Mechanistic Aspects of Wet and Dry CO Oxidation on Co$_3$O$_4$ Nanorod Surfaces: A NAP-UPS Study

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ABSTRACT: Catalytic activity, electronic structure, and the mechanistic aspects of Co$_3$O$_4$ nanorod (NR) surfaces have been explored for CO oxidation in dry and wet atmosphere using near-ambient pressure ultraviolet photoelectron spectroscopy. Presence of water with CO + O$_2$ plummets the catalytic activity because of the change in the electronic nature from predominantly oxide (without water in feed) to a Co$_3$O$_4$ surface covered by a few intermediates. However, at ≥375 K, the Co$_3$O$_4$ surface recovers and regains the oxidation activity, at least partially, even in the presence of water. This is fully supported by the changes observed in the work function of Co$_3$O$_4$ under wet (H$_2$O + CO + O$_2$) conditions compared with dry (CO + O$_2$) conditions. This study focuses on the comparative CO oxidation rate on Co$_3$O$_4$ NR surfaces and highlights the changes in the electronic structure that occur in the catalyst during the CO oxidation reaction.

INTRODUCTION

Developing a sustainable CO oxidation catalyst that works at ambient temperatures under relevant environmental conditions is an important challenge; indeed it is essential to improve the quality of life of the current and future generations.¹,² Various noble metal-based catalysts have been used for CO oxidation to lower the automotive emissions;³,⁴ however, owing to their high cost, sustainability issues, and active temperature regime limitations, the search is still on to find alternative, cost-effective, and noble metal-free catalysts. This led to the study of 3d transition metal and metal oxide-based catalysts for CO oxidation. One such system is the spinel form of cobalt oxide,⁵ and it was demonstrated to show high catalytic activity for the CO oxidation reaction at and below ambient temperatures.⁶ Although Co$_3$O$_4$ nanorods (Co$_3$O$_4$ NRs) show remarkable CO oxidation reaction at ambient and low temperatures, their reaction mechanism is still unclear. A simple mechanism proposed involves CO adsorption on the Co$^{3+}$ site, reaction with surface oxygen to form CO$_2$, and ready desorption from the surface.⁶ However, this does not explain the structure or morphology dependence as observed in the literature.⁷—⁹ It is also to be noted that CO oxidation was correlated with the number of surface Co$^{3+}$ sites.⁵

The interaction of transition metal oxide surface with H$_2$O plays an important role in catalysis and surface chemistry. It is well-known that the rate of CO oxidation is strongly affected by the presence of water. Addition of water with the reactant feed enhances the CO oxidation rate on supported nanogold.¹⁰,¹¹ However, water can dissociate on the catalyst surface and diminish the activity by deactivating the catalyst.¹² Xie et al.¹³ evaluated the CO oxidation using normal feed gas (3–10 ppm moisture) and suggested that Co$_3$O$_4$ NR was less sensitive to water. Nonetheless, innocuous water vapor is present everywhere to a large extent. Theoretical studies suggest that water molecules adsorb on the active sites of the metal oxide, which hinders the redox cycle of the reaction and leads to a decline in activity;¹⁴ however, there is no direct experimental evidence available to support the hypothesis. Hence, the question is wide open.

The above discussion underscores the importance of gas−solid interactions between reactants and catalyst surfaces,¹⁵ which is yet to be explored using relevant methods. However, until now, no direct experimental studies have been reported to identify the possible reaction pathway and the role of water vapor in suppressing the activity. In the present article, we report a systematic study of adsorption and oxidation of CO with O$_2$ on Co$_3$O$_4$ NR catalysts using near-ambient pressure ultraviolet photoelectron spectroscopy (NAP-UPS).¹⁶,¹⁷ We present direct spectroscopy and mass spectrometry evidence for the catalytic activity and the influence of moisture on the catalytic activity toward CO oxidation on Co$_3$O$_4$ NRs. A serious attempt has been made to explore the mechanistic insights into the CO oxidation activity at ambient temperatures and near-ambient pressures using NAP-UPS. Supplementary data obtained using X-ray photoelectron spectroscopy (XPS) under NAP conditions are also provided.
RESULTS AND DISCUSSION

