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A simple method to prepare ZnO and $Al(OH)_3$ nanorods by the reaction of the metals with liquid water

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Abstract

Reaction of liquid water with Zn and Al powders and foils have been investigated in the 25–75 °C range. The reaction of Zn metal powder with water in this temperature range yields ZnO nanorods. The diameter of the nanorods decreases slightly with the increase in the reaction temperature, accompanied by an increase in the relative intensity of UV emission band. Zn metal foils also yield ZnO nanorods on reaction with water in the 25–75 °C range. Reaction of Al metal powder or foil with water in the 25–75 °C range yields $Al(OH)_3$ nanorods. The formation of ZnO and $Al(OH)_3$ nanorods by the reaction of the metals with water is suggested to occur because of the decomposition of water by the metal giving hydrogen.

Keywords: Zinc oxide; Nanorods; Photoluminescence

1. Introduction

Zinc oxide is an important solid state material of contemporary interest, possessing several properties such as piezoelectricity, field emission and lasing action with potential technological applications [1,2]. One-dimensional (1D) nanostructures of ZnO have been of particular interest due to their tunable electronic and optoelectronic properties [1–7]. The methods employed to produce ZnO nanorods include chemical vapor deposition [8,9], physical vapor deposition [10–12], metal-organic vapor phase epitaxy [13] and the use of anodic aluminum oxide tempalates [14,15]. A low-temperature chemical-liquid deposition method has been employed to grow oriented ZnO nanorods by continuously supplying Zn ions from a Zn foil to a ZnO-coated substrate in aqueous formaldehyde solution [16]. Reaction of a Zn^{2+} salt with ethyl alcohol in the presence of an amine gives 1D nanostructures of ZnO [17]. Solvothermal reaction of zinc acetate with NaOH in the presence of polyvinylpyrolidone in ethanol has been employed to obtain ZnO nanorods [18]. Hydrothermal reactions have been used for the preparation of the ZnO nanorods as well. Thus, heating zinc nitrate and NaOH in a mixture of ethylenediamine and water at 180 °C for 20 h gives rise to ZnO nanorods [19]. In the presence of ethylenediamine, the reaction of Zn metal foil with water under hydrothermal conditions (150–230 °C) is also reported to yield ZnO nanorods [20]. It has been found recently that the C–O bond of the aliphatic alcohols is readily cleaved on zinc metal surfaces, giving rise to ZnO nanoparticles [21]. It occurred to us that the reaction of Zn metal with liquid water may also produce ZnO nanostuctures, since the reaction would be associated with the evolution of hydrogen [22,23]. We have, therefore, investigated the reaction of Zn metal powder and Zn foils with water at room temperature as well as with water maintained at a temperature in the 25–75 °C ranges. The present study differs from literature reports in that we have examined the interaction of zinc metal with liquid water at or close to room temperature with out any additives. The literature methods generally use amines and other additives or zinc compounds and employ higher temperatures. Encouraged by the results obtained by the reaction Zn

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metal with water, we have also examined the reaction of aluminum metal with water. The present study provides a very simple method of generating nanorods of ZnO and $Al(OH)_3$ by the reaction of liquid water with the metals. To our knowledge, $Al(OH)_3$ nanorods have been not reported in the literature.

2. Experimental section

In a typical synthesis of the ZnO nanorods from Zn metal powder (Ranbaxy, $\geqslant 10\,\mu m$ diameter), 10 mg of the powder was taken in a vial containing 10 ml of double distilled water (pH 6.5). The reaction mixture was kept at a desired temperature. At 25 °C (room temperature), the reaction mixture was kept for 72 h. Reaction of zinc foils with double distilled water carried out by immersion the foil in 10 ml of water and maintained the temperature at desired value at 25 °C for 72 h. At 50 and 75 °C, the reaction mixture was kept for 24 h. Reaction of Al powder (Ranbaxy, $\geqslant 10\,\mu m$ diameter) and Al foil with water was carried out similarly except that at 25 °C the reaction time was 120 h. The $Zn + H_2O$ reaction was also carried out at 25 °C by adding ethylenediamine (1 ml) to 10 ml of water.

