Enhanced Humidity Sensing Response of SnO$_2$/Silicon Nanopillar Array by UV Irradiation

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Abstract: In this work, a silicon nanopillar array was created with nanosphere lithography. SnO$_2$ film was deposited on this nanostructure by magnetron sputtering to form an SnO$_2$/silicon nanopillar array sensor. The humidity sensitivity, response time, and recovery time were all measured at room temperature (25 $^\circ$C) with UV or without UV irradiation. As a result, the humidity sensitivity properties were improved by enlarging the specific surface area with ordered nanopillars and irradiating with UV light. These results indicate that nanostructure sensors have potential applications in the field of sensors.

Keywords: humidity sensing; SnO$_2$ film; silicon nanopillar array; UV light

1. Introduction

Gas sensors with a metal oxide semiconductor (MOS) have received much attention in recent years [1–8]. MOS sensors depend on the change of a metal oxide semiconductor layer in resistance or capacitance, which is induced by the interaction between a surface and ambient gas. Many materials, such as ZnO, WO$_3$, and SnO$_2$, are designed as gas sensors [9–16]. Due to the large interaction energy of chemisorption, these MOS gas sensors have good performance at high temperatures to overcome the energy limitations of rapid response and recovery time. This places significant pressure on gas sensor reliability and durability at high temperatures. For this reason, many researchers have focused on the development of room temperature MOS sensors [17–20].

Tin oxide is a sensitive material with a band gap of $E_g$ = 3.7 eV. Some recent papers demonstrated that nanostructured SnO$_2$ as a gas sensor has considerable humidity sensitivity [21–23]. As mentioned above, the high operating temperature is still a significant issue. One possible solution is to enlarge the specific surface area [24,25]. With more surface area, more gas molecules are adsorbed. An alternative efficient and inexpensive method is to apply UV light irradiation [26–28].

In our previous papers, the preparation and characterization of a silicon nanopillar array sensor were reported [29,30]. In addition, enhanced humidity sensitivity of the silicon nanopillar array sensor by UV light was also achieved [31]. In this paper, SnO$_2$ film was prepared by magnetron sputtering on a silicon nanopillar array to form an SnO$_2$/silicon nanopillar array humidity sensor. With UV light irradiation, SnO$_2$/silicon nanopillar array humidity sensing activity was improved. These results indicate that nanostructure sensors have potential applications in the field of sensors.
2. Experiment

2.1. Preparation of the Large-Area and Ordered Polystyrene Spheres Array

In this experiment, the Si nanopillar array was created by nanosphere lithography. A P-type silicon wafer (110) was used in this work. A long-range ordered polystyrene (PS) sphere monolayer was deposited on the silicon substrate by self-assembly. The PS spheres suspension (10 wt%) with 220 nm diameters was purchased from Duke Scientific Corporation (California, USA). An approximate 5 µL solution was applied to the silicon substrate by micropipette. The substrate with PS spheres was slowly dipped into deionized water in a glass basin, at which point the PS nanospheres slipped from the Si wafer to form a monolayer on the water surface. The monolayer was then taken to the prepared silicon wafer.

2.2. Preparation of Ordered Silicon Nanopillar Array

This silicon wafer was put into a reactive-ion etching (RIE) chamber. It was etched with CF₄ (30 W RF, 20 Sccm) for 3 min. In this process, Si was etched with the following reactions:

\[ \text{CF}_4 + e^- \rightarrow \text{CF}_3^+ + F + 2e^- \]  
\[ \text{Si} + 4F \rightarrow \text{SiF}_4 \uparrow \]

Here, the reducing rate of PS spheres is smaller than that of silicon. PS spheres were used as a mask and were reduced by plasma bombardment. As a result, the nanoscale pattern with PS sphere was transferred to form a silicon pillar array. In the next process, the substrate was put into a tetrahydrofuran (THF) solvent to remove all of the PS spheres.

