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Influence of Aging and Environment on Nanoparticle Chemistry – Implication to Confinement Effects in Nanoceria

Satyanarayana VNT Kuchibhatla^{#,§,1,*}, A. S. Karakoti^{#,*}, D. R. Baer[§], S. Samudrala[#], M. H. Engelhard[§], J. E. Amonette[§], S. Thevuthasan[§], and S. Seal^{#,&}

[#]Advanced Materials Processing and Analysis Center, Mechanical, Materials Aerospace Eng, University of Central Florida, Orlando, FL-32816, USA

[&]Nanoscience and Technology Center, University of Central Florida, Orlando, FL-32816, USA

[§]EMSL, Pacific Northwest National Laboratory, Richland, WA-99354, USA

¹Battelle Science and Technology India, Pune, MH-411057, India

Abstract

The oxidation state switching of cerium in cerium oxide nanoparticles is studied in detail. The influence of synthesis medium, aging time and local environment on the oxidation state switching, between +3 and +4, is analyzed by tracking the absorption edge using UV-Visible spectroscopy. It is observed that by tuning the local environment, the chemistry of the nanoparticles could be altered. These time dependent, environmentally induced changes likely contribute to inconsistencies in the literature regarding quantum-confinement effects for ceria nanoparticles. The results in this article indicate that there is a need to carry out comprehensive analysis of nanoparticles while considering the influence of synthesis and processing conditions, aging time and local environment.

Introduction

Despite the significant attention and numerous publications devoted to nano-sized materials, the physics and chemistry driving their properties are sometimes not adequately explored. Hence, understanding and controlling the properties of nanoscale materials continue to be significant challenges to the scientific community^{1,2}. Cerium oxide, (CeO₂), ceria is among the frequently studied oxides because of uses as a catalyst and catalyst support^{3,4}, in solid-oxide fuel-cell technology^{5,6}, and for UV-blocking applications⁷. Chemical-mechanical planarization and solar cells⁸ are among the newer applications where the nanoceria particles may have an impact. Radical scavenging ability of ceria nanoparticles (NPs) to protect retinal cells (in vivo) from reactive oxygen species (ROS) and to protect human breast-line cells from radiation damage during cancer treatment, by mimicking superoxide dismutase (SOD) activity,^{9,10} has also been reported.

A key property of ceria NPs in either the traditional applications and likely in the nano-bio regime is their ability to effectively switch between the +3 and +4 oxidation states. Especially for NPs, the oxidation state observed is influenced by the synthesis and processing conditions, storage time (aging) and environment. These combine to influence physical (and chemical) properties of ceria NPs including lattice parameter and optical absorption^{7,11}. A reported blue shift in optical absorption with decreasing particle size, consistent with the exciton confinement (quantum size effect) that leads to blue shift in

*Equal contribution authors

optical transmission spectra widely observed in the semiconductors and some oxide NPs, has also attracted attention. The literature on such quantum confinement effects in ceria has been inconsistent^{12–14} and stimulated a lively debate^{15,16}.

Many researchers have seen a blue shift in the optical absorption edge with decrease in particle size and often used the effective mass approximation (EMA)* theory to interpret the particle size from the shift in the optical absorption edge. Examples of such observations are provided in Table 1. While some groups have attributed this to quantum confinement, others have ascribed it to the presence of the Ce³⁺ oxidation state in the NPs^{11,17}. Zhang et al¹⁸, reported that adsorbed hydroxyl radicals on the surface of the ceria NPs are capable of creating a surface-energy band and thereby causing absorption at longer wavelengths, compensating the confinement effect, for particle sizes below 4nm. The general tendency for an increased amount of Ce³⁺ with decreasing particle size below 10 nm has also been widely reported¹⁸. In either case researchers usually assume that the particles remain static (except when talking about agglomeration) with time and ignore any interaction with the environment, an assumption that, we find, does not always apply.

Although synthesis, processing, storage conditions, and local environment of NPs are known to play a significant role in determining their properties, this important information about particles and their history is often not reported.^{24,25} Lieber's group²⁶ has demonstrated large anisotropy in polarization and photoconductivity as a result of dielectric contrast between nanowires and the surrounding environment rather than the quantum-confinement effect. Structural changes in ZnO NPs in the presence of water and alcohol were observed by Zhang et al.²⁷. In other reported literature as well, we have seen indications of environmentally induced changes in NPs apparently of similar or identical size²⁸.