Field emission scanning electron microscope (FESEM) images were recorded with a FEI NOVA NANOSEM 600. X-ray diffraction (XRD) patterns of the samples were recorded in the $\theta{-}2\theta$ Bragg–Bretano geometry with a Siemens D5005 diffractometer using Cu$K\alpha$ ($\lambda = 0.151418$ nm) radiation. UV–vis absorption spectra of the nanorods dispersed in CCl_4 were recorded using a Perkin-Elmer Lamda 900 UV/vis/NIR spectrometer. Photoluminescence (PL) spectra were recorded with a Perkin-Elmer model LS55 luminescence spectrometer. Raman spectra were recorded with LabRAM HR high resolution Raman spectrometer (Horiba Jobin Yvon) using He–Ne Laser ($\lambda = 630$ nm). IR spectra were recorded on KBr pellet with Bruker IFS-66V. Transmission electron microscope (TEM) images were obtained with a JEOL JEM 3010 instrument.

3. Results and discussion

In Figs. 1a–c, we show FESEM images of ZnO nanorods obtained by the reaction of Zn metal powder with water at different temperatures. Of these, Fig. 1a shows a FESEM image of the nanorods obtained after the reaction at 25 °C for 72 h. The nanorods have diameters varying between 40 and 150 nm, with an average diameter of around 75 nm, and an average length of 300 nm (see inset in Fig. 1a). A FESEM image of the ZnO nanorods obtained after reaction at 50 °C for 24 h is shown in Fig. 1b. These nanorods have diameters in the range 20–100 nm, with an average diameter of 50 nm and the length ranging from 1 to 3 μm (see inset in Fig. 1b). The nanorods prepared at 75 °C

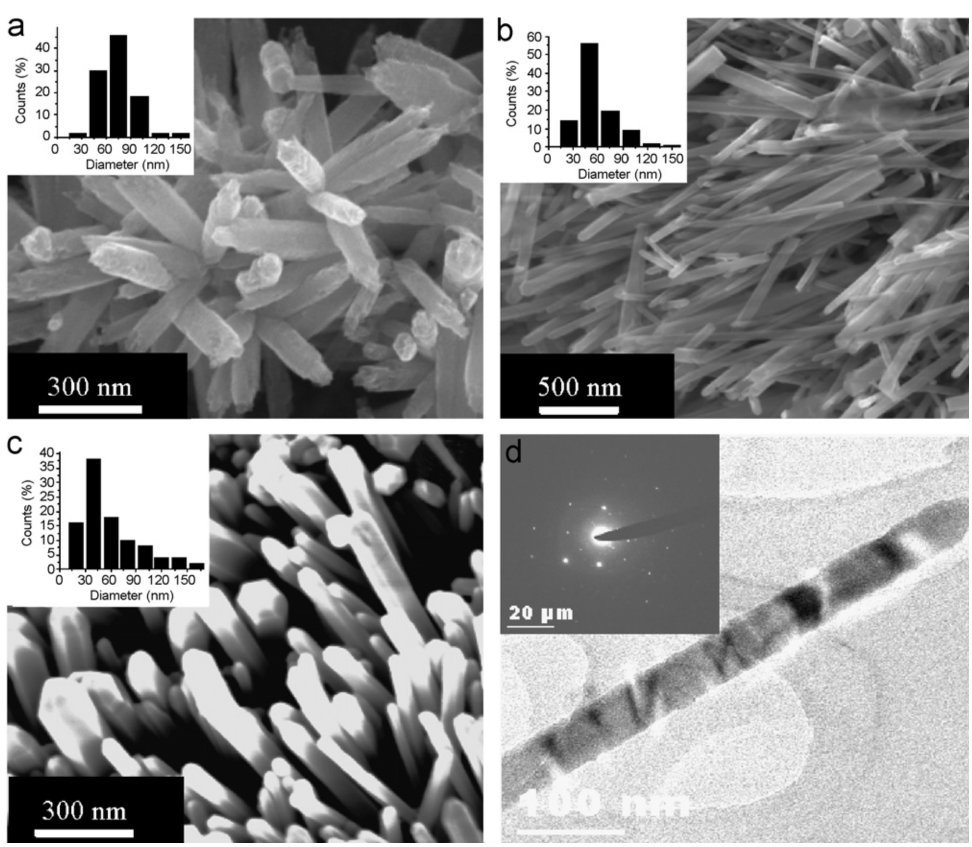

Fig. 1. (a–c) FESEM images of ZnO nanorods obtained by the reaction of Zn metal powder with water at 25, 50 and 75 °C, respectively. Insets in (a–c) show the particle size distribution, histogram. (d) TEM image of a ZnO nanorod prepared at 50 °C. Inset shows the SAED pattern.

