature](image)

**Fig. 3.24** UV-visible spectra of SNPs dispersed in n-hexane as a function of growth temperature. A single SPR band is observed in each spectrum which is centred at 404 nm, confirming the spherical morphology of nanostructures.

### 3.2.2.5 Effect of Growth Time ($G_t$)

Another important parameter that could affect the quality and quantity of SNPs is the growth time. To evaluate the effect of $G_t$ on the product, it was varied from 0.5 h - 8 h. No changes were made in the experimental protocols, which are described in section 3.2.2.1. Effect of $G_t$ on the yield of SNPs is shown in Fig. 3.25. SNPs yield increases linearly with $G_t$. The highest yield (76%) was observed when $G_t = 8$ h. When $G_t = 6$ h, the yield of SNPs drastically decreases to 12.5%. Despite of several repetitions of this experiment, same result was observed. The reasons behind low yield for $G_t = 6$ h is unclear.
Fig. 3.25 Variation in % yield of SNPs with growth time. Trend line is drawn for the sake of clear viewing.

Fig. 3.26 shows the effect of $G_t$ on the crystallite size of nanostructures calculated from the X-ray diffraction data presented in Fig. 3.27. The crystallite size varies between 3 nm - 6 nm when $G_t$ is varied from 0.5 h - 8 h. The crystallite size jumps to 8 nm when $G_t$ is 6 h. Except for $G_t = 6$ h, the crystallite size does not vary much with $G_t$ and hence can be considered as independent of $G_t$.

Fig. 3.26 Variation in the crystallite, physical and hydrodynamic particle size of SNPs as a function of growth time. Trend lines are drawn for the sake of clear viewing.
The variation of lattice strain as a function of growth time is shown in Fig. 3.5(e). It decreases exponentially when \( G_t \) increases from 0.5 h - 6 h. Beyond this, there is a little increase in the lattice strain of SNPs. This might be because of change in crystallite size trend (increases up to \( G_t = 6 \) h followed by a decrease) at \( G_t = 6 \) h. The TEM micrographs of SNPs corresponding to different \( G_t \) are shown in Fig. 3.28. Irrespective of \( G_t \), self-assembled HCP structures are observed; indicating that the tight size dispersion of SNPs can be obtained in the studied range of \( G_t \). Variation in the physical size of SNPs obtained from TEM is also plotted in Fig. 3.26. The particle size ranges between 7-10 nm. The large difference between the crystallite and physical size of nanoparticles for \( G_t = 6 \) h and \( G_t = 8 \) h might be due to the polycrystalline nature of SNPs. The hydrodynamic size is independent of \( G_t \) (Fig. 3.26). Irrespective of \( G_t \), the mean hydrodynamic size is between 10-12 nm except for \( G_t = 6 \) h where the size is 17.73 nm. This could be due to the large physical size (12.7 nm) of the SNPs for \( G_t = 6 \) h. The conclusion drawn from these experiments is that the coating process is independent of \( G_t \), while it strongly depends on the nucleation and growth temperatures.
Fig. 3.28 TEM micrographs of SNPs prepared at different growth time.

The UV-visible absorption spectra of SNPs prepared with different growth time (0.5 h - 8 h) is shown in Fig. 3.29. A single plasmon resonance band is observed which is centred at 397 nm - 408 nm. No other spectral signatures are found in the UV-visible spectra. It means that the morphology of SNPs, which is spherical in this case, is independent of growth time.

Fig. 3.29 UV-visible spectra of SNPs dispersed in n-hexane as a function of growth time. A single SPR band is observed in each spectrum which is centred at 404 nm, confirming the spherical morphology of nanostructures.
High resolution transmission electron microscopy image of the SNPs prepared with optimized conditions, (i.e. concentration of reducing cum capping agent-oleylamine = 15 mM, nucleation temperature = 200 °C, nucleation time = 30 min, growth temperature = 150 °C and growth time = 4 h) is shown in Fig. 3.30. Monodispersed nanoparticles with well-defined spherical morphology can be observed in Fig. 3.30. The top inset shows the specific area electron diffraction (SAED) image of SNPs. Four well distinguish rings can be observed in the SAED pattern, which confirms the polycrystalline nature of the nanoparticles. The bottom inset is the high resolution lattice fringe image of a silver nanoparticle. The average inter-planner spacing is 0.162 nm corresponding to (220) lattice plane. Silver nanoparticle is made up of six domains, which also confirms the polycrystalline nature of the particle.

![High resolution transmission electron microscopy image of the SNPs](image)

**Fig. 3.30** HRTEM micrograph of SNPs. Inset (top) shows the specific area electron diffraction pattern (SAED) and inset (bottom) shows the lattice fringe image of a single silver nanoparticle.

The inhibition of delayed nucleation during growth, in other words, the complete separation of nucleation and growth, is critical for the successful synthesis of monodispersed nanoparticles [18]. Although the mechanism leading to monodispersed SNPs presented here is not completely clear but the experimental observations suggest that the formation of SNPs follows the classical condensation mechanism during the
growth process [18]. SNPs were built up by the stacking of atomic species of Ag. These atomic species were derived from the chemical reduction of AgNO$_3$ by OA. The clustering of the Ag atoms gives numerous nuclei that are saturated in the reaction medium and aggregated into SNPs. The solubility of the nuclei in the dispersion decides the stage at which the nucleation stops and the aggregation of the nuclei dominates the growth process [18]. The particles cannot be formed if the nuclei are not saturated in the dispersion medium. Above the saturation threshold, the aggregation of the nuclei becomes spontaneous until the particles sinter from the dispersion.

3.2.3 Phase Transfer

OA coating on SNPs renders them hydrophobic. To investigate the antimicrobial properties of SNPs, they need to be dispersible in water/biological media. Hence as-synthesized hydrophobic SNPs were phase transferred from n-hexane to water by the facile phase transfer protocols [19]. Pluronic F-127 was used as phase transfer ligand. Pluronic F-127 has two hydrophilic A chains of poly ethylene oxide (PEO) and one hydrophobic B chain of poly propylene oxide (PPO) in an ABA configuration. For the phase transfer of SNPs; 20 mL, 0.2 M aqueous solution of pluronic F-127 was mixed with equal volume of stock solution of SNPs in n-hexane in a 100 mL beaker. It was covered with a perforated aluminium foil to control the evaporation of n-hexane. The mixture was magnetically stirred until the n-hexane evaporates completely. To confirm the phase transfer of SNPs, fresh n-hexane was poured on the aqueous solution of SNPs. On successful phase transfer, both aqueous and organic phases would remain immiscible (Fig. 3.31). The added organic phase was isolated from the aqueous phase by centrifugation. The phase transferred aqueous dispersion of silver was preserved at 4 °C.