In Situ Catalytic Activity Measurement. A series of controlled experiments were performed to understand the CO oxidation activity, catalyst sustainability, and mechanism of varied CO₂ production in the presence and absence of moisture. To explore the electronic structure and the mechanistic aspects, we studied the CO oxidation reaction using NAP-UPS at a total pressure of 0.1 mbar under dynamic dosing conditions between ambient temperature and 400 K, along with mass spectral analysis. The reaction was studied in the presence and absence of water vapor with various CO/O₂ ratios; the best activity results were observed for the 1:3 ratio, and hence this ratio was used to explore the electronic structure aspects of the reaction. Individual reactants were bubbled through liquid water at room temperature (RT) to create a wet reaction environment for the reaction. A simple ratio of partial pressure of water to total pressure of all reactant and product components observed using a quadrupole mass spectrometer (QMS) indicates it to be 0.2% (approx. 1–2 × 10⁻⁹ mbar); however, this is an underestimated value considering the difficulty in quantifying condensed water [on the ultrahigh vacuum (UHV) chamber walls] from the dosing point to the measurement point using a QMS. In spite of these limitations in the quantification of water vapor, a large change in the reactivity and spectral data was observed because the water vapor present at the dosing point (before condensation into chamber walls) underscores its influence toward the catalytic activity. Under real-world conditions, such CO oxidation catalysts are expected to work with less percentage of water vapor, and it also depends on the application. Figure 1a,b shows the mass spectrum measured for the kinetic results of CO conversion to CO₂ between 300 and 400 K (a) in the absence of water vapor and (b) in the presence of 0.2% water vapor in the reaction mixture. Blue, olive green, red, and cyan indicate the change in the partial pressure of CO, O₂, CO₂, and H₂O, respectively.

Figure 1. Mass spectra recorded at 0.1 mbar total pressure with 1:3 CO/O₂ ratio, between 300 and 400 K (a) in the absence of water vapor and (b) in the presence of 0.2% water vapor in the reaction mixture. Blue, olive green, red, and cyan indicate the change in the partial pressure of CO, O₂, CO₂, and H₂O, respectively.

the mass spectrum measured for the kinetic results of CO conversion to CO₂ between 300 and 400 K under dry and wet conditions, respectively. The mass spectral analysis shows that the formation of CO₂ observed at 300 K remains unaffected at increasing temperature, under the moisture-free condition. However, a similar analysis performed in the presence of water vapor showed that CO₂ production drastically decreases by more than an order of magnitude. Gradually increasing amounts of CO₂ and O₂ in the first few minutes, as can be observed in Figure 1a,b, is due to diffusion limitation; contrarily, CO diffuses very fast (see Experimental Section for diffusion coefficients), and a sudden spurt in its partial pressure could be observed at the beginning of the reaction. It is to be mentioned that the QMS is kept in the preparation chamber 1.5 m away from the NAP-UPS measurement spot. The total pressure, which was measured to be 0.1 mbar, very close to the analysis spot, throughout the experiment, confirms that the Co₃O₄ NR experiences the pressure applied.

NAP-UPS Studies. In situ NAP-UPS analysis was used to explore the nature of the catalyst surface under dry and wet reaction conditions. The valence band (VB) spectra of Co₃O₄ NRs measured at UHV-RT are shown in Figure 2a (Figure S1a). According to the literature, the VB spectrum of the Co₃O₄ NR can be deconvoluted into various bonding features of Co³⁺ and Co²⁺. The features at 1.2 (red), 5.6 (dashed red), and 9.3 eV (dash-dotted orange) correspond to Co³⁺ 3d, Co³⁺—O 2p, and the corresponding satellite peak, respectively. However, Co²⁺ 3d (1.5 eV, solid purple) and Co²⁺—O 2p (3.9 eV, blue) feature with the corresponding satellite peaks at 2.3 (dotted purple) and 7.3 eV (dash-dotted blue), respectively. A detailed explanation of the spectra is given in Figure S1a,b. When the reactant was fed to the catalyst, the following major changes were observed: (i) The characteristic peak for Co³⁺ 3d tends to shift to 1.3 eV at 300 K (compared with UHV-RT VB) and again returns to 1.1 eV at 400 K (red arrow), whereas the Co³⁺—O 2p peak at 5.6 eV hardly shows any shift due to reaction environment and temperature up to 400 K. (ii) The satellite feature of Co³⁺ at 9.2 eV shifts to 9.6 eV up to 350 K and returns to 9.4 eV at 400 K (orange dash-dot arrow). (iii) The satellite feature of Co²⁺ at 2.3 eV displays a shift of 0.35 eV toward higher binding energy (BE) under reaction conditions (purple arrow). (iv) The presence of CO₂ vibrational features along with those of reactants fully support CO₂ formation at RT with characteristic vibrational features at 8.6, 6.7, and 8.3 eV for CO, O₂, and CO₂, respectively. An additional vibrational feature of CO₂ is also observed at 12.7 eV, which further confirms the CO oxidation at RT. (v) A shift and broadening of CO and O₂ vibrational features was observed (0.23 eV), whereas that of CO₂ shifts by 0.15 eV on catalyst surfaces between 300 and 400 K. (vi) VB_max shifts to a lower BE (5.1 eV) at 300 K and broadens compared with single VB_max at UHV-RT (5.4 eV) spectrum; it shifts further down to 4.8 eV with increasing temperature at 400 K. This directly indicates the interaction of the surface with gas-phase reactants. A considerable broadening in the reactants and CO₂ vibrational features is also observed, likely due to the participation of various intermediates in the reaction (Figure 2f), whereas no broadening was observed in the gas-phase feature of gases even at 400 K (Figure S2).