2.3. Preparation of SnO₂/Silicon Nanopillar Array Sensor

SnO₂ film was deposited on the silicon nanopillar array by a sputtering instrument (JGP-560, SKY Technology Development, China) with the pressure of 1 × 10⁻⁴ Pa. A 99.99% pure SnO₂ target was deposited on the above Si substrate under a current density of 60 mA/cm², a power of 90 mW, and a deposition time of 2 min. After the sputtering process, the sample was thermally annealed at 1000 °C with oxygen for 1 h. The interdigital measurement electrodes of 1 × 1 cm² were prepared on the SnO₂ film surface. It was performed by electron-beam evaporation (EBV) in a vacuum of 3 × 10⁻⁴ Pa, with an evaporation current of 25 mA and a deposition time of 30 s. The width of the finger was 2 mm and the length was 10 mm. The gap parameters were the same as those of the finger.

2.4. Measurement of Humidity Sensing Properties

The humidity sensing properties of the SnO₂/silicon nanopillar array were assessed by measuring its capacitance variation with relative humidity (RH) levels of 11%, 34%, 56%, 75%, and 90% at room temperature. These humidity environments were provided by containing salt solution (MgCl₂, LiCl, KNO₃, NaCl, KCl, and Mg(NO₃)₂) in air–glass chambers.

3. Discussion and Results

Figure 1a shows a scanning electron microscopy (SEM) image of the ordered PS sphere array. The periodic single layer PS sphere array was fabricated on a silicon wafer, which displayed a classic honeycomb, close-packed structure with a period of 220 nm (PS sphere diameter). Figure 1b shows an SEM image of the Si nanopillar array. The diameter of the pillar was approximately 120 nm. This demonstrates that the honeycomb, close-packed structure was well transferred from the PS sphere to the silicon wafer surface. As shown in Figure 1c, the SnO₂ film was deposited onto the silicon nanopillar array. The surface morphology of the silicon nanopillar array with SnO₂ was maintained without decomposition. The size was 130 nm, which was bigger than the fresh silicon nanopillar array.
Figure 1d is an atomic force microscopy (AFM) image of the silicon nanopillar array with SnO$_2$ film. It demonstrates the oblique view of the silicon nanopillar array with SnO$_2$ film. The height of pillar was approximately 110 nm. The X-ray diffraction patterns of the SnO$_2$ film are shown in Figure 2. These indicate that a SnO$_2$ film with a crystalline property was homogeneously deposited on the Si nanopillar array.

![Figure 1. (a) Scanning electron microscopy (SEM) image of the ordered polystyrene (PS) sphere array. (b) SEM image of the silicon nanopillar array. (c) SEM image of the silicon nanopillar array with SnO$_2$. (d) Atomic force microscopy (AFM) image of the silicon nanopillar array with SnO$_2$.](image)

![Figure 2. X-ray diffraction patterns of SnO$_2$.](image)

In our case, the capacitance response was measured under four different frequencies—50 Hz, 200 Hz, 1 kHz, and 5 kHz. The SnO$_2$/silicon nanopillar array humidity sensing activity was studied with UV light irradiation. As a point of comparison, the SnO$_2$ film on the flat surface silicon wafer (SnO$_2$/Si) was also studied. Here, the humidity response $R$ is defined as:

$$R = \frac{C_{RH}}{C_{11}}$$  \hspace{1cm} (3)
where \( C_{11} \) is the capacitance at RH = 11% and \( C_{RH} \) is the capacitance at a certain RH (34%, 56%, 75%, and 90%). Figure 3 shows the humidity response curves measured under four frequencies. As seen in Figure 3, all four figures show the same result, that humidity response for SnO\(_2\)/silicon nanopillar array sensors increased with RH increasing, which indicates that SnO\(_2\)/silicon nanopillar arrays can be used as humidity sensors. The response of the SnO\(_2\)/silicon nanopillar arrays was better than that of SnO\(_2\)/Si, as shown in Figure 3. This phenomenon might have been caused by enlarging the specific surface area with an ordered nanopillar array. The more specific surface area, the more water vapor was adsorbed. Furthermore, humidity responses decreased with the increase in applied frequency. It is because of this that water molecules can be polarized in an alternating electric field. Past studies have reported that polar water molecules are able to follow an alternating electric field with a relatively short relaxing time at low frequency, but a long relaxing time at a high frequency \([32,33]\). Capacitance is proportional to dielectric constant. When the testing frequency was 50 Hz (low frequency), the speed of the alternating electric field was low and the polarized water molecules were likely to follow. At this frequency, the dielectric constant remained stable. When the testing was 200 Hz, 1 kHz, and 5 kHz (high frequency), the speed of the alternating electric field was high and it was difficult for polarized water molecules to catch up. This results in the decrease of the dielectric constant, which causes an abatement of the sensor capacitance.