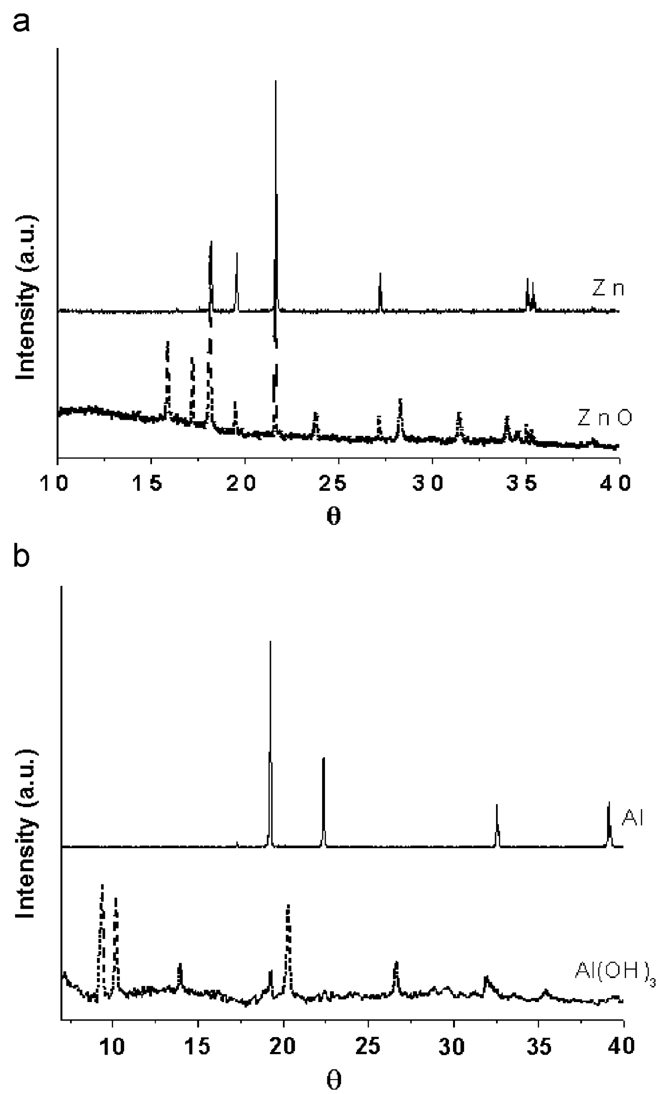

Fig. 2. XRD patterns of (a) ZnO and (b) $Al(OH)_3$ nanorods along with those of the starting metal samples.