Co₃O₄ NRs were subjected to the wet reactant stream to examine the change in the catalyst structure under the influence of water vapor, and the NAP-UPS results obtained are shown in Figure 3. The VB feature of Co₃O₄ NRs recorded under dry conditions at 300 K (similar to Figure 2b) is shown in Figure 3a for comparison. In the presence of water vapor, there is no ambient temperature activity, and no CO₂ feature was observed for the catalyst. At 300 K, the presence of water vapor severely hampers the gas-phase features of CO and O₂. The intensity of the CO and O₂ vibrational features shows a large decrease and a broadening along with a shift to a high BE (Figure 3f) compared with the spectrum under dry conditions at 300 K (Figure 2f). Whereas O₂ vibrational features recover to the lower BE, CO features are observed at the same BE at 400 K (red arrow in Figure 3). A broadening observed with CO features is attributed to the formation of CO₂ or —HCO/COOH species on the surface. A broad VB_max observed between 4 and 6 eV under dry conditions (Figure 3a) contracts to ~6 eV, with a significant decrease in the intensity between
4 and 5 eV under wet conditions (Figure 3b−d). The satellite feature of Co$^{3+}$ at 9.6 eV (under dry conditions at 300 K) shifts to 9.9 eV up to 350 K and returns to 9.6 eV at 400 K (under wet conditions). The presence of a broad hydroxyl feature at 12.6 eV confirms that water is adsorbed dissociatively on the catalyst surface.\textsuperscript{13,17} It is to be noted that the same hydroxyl

**Figure 2.** (a) Ultraviolet photoelectron spectroscopy (UVPES) VB spectra of Co$_3$O$_4$ NRs at UHV-RT. NAP-UPS VB features of Co$_3$O$_4$ NRs recorded under dry conditions with 1:3 CO/O$_2$ ratio at 0.1 mbar at (b) 300, (c) 350 K, and (d) 400 K. (e) O$_2$ and (f) CO and CO$_2$ vibrational features show a shift to lower BE.

**Figure 3.** (a) UVPES VB spectra in a moisture-free reaction environment at 300 K; (b−d) VB change of Co$_3$O$_4$ NRs on varying the temperature from 300 to 400 K in the presence of water vapor in the reaction mixture (approx. 0.2%); (e) deconvoluted CO vibrational features at 300 and 400 K; and (f) gradual shift and broadening of CO vibrational features with temperature under wet reaction conditions.
feature was observed with a low intensity at UHV-RT (refer Figure 5a) using NAP-UPS, as shown in Figure 2; this is due to the residual water present in the vacuum chamber. The water molecules adsorbed dissociatively on the catalyst change the nature of the surface from predominantly oxide to hydroxide and make it electron-rich; CO adsorption on such a surface converts it to carbonate and/or formyl species. These side reactions change the nature of the surface toward carbonate-enriched species and hinder the activity for primary CO oxidation. Hence, H2O creates a reducing environment and converts the active site on the catalyst. It is also to be mentioned that under high pressure measurement (0.1 mbar) conditions, no static charge development occurs; even if such charging occurs, it is nullified by the gas phase.