![Figure 3. Humidity response curves measured under four frequencies: (a) 50 Hz, (b) 200 Hz, (c) 1 kHz, (d) 5 kHz.](image)

To improve humidity sensitivity, UV-activated irradiation was carried out. These measurements were studied in a quartz glass under UV light irradiation at room temperature (25 °C). UV light was provided by a light-emitting diode (LED). Considering both the linearity and the response of the abovementioned studies, the applied frequency was 1 kHz. The humidity responses with and without UV are shown in Figure 4. The inset illustrates the schematic diagram of the SnO\(_2\)/silicon nanopillar array sensor with UV light. Three different power intensities (25 mW/cm\(^2\), 15 mW/cm\(^2\), and 5 mW/cm\(^2\)) of UV light with a wavelength of 300 nm were applied in our work. As shown, increasing power produced a greater response. The optimal response was obtained with 25 mW/cm\(^2\). The response increased across the entire testing RH range with UV light. Table 1 shows the outcome of the humidity
response with UV (25 mW/cm²) and without UV. As can be seen from Table 1, the increase was 20% at 11% RH. In the other case, the increase was approximately 50%. The maximum response increase was 58% at 56% RH.

![Figure 4](image-url)  
**Figure 4.** The humidity responses with and without UV. The inset illustrates the schematic diagram of the SnO₂/silicon nanopillar array sensor with UV light.

| 11% RH | 34% RH | 56% RH | 75% RH | 90% RH |
|--------|--------|--------|--------|--------|
| Without UV Response | 1 | 2.3 | 4.8 | 7.3 | 10.1 |
| With UV Response | 1.2 | 3.5 | 8.6 | 10.8 | 15.4 |
| Response Increase | 20% | 52% | 58% | 48% | 52% |

The humidity sensing mechanism of the UV-activated silicon nanopillar array sensor is illustrated in Figure 5. The photogenerated electrons and holes, induced by UV light, might be a major contributor. Without UV irradiation, the chemisorbed oxygen ion (O₂⁻) is thermally stable. Due to the large adsorption energy, it is difficult to be removed from the SnO₂ surface (Figure 5a) [34]. With UV irradiation, the electrons and holes are generated on the interface between SnO₂ and the silicon nanopillar array. The adsorbed oxygen ions interact with the photoinduced hole, causing the oxygen gas to be desorbed according to the following reaction (Figure 5b):

$$hv \rightarrow h^+ + e^-$$  \hspace{1cm} (4)

$$O_2^- + h^+ \rightarrow O_2 \uparrow.$$  \hspace{1cm} (5)

Meanwhile, the ambient oxygen molecules interact with photoelectrons to form the additional photoinduced oxygen ions as shown in the following scheme (Figure 5c):

$$O_2 + e^- \rightarrow O_2^-.$$  \hspace{1cm} (6)

These additional photoinduced oxygen ions are combined with water molecules by covalent bonds (Figure 5d). Figure 6 shows the energy band diagram of the nanostructure of SnO₂/Si according to the Anderson model. E_F is the Fermi level position, E_c and E_v are the conduction and valence band edge, E_g is the band gap, ΔE_c and ΔE_F are the band discontinuities, ΔE_S is the electron affinity energies of Si and SnO₂. Under UV irradiation, SnO₂ and Si absorb photon energy to generate
electrons and holes. As $\chi_{\text{Si}}$ is smaller than $\chi_{\text{SnO}_2}$, the electrons flow from the Si conduction band to SnO$_2$. The process was enhanced as more electrons appeared on the surface of SnO$_2$. Therefore, more water molecules were absorbed with UV irradiation to condense liquid water than without UV. It was found that the sensor capacitance raises rapidly to improve the humidity sensitivity.

![Figure 5. The UV-activated humidity sensing mechanism of the silicon nanopillar array sensor.](image)

Figure 6. The energy band diagram of the nanostructure of SnO$_2$/Si.

