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# Application of Statistical Design Strategies to Optimize the Preparation of CuO Nanoparticles by Hydrothermal Technique

**Reda Mohamed[1,2*], Ibreheem Mkhalid[1], Elham Azaam[1]**

[1]Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah, KSA; [2]Central Metallurgical R&D Institute, CMRDI, Cairo, Egypt.
Email: *redama123@yahoo.com

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## ABSTRACT

*Synthesis of CuO nanoparticles by hydrothermal technique in presence of cetyltrimethylammonium bromide* (*CTAB*) *as surfactant was carried out by statistically designed experiments based on Box Behnken method. Reaction parameters as time*, *temperature and surfactant concentration have been studied to show their effect on CuO particle size and morphology. The results of experimental design indicate that the surfactant concentration*, *reaction time and temperature were significant in CuO particles were characterized using XRD and SEM. These work findings showed that CuO nanoparticles were formed at* 100*˚C. On other hand, their crystallinity was improved with rising temperature from* 100 *to* 200*˚C to achieve particle size of CuO in the range of* 49 - 92 *nm.*

***Keywords***: *Statistical Design*, *CuO*, *Nanoparticles*, *Surfactant*, *Hydrothermal*

## 1. Introduction

Nanocrystalline semiconductor particles have drawn considerable interest in recent years because of their special properties such as a large surface to-volume ratio, increased activity, special electronic properties and unique optical properties as compared to those of the bulk materials [1,2]. The oxides of transition metals are an important class of semiconductors, which have applications in magnetic storage media, solar energy transformation, electronics and catalysis [3-12]. Among the oxides of transition metals, CuO has attracted much attention because it is the basis of several high-Tc superconductors. CuO is a semiconducting compound with a narrow band gap and used for photoconductive and photothermal applications [13]. However, up to now, the reports on the preparation and characterization of nanocrystalline CuO are relatively few contrariwise to other transition metal oxides such as zinc oxide, titanium dioxide, tin dioxide and iron oxide. Recently methods for the preparation of nanocrystalline CuO have been reported as the sonochemical method [14], sol-gel technique [15], one-step solid state reaction method at room temperature [16], electrochemical method [17], thermal decomposition of precursors [18], and co-implantation of metal and oxygen ions [19], hydrothermal [20-22]. The optimum conditions and the interaction between the parameters for preparation of CuO nanosized particles are not determined yet; in this work statistically designed experiments (Box Behnken method) have been performed to study the synthesis of nanoparticles CuO via a low-temperature hydrothermal technique with and without surfactant as a function of the surfactant concentration, reaction time, and temperature.

## 2. Experimental

CuO nanoparticles were synthesized as follow: equal volume of $Cu(NO_3)_2 \cdot 3H_2O$ and urea NaOH are mixed in presence of a cetyltrimethylammonium bromide (0 - 5 m mol) at room temperature with magnetic stirring. $Cu(OH)_2$ precipitate are formed instantaneously. The $Cu(OH)_2$ precipitate was separated by decantation and washed by water several times. Suspension of $Cu(OH)_2$ hydrothermally treated in a teflon-lined autoclave at 100, 150 and 200˚C for different period from 1-5 hours. After hydrothermal treatment, the samples were centrifuged and dried at 110˚C for 24 hours. Observation of surface morphology was performed using a scanning electron microscope (SEM JEOL model JSM5410). X-ray powder

diffraction (XRD) patterns were conducted at room temperature (RT) using Bruker axs, D8 advance using Cu Kα radiation at a wavelength 0.154 nm. Box Benhken experimental design for the variables is shown **Table 1**. Plots of the response surface, contours, and the best predictive models for estimating the variable response were developed. The Box-Behnken design in **Table 1** can fit the following model [23];

$$E(y) = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \sum_{j=1}^{3} \beta_{ij} x_i x_j \quad (1)$$

where y is the estimate of the response variable and Xi's are the independent variables [surfactant concentration, time and temperature] that are known for each experimental run. The parameters $\beta_0, \beta_i$, and $\beta_{ij}$ are the regression parameters.