As the temperature increases, the oxygen vibrational features regain the intensity, which indicates that the presence of H2O diminishes the affinity of the surface toward O; H2O begins to desorb above its boiling point, and simultaneously the surface regains the affinity toward O2. By contrast, CO features show an entirely different behavior; they begin to diminish in intensity, giving rise to a broad feature. This broad feature can be deconvoluted into two features; the lower BE peak corresponds to the CO vibrations, whereas the other feature appearing at a high BE is due to the reaction intermediates (HCO/COO2−) (Figure 3e,f). However, with increasing temperature, the broadening of the peak increases; the broad feature contains CO2 and CO at ≥375 K and shifts to a lower BE.

A detailed data analysis of the VB spectra indicates that the nature of catalyst surface structure changed during the course of reaction because of which the vibration feature of all of the gas-phase features shifted from their original BE. These vibration features appear at a comparatively higher BE in the presence of water, which indicates less interaction of the incoming molecules with the catalyst surface. The experimental results also indicate that the Co 3d electron density of the VB feature and the corresponding interaction with O 2p has a good correlation with the catalytic activity. No clear correlation was recorded at 400 K resembles that recorded at 300 K, but the intensity of this hydroxyl feature decreases; however, the adsorbed reactant feature remains unaffected. O 1s spectrum recorded at 400 K resembles that recorded at 300 K but with a very low intense hydroxyl component, indicating the desorption of the hydroxyl group at high temperatures and supporting the partial recovery of Co3O4 NR surfaces.

Under the same conditions, C 1s spectra obtained were deconvoluted into three main features at 284.2 (dark cyan), 286.5 (wine red), and 288.4 eV (purple). The peaks at 284.2 and 286.5 eV correspond to the adventitious carbon and the adsorbed CO molecules on the surface. However, the peak at 288.4 eV was assigned to the weakly adsorbed ions of the CO2 species (CO2−) present on the catalyst surface, which is a reaction intermediate, and subsequently desorbed to form the actual product, CO2. Apart from the above features, the C 1s spectrum also shows the gas-phase features of CO (291.1 eV) (dotted wine red) and CO2 (292.1 eV) (blue). The appearance of the product gas-phase feature confirms the formation of CO2 at RT. It should be noted that surface carbonate (Supporting Information 4) is an intermediate for CO oxidation on metal oxide; however, there was no carbonate feature observed during the dry reactant stream under our experimental conditions.

A broad C 1s spectrum was observed under wet conditions, which was deconvoluted to understand the nature of reaction intermediates, responsible for the diminished CO oxidation activity under wet reaction conditions. Similar to the dry reaction conditions, various peaks were observed under wet conditions for adsorbed CO (286.7 eV) (solid wine red), CO2− (288.4 eV) (orange), gas-phase CO (291.1−291.3 eV) (dotted wine red), and molecules with adventitious C species at 284.4 eV (dark cyan) (Supporting Information 4). Shifts in the BE of various fitted components indicate that the surface electronic structure was altered in the presence of water vapor. Crucially, no peak was observed at 292.2 eV for gas-phase CO2. The absence of gas-phase CO2 feature at 300 K supports the mass spectral results and suggests the deactivation of the catalyst under wet reaction conditions. Indeed, some new features observed at 287.4 (green, formyl) and 289.3 (dark yellow, carbonate) correspond to new reaction intermediates because of the interaction of water molecules with the catalyst surface and the reactant species. When the temperature increases above 375 K, the corresponding peak area of features at 287.7 and 289.3 eV shows a decrease (as compared with 300 K) with the appearance of CO2 features; however, at 400 K, sufficient change in the concentration of various intermediates.

**Figure 4.** NAP-XPS C 1s and O 1s spectra recorded under dry and wet reaction conditions: C 1s and O 1s spectra recorded under (a,d) dry reaction conditions at 300 K, (b,e) wet reaction conditions at 300 K, and (c,f) wet reaction conditions at 400 K.
with the enhancement of CO₂ gas-phase feature was observed, indicating the decomposition of the latter intermediate (peak at 289.3 eV), facilitating CO₂ production. An enhancement was observed with the feature at 287.3 eV, which seems to be a spectator/stable intermediate for the reaction.

