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Highly integrated synthesis of heterogeneous nanostructures on nanowire heater array†

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We have proposed a new method for the multiplexed synthesis of heterogeneous nanostructures using a top-down fabricated nanowire heater array. Hydrothermally synthesized nanostructures can be grown only on the heated nanowire through nanoscale temperature control using a Joule heated nanowire. We have demonstrated the selective synthesis of zinc oxide (ZnO) nanowires and copper oxide (CuO) nanostructures, as well as their surface modification with noble metal nanoparticles, using a nanowire heater array. Furthermore, we could fabricate an array of heterogeneous nanostructures *via* Joule heating of individual nanowire heaters and changing of the precursor solutions in a sequential manner. We have formed a parallel array of palladium (Pd) coated ZnO nanowires and gold (Au) coated ZnO nanowires, as well as a parallel array of ZnO nanowires and CuO nanospikes, in the microscale region by using the developed method.

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There has been great interest in and active research on localized temperature control in the micro/nanoscale because it can provide novel platforms for studying and manipulating local chemical and biological phenomena. Individually controllable microheaters have been developed for selective cell lysis based on local temperature control without disturbing the surrounding areas.^{1,2} The small heat capacity of micro-heaters enables fast temperature switching as well as localized chemical reaction control.^{3–6} Localized heating by micro-heaters has also been utilized for the selective chemical synthesis of nanomaterials such as silicon nanowires,³ zinc oxide (ZnO) nanowires,⁴ carbon nanotubes⁵ and gallium nitride/ZnO coaxial nanorods,⁶ which can be integrated as active components into functional micro/nano-electronic devices such as chemical sensors, biosensors and optoelectronic devices.⁷

Recently, efforts on temperature localization have progressed from microscale down to nanoscale, due to the need to control a temperature field with higher spatial resolution. Nanoscale localized heating has been applied in various fields

that require temperature controllability in nanoscale areas such as cell manipulation,⁸ modulation of electrical properties of materials^{9–11} and enhancement of sensing responses.^{12–14} Researchers have suggested several methods for the heating of nanoscale regions, in order to satisfy specific purposes. Precise cancer cell lysis was conducted using a selective cluster of light absorbing nanoparticles on cancer cell membranes and providing local heating through irradiation with a laser beam.⁸ Phase change materials could be integrated into a nanoscale region through the self-heating of phase-change nanowires or Joule heating of carbon nanotubes.^{9–11} A fast response time for hydrogen sensing was obtained when sensing materials such as palladium nanowires and palladium-decorated silicon nanowires were self-heated by applying an appropriate electrical voltage.^{12–14} In our previous work,^{14–16} a nanoscale temperature field, created by a top-down fabricated nanowire array, was used for the chemical manipulation of polymeric materials (*e.g.* polymer decomposition or crosslinking),^{15,16} selective surface functionalization of nanowire sensors^{14,16} and localized synthesis of one dimensional nanomaterials.¹⁵ We have demonstrated the great potential and versatile capabilities of top-down fabricated nanowire array heaters.

In the present work, we have developed a novel method for the fabrication of a highly integrated, multiplexed array of heterogeneous nanostructures in a microscale region by using an array of top-down fabricated nanowire heaters and modulation of the chemical environment for a liquid-phase reaction. Individually addressable nanowire heaters create a localized temperature field in the nanoscale region and thus induce the selective synthesis of nanomaterials. By switching the heated

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nanowire and the precursor solution, one can fabricate a multiplexed array of different nanomaterials on individual nanowire heaters. Here, we have synthesized an array of metal oxide nanostructures and functionalized them with catalytic metal nanoparticles, all in the liquid phase. We demonstrate the fabrication of (1) an array of two ZnO nanowire bundles functionalized with different metal nanoparticles (gold (Au) and palladium (Pd)) and (2) an array of two different metal oxide nanostructures (ZnO nanowires and CuO nanospikes) as a proof-of-concept for our method.

Multiplexed arrays of heterogeneous nanostructures can be fabricated by utilizing selective Joule heating of nanowire heaters and different liquid precursor chemicals, as shown in Fig. 1. As reported in our previous paper,¹⁵ the temperature increase generated by the Joule heating of a single nanowire heater is highly localized in the nanoscale region. Nanostructures are synthesized within the heated nanoscale region by an endothermal chemical reaction of precursor chemicals that absorb heat from the nanowire heater. Different types of nanostructures can be synthesized by employing different precursor chemicals. Also, pre-synthesized nanostructures can be heated again using underlying nanowire heaters for further surface decoration with nanoparticles to enhance the functionality of the nanostructures.