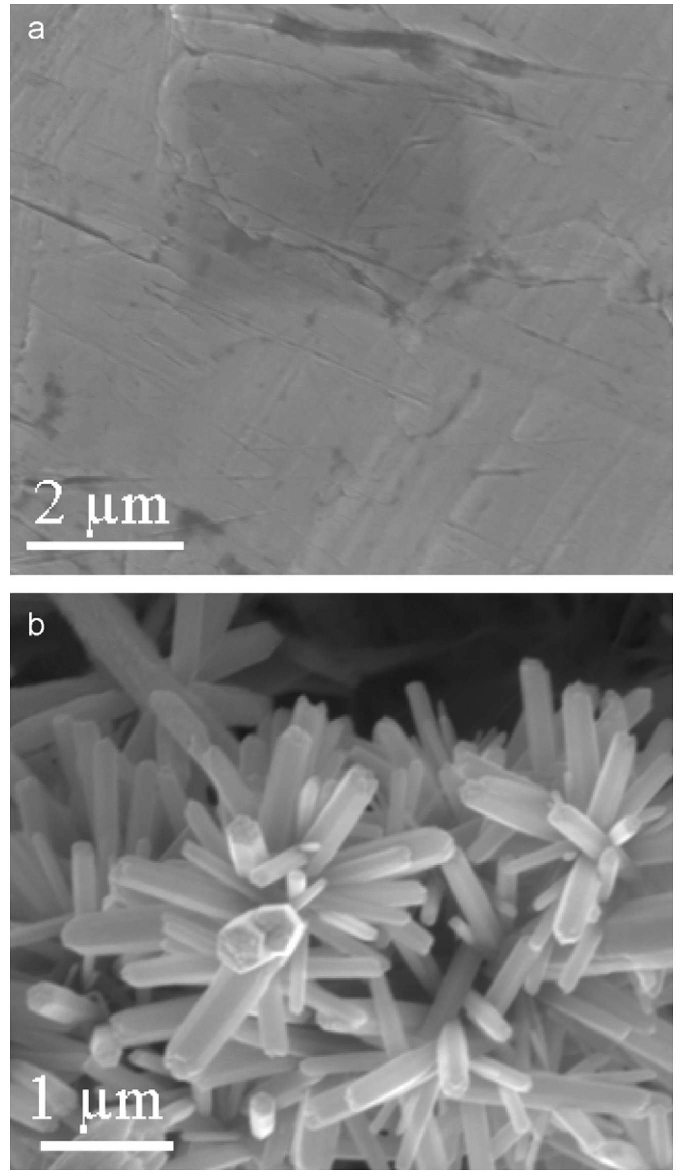

Fig. 3. FESEM images of (a) ZnO foil and (b) ZnO nanorods obtained at 50 °C by the reaction of water with the Zn foil.

have diameters in the 20–140 nm range, with an average diameter of 40 nm and the length in the 1–3 μm range (Fig. 1c). Inset in Fig. 1c shows the particle size distribution, histogram. In Fig. 1d, we show a TEM image of a ZnO nanorod (diameter~40 nm) prepared at 50 °C. The selected area electron diffraction (SAED) pattern shown as an inset in Fig. 1d confirms the single crystalline nature of the nanorod. The XRD patterns of the ZnO nanorods (Fig. 2a) obtained from the different preparations could be indexed on the hexagonal wurtzite structure (space group: $P6_3mc$; $a = 0.3249$ nm, $c = 0.5206$ nm, JCPDS card no. 36-1451). Our studies of the reaction of Zn powder with liquid water in the 25–75 °C range indicate that the average diameter of the ZnO nanorods decreases with the increase in temperature, accompanied by an increase in the aspect ratio.

We have examined the effect of addition of ethylenediamine on the formation of ZnO nanorods by the reaction of water with Zn metal powder. By adding 1 ml of ethylenediamine to 10 ml of water, we found that the reaction occurs faster. Thus, at 25 °C a good quantity of ZnO nanorods was produced just after 36 h. The diameter of the nanorods was, however, a little larger.

In Fig. 3a, we show the FESEM image of a Zn foil. In Fig. 3b, we show a FESEM image of ZnO nanorods obtained by the reaction of the Zn foil with water at 50 °C. The diameter of the nanorods varies between 80 and 400 nm, with an average value of 150 nm. The average length of the nanorods is 1 μm. The XRD pattern of these nanorods was also characteristic of the wurtzite structure.

The UV absorption spectrum of the ZnO nanorods gives the characteristic band round 365 nm (see inset in Fig. 4a) [24]. The room-temperature PL spectra of the ZnO nanorods (Fig. 4a) show a UV emission band at 380 nm