![Fig. 3.31](image)

Fig. 3.31 SNPs (A) before phase transfer (dispersion in hexane) and (B) after phase transfer (dispersion in water).
Reduction of AgNO₃ by OA produces SNPs with hydrophobic surfaces. OA is chemically bound on the surface of silver due to the formation of Ag – N bond [25], which keeps them hydrophobic and dispersible in hexane. Pluronic F-127 is used to transfer hydrophobic SNPs into aqueous medium. Pluronic F-127 is made up of two hydrophilic A chains of poly ethylene oxide (PEO) and one hydrophobic B chain of poly propylene oxide (PPO). The transfer mechanism (Fig. 3.32) shows pluronic replaces the original OA ligand on the surface of nanoparticles and become the new ligand. Hydrophilic nature of PEO segments of pluronic-capped nanoparticles transfer them into the aqueous medium and keeps them dispersible in water. By exchanging the original ligands (oleylamine) with block-co-polymer pluronic F-127, the transferred nanoparticles exhibited good stability in water, even after being washed with hexane.

![Diagram](image)

**Fig. 3.32** Schematic representation of phase transfer of hydrophobic SNPs into hydrophilic using pluronic F-127.

UV-visible spectra of as-synthesized (in n-hexane) and phase transferred SNPs are shown in Fig. 3.33. A single SPR peak was observed both before and after the phase transfer. The spectral band after the phase transfer shifts to higher wavelength, i.e. a red shift is observed after the phase transfer. This might be because of difference in surface adsorbed species on SNPs before and after the phase transfer. The presence of single SPR band after the phase transfer indicates that the particle morphology is not affected by phase transfer. According to the Mie’s theory, only a single SPR band is expected in the absorption spectra of spherical metal nanoparticles, whereas anisotropic particles could give two or more SPR bands depending on the shape of the particles [26]. In this case, a single SPR band is observed, indicating that SNPs are spherical. Further, phase transfer does not alter the shape of the SPR band, which excludes the possibility of formation of agglomerates during the phase transfer. Reduction in the intensity of SPR band for the phase transferred SNPs is due to their lower concentration.
Fig. 3.33 UV-visible spectra of SNPs (—) before and ( - - - ) after the phase transfer. A single SPR peak centred at 404 nm indicating the spherical geometry of nanoparticles. The SPR band is red shifted to 413 nm after the phase transfer.

Hydrodynamic particle size distribution histograms of SNPs before and after the phase transfer are shown in Fig. 3.34. Each histogram is fitted with lognormal particle size distribution function and from the fitting, the mean hydrodynamic size and polydispersity indices are determined. The hydrodynamic size of SNPs before the phase transfer is 9.2 ± 0.06 nm and after the phase transfer, it is 59.1 ± 0.14 nm. The size difference of ≈ 50 nm between as-synthesized and phase-transferred nanoparticles is doubled compared to the micellar size (23 nm) of pluronic [27].

Fourier transform infrared spectroscopy was employed to understand the surface functionalization of SNPs before and after the phase transfer. FTIR spectra of SNPs before and after the phase transfer are shown in Fig. 3.35 and analysed in Table 3.1. Only the salient features of each spectrum are described here. In case of oleylamine capped SNPs (before phase transfer), the bands at 2850 and 2915 cm\(^{-1}\) originate from the symmetric and asymmetric stretching vibrations of C – H [28]. The broad absorption band centred at 3432 cm\(^{-1}\) is attributed to the N – H stretching vibrations [28]. An additional band appeared at 1591 cm\(^{-1}\) is due to the asymmetric stretching of the Ag – N, suggesting that – NH\(_2\) group of OA coordinates with the Ag on the surface of the SNPs [9]. In the FTIR spectra of phase transferred SNPs, bands at 949 and 1113 cm\(^{-1}\) are
observed. These bands correspond to the CH$_2$ rocking and C – O – C stretching vibrations of pluronic F-127 [29]. The bands at 1543 and 1638 cm$^{-1}$ are due to the aromatic rings in pluronic F-127. Absorption bands corresponding N – H vibrations and Ag – N present in the FTIR spectra of SNPs before the phase transfer are missing in the FTIR spectrum of SNPs after the phase transfer. This observation strengthens our claim that OA is replaced by block copolymer, pluronic F-127 during the legend exchange reaction [9].

![Hydrodynamic size distribution histograms of SNPs](image)

**Fig. 3.34** Hydrodynamic size distribution histograms of SNPs (a) before and (b) after the phase transfer. Each histogram is fitted with lognormal particle size distribution function.

![FTIR spectra of SNPs](image)

**Fig. 3.35** FTIR spectra of SNPs before and after phase transfer.
Table 3.1 Band Assignments of FTIR spectra (Fig. 3.35) of SNPs before and after phase transfer.

<table>
<thead>
<tr>
<th>SNPs</th>
<th>Band position (cm⁻¹)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before phase transfer</td>
<td>1591</td>
<td>Asymmetric stretching of the Ag – N</td>
</tr>
<tr>
<td></td>
<td>2850</td>
<td>Symmetric stretching vibrations of C – H bonds</td>
</tr>
<tr>
<td></td>
<td>2915</td>
<td>Asymmetric stretching vibrations of C – H bonds</td>
</tr>
<tr>
<td></td>
<td>3432</td>
<td>N – H stretching vibrations</td>
</tr>
<tr>
<td>After phase transfer</td>
<td>949</td>
<td>CH₂ rocking vibration</td>
</tr>
<tr>
<td></td>
<td>1113</td>
<td>C – O – C stretching vibration</td>
</tr>
<tr>
<td></td>
<td>1249</td>
<td>CH₂ twist</td>
</tr>
<tr>
<td></td>
<td>1294</td>
<td>CH₂ twist</td>
</tr>
<tr>
<td></td>
<td>1362</td>
<td>CH₂ wag</td>
</tr>
<tr>
<td></td>
<td>1464</td>
<td>= CH₂ bending</td>
</tr>
<tr>
<td></td>
<td>1543</td>
<td>Aromatic C = C stretching</td>
</tr>
<tr>
<td></td>
<td>1638</td>
<td>Aromatic C = C stretching</td>
</tr>
<tr>
<td></td>
<td>2874</td>
<td>Symmetric stretching of C – H</td>
</tr>
</tbody>
</table>

3.3 Synthesis of Copper Nanoparticles (CNPs)

3.3.1 Materials

Copper (II) chloride dihydrate (≥ 99%), polyvinylpyrrolidone (PVP) (average mol. wt. 10,000) and sodium borohydride (NaBH₄) (≥ 98%) were obtained from Sigma Aldrich. L-ascorbic acid (AA) was procured from Merck. Aqueous solutions were prepared in Millipore ultrapure water (ρ = 18.2 MΩ). All chemicals were used as-received without purification.