Material selection and geometry design of the nanowire heater device are crucial factors for achieving accurate heat localization in the nanoscale. Top-down nanofabrication of a nanowire heater array is clearly advantageous for integration purposes since the nanowire heaters can be patterned with accurate and arbitrary geometries at precise locations in a wafer scale. Using the advantages of a top-down approach, a

nanowire heater array was fabricated by the following process: first, a 330 nm thick silicon oxide (SiO_2) layer was formed on a silicon (Si) substrate *via* thermal oxidation. Then, electron beam lithography was performed on a polymethylglutarimide/poly(methyl methacrylate) (PMGI/PMMA)-coated substrate with an acceleration voltage of 30 kV. The PMGI and PMMA were used as a lift-off layer and an electron beam resist layer, respectively. After the development of an exposed area, chromium (10 nm) and gold (60 nm) layers were deposited using electron beam evaporation, followed by a lift-off process. A silicon nitride layer with a thickness of 300 nm was deposited, using a plasma enhanced chemical vapor deposition (PECVD) process, on the metal nanowire heater array device to prevent any unwanted electrochemical reactions occurring during the hydrothermal synthetic process.

A ZnO thin film, as a seed layer for the ZnO nanowire synthesis, was coated onto the entire surface of the nanowire heater array device using DC sputtering. The precursor solution for ZnO nanowire synthesis was prepared using a mixture of zinc nitrate (25 mM), hexamethylenetetramine (25 mM) and polyethylenimine (6 mM) in deionized (DI) water.¹⁷ The precursor solution was dispensed using a small PDMS-based liquid container mounted on the nanowire heater array device. Then, an electrical bias was applied across the nanowire heater to generate localized heat for the hydrothermal synthesis of ZnO nanowires. As shown in Fig. 2(a), ZnO nanowires were formed along the central region of the nanowire heater. The lengths of the ZnO nanowires were at a maximum at the center of the nanowire heater and gradually decreased to zero at a distance

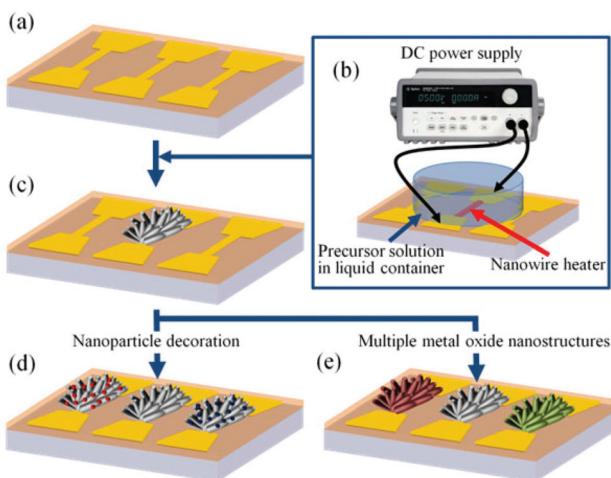


Fig. 1 Schematic of the fabrication process for a multiplexed array of heterogeneous nanostructures: (a) top-down fabricated nanowire heater array, (b) simple setup for the fabrication process based on localized hydrothermal synthesis by Joule heating of a nanowire array, (c) hydrothermally synthesized nanostructures by selective heating of a nanowire heater, (d) selective surface functionalization of pre-synthesized nanostructures, and (e) synthesis of heterogeneous nanostructures onto each nanowire heater.

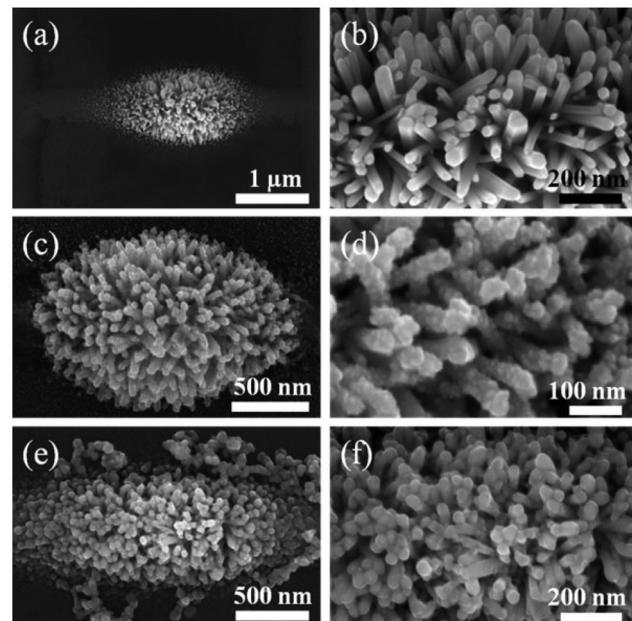


Fig. 2 SEM images of (a, b) ZnO nanowires synthesized on a nanowire heater by applying the electrical bias of 0.58 V for 300 s; (c, d) Au nanoparticle coated ZnO nanowires, formed by applying an electrical bias of 0.50 V for 60 s; and (e, f) Pd nanoparticle coated ZnO nanowires, formed by applying an electrical bias of 0.49 V for 60 s.

of 1 μm from the center. This phenomenon is due to the localized temperature distribution that occurs along the nanowire heater with a parabolic temperature profile and a maximum at the center. The results of numerical simulation in Fig. S1(a) and S2(a)[†] show that the maximum temperature of the nanowire heater is 92 °C when 0.6 V is applied across the nanowire heater and that the temperature distribution on the top surface of the silicon nitride layer has a parabolic profile.