## 3. Results and Discussions

In the precipitation and hydrothermal process, the CuO powders form by two reactions according to the following equations:

$$Cu(NO_3)_2 + 2\ NaOH \rightarrow Cu(OH)_2 + 2\ NaNO_3 \quad (2)$$

$$Cu(OH)_2 \xrightarrow{Hydrothermal} CuO + H_2O \quad (3)$$

Copper nitrate reacts with sodium hydroxide to form copper hydroxide that needs to be converted into the desired CuO product by hydrothermal method. X-ray diffraction and SEM results confirm the crystallinity of CuO with a small primary crystal size below 70 nm, respectively. There are three variables for preparation of CuO nanoparticles via hydrothermal process: surfactant concentration, temperature and time. The optimum conditions using experimental design have been revealed.

### 3.1. Effect of Synthetic Variables on CuO Particles Size

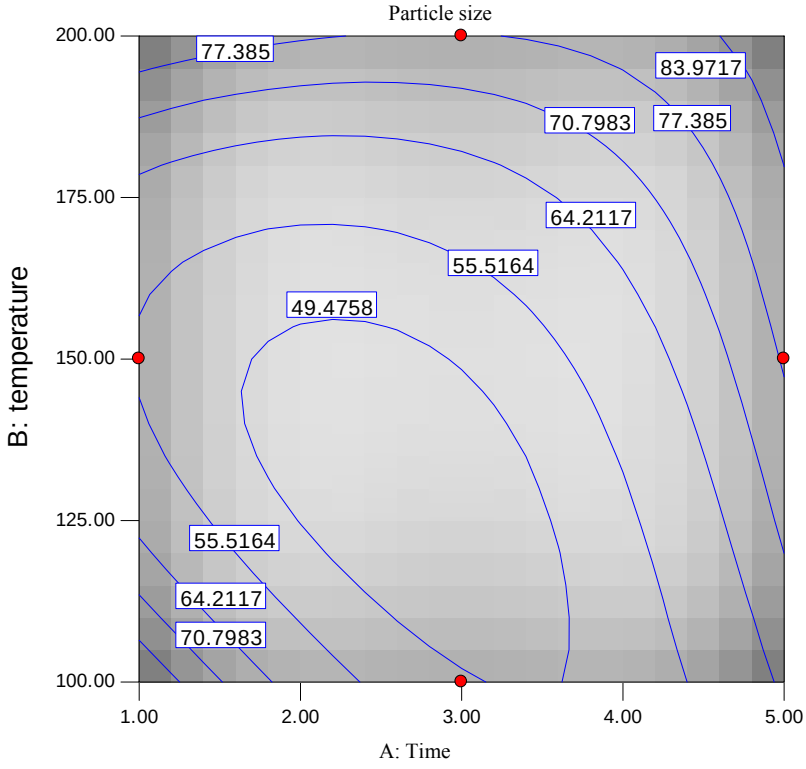
**Figure 1** shows that the effect of reaction time and temperature on CuO particle size (0, 2.5 and 5 mmol surfactant). The particles size was increased from 50 to 84 nm with increasing hydrothermal time from 1 to 5 hours in absence of surfactant as shown in **Figure 1(a)**. Moreover, we noticed that with increasing temperature from 100 - 200˚C the particles size increased from 64 to 84 nm after 3 hours. The lowest particle size, 49 nm, was achieved at low surfactant concentrations and temperature 125˚C. At 3 mmol surfactant concentration, the particles size growth was dependent on reaction time, (**Figure 1(b)**). Moreover, the particles size increment can be performed with rising the reaction temperature. The contour shown in **Figure 1(c)**, at 5 mmol surfactant concentration, illustrates that the particles size can be controlled through tuning reaction time and temperature. The surfactant addition showed pronounceable influence on growth of CuO nanoparticle that can be followed by observing the particles size of sample prepared in absence and presence of surfactant. However the lowest particle size can be achieved at 150˚C for 1 hour without surfactant. Interaction graph for the particles size of CuO as a function of temperature and time at 2.5 mmol surfactant concentration is shown in **Figure 1(d)**. It reveals that the particles size of sample prepared at 100˚C is much larger than 200˚. This unexpected behavior might be due to removal part of CTAB attached the $Cu(OH)_2$ surface during washing step the before the hydrothermal treatment. Surfactant concentration, temperature and time have a significant role for reducing CuO particle size.