3.3.2 Synthesis Process

Synthesis of CNPs was carried out by chemical reduction at elevated temperatures. CNPs were prepared by reducing copper (II) chloride with strong (NaBH₄) and weak (L-ascorbic acid) reducing agents. To achieve fast and homogenous nucleation of CNPs, aqueous solution of copper (II) chloride was added into the preheated mixture of reducing (NaBH₄ + L-ascorbic acid) and capping (PVP) agents. The role of reducing and capping agent on the product quality of CNPs has been evaluated in terms of their size and size distribution, crystal phase and morphology. It has been found that all the three components, i.e. PVP, NaBH₄ and L-ascorbic acid were essential for the synthesis of stable CNPs. In the absence of one of these components, either CNPs did not form or
were not stable. Schematic representation of protocols followed for the synthesis of CNPs is presented in Fig. 3.36.

3.3.2.1 Effect of Weak Reducing Agent (L-ascorbic acid)

Effect of weak reducing agent (L-ascorbic acid) on the formation of CNPs, their stability and quality in terms of size and size distribution have been investigated by preparing series of samples with 0-15 mM L-ascorbic acid. In brief, 25 mL aqueous solution of PVP (10 mM) was prepared. To this, 15 mL aqueous solution of NaBH₄ (10 mM) and AA (0 mM-15 mM) was added under continuous magnetic stirring. The mixture was heated to 80 °C at a rate of 3 °C/min. 10 mL aqueous solution of copper chloride (1.16 mM) was added drop-wise. The solution was heated at 80 °C till the color of mixture turned bright red. This intense red color is due to the surface plasmon resonance (SPR) of CNPs. The mixture was cooled to 25 °C. The sample was collected by centrifugation for 10 min at a relative centrifugal force (RCF) of 15471 x g (12000 rpm). Well dispersed CNPs were obtained as supernal and larger cluster of CNPs, if any, are discarded as sediment.

![Schematic presentation of protocols followed for the synthesis of colloidal CNPs.](image)

**Fig. 3.36** Schematic presentation of protocols followed for the synthesis of colloidal CNPs. Image at the end of the flow chart shows intense red color due to the surface plasmon resonance in copper nanoparticles confirming their formation.

Effect of weak reducing agent (L-ascorbic acid) on the formation of CNPs was evaluated by UV-visible spectroscopy. **Fig. 3.37** shows the UV-visible spectra of CNPs prepared with different L-ascorbic acid concentration (0-15 mM).
For 0 mM AA, the SPR band is observed at 450 nm, a typical characteristic of Cu$_2$O nanoparticles [30]. No SPR peak corresponding to metallic phase of CNPs was observed, which is expected at 575 nm [30]. This means AA is essential for the synthesis of pure metallic phase of CNPs. In case of 5 mM AA, no SPR peak was observed in the UV-visible spectra, indicating the formation of larger size particles, as large size metallic particles do not show plasmonic characteristics [31, 32]. A single plasmon resonance band was observed at 566 nm when AA concentration is ≥ 10 mM. No SPR band below 500 nm was observed. This means as-synthesized nanoparticles did not possess any oxide phases (CuO or Cu$_2$O) as absorption maximum corresponding to CuO and Cu$_2$O phases would have been observed at 370 nm and 450 nm, respectively [30]. Observation of single SPR peak (at 566 nm) also indicates that the synthesized CNPs have spherical morphology as multiple SPR bands are expected from asymmetric metal nanoparticles [23, 33].

Hydrodynamic particle size distributions of CNPs prepared with different AA concentrations (0-15 mM) are shown in Fig. 3.38. Each histogram is fitted with lognormal particle size distribution function [21] and from the fit, mean hydrodynamic size and polydispersity indices are determined. For 0 mM AA, the mean hydrodynamic size and polydispersity index of as-synthesized nanoparticles are 393.7 nm and 0.44,
respectively. With increase in AA concentration, the mean hydrodynamic size decreases and saturates at 17.4 nm at 10 mM AA (Fig. 3.39). The minimum in polydispersity index (0.13) was also observed for 10 mM AA.

**Fig. 3.38** Size distribution histograms of CNPs prepared with different concentration of L-ascorbic acid (NaBH₄ and PVP = 10 mM).

**Fig. 3.39** Variation in hydrodynamic size (○) and polydispersity index (□) of CNPs as a function of L-ascorbic acid (NaBH₄ and PVP = 10 mM) concentration.
Ascorbic acid has a dual functionality. It is acting as reducing and capping agent, which helps in controlling the particle size and its distribution by electrostatic stabilization of nanoparticles. From the results of UV-visible and photon correlation spectroscopy, it is concluded that 10 mM of AA is the optimum concentration required to prepare ultra-small, stable, single phase CNPs.

3.3.2.2 Effect of Strong Reducing Agent (NaBH₄)

To understand the effect of strong reducing agent on phase formation of CNPs, their size and size distribution; five samples were prepared with 0-12.5 mM NaBH₄. PVP and AA concentration were kept constant at 10 mM. Rest of the synthesis protocols were same as described in section 3.3.2.

![Fig. 3.40](image-url)

**Fig. 3.40** shows the UV-visible spectra of CNPs prepared with different NaBH₄ concentrations (0-12.5 mM). No SPR band is observed for low NaBH₄ concentration (≤ 5 mM). There could be two possible reasons behind the absence of SPR bands in the UV-visible spectra of CNPs prepared with lower (≤ 5 mM) NaBH₄ concentration. Either no phase of copper (Cu/CuO/Cu₂O) is formed or their particle size is larger than the excitonic radius of copper.

![Fig. 3.40](image-url)

**Fig. 3.40** UV-visible spectra of as-synthesized CNPs prepared with different concentrations of NaBH₄ (L-ascorbic acid and PVP = 10 mM).
To confirm this, photon correlation spectroscopy was employed. Fig. 3.41 shows the hydrodynamic size distribution histograms of CNPs prepared at different NaBH₄ concentration (0-12.5 mM). At low NaBH₄ concentration (≤ 5 mM), the hydrodynamic size of CNPs is very large (> 100 nm). For 0 mM NaBH₄, the hydrodynamic size is 388.6 nm and at 5 mM, it is 127 nm. With increase in NaBH₄ concentration, the hydrodynamic size of CNPs decreases. This might be due to the change in nucleation density. At low NaBH₄ concentration, the nucleation density might be low, which leads to the growth of fewer number of larger size particles. As NaBH₄ concentration increases, the nucleation density increases and hence the hydrodynamic size decreases.

Fig. 3.41 Size distribution histograms of CNPs prepared with different concentration of NaBH₄ (L-ascorbic acid and PVP = 10 mM).

Fig. 3.42 shows the variation in hydrodynamic size and polydispersity index of CNPs prepared with different concentration of NaBH₄. Hydrodynamic size is minimum (11.6 nm) for 12.5 mM of NaBH₄ but the polydispersity is high (0.31). Minimum in polydispersity (0.13) of CNPs is observed when NaBH₄ is 10 mM. From the mean hydrodynamic size and polydispersity data of CNPs, it is concluded that 10 mM of NaBH₄ is the optimum concentration for the preparation of nearly monodisperse ultrafine
CNPs. Further, a single SPR band centred at 566 nm is observed when NaBH₄ concentration is 10 mM. Single SPR band centred at 566 nm originates from the spherical single phase metallic CNPs whose physical size is smaller than the excitonic radius of copper. For NaBH₄ concentration > 10 mM, the SPR band gets broaden and red shifts.