Here, we examine the time-dependent chemical-state switching of ceria NPs suspended in aqueous solutions as a function of local environment and aging time. An overview of this phenomenon is shown in figure 1. It is important to recognize that the effects are reversible. Because these chemical-state changes influence both physical and chemical properties of the particles they will impact NP characteristics important for specific applications such as catalysis or biomedical materials. Previous measurements²⁹ have demonstrated that the interaction of ceria NPs with the polymers and organic molecules is dynamic and depends on the solvent and processing conditions. In particular, solvent properties have been observed to influence both the particle size and chemistry as a result of surface interactions²⁰. Although the chemical state of the NPs is assumed to be reversible, systematic analysis and a detailed mechanistic understanding of this phenomenon as a function of aging and environment are not available^{20,29}. Here we examine the ability of ceria NPs to switch their oxidation state in aqueous media, propose a mechanism for these changes, and suggest how these changes may influence reported observations of quantum confinement. This article mainly focuses on these observations and discusses some mechanistic aspects.

*EMA theory: When the dimensions of a material reach those of its Bohr exciton radius, the energy of the lowest excited state increases, i.e. blue shift occurs in the optical absorption with decrease in size. The combination of quantum confinement and effective mass approximation theory can be used to derive a R⁻² dependence of the band gap energy for a spherical particle and the relation can be written as:

$$\Delta E_g = E_g(R) - E_g = \frac{h^2}{8R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right)$$

Experimental Work- Synthesis and characterization of ceria NPs

Unless specifically noted, the ceria NPs used in this work were synthesized by a room-temperature wet-chemical route without any surfactants or additives. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, was dissolved in DI water (18.2 M.Ω.), and a calculated amount of 30% H_2O_2 was added drop-wise to yield a final 30mM ceria NP suspension. As the drops are added, the colorless solution slowly turned to a characteristic yellow color indicating the oxidation of Ce^{3+} to Ce^{4+} . A Varian Cary-1 UV-Visible (UV-Vis) spectrophotometer was used to characterize the ceria NPs suspended in solution. Characteristic Ce^{4+} and Ce^{3+} spectra were collected using control solutions made from Ce^{4+} -ammonium nitrate and Ce^{3+} -nitrate in DI water, respectively. Transmission spectra were obtained at two-minute intervals during the first sixty minutes (Figure 2) of particle formation. Later, the spectra were collected every day for 1 week and then after 2, 3 and 4 weeks of aging (Figure 1b). The absorbance values were calculated from the transmission data using the Beer-Lambert law and were used to estimate the band-edge. Transmission electron microscopy (TEM) and x-ray photo electron spectroscopy (XPS) were carried out on various particle samples and representative data are quoted in relevant contexts.

The concentration of Ce^{4+} initially increases imparting the characteristic yellow color with a maximum in intensity after 1-day of aging (Fig. 1). The intensity of yellow color starts fading away after 1 week or longer aging indicating a decrease in the amount of Ce^{4+} in the solution. After 3 weeks of aging, the solution appears pale yellow in color indicating the further reduction of Ce^{4+} and regeneration of Ce^{3+} . At this stage, the environment is significantly less oxidizing and the ceria NPs are stable in a predominantly Ce^{3+} oxidation state. A simple filtration experiment (Figure 3) was carried out to confirm that the color of the solution is a result of the variations in the chemistry of the NPs. The solution with nanoparticles was filtered using a 20-nm alumina filter from Millipore(TM) after 1 day of aging. Both the spectral and visual confirmations are provided in figure 3. The solutions before and after filtration show clear difference and the filter paper shows the presence of yellow colored ceria nanoparticles. The post filtration solution was found colorless ascertaining the role of nanoparticles in its color and the optical absorption spectrum confirms the absence of Ce^{4+} remaining in the solution. The solution shown in the picture, figure 3, has 5 times more hydrogen peroxide than the optimal amount and is purely used to show the pronounce effect of the particle oxidation state induced color changes. The HRTEM image in figure 3 was obtained by dipping a carbon coated copper grid in the ceria nanoparticle suspension, before filtration. It is clear from the image that the agglomerates are, ~20nm constituted by 3–5nm individual particles. The XPS data (figure 3-e) also confirms the 4+ oxidation state of the nanoparticles on the filter. It is clear from the images and the analysis presented in the manuscript that all the changes are indeed occurring on the NPs. The ceria NPs synthesized in various aqueous media such as poly(ethylene glycol), ethylene glycol, dextran and glucose using similar conditions as mentioned above were used to understand the role of additives on the oxidation state changes.