All the experimental data was collected at the 3-D cu-

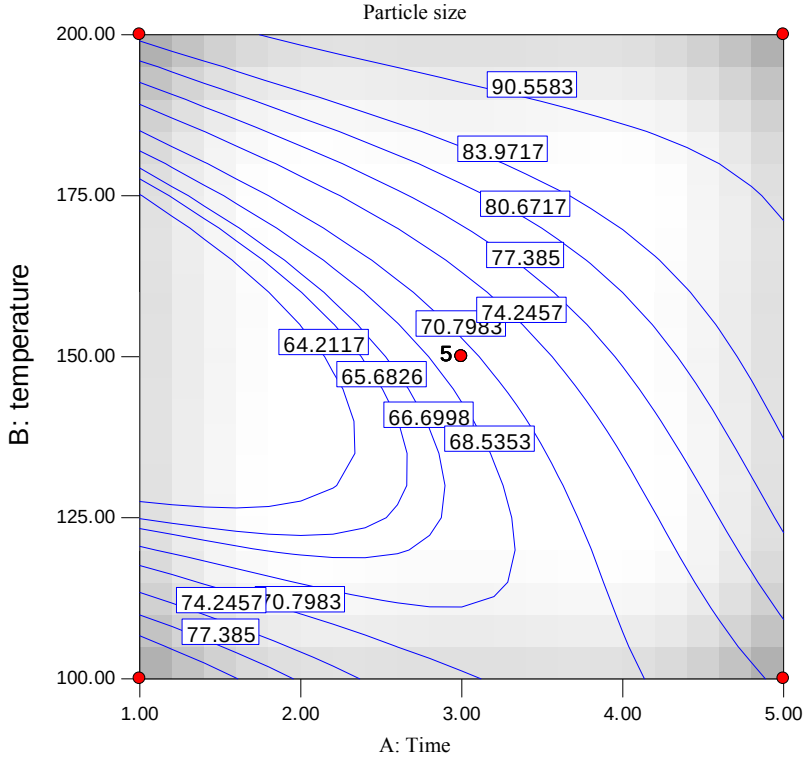
**Table 1. Experimental Box Behnken Design with the 3 levels and 3 variables utilized in the experiment.**

| Run No. | Coded Factor Levels | | | Particle size, nm |
|---|---|---|---|---|
| | Time, hr | Temperature, °C | Surfactant concentration, mmol | |
| R1 | 1.00 | 100.00 | 2.50 | 88 |
| R2 | 5.00 | 100.00 | 2.50 | 75 |
| R3 | 3.00 | 150.00 | 2.50 | 70 |
| R4 | 5.00 | 200.00 | 2.50 | 95 |
| R5 | 1.00 | 100.00 | 2.50 | 88 |
| R6 | 3.00 | 100.00 | 0.00 | 50 |
| R7 | 3.00 | 150.00 | 2.50 | 70 |
| R8 | 3.00 | 100.00 | 5.00 | 82 |
| R9 | 1.00 | 200.00 | 2.50 | 85 |
| R10 | 3.00 | 150.00 | 2.50 | 69 |
| R11 | 3.00 | 200.00 | 5.00 | 105 |
| R12 | 5.00 | 150.00 | 5.00 | 85 |
| R13 | 3.00 | 150.00 | 2.50 | 71 |
| R14 | 3.00 | 150.00 | 2.50 | 70 |
| R15 | 3.00 | 200.00 | 0.00 | 77 |
| R16 | 1.00 | 150.00 | 0.00 | 55 |
| R17 | 5.00 | 150.00 | 0.00 | 78 |