![Graph showing variation in hydrodynamic size and polydispersity index as a function of NaBH₄ concentration.](image)

**Fig. 3.42** Variation in hydrodynamic size (○) and polydispersity index (□) as a function of NaBH₄ (L-ascorbic acid and PVP = 10 mM) concentration.

### 3.3.2.3 Effect of Surfactant (PVP)

To investigate the effect of stabilizer, PVP on the quantity and quality of CNPs, a series of samples were prepared by varying the PVP concentration from 0-12.5 mM. Rest of the variables were kept constant as per the conditions of section 3.3.2. NaBH₄ and AA concentrations were 10 mM each.

Effect of concentration of reducing agent on the quality of nanostructures has been evaluated in terms of size and size distribution, crystal phase and morphology. It is observed that at least 2.5 mM of PVP is required to form metallic phase CNPs. UV-visible spectra of CNPs prepared with 0-12.5 mM PVP are shown in **Fig. 3.43**. No SPR is observed when nanoparticles are prepared in the absence of PVP. The SPR band is observed at 572 nm when PVP is 2.5 mM and it blue shifts to 566 nm when PVP ≥ 5 mM. The observation of single SPR band at 566 nm for PVP concentration ≥ 5 mM indicates that ultra-small single phase metallic CNPs are formed. No SPR band corresponding to
oxide phases of copper are observed. This study reveals that to prepare ultra-small, spherical, plasmonic CNPs; at least 5 mM of PVP is essential.

Fig. 3.43 UV-visible spectra of as-synthesized CNPs prepared with different concentrations of PVP (L-ascorbic acid and NaBH₄ = 10 mM).

Fig. 3.44 shows the hydrodynamic size distribution histograms of CNPs prepared with different concentration of PVP while keeping AA and NaBH₄ concentration constant at 10 mM. Without PVP (0 mM), the hydrodynamic size and polydispersity index of CNPs are 313 nm and 0.26, respectively. The hydrodynamic size of CNPs decreases as PVP concentration increases and levels off when the concentration is ≥ 7.5 mM (Fig. 3.45). Lower PVP concentration in the medium during the synthesis of CNPs cannot control the aggregation and hence results in the clusters of CNPs with higher size and broader size distribution. As the concentration of PVP increases, it decreases the tendency of agglomeration of CNPs by increasing the electrostatic repulsion between them. The average hydrodynamic size is 17.4 nm when PVP concentration is 10 mM. At this concentration, each nanoparticle is protected against aggregation by a thin layer of PVP. For CNPs prepared with 10 mM PVP, both hydrodynamic size (17.4 nm) and polydispersity (0.13) are minimum. Synthesis of CNPs with 10 mM PVP produces single phase nanoparticles with smaller size and narrow size distribution.
Fig. 3.44 Size distribution histograms of CNPs prepared with different concentration of PVP (L-ascorbic acid and NABH₄ = 10 mM). Each histogram is fitted with lognormal particle size distribution function.

Fig. 3.45 Variation in hydrodynamic size (○) and polydispersity index (□) as a function of PVP (L-ascorbic acid = NABH₄ = 10 mM) concentration.
Optimized conditions to prepare uniform, ultra-small, spherical metallic single phase CNPs are summarized in Fig. 3.36. The optimized concentration of L-ascorbic acid, PVP and NaBH₄ is 10 mM, each. The X-ray diffraction pattern of as-synthesized CNPs prepared with 10 mM each of PVP, NaBH₄ and AA is shown in Fig. 3.46. X-ray diffractogram shows three distinct diffraction peaks corresponding to FCC structure of copper. The indexed peaks matched well with the PCPDF card no. 04-0836 of copper. The broadening of X-ray diffraction peaks shows that the as-synthesized CNPs are very small. No peak corresponding to oxide or any other impurity phases of copper is observed in the diffractogram. The synthesis protocols developed here produces single phase metallic CNPs directly in air without any secondary oxide phase. CNPs are stable against both the aggregation and oxidation.

![X-ray diffraction pattern of CNPs][1]

**Fig. 3.46** X-ray diffraction pattern of CNPs prepared under optimized condition (i.e. concentration of PVP = NaBH₄ = L-ascorbic acid = 10 mM).

**Fig. 3.47** shows the TEM micrographs of CNPs prepared under optimized conditions. As seen in the micrograph (**Fig. 3.47(a)**), CNPs formed a macromolecule with needle like morphology. Similar self-assembly for silver nanoparticles is reported by Li et al [34]. The macromolecule formed by the self-assembly of ultra-small CNPs is very large (≈ 500 nm in length). **Fig. 3.47(b)** shows the magnified view of the encircled region of **Fig. 3.47(a)**. HRTEM image of the same region is also shown in **Fig. 3.47(c)**. Self-
assembly of ultra-small CNPs each of 2 nm into hexagonal closed pack lattice can be seen in Fig. 3.47(c), indicating the high quality of the synthesized product.

Fig. 3.47 (a) Low resolution TEM micrographs of CNPs prepared under optimized condition, (b) Magnified view of the encircled region of (a) and (c) HRTEM micrograph of CNPs.

3.3.3 Reduction Mechanism

To understand the formation of single phase metallic CNPs and its growth mechanism, large number of experiments were carried out. From these experiments, it is concluded that both the strong (NaBH₄) and the weak (AA) reducing agents are essential in addition to stabilizing agent (PVP) for the formation of stable, single phase metallic CNPs. This observation is contradictory to previous reports in which synthesis of stable metallic CNPs by reducing Cu²⁺ ions with either NaBH₄ or AA [33, 34] is reported. In the absence
of any of the reducing agent (AA or NaBH₄), either copper oxide or unstable metallic Cu phase is formed, which is not stable and within minutes gets converted into one of the stable oxide (CuO or Cu₂O) phases.

To understand the phase formation, systematic investigation of the reduction of CuCl₂ was carried out. The reduction reaction was monitored in terms of color change as first indicator followed by UV-visible spectroscopy as the confirmation. It has been observed that PVP alone cannot reduce CuCl₂. This was evidenced from the fact that no color change was observed even if CuCl₂-PVP mixture was heated at 80 °C for long time (> 24 h). When 10 mM NaBH₄ was added into the reaction medium containing 1.16 mM CuCl₂ and 10 mM PVP at 80 °C; Cu²⁺ ions immediately reduced to Cu⁰, which was evidenced from the red color of the solution. But within minutes, solution turned into dark green, indicating the oxidation of CNPs (tube - b in Fig. 3.48). The corresponding UV-visible spectrum is shown in Fig. 3.49. The SPR band positioned at 465 nm corresponds to the Cu₂O phase. The characteristic absorption maximum at 560 nm is missing indicating that no metallic copper is present in the sample.