There is no significant shift observed in the Co 2p XPS spectrum, which indicates that under reaction conditions, the bulk chemical nature of the Co₃O₄ NRs remains unchanged as identified at RT; however, the ratio of Co³⁺/Co²⁺ shows an 8–10% change with temperature under dry to wet reaction conditions. It is also to be noted that the probing depth is approximately 5–6 nm for NAP-XPS compared with approximately 1 nm for NAP-UPS; this allows the surface changes to reflect much better with the latter than the former.

A simple comparison of spectra recorded at 300 and 400 K, with and without water vapor, underscores the changes in the work function (WF) (Supporting Information 5) of the material, depending on the measurement conditions (Figure 5). Whereas the 400 K spectrum displays a comparable WF for wet (5.55 eV) and dry (5.6 eV) conditions, the 300 K spectrum shows 5.7 eV (5.0 eV) for dry (wet) conditions, highlighting the enormous influence of water vapor at ambient temperatures. It is also to be noted that the Co₃O₄ NR exhibits the same WF (5.6–5.7 eV) between 300 and 400 K under dry conditions. The above observation indicates that desorption of water molecules/intermediates from the catalyst surface occurs with increase in temperature and reverts the passive/low active catalyst surface to the active surface. Broadening of VB under wet conditions, compared with dry conditions, at 300 K underscores the formation of stable species. A careful analysis reveals the introduction of a highly populated band at 12.3 eV under wet conditions at 300 K, at the cost of 11.3 eV band observed under dry conditions, whereas there are no significant changes observed at 400 K between wet and dry conditions. This highlights the negligible (strong) influence of water above 375 K (at 300 K). Co³⁺ feature at 1.2 eV shows a higher intensity under wet conditions than under dry conditions at 300–400 K. This hints at the availability of Co³⁺ even under wet conditions but with different anions such as hydroxyl, formyl, or carbonate groups (see Figure 5).

**Water-Induced Surface Modification and Catalyst Deactivation.** Water has a significant effect on the activity and selectivity of various catalytic reactions, and it strongly alters the rate of CO oxidation depending on the catalytic systems and conditions (see Figure 6). In the present study, we observed a diminished ambient temperature catalytic activity for CO oxidation to CO₂ in the presence of moisture (Figure 6). This can be accounted as follows: Water molecules dissociatively adsorb and change the electronic nature of the catalyst surface from oxide to hydroxide/oxhydroxide at least partially by hydroxylating the catalyst surface. Co₃O₄ is known to be highly electrophilic in nature and can be hydroxylated easily at RT. On the basis of the present experimental findings, it is evident that the dissociative adsorption of water forms a layer of OH groups on the catalyst surface. The OH groups on the Co₃O₄ surface hinder a direct interaction of reactant molecules (CO and O₂) with the catalyst surface, thus resulting in a diminished catalytic activity. The presence of moisture alters the surface electronic nature of Co₃O₄ from oxide to predominantly hydroxide. The hydroxide layer (and protons) on the surface facilitates the formation of carboxylate/formate intermediates with the incoming CO molecules (see Figure 6b).

Interestingly, the analysis of mass spectra shows a high consumption of CO under humid conditions at temperature ≤350 K. It is known that CO has a high affinity toward Co³⁺, and hence under humid conditions, the CO molecules adsorb on the pseudo Co³⁺ site; however, the catalyst surface is found to be significantly oxyphobic in the presence of water vapor. The adsorption of CO on the Co³⁺ site does lead to CO₂ in the absence of water vapor and to stable reaction intermediates, such as carbonate and formyl, in the presence of water vapor. When the temperature reaches ≥375 K, the OH group layer starts depleting, and the affinity of the catalyst surface toward O₂ regenerates. Hence, the dissociative adsorption of water is apparently reversible, and the catalyst surface partially regains...
its activity because of its reoxidation to Co₃O₄ surface at T ≥ 375 K (see Figure 6c).