To understand the actual time-dependent behavior of ceria NPs we 1) analyzed the optical absorption data using the conventional data analysis techniques existing in literature, 2) examined the chemical changes occurring in the ceria NPs with time and the environment, and 3) interpreted the results of (1) and (2) in terms of the quantum-confinement effect in ceria NPs.

Inferring band gaps from conventional analysis of UV-Vis data

The absorbance can be calculated from transmission data using the Beer-Lambert law:

$$\text{Absorbance (A)} = \log(100/\%T) = \epsilon C l$$

Where ϵ is the molar absorptivity, [L.mol⁻¹cm⁻¹], C is the chromophore concentration in solution, [mol. L⁻¹], and l is the path length [cm], T is the transmittance. Band-gap values can be calculated by plotting $(\alpha E)^2$ Vs E for direct and $\alpha^{0.5}$ Vs E for indirect transitions⁷ and extrapolating these plots to zero absorbance. Here, E is the energy ($= hc/\lambda$ (1248.62/ λ), λ is the wavelength [nm]; α is the optical absorption coefficient ($= (2.303 \times 10^3 A.\rho) / l.c$, ρ is the solid-phase density (7.13 g/cc for CeO₂)).

Because it was shown earlier that the transitions in ceria NPs are direct in nature,⁷ we confine our analysis to $(\alpha E)^2$ Vs E plots only. These are shown for ceria NPs that were aged in as-synthesized condition at room temperature for various time periods (Figure 4). The method of extrapolating the plots to obtain the band edge value is also shown for a representative data set from freshly synthesized NPs. The band gap values obtained from this method are plotted in Figure 5.

Correlation of band-gap analysis with microscopic and visual observations

The TEM images collected initially after synthesis (~15–30 minutes) have shown 15- to 20-nm agglomerates of 3- to 5-nm particles, which is in the range of the Bohr-exciton radius (~7 nm for ceria NPs). Particle sizes in this range and smaller are of major interest when considering the quantum confinement effect¹⁵. The optical absorption edge in ceria is expected to be a result of overlapping O_{2p} and Ce_{4f} charge-transfer bands and the spin-orbit splitting of Ce_{4f}³⁰. Time-dependent UV-Vis spectra show absorption in the visible region with a clear red shift in the first sixty minutes after synthesis (figure 2). This shift is based on the assumption that the particles are growing with time which would be consistent with a blue-shift for particles with decreasing size. This red-shift and the increasing particle size could be interpreted as a result of contribution from confinement effects²³. However, it should be noted that at least two significant changes occur after the oxidizer is added, the ceria NP nucleation and growth with a simultaneous change in oxidation state from +3 to +4. Because of the changes in chemical state, the observed red shift may not be due, solely, to the changes in particle size but also a result of the change in oxidation state. Based upon the measurements from the dissolved salts, the absorption edges for Ce³⁺ and Ce⁴⁺ are 3.76eV and 3.2eV, respectively. This indicates that the change in the oxidation state from Ce³⁺ to Ce⁴⁺ also leads to notable changes in the band edge values.

Extending the analysis of the NP suspension to 1-day at room temperature, there was a significant red shift in the absorption edge from ~3.9eV to 3.6eV (Fig. 5). There was no significant difference in either the color of the solution or the change in band edge value for up to one week of aging (data not shown). Aging of the ceria suspension beyond 1 week resulted in gradual reversal of the oxidation state to 3+. The absorption spectrum for the sample aged for 3-weeks almost overlaps with that of the fresh sample (Fig. 1b). At this point, the solution is mostly colorless and there is no significant precipitation. The band edge values and the color of the solution indicate the dominance of Ce³⁺ species. This indicates that the ceria NPs have switched their oxidation state from Ce 3+ to 4+ and eventually back to 3+ again. During this entire oxidation/reduction process we did not see any significant changes in NP size based on TEM analysis, despite the variation in the agglomeration for different solutions as discussed below. We were able to observe this interesting behavior of ceria NPs because of the long term studies carried out in our lab. Some of the reported studies on ceria NPs have been confined to first few minutes or hours after synthesis. In order to effectively use the NPs in many useful applications, it is

important to understand their long and short term stability and the associated chemical changes.