![Fig. 3.48 The photographic view of as-synthesized nanoparticles with (a) 10 mM L- ascorbic acid and 0 mM NaBH₄; (b) 0 mM L-ascorbic acid and 10 mM NaBH₄ and (c) 10 mM L-ascorbic acid and 10 mM NaBH₄.](image)

Now, when the same experiment was carried out with weak reducing agent, i.e. when NaBH₄ was replaced with 10 mM AA; in that case no evidence of formation of
metallic Cu was observed as the final color of the solution remains dark yellow even after prolonged heating (tube - a in Fig. 3.48). The same is further confirmed from the UV-visible spectroscopy of the product (Fig. 3.49) where no signature of copper or any of their oxides phases are observed.

![UV-visible spectra of nanoparticles prepared with 10 mM PVP as stabilizing agent](image)

**Fig. 3.49** UV-visible spectra of nanoparticles prepared with 10 mM PVP as stabilizing agent (a) 10 mM L-ascorbic acid and 0 mM NaBH₄; (b) 0 mM L-ascorbic acid and 10 mM NaBH₄; (c) 10 mM L-ascorbic acid and 10 mM NaBH₄.

In the next experiment, both the strong (10 mM NaBH₄) and weak (10 mM AA) reducing agents were added into the preheated CuCl₂-PVP mixture. Immediately upon addition, the solution color changes to dark red (tube - c in Fig. 3.48). On further heating, it did not change even if kept under oxidizing environment for long, indicating that Cu²⁺ has been reduced into stable Cu⁰ phase. This is further confirmed by UV-visible spectroscopy (Fig. 3.49). A characteristic SPR band of CNPs centred at 560 nm is observed. No signatures of CuO or Cu₂O phases are observed in the spectra indicating that nanoparticles do not possess any oxide phase.

To understand the reduction mechanism, we did the serial addition of various components (PVP, NaBH₄ and AA) into the aqueous solution of CuCl₂. First 10 mM PVP was added into 1.16 mM CuCl₂ and heated to 80 °C. The UV-visible spectrum of the sample is shown in Fig. 3.50. For reference, the UV-visible spectrum of aqueous PVP is also shown in Fig. 3.50.
**Fig. 3.50** UV-visible spectra of PVP and PVP-copper complex.

The UV-visible spectrum of CuCl$_2$ containing PVP shows a broad absorption band centred at 432 nm. This absorption band is ascribed to the formation of Cu-PVP complex. No such characteristic absorption maximum is observed for the aqueous PVP. Similar results are reported by Zhang et al. [35] when AgNO$_3$ was introduced into PVP solution. They have concluded that the observed absorption band was due to the formation of Ag-PVP complex. The formation of Ag-PVP complex reduces the reduction potential of Ag$^{+1}$ [35]. It is proposed that Cu$^{2+}$ ions make an organometallic complex with PVP via following chemical reaction.

$$
\begin{align*}
2 \left[ \begin{array}{c}
\text{H}_2\text{C} \\
\text{N} \\
\text{O} \\
\text{O:Cu}^{2+}
\end{array} \right] \\
\text{(PVP)}
+ \text{Cu}^{+2} & \rightarrow & \rightarrow \\
\text{H}_2\text{C} & \text{CH} & \text{H}_2\text{C} \\
\text{N} & \text{O:Cu}^{+2} & \text{O:Cu}^{+2}
\end{align*}
$$

Step-I: Formation of PVP-Cu$^{2+}$ complex.

This complex formation between PVP and Cu$^{2+}$ is proposed on the basis of the structural features of PVP. PVP has polyvinyl skeleton with nitrogen and oxygen polar groups [36-38]. These polar groups form a coordinative interaction between PVP and Cu$^{2+}$ ions by donating their lone pair electrons to Cu$^{2+}$. The organometallic complex formation between Cu$^{2+}$ and PVP was previously reported by several groups [36-38]. The proposed mechanism of complex formation between Cu$^{2+}$ and PVP is in line with that proposed by...
these groups [36-38]. When 10 mM NaBH₄ was added into the solution, it immediately reduced Cu²⁺ in the PVP- Cu²⁺ complex into Cu⁰. NaBH₄ ionizes and forms a (BH₄)⁻ ligand, which then reacted with hydroxyl anions (Step-II). During this reaction, eight electrons are liberated from the hydroxyl ions. These electrons react with Cu²⁺ ions in the PVP-Cu²⁺ complex and reduce them to Cu⁰.

\[
\begin{align*}
\text{NaBH}_4 & \rightarrow \text{Na}^+ + (\text{BH}_4)^- \\
\text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{OH}^-
\end{align*}
\]

\[
(\text{BH}_4)^- + 8\text{OH}^- \rightarrow \text{B}(\text{OH})_3^- + 4\text{H}_2\text{O} + 8\text{e}^-
\]

Step-II: Ionization of NaBH₄ and release of electrons from hydroxyl ions.

Step-III: Reduction of Cu²⁺ ions by NaBH₄ (product of step-II).

The execution of reduction reaction (Step-III) is evidenced from the change in the solution color from light yellow to dark red. Since, the product was in the oxidizing environment so within minutes it oxidized to Cu²⁺ and the solution color turned from red to dark green. Now, 10 mM AA was added into the solution (product of step-III). Within few minutes,

\[
\begin{align*}
\text{HO} & \rightarrow \text{HO} \\
\text{HO} & \rightarrow \text{HO} + 2\text{H}^+ + 2\text{e}^-
\end{align*}
\]

L-ascorbic acid \hspace{2cm} \text{Dehydroascorbic acid}

Step-IV: Oxidation of L-ascorbic acid into dehydroascorbic acid.
the solution color again changes back from green to dark red. AA oxidizes into dehydroascorbic acid with a release of two electrons [39]. These electrons react with the oxidized product of step-III and reduce Cu\textsuperscript{2+} back into Cu\textsuperscript{0}. The oxidation by-product of AA, i.e. “dehydroascorbic acid” simulates a dynamic equilibrium (Step-V) around the Cu\textsuperscript{0}, which stabilizes CNPs against the oxidation [39]. The entire reduction mechanism is summarized as a schematic in Fig. 3.51.

Step-V: Reduction of PVP-CuO complex by L-ascorbic acid and its stabilization by dehydroascorbic acid.