The response and recovery time of the sensor was also measured. $C$ is the instantaneous capacitance of this SnO$_2$/silicon nanopillar array sensor, and $C_0$ is either the final or initial value. The response time is defined as the time taken to go from $C/C_0 = 0\%$ to $90\%$. The recovery time is defined as the time taken to go from $C/C_0 = 100\%$ to $10\%$. Here, the response and recovery times were measured by switching the humidity between RH = 11\% and 90\% under the frequency of 1 kHz. Figure 7 shows the response and recovery time under RH = 90\%. With UV, the response time was 19\ s and the recovery time was 180\ s. Without UV, the response time was 28\ s and the recovery time was 155\ s. Furthermore, Figures 8a and 8b show the response and recovery times when the relative humidity switches from 11\% RH to 34\%, 56\%, 75\%, and 90\%, respectively. Both with and without UV irradiation, the response time decreased with the increase of humidity. However, the recovery time increased with the increase of humidity under UV irradiation. This is mainly because more water vapor condenses liquid water on the surface of SnO$_2$/silicon nanopillar array at the same time under a high RH, but the liquid water becomes more difficult to desorb with the increase of humidity. The fastest response time was 19\ s at 90\% RH with UV and the fastest recovery time was 65\ s at 11\% RH without UV. Table 2 summarizes the humidity sensing performances of our work and other humidity sensors.
reported. It notes that the performances of our sensors are significantly superior to others, not only in terms of sensitivity but also in response and recovery times.

**Figure 7.** The response and recovery times under RH = 90%.

**Table 2.** The performances of humidity sensors from this work and other reports.

| Materials                        | RH  | Sensitivity | Response Time (s) | Recovery Time (s) | Reference |
|----------------------------------|-----|-------------|-------------------|-------------------|-----------|
| SnO₂/silicon nanopillar array    | 90% | 16          | 19                | 180               | This work |
| SnO₂                             | 95% | ~2          | 26                | 45                | [35]      |
| SnWO₄-SnO₂                        | 90% | ~4          | 30                | 100               | [36]      |
| MoS₂/Si                          | 90% | 3           | 36.3              | 57.6              | [37]      |
| Graphene                         | 84% | 2           | 180               | 180               | [38]      |
4. Conclusions

In this study, SnO$_2$/silicon nanopillar array sensors were prepared. With UV light irradiation, SnO$_2$/silicon nanopillar array humidity sensing activity was improved. As a result, the humidity sensitivity response showed better linearity at the testing frequency of 1 kHz. Furthermore, the increase in response reached above 50% with UV irradiation. With the increase of humidity, the response time decreased and the recovery time increased. The fastest response time was 19 s and the lowest recovery time was 180 s at 90% RH with UV. The lowest time was 50 s and the fastest recovery time was 65 s at 11% RH without UV.

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References

1. Song, X.; Qi, Q.; Zhang, T.; Wang, C. A humidity sensor based on KCl-doped SnO$_2$ nanofibers. *Sens. Actuators B Chem.* 2009, 138, 368–373. [CrossRef]

2. Tricoli, A.; Righettoni, M.; Teleki, A. Semiconductor gas sensors: Dry synthesis and application. *Angew. Chem. Int. Ed.* 2010, 49, 7632–7659. [CrossRef] [PubMed]

3. Miller, D.R.; Akbar, S.A.; Morris, P.A. Nanoscale metal oxide-based heterojunctions for gas sensing: A review. *Sens. Actuators B Chem.* 2014, 204, 250–272. [CrossRef]

4. Jung, D.; Kim, J.; Lee, G.S. Enhanced humidity-sensing response of metal oxide coated carbon nanotube. *Sens. Actuators A Phys.* 2015, 223, 11–17. [CrossRef]

5. Tian, H.L.; Fan, H.Q.; Li, M.M.; Ma, L. Zeolitic Imidazolate Framework Coated ZnO Nanorods as Molecular Sieving to Improve Selectivity of Formaldehyde Gas Sensor. *ACS Sens.* 2016, 1, 243–250. [CrossRef]

6. Staerz, A.; Berthold, C.; Russ, T. The oxidizing effect of humidity on WO$_3$ based sensors. *Sens. Actuators B Chem.* 2016, 237, 54–58. [CrossRef]

7. Tyagi, P.; Sharma, A.; Tomar, M.; Gupta, V. A comparative study of RGO-SnO$_2$ and MWCNT-SnO$_2$ nanocomposites based SO$_2$ gas sensors. *Sens. Actuators B Chem.* 2017, 248, 980–986. [CrossRef]