Linking the dynamic nature of ceria NPs to solution chemistry

When the ceria NPs are synthesized by adding peroxide to the initial solution, the oxidizing agent starts both the oxidation of Ce^{3+} to Ce^{4+} and the nucleation and/growth of NPs. It is important to account for the chemical changes in the ceria system during and after the synthesis stages to understand the observed variations in the band edge values of ceria. The two overall chemical reactions associated with the formation of ceria NPs³¹ as the precursor is initially oxidized are the following:

There is a well established literature on oxidation and reduction kinetics of $\text{Ce}^{4+}/\text{Ce}^{3+}$ in the presence of hydrogen peroxide^{32–37}. As identified by critical reviews of the literature regarding the catalytic oxidation of Ce^{3+} to Ce^{4+} in the presence of hydrogen peroxide,^{32–37} a key aspect of the hydrogen peroxide dissociation is the formation of hydroperoxy or the perhydroxyl radicals. Formation of perhydroxyl species during the reaction of Ce^{4+} with hydrogen peroxide has been confirmed by electron spin resonance spectroscopy³⁸. The hydroperoxy radical is known to disproportionate in the oxidation and reduction of solutions with cations of multiple valence states (equation 3b).

Our experiments are consistent with these observations indicating that ceria NPs can be stable in either Ce^{3+} or Ce^{4+} oxidation state in aqueous media under suitable conditions. Hence, Ce^{3+} is formed from the Ce^{4+} oxidation state in the presence of the hydroperoxy species, following the chemical reaction (4).

Hydrogen peroxide converts the Ce^{3+} to Ce^{4+} immediately after it is added to the Ce^{3+} solution. The Ce^{4+} ions quickly bond with the available hydroxyl radicals and nucleate the hydrated ceria particles to form a stable suspension at a pH of ~3.5. After this stage, the solution will become depleted of the Ce^{3+} ions and will be rich in Ce^{4+} (in the particles) and HO_2 radicals. This will drive the reaction 4 and leads to the reduction of Ce^{4+} to Ce^{3+} . Hence, there appear to be competing reactions occurring simultaneously as long as the relative concentrations of Ce^{4+} , Ce^{3+} and HO_2 radical provide the driving force. The detailed thermodynamics and kinetics of these reactions will be part of future research.

Once the solution is depleted of the oxidizing species, cerium will revert back to its stable oxidation state in aqueous medium i.e., Ce^{3+} oxidation state. So, we propose that the oxidation state cycling capability of ceria NPs is determined by immediate environment of the particle. This implies that the Ce^{4+} ions can be reduced and regenerated as the

environment changes. Such a mechanism has been suggested in the oxidation of reactive oxygen species (ROS) to protect retinal cells⁹. Our observations indicate that the formation of Ce^{4+} by reaction with H_2O_2 is much faster than the reduction by hydroperoxyl species. One reason may be that the reduction reaction involves solid NPs whereas the initial oxidation reaction involves ions in solution to form solid NPs. Once the NPs have formed, the process of reduction is reversible and oxidation of the NPs can be induced by the addition of oxidizing species like H_2O_2 . This is demonstrated in figure 6, where addition of H_2O_2 to a NP suspension that had been aged for three weeks (and contained predominantly Ce^{3+} NPs) regenerates the Ce^{4+} oxidation state. However, the process of re-oxidation is slower than the initial oxidation reaction.