Fig. 3.51 Schematic representation of various steps that leads to the formation of ultra-small CNPs and its stabilization by dehydroascorbic acid.
3.3.4 Effect of Aging on the Stability of CNPs

Stability of the oxidation state of CNPs is very crucial. CNPs have a tendency to oxidise to CuO or Cu$_2$O phase. To evaluate the aging effect on the stability of CNPs against oxidation and aggregation, UV-visible and photon correlation spectroscopy were employed. Fig. 3.52 shows the UV-visible spectra of as-synthesized and aged CNPs. The aging period was 120 days. Upon aging, no change in the position of SPR band (at 566 nm) corresponding to pure metallic phase of copper is observed. In addition, no signature of evolvement of CuO or Cu$_2$O phase is found in the UV-visible spectra of aged CNPs. This shows that CNPs are stable and resistant to oxidation in ambient condition.

![Absorbance vs Wavelength](image)

**Fig. 3.52** UV-visible spectra of as-synthesized (——) and aged (---) CNPs. The aging period is 120 days. No signature corresponding to CuO or Cu$_2$O is observed in the aged sample indicating that CNPs are resistant to oxidation.

Particle size distribution histograms of as-synthesized CNPs prepared under optimized conditions and CNPs aged for 120 days are shown in **Fig. 3.53**. The mean hydrodynamic size of CNPs before and after the aging is 17.4 nm and 19.7 nm, respectively. The polydispersity index of as-synthesized CNPs is 0.13 and after aging, it increases to 0.16. Little increase in the hydrodynamic size and polydispersity of CNPs might be caused by formation of few aggregates of CNPs. Even though the CNPs are aged for a significantly large period of 120 days in ambient conditions, their particle size
and polydispersity indices are almost constant revealing their impressive stability against aggregation.

![Size distribution histograms fitted with lognormal particle size distribution function of as-synthesized (—) and aged (- - -) CNPs.](image)

**Fig. 3.53** Size distribution histograms fitted with lognormal particle size distribution function of as-synthesized (—) and aged (- - -) CNPs.

### 3.4 Synthesis of Titanium dioxide Nanoparticles (TNPs)

#### 3.4.1 Materials

Titanium (IV) isopropoxide (97%) and cobalt (II) nitrate hexahydrate (≥ 99%) were obtained from Sigma Aldrich. Ethanol was procured from Merck. Millipore ultrapure water (ρ = 18.2 MΩ) was used for hydrolysis of Titanium (IV) isopropoxide. Concentrated nitric acid (70%) and concentrated hydrochloric acid (37%) were purchased from Loba chemie. All chemicals were used as-received without purification.

#### 3.4.2 Synthesis of Undoped TNPs

Synthesis of TNPs was carried out by sol-gel technique [40]. Synthesis protocols followed in these experiments are summarized as schematic in **Fig. 3.54**. In a typical synthesis, a sol was prepared by mixing 35 mM titanium isopropoxide with 25.5 mL ethanol under constant magnetic stirring. The solution was stirred for 5 min at 500 rpm. To this, 2.55 mL ethanoic solution of conc. HNO₃ having acid to titanium isopropoxide
A molar ratio of 0.2 was added. The mixture was stirred for another 30 min. To induce gelation, a mixture of ethanol (16.1 mL) and water (2.55 mL) was added drop-wise. The molar ratio of water and titanium isopropoxide was maintained at 4. After the addition of water-ethanol mixture, it is stirred at room temperature until gelation. The gel was dried over night at 100 °C. The dried crystallites were ground and washed with distilled water multiple times. The powder was air dried at 150 °C and calcine at 500 °C for 4 h.

**Fig. 3.54** Schematic presentation of the synthesis protocols followed for the preparation of undoped and cobalt doped TNPs by sol-gel technique.
3.4.3 Synthesis of Co-doped TNPs

Cobalt doped TNPs were also prepared by the sol-gel technique where the same protocols described for the synthesis of undoped TNPs in section 3.4.2 and summarized in Fig. 3.54 were followed. Dopant concentration was varied from 0.05 wt % - 2 wt % of TiO₂. In brief, ethanoic solution of Co(NO₃)₂·6H₂O was prepared for each wt % of Co by dissolving appropriate quantity of Co(NO₃)₂·6H₂O in required volume of ethanol so that its final concentration was adjusted to 0.1 M. To this, 25.5 mL ethanol was added and stirred for 5 min. In this solution, 10.5 mL titanium isopropoxide was added drop-wise under constant magnetic stirring. After 5 min, 2.55 mL ethanoic solution of conc. HNO₃ was added. The molar ratio of acid to titanium isopropoxide was 0.2. The solution was stirred for another 30 min. To induce gelation, ethanol (16.1 mL)-water (2.55 mL) mixture was added drop-wise. The molar ratio of water to titanium isopropoxide was 4. This will initiate the hydrolysis reaction. After adding the water-ethanol solution, the mixture was stirred at room temperature till gelation. The gel was dried over night at 100 °C and washed with distilled water multiple times. It was dried at 150 °C and calcined at 500 °C for 4 h.

3.4.4 Mechanism

Synthesis of TNPs via sol-gel process is a two-step approach [41,42]. In the first step, the organometallic source of Titanium (e.g. titanium isopropoxide) is hydrolysed via following chemical reaction:

\[ \text{Ti} - \text{(OC₃H₈)} + \text{H₂O} \rightarrow \text{Ti} - \text{OH} + \text{C₃H₈OH} \]

During the hydrolysis, water molecule attacks the titanium isopropoxide and suppresses the condensation stage, which leads to the formation of TNPs. The presence of residual alkoxy groups also reduces the rate of crystallization of TNPs, which will also favor the formation of less dense anatase phase of TiO₂ [43]. In the second step, condensation of Ti – OH progresses with elimination of alcohol or water groups via alcohol or water condensation.

\[ \text{Ti} - \text{OH} + \text{C₃H₈} - \text{Ti} \rightarrow \text{Ti} - \text{O} - \text{Ti} + \text{C₃H₈OH} \]

(Alcohol Condensation)
Ti – OH + HO – Ti \[\rightarrow\] Ti – O – Ti + H₂O

(Water Condensation)

Here, acid acts as a catalyst, which controls the kinetics of hydrolysis and condensation of titanium isopropoxide. Generally, the low pH in the reaction medium provides a good chance of preformation of TNPs which could suppress further crystallization of TiO₂. The presence of excess anions of acid (NO₃⁻ or Cl⁻) adsorbed on the surface of TNPs also suppress their further growth [43]. Addition of acid does not form any residual impurity phases on the surface of TNPs after the calcination, which is confirmed from the X-ray diffraction measurement.

To find out appropriate value of crystallization temperature, the as-synthesized pristine and Co-doped TNPs are subjected to differential scanning calorimetry (DSC) measurement. The DSC thermograms of as-synthesized TNPs are shown in Fig. 3.55. An exothermic peak is observed between 400-460 °C. This peak corresponds to the transformation of amorphous TiO₂ to crystalline phase. The crystallization temperature corresponding to anatase phase for different cobalt doping is also represented in Table - 3.2.