8. Abbasi, A.; Sardroodi, J.J. Investigation of the adsorption of ozone molecules on TiO$_2$/WSe$_2$ nanocomposites by DFT computations: Applications to gas sensor devices. *Appl. Surf. Sci.* 2018, 436, 27–41. [CrossRef]

9. Liu, X.; Chen, N.; Han, B.Q.; Xiao, X.; Chen, G.; Djerdj, I.; Wang, Y. Nanoparticle cluster gas sensor: Pt activated SnO$_2$ nanoparticles for NH$_3$ detection with ultrahigh sensitivity. *Nanoscale* 2015, 7, 14872–14880. [CrossRef] [PubMed]

10. Li, W.; Liu, J.; Chao, D.; Bai, G.; Xu, J.; Ren, Q.; Li, J. Fabrication of Ordered SnO$_2$ Nanostructures with Enhanced Humidity Sensing Performance. *Sensors B Chem.* 2017, 17, 2392. [CrossRef] [PubMed]

11. Yao, Y.; Ji, F.; Yin, M.L.; Ren, X.; Ma, Q.; Yan, J.; Liu, S.F. Ag Nanoparticle-Sensitized WO$_3$ Hollow Nanosphere for Localized Surface Plasmon Enhanced Gas Sensors. *ACS Appl. Mater. Interfaces* 2016, 8, 18165–18172.

12. Tomer, V.K.; Duhan, S. Highly sensitive and stable relative humidity sensors based on WO$_3$ modified mesoporous silica. *Appl. Phys. Lett.* 2015, 106, 063105. [CrossRef]

13. Hsu, C.L.; Su, I.L.; Hsueh, T.J. Tunable Schottky contact humidity sensor based on S-doped ZnO nanowires on flexible PET substrate with piezotronic effect. *J. Alloys Compd.* 2017, 705, 722–733. [CrossRef]

14. Mahjoub, M.A.; Monier, G.; Robert-Goumet, C. Synthesis and Study of Stable and Size-Controlled ZnO-SiO$_2$ Quantum Dots: Application as a Humidity Sensor. *J. Phys. Chem. C* 2016, 120, 11652–11662. [CrossRef]

15. Li, X.G.; Zhao, Y.Y.; Wang, X.Y.; Wang, J.; Gaskov, A.M.; Akbar, S.A. Reduced graphene oxide (rGO) decorated TiO$_2$ microspheres for selective room-temperature gas sensors. *Sens. Actuators B Chem.* 2016, 230, 330–336. [CrossRef]