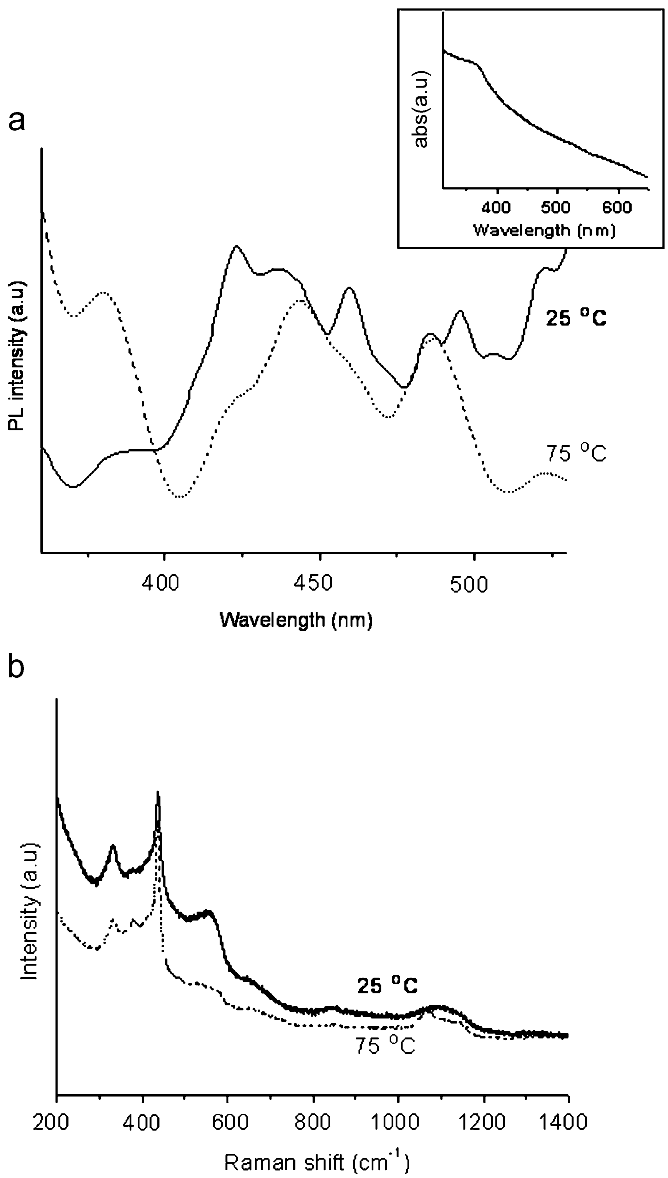

Fig. 4. (a) PL spectra of ZnO nanorods obtained at 25 and 75 °C, inset shows the UV–vis spectrum and (b) Raman spectra of ZnO nanorods at 25 and 75 °C.

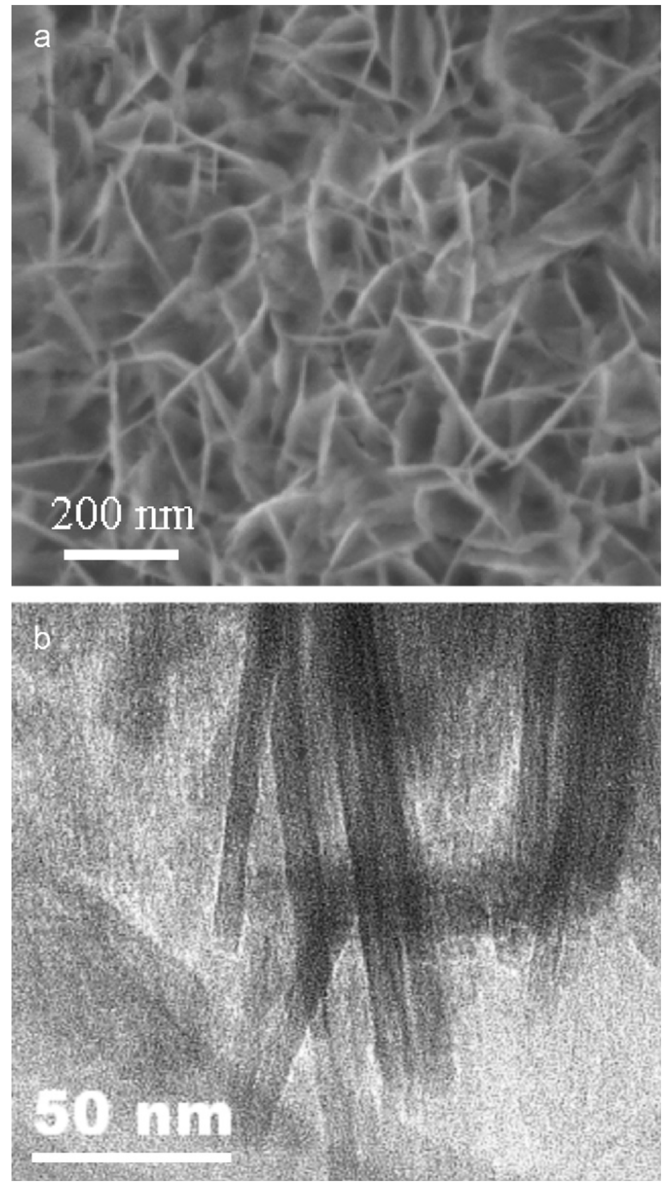

Fig. 5. (a) FESEM image of the $Al(OH)_3$ nanorods obtained by the reaction of Al metal powder with water at 75 °C and (b) TEM image of the $Al(OH)_3$ nanorods obtained at 50 °C.