**Fig. 3.55** DSC thermograms of cobalt (0-2 %) doped TNPs.

The crystallization temperature increases with Co-doping, indicating that the presence of cobalt ions in the TiO₂ matrix hinders the amorphous to anatase phase transition. From the obtained crystallization temperature data, 500 °C is chosen as the calcination temperature for all the samples of TNPs.
<table>
<thead>
<tr>
<th>Dopant Concentration (Cobalt) (wt %)</th>
<th>Crystallization Temperature (°C)</th>
<th>Band Gap (eV)</th>
<th>Elemental Compositions obtained from EDS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ti (in wt %)</td>
</tr>
<tr>
<td>0%</td>
<td>404</td>
<td>3.03</td>
<td>59.95</td>
</tr>
<tr>
<td>0.05%</td>
<td>392</td>
<td>2.95</td>
<td>59.91</td>
</tr>
<tr>
<td>0.10%</td>
<td>408</td>
<td>2.66</td>
<td>59.875</td>
</tr>
<tr>
<td>0.25%</td>
<td>408</td>
<td>2.56</td>
<td>59.78</td>
</tr>
<tr>
<td>0.50%</td>
<td>416</td>
<td>2.24</td>
<td>59.61</td>
</tr>
<tr>
<td>1%</td>
<td>427</td>
<td>1.97</td>
<td>59.21</td>
</tr>
<tr>
<td>2%</td>
<td>454</td>
<td>1.93</td>
<td>58.36</td>
</tr>
</tbody>
</table>
3.4.5 Investigation of TNPs

XRD patterns of undoped and cobalt doped TNPs are shown in Fig. 3.56.

![XRD patterns of undoped and cobalt doped TNPs](image)

**Fig. 3.56** XRD patterns of undoped and cobalt (0-2 %) doped TNPs.
Each diffractogram shows ten well resolved reflections. Peak positions of these reflections are in good agreement with the standard X-ray diffraction pattern of tetragonal anatase phase of TiO$_2$ (JCPDS card no. 21-1272). The (hkl) indices corresponding to each reflections are shown in Fig. 3.56. No signatures of rutile phase, pure cobalt or cobalt oxide are observed. The highest intense reflections of rutile and brookite phases are expected at 27.4° and 30.8°, respectively. The absence of these signatures in the X-ray diffractograms confirms the formation of single anatase phase TNPs. A slight shifting in the peak positions is observed. This shift is due to changes in the local structure around Ti$^{4+}$ after Co$^{2+}$ substitution [44]. Average crystallite size of TNPs is determined from the X-ray diffractograms by analysing them with Williamson-Hall analysis [Equation 3.1]. The crystallite sizes thus obtained are reported in Table - 3.3. The crystallite size varies between 8.5-11.7 nm. For undoped TNPs, the crystallite size is 8.5 nm. Upon Co doping, it increases and lies in the range of 9.5-11.7 nm. The crystallite size of Co doped TNPs is larger than the pristine TNPs. This result indicates that increasing Co concentration is not inhibiting the grain growth and hence it is likely that Co is entering into the TiO$_2$ lattice at interstitial or substitutional sites. From the Williamson-Hall analysis, the lattice strain has been calculated, which comes out to be of the order of 10^{-4}. This strain is one order smaller than that observed for SNPs. This might be because of lattice relaxation during sintering of amorphous titania.

In order to understand the effect of Co-doping on TiO$_2$ lattice, each XRD pattern is refined by Rietveld refinement technique by using Fullprof software package. XRD patterns are refined by assuming tetragonal symmetry with I4$_1$/amd space group. The refined unit cell parameters of undoped and Co-doped TNPs are reported in Table - 3.3. R$_{wp}$ < 10% and $\chi^2 \rightarrow 1$ indicate that the experimental patterns are in close correlation with the simulated patterns. The lattice parameter a = b do not show any significant deviation from the reported value of 3.7852 Å (JCPDS card no. 21-1272). Contrary to this, the lattice parameter c, which is along the long axis of the tetragonal unit cell shows a decrease in comparison to the reported value of 9.5139 Å. With increasing Co concentration, lattice parameter ‘c’ also increases and assumes maxima for 0.1 wt% Co. Further addition of Co in the TiO$_2$ matrix compresses the TiO$_2$ unit cell. For dopant concentration $\geq 0.5$ wt%, the ‘c’ value is independent of doping. The same trend is also observed for unit cell volume (Table - 3.3). The Wyckoff positions of Ti, Co and O are also reported in Table - 3.3.
Table 3.3 Crystallographic parameters of Co (0-2%) doped TNPs obtained from Rietveld Refinement of XRD.

<table>
<thead>
<tr>
<th>Dopant Concentration (Cobalt) (wt %)</th>
<th>Crystallite Size (nm)</th>
<th>Atom</th>
<th>Site</th>
<th>Wyckoff positions</th>
<th>Lattice Parameters</th>
<th>Unit Cell Volume (Å³)</th>
<th>Goodness of fit parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x y z a = b c</td>
<td></td>
<td></td>
<td>χ² Rwp (%)</td>
</tr>
<tr>
<td>0%</td>
<td>8.5</td>
<td>Ti</td>
<td>4b</td>
<td>0 0.25 0.3750</td>
<td>3.7823(19) 9.4950(5)</td>
<td>135.83</td>
<td>1.15 8.98</td>
</tr>
<tr>
<td>0.05%</td>
<td>11.6</td>
<td>O</td>
<td>8e</td>
<td>0 0.25 0.1621(8)</td>
<td>3.7863(11) 9.5100(3)</td>
<td>136.34</td>
<td>1.23 9.41</td>
</tr>
<tr>
<td>0.10%</td>
<td>10.7</td>
<td>Co</td>
<td>4b</td>
<td>0 0.25 0.3750</td>
<td>3.7900(8) 9.5160(2)</td>
<td>136.69</td>
<td>1.27 6.68</td>
</tr>
<tr>
<td>0.25%</td>
<td>10.8</td>
<td>Ti</td>
<td>4b</td>
<td>0 0.25 0.3750</td>
<td>3.7856(4) 9.5072(11)</td>
<td>136.24</td>
<td>1.14 8.88</td>
</tr>
<tr>
<td>0.50%</td>
<td>9.5</td>
<td>O</td>
<td>8e</td>
<td>0 0.25 0.1620(7)</td>
<td>3.784(17) 9.5020(4)</td>
<td>136.06</td>
<td>1.17 8.51</td>
</tr>
<tr>
<td>1%</td>
<td>10.2</td>
<td>Co</td>
<td>4b</td>
<td>0 0.25 0.3750</td>
<td>3.7839(11) 9.4950(3)</td>
<td>135.95</td>
<td>1.15 5.96</td>
</tr>
<tr>
<td>2%</td>
<td>11.7</td>
<td>O</td>
<td>8e</td>
<td>0 0.25 0.1629(7)</td>
<td>3.7830(8) 9.4990(2)</td>
<td>135.94</td>
<td>1.15 5.76</td>
</tr>
</tbody>
</table>
No significant changes in the Wyckoff positions of O-atoms have been observed. This indicates that Co might have substituted at the Ti site. The observed little variation in the lattice parameter c and unit cell volume might be due to the difference in the ionic radii of Ti$^{4+}$ (60.5 pm) and Co$^{2+}$ (53 pm).