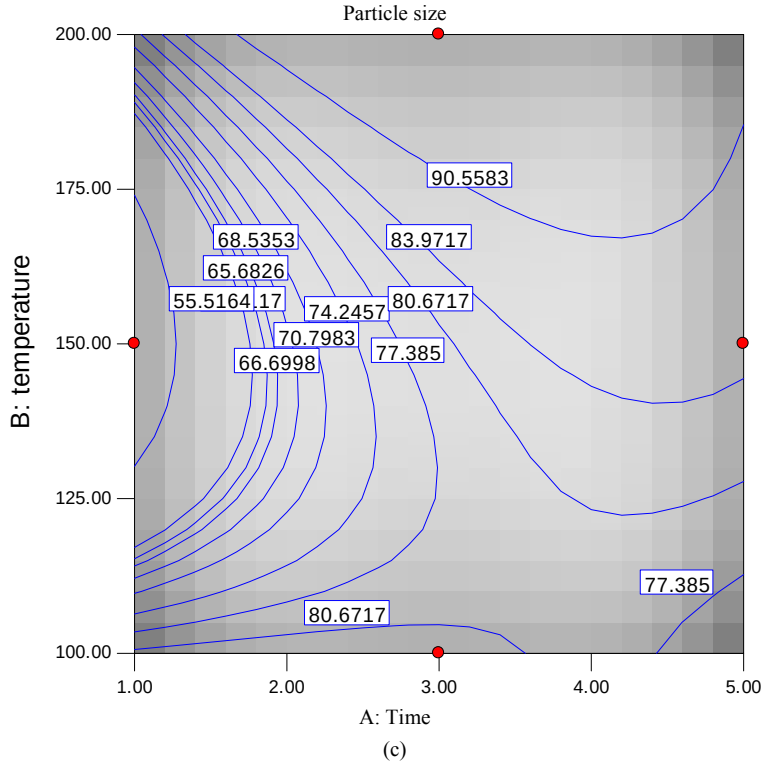



(a)

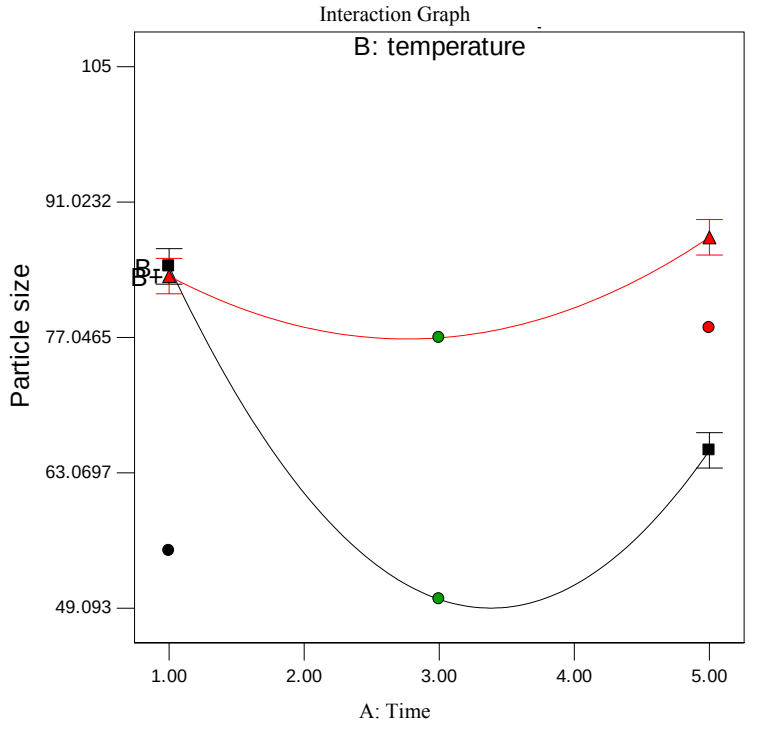



(b)




(c)




(d)

**Figure 1. (a) Contour plots for the effects of time and temperature on CuO particles size at surfactant conc. = Zero; (b) Contour plots for the effects of time and temperature on CuO particles size at surfactant concentration 2.5 mmol; (c) Contour plots for the effects of time and temperature on CuO particles size at surfactant concentration 5 mmol; (d) Interaction graph for the effect of time and temperature at zero surfactant concentration.**

bic as shown in **Figure 4**. The data revealed that particles size was ranged from 65 to 92 nm. At low temperature, 100˚C, and long reaction time without surfactant, the particle size was 65 nm. Rising temperature to 200˚C the particles size increased to 83 nm. On the other hand, at low temperature and short reaction time without surfactant the particle size was 88 nm. With rising temperature to 200˚C and surfactant concentration to 5mmol, the particles size was increased to 92 nm. Under such conditions, low surfactant concentration would be desirable for less aggregation.