16. Nikfarjam, A.; Salehifar, N. Improvement in gas-sensing properties of TiO$_2$ nanofiber sensor by UV irradiation. *Sens. Actuators B Chem.* 2015, 211, 146–156. [CrossRef]
17. De Lacy Costello, B.P.J.; Ewen, R.J.; Ratcliffe, N.M.; Richards, M. Highly sensitive room temperature sensors based on the UV-LED activation of zinc oxide nanoparticles. *Sens. Actuators B Chem.* 2008, 134, 945–952. [CrossRef]
18. Zhang, Y.; Kolmakov, A.; Lilach, Y.; Moskovits, M. Electronic control of chemistry and catalysis at the surface of an individual Tin oxide nanowire. *J. Phys. Chem. B* 2005, 109, 1923–1929. [CrossRef]
19. Tian, Z.R.; Voigt, J.A.; Liu, J.; McKernie, B.; Mcdermott, M.J.; Rodriguez, M.A.; Konishi, H.; Xu, H. Complex and oriented ZnO nanostructures. *Nat. Mater.* 2003, 2, 821–826. [CrossRef]
20. Arena, A.; Donato, N.; Saitta, G.; Bonavita, A.; Rizzo, G.; Neri, G. Flexible ethanol sensors on glossy paper substrates operating at room temperature. *Sens. Actuators B Chem.* 2010, 145, 488–494. [CrossRef]
21. Tomer, V.K.; Duhan, S. In-situ synthesis of SnO$_2$SBA-15 hybrid nanocomposite as highly efficient humidity sensor. *Sens. Actuators B Chem.* 2015, 212, 517–525. [CrossRef]
22. Georgieva, B.; Podolesheva, I.; Spasov, G.; Pirov, J. Nanosized thin SnO$_2$ layers doped with Te and TeO$_2$ as room temperature humidity sensors. *Sensors* 2014, 14, 8950–8960. [CrossRef]
23. Feng, H.L.; Li, C.; Li, T.; Diao, F.; Xin, T.; Liu, B.; Wang, Y. Three-dimensional hierarchical SnO$_2$ dodecahedral nanocrystals with enhanced humidity sensing properties. *Sens. Actuators B Chem.* 2017, 243, 704–714. [CrossRef]
24. Zhu, Y.H.; Yuan, H.; Xu, J.Q.; Xu, P.C.; Pan, Q.Y. Highly stable and sensitive humidity sensors based on quartz crystal microbalance coated with hexagonal lamelliform monodisperse mesoporous silica SBA-15 thin film. *Sens. Actuators B Chem.* 2010, 144, 164–169. [CrossRef]
25. Tu, J.C.; Wang, R.; Geng, W.C.; Lai, X.Y.; Zhang, T.; Li, N.; Yue, N.L.; Li, X.T. Humidity sensitive property of Li-doped 3D periodic mesoporous silica SBA-16. *Sens. Actuators B Chem.* 2009, 136, 392–398. [CrossRef]
26. Korotcenkov, G.; Cho, B.K. Ozone measuring: What can limit application of SnO$_2$-based conductometric gas sensors. *Sens. Actuators B Chem.* 2012, 161, 28–44. [CrossRef]
27. Park, S.; An, S.; Mun, Y.; Lee, C. UV-enhanced NO$_2$ gas sensing properties of SnO$_2$-core/ZnO-shell nanowires at room temperature. *ACS Appl. Mater. Interfaces* 2013, 5, 4285–4292. [CrossRef]
28. Nguyen, D.C.; Nguyen, D.Q. NO gas sensing kinetics at room temperature under UV light irradiation of In$_2$O$_3$ nanostructures. *Sci. Rep.* 2016, 6, 35066.
29. Li, W.; Hu, M.Y.; Ge, P.P.; Wang, J.; Guo, Y. Humidity sensing properties of morphology-controlled ordered silicon nanopillar. *Appl. Surf. Sci.* 2014, 317, 970–973. [CrossRef]
30. Li, W.; Dai, E.; Bai, G.; Xu, J. Depth-dependent humidity sensing properties of silicon nanopillar array. *Sens. Actuators B Chem.* 2016, 237, 526–533. [CrossRef]
31. Li, W.; Ding, C.; Cai, Y.; Liu, J.; Wang, L.; Ren, Q.; Xu, J. Enhanced humidity sensitivity with silicon nanopillar array by UV light. *Sensors* 2018, 18, 660. [CrossRef]
32. Sauerbrey, G. The use of quartz oscillators for weighing thin layers and for micro-weighing. *Z. Phys.* 1959, 155, 206–222. [CrossRef]
33. Morrison, S.R. *The Chemical Physics of Surface*; Plenum Press: New York, NJ, USA, 1977.
34. Shukla, S.K.; Rastogi, R.P.; Singh, N.B. Nanosize SnO$_2$ through nitrate eutectic mixture for humidity sensors. *Emerg. Mater. Res.* 2015, 4, 12–17. [CrossRef]
35. Sundaram, R. Comparative study on micromorphology and humidity sensitive properties of thick film and disc humidity sensors based on semiconducting SnWO$_4$–SnO$_2$ composites. *Sens. Actuators B Chem.* 2007, 124, 429–436. [CrossRef]
36. Liu, Y.J.; Hao, L.Z.; Gao, W.; Liu, Y.M.; Li, G.X.; Xue, Q.Z.; Guo, W.Y.; Wu, Z.P.; Liu, X.H.; Zeng, H.Z.; et al. Growth and humidity-dependent electrical properties of bulk-like MoS$_2$ thin films on Si. *RSC Adv.* 2015, 5, 74329–74335. [CrossRef]
37. Ghosh, A.; Late, D.J.; Panchakarla, L.S.; Govindaraj, A.; Rao, C.N.R. NO$_2$ and humidity sensing characteristics of few-layer graphenenes. *J. Exp. Nanosci.* 2009, 4, 313–322. [CrossRef]

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