The SEM images of 0%, 0.1%, 1% and 2% cobalt doped TNPs are shown in Fig. 3.57. Irrespective of Co doping, nanoparticle clusters are observed in each micrograph with near spherical morphology. The average size of nanoparticles is 20 nm. The size distribution is uniform. Due to high density of particles in each micrograph, it is difficult to plot size distribution histograms from these micrographs and hence excluded from the study.

![SEM micrographs of undoped and cobalt doped TNPs](image)

**Fig. 3.57** SEM micrographs of undoped and cobalt doped TNPs.

The EDX patterns of pristine and Co doped TNPs are shown in Fig. 3.58.
Fig. 3.58 EDX patterns of TNPs with different cobalt concentrations. X-axis represents energy of X-rays emitted by the specimen in keV.
The detail analysis of elemental analysis for each sample is presented in Table - 3.2. In the case of pristine TNPs, only titanium and oxygen are detected. The absence of foreign elements shows that the synthesized product has high chemical purity. The EDX spectra of doped samples also show the presence of cobalt. The detected cobalt content is in agreement with the expected concentration. The weight fraction of oxygen atoms decreases with increase in Co-doping. The observed % weight of oxygen in the sample is less than its accepted stoichiometric proportion. This data suggest that in the TiO$_2$ matrix, Ti$^{4+}$ has been substituted by Co$^{2+}$ and to compensate the extra charge and maintain charge neutrality of the sample, it creates additional vacancies at oxygen site [45]. The similar distortion of TiO$_2$ unit cell was also predicted from the XRD analysis.

A representative transmission electron microscopy image of undoped TNPs, which are calcined at 500 °C is shown in Fig. 3.59. Small nanoparticles with near spherical geometry can be observed in the TEM micrograph. Most of the nanoparticles are agglomerated, a typical character of nanoparticles generally observed when prepared via sol-gel route [46]. The average size of TNPs is 20 nm, which is in agreement with the results of scanning electron microscopy. Due to the heavy clustering, it is not possible to prepare their size distribution histograms.

**Fig. 3.59** TEM micrograph of undoped TNPs. The inset shows the selected area electron diffraction pattern of TNPs.
The top inset in Fig. 3.59 shows the specific area electron diffraction image of TNPs. Well distinguish rings can be observed in the SAED pattern of TNPs confirming the polycrystalline nature of the nanoparticles. The SAED pattern is in well agreement with the anatase phase of TNPs. This result is also in good agreement with the results of X-ray diffraction studies.

Diffuse reflectance UV-visible spectroscopy is used to understand the substitution effect of dopant on host lattice and its co-ordination environment. Diffused reflectance spectra of undoped and Co-doped TNPs are shown in Fig. 3.60. Two small peaks at 497 nm and 584 nm are observed in 2% cobalt doped TNPs. These peaks are absent in case of pristine TNPs. The peak at 497 nm is due to the $^{4}T_{1g}$ to $^{4}T_{1g}(P)$ and at 584 nm is due to $^{4}T_{1g}$ to $^{4}A_{2g}$ transitions, which are due to the presence of Co$^{2+}$ in the octahedral or pseudo octahedral coordination [47]. In case of anatase TiO$_2$, each Ti$^{4+}$ is coordinated with six oxygen atoms. When Ti$^{4+}$ is substituted by Co$^{2+}$ then electrons in the d-orbital of Co$^{2+}$ will undergo repulsion, which results in the splitting of d-orbitals of Co$^{2+}$. Kubelka-Munk equation [48] is used to relate the reflectance of the samples with their absorption. It is written as:

$$F(R) = \frac{(100-R)^2}{200 R}$$

where R is the reflectance (in %) of the sample and F(R) is the corresponding absorbance [48].

![Diffuse Reflectance UV-visible spectra of TNPs doped with Co](image)

**Fig. 3.60** Diffuse Reflectance UV-visible spectra of TNPs doped with (a) 0% Co, (b) 0.05% Co, (c) 0.1% Co, (d) 0.25% Co, (e) 0.5% Co, (f) 1% Co and (g) 2% Co.
To understand the effect of Co-doping on the energy band gap of TNPs, a graph of $[F(R)h\nu]^{1/2} \rightarrow h\nu$ is plotted in Fig. 3.61. The exponent $½$ signifies that the band to band transition is of indirect nature. In order to determine the energy band, the linear portion of the curves are fitted and extrapolated for zero absorbance i.e. $F[R] = 0$. The point at which the extrapolated straight line intersects the X-axis is the band gap of the nanoparticles. The energy band gap of TNPs decreases with increasing dopant concentration (Table - 3.2).

**Fig. 3.61** The plots of $[F(R)h\nu]^{1/2} \rightarrow h\nu$ for Co (0-2%) doped TNPs.
The energy band gap of TNPs as a function of Co-doping is plotted in Fig. 3.62. The energy band gap of pristine TNPs is 3.03 eV. This energy band gap is lower than the reported band gap of anatase TiO$_2$ in bulk (3.2 eV) [45]. Generally decreasing particle size widens the energy gap [49]. Contrary to that, a band narrowing is observed in the present case. This decrease in energy band gap of pristine TNPs in reference to the reported band gap of bulk TiO$_2$ could be ascribed to the defect structure (oxygen vacancies) in the TNPs that introduces extra energy levels in the forbidden zone. The origin of such energy levels might be due to the change in the local distribution around Ti$^{4+}$ or partial conversion of Ti$^{4+}$ to Ti$^{3+}$ and creation of oxygen vacant sites [45, 50-52].

![Fig. 3.62 Variation in the band gap of TNPs as a function of cobalt concentration. Inset shows the schematic representation of band narrowing in TNPs due to cobalt doping.](image)

With increase in the Co-doping, the energy band gap of TNPs decreases drastically. Without Co, the band gap of TNPs is 3.03 eV, which decreases to 1.93 eV with 2 wt % Co-doping. The decrease in the energy band gap of TNPs with increasing cobalt doping can be assigned to the introduction of new d-states near the valence band edge which narrows the energy band gap of the system. In addition, the substitution of Co$^{2+}$ at the Ti$^{4+}$ site also introduces oxygen vacancy related defect states in the forbidden zone of the energy band gap of TiO$_2$. Both these mechanisms are responsible for band narrowing in cobalt doped TNPs. The schematic representation of band narrowing due to Co-doping is shown in the inset of Fig. 3.62.
References

49. A. M. Smith and S. Nie, Accounts of Chemical Research 43, 190-200 (2010).