The diagnostic results provide plot that can be used to analyze the data, which is plot of predicted values as a function of experimentally observed values for the particle size of CuO when the surfactant concentration, time and temperature are changed. These plot show that there is a linear relationship between the experimentally observed and predicted values from the model, and also that the differences between observed and predicted values are in the range of ± 1%. These indicate that experiments were conducted well and the results are not carrying any significant error. Also the standard deviation was 0.71 and $R^2$ 0.9994.

### 3.2. XRD Patterns

The XRD patterns of five CuO powders were determined and similar results were obtained. Here, R2, R3, R11 and R15 were selected as an example to reveal the effect of temperature and surfactant concentration on the XRD patterns as shown in **Fiure 3**. There are no noticeable changes in the crystallographic patterns and intensity ratios among peaks. But, a clear sharpening and attenuation of peaks can be observed with increasing the temperature. Pure CuO powder is formed only after hydro-

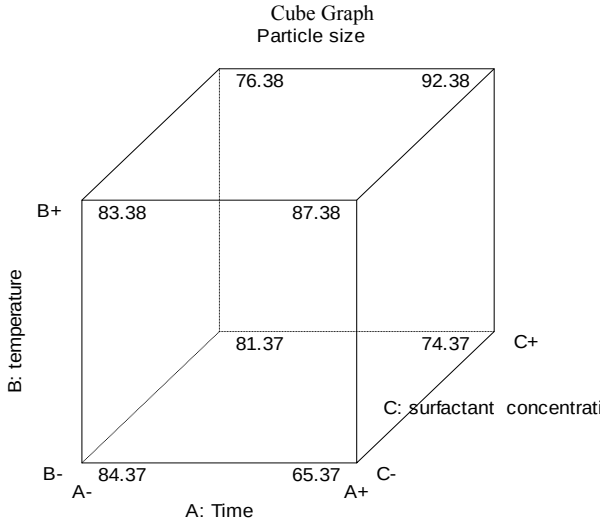



**Figure 2. 3-D plot for all experimental data.**

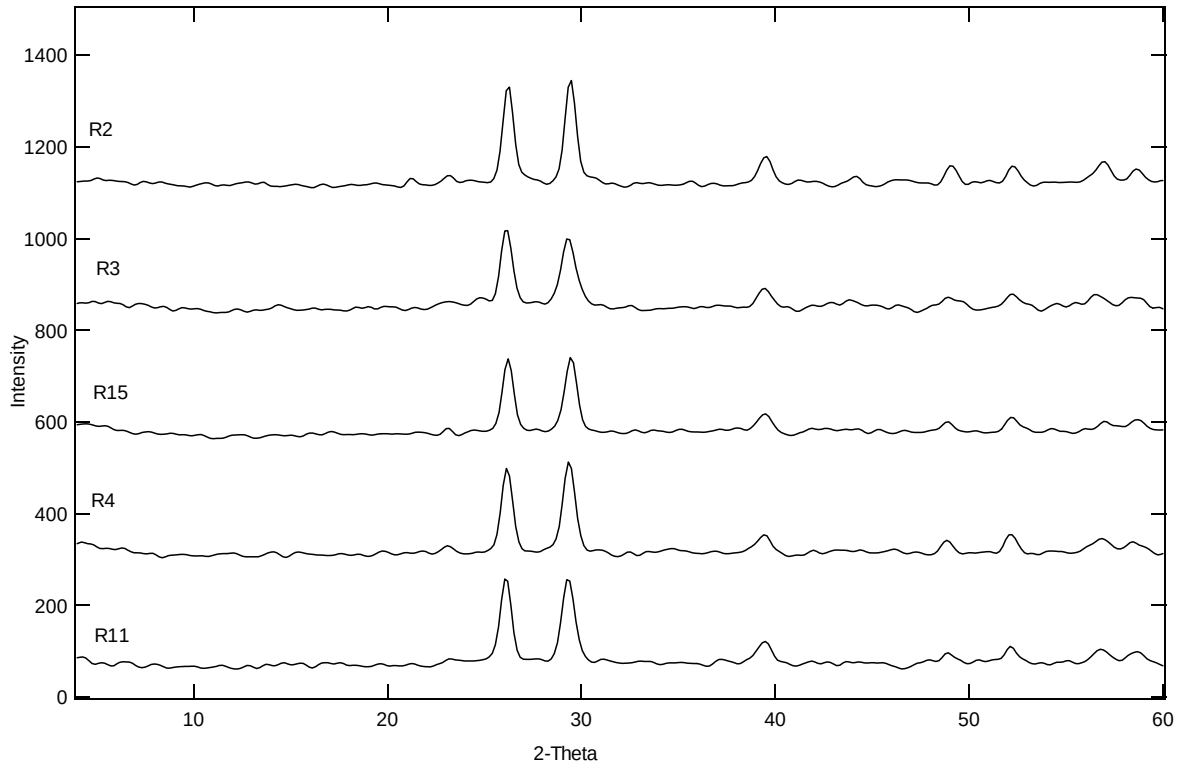



**Figure 3. XRD patterns of CuO nanoparticles for R2, R3, R11 and R15 samples.**

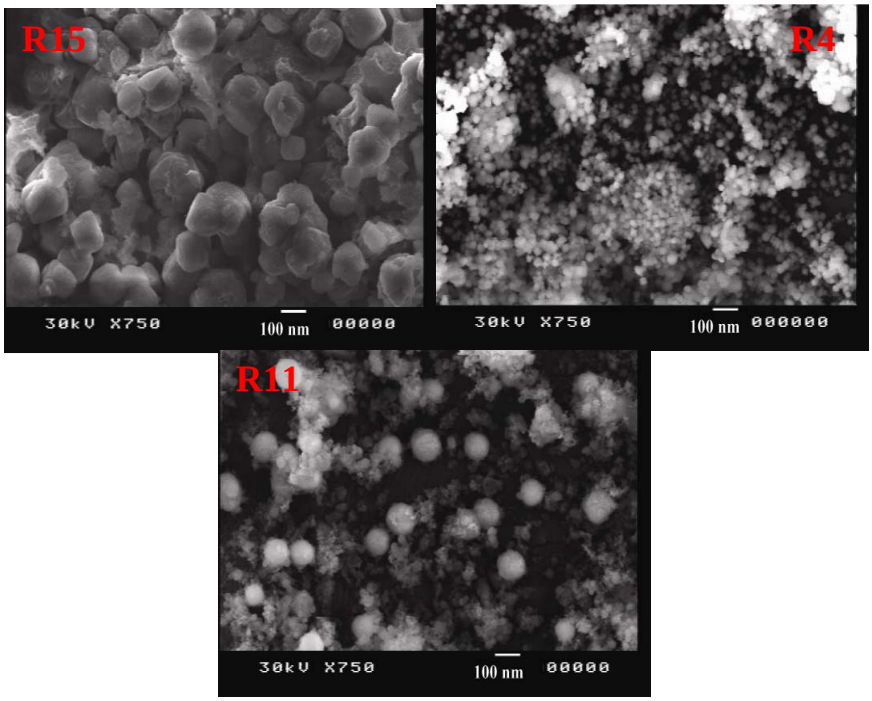