**CONCLUSIONS**

In summary, findings from NAP-UPS support Co₃O₄ NRs as the most active metal oxide for CO oxidation at RT in the absence of water vapor. However, in the presence of water vapor, the reaction is not active below 375 K because of the surface hydroxylation (or oxohydroxide) and associated changes in the electronic structure. Above 375 K, CO oxidation activity was regained underscoring the desorption of water above its boiling point leading to activity resumption; however, the dissociative water adsorption poisons the surface below 375 K. The decrease in WF under the wet reaction conditions underscores that the contaminated surface is more stable than the reactive surface found under dry reaction conditions with a high WF. Our future work will focus on the detailed electronic structure analysis to get the mechanistic pathway of the reaction and also to understand how water molecules turn the reaction path and cause concomitant decline in the catalytic activity.

**EXPERIMENTAL SECTION**

The Co₃O₄ NR was prepared using a wet chemical synthesis method by following the procedure reported in the literature. Typical material characterization details are given along with the X-ray diffraction (XRD) (Figure S6) and high-resolution transmission electron microscopy (HRTEM) (Figure S7) results in the Supporting Information. XRD and HRTEM for the Co₃O₄ NR were conducted and found to be similar to those of the literature report. The surface electronic structure of the catalyst during reaction conditions was studied using a custom-built NAP photoelectron spectrometer (NAP-UPS) at the National Chemical Laboratory, Pune. The core-level electronic structure was identified with Al Kα generated by a twin-anode X-ray source; however, the VB electronic structure was explored using UVPES recorded with He I source, and core-level studies were explored with Al Kα. A distance of 1.5 mm was maintained between the material surface and the cone. The NAP-UPS measurements were taken using a R3000HP (VG Sciencia) analyzer. The core level XPS measurements were taken at a pass energy of 100 eV for XPS and 5 eV for UVPES with the analyzer cone aperture (aperture = D) of 1.2 mm. A distance of 1.5 mm was maintained between the material surface and the cone. The NAP-UPS measurements were taken using a R3000HP (VG Sciencia) analyzer. The core level XPS measurements were taken at a pass energy of 100 eV for XPS and 5 eV for UVPES. The spectral analysis and peak deconvolution were carried out using CASA software. Shirley background subtraction was used for background removal. All VB studies were restricted with the He I source, and core-level studies were explored with Al Kα. A detailed NAP-UPS data analysis was carried out with peak deconvolution and assignment (see Figure S1a). The appearance of characteristic peaks of Co³⁺ and Co²⁺ with a weak shake-up satellite feature in XPS²²,²³ (Figure S1b) and UVPES²⁴ confirms the surface nature of the spinel.

A very thin pellet was used for the NAP-UPS analysis in the presence of reactants at different temperatures. All high pressure data presented in this article were obtained at 0.1 mbar reactant pressure; NAP-UPS data collection was recorded between 300 and 400 K. The reaction was studied in the presence and absence of water vapor with 1:3 CO/O₂ ratio. To create a wet reaction environment, the individual reactants were bubbled through liquid water at RT. Condensation of water molecules was observed throughout the chamber, which is unavoidable. The mass spectral analysis was carried out by interconnecting the analysis chamber to the QMS (SRS RGA 200) placed in the preparation chamber through a bellow and a leak valve kept close to the QMS. All of the reactants and products diffuse from the analysis chamber to a long distance (~1.5 m) and leaked through the leak valve for measurements. Hence, QMS measurements can be considered, at best, as semiquantitative. However, the diffusion coefficient of the relevant gas-phase species in air at 1 atm is as follows: CO = 2020 m²/s; O₂ = 1880 m²/s; and CO₂ = 1570 m²/s; this supports the pressure changes observed in Figure 1. Several control experiments, including CO + O₂ dosing in the absence of catalyst, were carried out to confirm that the CO oxidation activity arises only from the catalyst; however, no CO₂ production was observed, demonstrating that there is no inherent activity of the UHV chamber walls or any component within the NAP-UPS system for the reaction. The ambient temperature activity of the catalyst was also confirmed in a typical fixed-bed atmospheric pressure reactor, and the ambient temperature activity was confirmed.

**ASSOCIATED CONTENT**

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00471.

UVPES and XPS results of Co₃O₄ under UHV conditions, UVPES of Co₃O₄ in the presence of CO or O₂, Co 2p core-level spectra under wet and dry conditions, WF calculation, assignment of deconvoluted features, and characterization of catalyst using XRD and HRTEM (PDF).

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

R.J. thanks CSIR, New Delhi, for research fellowships. This work is partly supported by CSIR through CSC-0404.

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