Irrespective of the nature of the NPs – i.e. individual particles, small and large agglomerates – we have observed reversible oxidation state changes in various aqueous media. The effect of different solvents, (such as ethylene glycol, polyethylene glycol(600Mw)) on the oxidation state and size of as synthesized ceria NPs is clearly shown in figure 7, 8. Each additive has its own effect and significantly influences the chemical nature of the NP suspension as evidenced by the differences in the optical absorption data. The effect of dextran and glucose in acidic and basic environments is critically discussed in a previous publication²⁹. In our studies, we have not seen any significant difference in the variation of absorption edge as a function of agglomeration. Studies carried out with NPs synthesized in various aqueous media such as ethylene glycol, poly (ethylene glycol), dextran and glucose at different concentrations also support this observation. The most important point to be noted is that irrespective of the media, the individual ceria NPs remained 3–7nm in size, below the Bohr radius (~7nm), figure 8. ^{14,29} However, the kinetics of oxidation state vary among different solutions (figure 7). This result confirms that the solution environment plays a significant role in influencing the oxidation state (or the rate of oxidation state transition) and thereby the band edge as a function of time. We have found that the individual NPs of ceria remain 3–5nm even after aging for 4–6 weeks and observed they remain the same even after ~400 days of aging (not shown here) ¹⁴. Thus, after the initial nucleation stage the size of the NPs does not change. These measurement show that ceria NPs produced as described in this paper have dynamic oxidation states, which can be tuned by choosing suitable environments and aging conditions.

Implications of chemical state changes to the band gap analysis

A number of researchers have shown that the lattice-parameter expansion in the ceria NP system with reduction in particle size is a result of an increase in the fraction of cerium species in the Ce^{3+} oxidation state and the associated oxygen-vacancy formation. However, the same fact has not always been considered in analyzing the optical absorption data of ceria NPs. Henceforth, data presented in this article and the dynamic nature of the ceria NPs chemistry should be carefully considered while analyzing the confinement effects in ceria NPs. As usually applied, the effective mass approximation (EMA) theory presents only the radial dependence of the band gap in the quantum dots and does not consider a change in the chemical state of the semiconductor NPs. Hence, the validity of the EMA theory to interpret quantum confinement is questionable for species having variable chemistry, such as cerium oxide NPs. The role of local environment in influencing the “chemistry” of ceria nanoparticles also indicates that the interpretation of confinement effects may not, always, be appropriate without accounting for their influence.

In ongoing studies, we are finding that for the smallest particles the changes observed when oxidation state switches from +3 to +4 may be more complex and a possible influence of the nanoparticle size is also being critically studied. The influence of storage conditions such as presence and absence of light, temperature are also under investigation. The combination of

in situ Raman and microXRD studies are being used to examine these states in some detail and will be part of a future publication.

Conclusion

Both qualitative analysis of experimental data and more detailed data analysis show the dynamic nature of ceria NPs and the changes of their oxidation state as a function of aging (time) and environmental conditions. During the stage of particle nucleation and growth, both the particle size and chemical state change with time. After the particles reach 3nm to 5 nm, size remains (except for soft agglomeration) constant and the oxidation state depends primarily on the environment (and time). Often, the synthesis, analysis and relevant operational (in various applications) conditions are not the same. In such cases, aging time and environmentally induced changes in particles may play a significant role in the results reported and hence lead to discrepancies in various studies.

By simultaneously studying the NPs both in the presence and absence of organic additives over a period of time (long term studies) there is an increased scope for properly interpreting the complex nature of NPs. It appears that the band edge in ceria NPs can be chemistry driven and may not, in most cases, be due to pure quantum confinement effects driven by particle size changes. Having appreciated the facts, measurements of the effects of other parameters including temperature and storage conditions are important aspects of appropriate particle characterization and documentation. Similar studies in other systems might reveal additional useful information about NPs.

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Figure 1.

a) Schematic representation of the regenerative capability and oxidation state switching of ceria NPs in an aqueous environment. The pictures of bottles containing the NP suspension in DI water indicate the color changes after different aging periods. The mechanism of oxidation-state change in the presence of hydrogen peroxide and hydroperoxyl radicals is shown (b) UV-Vis absorption spectra of ceria NP suspension indicate the shift in the absorption as a function of time. It is evident from the plots that the absorption spectra for freshly synthesized ceria NPs and those after 3 weeks of aging are almost identical.

Figure 2.

The absorbance values of ceria nanoparticles synthesized in DI water as a function of time. Data collected at every two minutes during first 60 minutes, from which data at every 10 minutes is presented here, indicates a clear red shift.

Figure 3.

Pictorial representation of the filtration experiment a) with the pre and post filtration solutions b) the filter paper with nanoparticles c) the corresponding transmission spectra along with the control Ce³⁺ and Ce⁴⁺ spectra d) representative TEM image (inset) SAED pattern confirming the fluorite structure of ceria and e) Ce_{3d} x-ray photoelectron spectrum of the nanoparticles on the filter paper

Figure 4. αE^2 Vs E plots for ceria nanoparticle suspension in DI water after various aging periods. An estimate of the band gap can be obtained with $\alpha E = \text{const} (E - E_g)^n$ {E is the energy and E_g is the band gap “n” is 0.5 for a direct allowed transition}. The band gap value can be obtained from the energy intercept of the plot between αE^2 and E, as shown by the black line for the data corresponding to 1-day aged sample.