**Figure 4. SEM surface morphology of R4, R11 and R15.**

thermal heating at 100˚C. In general, the peak sharpening in XRD patterns can be ascribed to the increasing of crystallite size. On other word, the increase in the intensity of diffraction peaks is attributed to the increase in the crystallinity of the obtained powder [24-25].

### 3.3. SEM Morphology

The SEM micrographs of CuO powder prepared at different conditions are presented in **Figure 4**. R4, R11 and R15 are selected to be representative samples for all different conditions. At R15 without surfactant, particle shape of CuO powder is cubic. R4 and R11 with surfactant concentration of 2.5 and 5 mmol, the particle morphology are become spherical after surfactant addition. This means that, CTAB as surfactant is playing an important role for modifying the particles morphology.

## 4. Conclusions

Statistically designed experiments based on Box Behnken method were achieved to synthesize CuO nanoparticle in presence CTAB as surfactant by hydrothermal technique. CuO is formed only after hydrothermal heating at 100˚C. Compared to other method for synthesizing copper oxide powders, the reaction conditions are considerably moderate. It was found that, the surfactant concentration, reaction time and temperature were significant in tuning the particle size. The morphology of CuO particles was modified, from cubic structure to spherical one, using CTAB surfactant. The particle sizes of the CuO produced are ranged from 49 to 92 nm.

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