due to the radiative recombination between the electrons in the conduction band and the holes in the valence band [20,25], and broad bands in the 420–530 nm range. The visible emission originates from the localized levels in the band gap [20]. The UV emission band is present prominently in the sample prepared at 75 °C, but is weak in the one prepared at 25 °C. The intensity of the UV emission band increases with the temperature of preparation of the nanorods, where as the intensity of the bands in the visible region decreases (Fig. 4a). This variation correlates well with that of the 580 cm^{-1} Raman band (Fig. 4b) which arises from intrinsic lattice defects [26]. The intensity of the 580 cm^{-1} Raman band decreases with the increasing temperature of the reaction. The Raman bands at 433 and 378 cm^{-1} are attributed to E_2 mode and A_1 (TO) modes, respectively [25,27]. The band at 331 cm^{-1} could arise from a multiphonon process [27].

The mechanism of the formation of ZnO nanorods can be described as follows. Zinc metal on reaction with water slowly gives out hydrogen. The oxygen liberated reacts with Zn metal to give the oxide as given by the following reaction:

$$Zn(s) + H_2O(l) \rightarrow ZnO(s) + H_2(g).$$

Here (s), (l) and (g) represent solid, liquid and gas, respectively. It may be noted that the evolution of hydrogen accompanying the reaction of Zn metal with water has been documented in the literature [22,23]. In the reaction of zinc metal with water, it is reported that ZnO is formed first and $Zn(OH)_2$ at a later stage [28,29]. The growth of ZnO nanorods probably occurs by making use of the oxide nuclei that may be present on the metal surface.

We have carried out the reaction of Al metal powder as well as of Al foil with water. Fig. 5a shows a FESEM image of the nanorods obtained by the reaction of Al powder with water at 75 °C. The nanorods are uniform in diameter varying between 7 and 14 nm, with an average diameter of 10 nm and an average length of 300 nm. Fig. 5b shows a TEM image of the $Al(OH)_3$ nanorods obtained at 50 °C. The diameters of the nanorods are in the 8–14 nm range with an average length of 250 nm. The XRD patterns of the nanorods (Fig. 2b) were characteristic of the bayerite phase of $Al(OH)_3$ ($a = 0.501$ nm, $c = 0.469$ nm, JCPDS data, card no. 12-0457). The reaction of Al foil with water also gave rise to $Al(OH)_3$ nanorods.

The formation of $Al(OH)_3$ nanorods by the reaction of Al metal with water can be explained as follows. Al metal also gives hydrogen on reaction with water [22,23]:

$$2Al(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3/2H_2(g).$$

Unlike the reaction of Zn metal with water, the reaction of Al metal with water gives rise to the hydroxide instead of the oxide. Formation of $Al(OH)_3$ by reaction of Al metal with water has been reported in the literature [30,31]. The formation of $Al(OH)_3$ is also promoted by the presence of Al_2O_3 [32]. We have confirmed the formation of $Al(OH)_3$ by IR spectroscopy. The Raman bands agree with those reported in the literature [33].

4. Conclusions

In conclusion, we have found a new and simple method for preparing ZnO nanorods by the reaction of the zinc powder or zinc foils with water at relatively low temperatures. Addition of ethylenediamine to water favors the formation of the ZnO nanorods. Thus, the reaction time is considerably reduced in the presence of ethylenediamine. Detailed and systematic studies would be necessary to optimize the conditions for obtaining nanorods of the desired dimensions and other characteristics. Reaction of Al powder or Al foils with water gives rise to $Al(OH)_3$ nanorods. The formation of ZnO and $Al(OH)_3$ nanorods from the metals are both governed by the basic reaction between the metals and water giving hydrogen. The growth of the nanorods could be occurring at the small oxide nuclei that may be present on the metal surfaces.

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