Figure 5.

Band gap variation in water based ceria nanoparticles as a function of time. Data was collected at 2 minutes interval immediately after the oxidizer is added. Selective data points corresponding to 0 – 60 minutes are presented. The data clearly shows that the band gap values dropped from ~3.9eV to 3.75eV within first 60min. The lowest band gap value for 1-day aged sample is indicative of the contribution from Ce⁴⁺. Increase in the band gap from 1 week of aging is indicative of the change in the oxidation state to Ce³⁺. It should be noted that the individual particle size did not increase beyond 3 – 5nm, after first 60 minutes.

Figure 6.

UV-Vis transmission spectra indicating the effect of H₂O₂ addition on the ceria NPs aged for 3 weeks at room temperature in DI water. (change in environment) Change in the color of the solution is an indication of change in the oxidation state. The inset pictures represent the corresponding color changes with the addition of H₂O₂. (see text for a detailed explanation)

Figure 7.

Representative color of 30mM ceria NP solutions (immediately after synthesis) in (a) DI water (b) 20%ethylene glycol (c) 20% poly (ethylene glycol), (d) 100% ethylene glycol (e) 100% poly (ethylene glycol) solutions. Darker yellow/orange brown color indicates higher amounts of Ce^{4+} as a function of variation in the environment and the light yellow color indicates predominant Ce^{3+} . The number (XX) shown at the bottom of each image is the band edge value obtained from the transmission data. All the systems in as synthesized conditions have shown a particle size $\sim 3\text{--}5\text{nm}$ and agglomerate sizes of $10\text{--}20\text{nm}$ (TEM images are available in Fig. 8).

Figure 8.

HRTEM images of ceria nanoparticles synthesized in a) 20 PEG b) 20 EG c) 100EG d) 100PEG e) DI water are shown. It is clear from the in set images that irrespective of the synthesis medium individual nanoparticles are 3 – 5 nm with agglomerate size ranging from 10–20nm.

Table 1

Summary of ceria synthesis and analysis from open literature

Precursor/Method of Synthesis/Oxidizer	Particle Size, nm	Band Gap, (eV)	Comments	ref
Ce(III)/Micro emulsion/TMAOH Heptane and dodecane solvents	5 – 10	2.92	a. support QC but no size dependence was reported b. attribute the effects observed to Ce ³⁺ and some unknown physicochemical aspects	15
Ce(III) / Composite hydroxide mediated approach/ powders suspended in ethanol	varies with time and temperature 3 – 7	blue shift with decrease in size	a. do not make any comment about confinement effects	19
Ce(III)/ Sonochemical/ TAAOH/Azocarbonamide	3 – 5	3.68 – 3.0	a. support QC b. variation in particle size is attributed to the alkyl chain length in TAAOH	20
Ce(III)/ homogeneous precipitation/ Alcohol + water/ NaOH	varies with the amount of alcohol 4 – 9	no comments	a. attribute the variation in the particle size to dielectric properties of the solvent b. no comments on QC	21
Ce(III)/ hydrothermal/ size fractionation/ Alcohol + surfactant	varies with surfactant 2 – 3	3.18 – 2.83	a. support QC b. propose the possible contribution of Ce ³⁺ c. increase in Ce ³⁺ with decrease in particle size	22
Ce(III)/ Successive microemulsion	2 – 3	4.2 – 3.6	a. deny the QC b. possible contribution of Ce ³⁺ c. propose that the charge transfer is direct	7
Ce(III)/NH ₄ OH/particles dispersed in alcohol	2.6 and 4.1	3.44 and 3.38	a. band gap variation is negligible b. deny the QC c. propose the charge transfer to be both direct and indirect	16
Ce(III) nitrate/ hexamethyl tetramine	3 – 12	blue shift with decrease in particle size	a. support QC b. no consideration of chemistry c. lattice expansion due to Ce ³⁺ but do not consider the same in case of UV-Vis analysis	23