Surface modification is crucially important for improving or modifying the functionalities of nanomaterials. Accordingly, numerous methods for the surface modification of nanomaterials based on physical and chemical processes have been developed.^{18,19} In the present study, we have developed an alternative route to the multiplexed and selective surface modification of nanomaterials by using localized heating with nanowire heaters in a liquid environment. The surface of the synthesized nanowires can be further modified with functional nanoparticles by localized hydrothermal synthesis using an underlying nanowire heater. In this work, we have used Au and Pd nanoparticles for the surface decoration of ZnO nanowires. Au and Pd precursor solutions were prepared by adding a sodium citrate solution (30 mM, sodium citrate dihydrate dissolved in DI water) into aqueous solutions of NaAuCl₄ (1 mM, dissolved in DI water) or K₂PdCl₄ (1 mM, dissolved in DI water), respectively, and by adjusting the pH of the metal precursor solution to 11 using sodium hydroxide (NaOH).²⁰ Then, the Au or Pd precursor solution was dispensed using a PDMS container attached to the device with pre-synthesized ZnO nanowires. Selective surface modification was realized by individual Joule heating of a nanowire heater located underneath the ZnO nanowires. Since the nanowire heaters could be used for both the synthesis of ZnO nanowires and their surface modification with metal nanoparticles, selective synthesis and localized surface modification of nanowires could be achieved in a self-aligned manner without any complicated alignment processes.

In order to decorate the ZnO nanowires with Au nanoparticles, an electrical bias of 0.50 V was applied across the nanowire heater. This electrical bias was lower than that required for the ZnO nanowire synthesis since the reduction of Au ions occurs at a lower temperature (~90 °C) than that for the ZnO nanowire synthesis (~95 °C).²¹ For the same reason, the electrical bias used for the Pd nanoparticle synthesis was also lower than that used for the ZnO nanowire synthesis. Fig. 2(c and d) show the surface morphology of ZnO nanowires decorated with Au nanoparticles after a localized reduction of Au precursors. Au nanoparticles with an average size of 10–20 nm were densely and uniformly decorated along the surface of the ZnO nanowires. Discrete nanoparticles, instead of a continuous and smooth thin film, were formed on the surface of the ZnO nanowires (see Fig. S3[†] for high resolution SEM image). As shown in Fig. 2(e and f), Pd nanoparticles were also formed on the surface of the ZnO nanowires, but with a much lower surface density than that of the Au nanoparticles.

We further investigated the effects of an applied electrical bias across the nanowire heater and heating time on the

surface morphology of Au nanoparticle coated ZnO nanowires. Fig. 3 shows the SEM images and electron dispersive spectroscopy (EDS) spectra of Au nanoparticle coated ZnO nanowires formed under different electrical bias and time periods. Faster reduction of the Au ions and formation of denser and larger Au nanoparticles on the ZnO nanowires was observed at higher electrical bias across the nanowire heater. When an electrical bias of 0.46 V was applied across the nanowire heater for 60 seconds, Au nanoparticles with diameters of 10–20 nm were formed along the ZnO nanowires with low surface density (<10%), as shown in Fig. 3(b). On the other hand, when a higher electrical bias (0.50 V) was applied for the same period of nanowire heating, Au nanoparticles were coated on the ZnO nanowires with much higher density (>50%), as shown in Fig. 3(c). Fig. 3(d–f) show the surface morphology of the ZnO nanowires coated with Au nanoparticles after different heating times (30, 60 and 120 s), with the same electrical bias (0.50 V) applied across the nanowire heater. After 30 seconds (Fig. 3(d)), a few small Au nanoparticles had been formed on the surface of the ZnO nanowires with very low surface density. Here, it should be noted that the small atomic concentration (0.67%) of Au shown in Fig. 3(g) may also be due to the underlying Au nanowire heater as well as instrument noise during EDS analysis. On the contrary, many Au nanoparticles were densely coated on the surface of the ZnO nanowires after 60 seconds. After 120 seconds, more Au nanoparticles were formed around the surface of the nanowires (see Fig. 3(f) for a low resolution SEM image, Fig. 3(i) for EDS results and Fig. S4[†] for a high resolution SEM image). However, it can be observed that the ZnO nanowires were partially etched and damaged during the formation of the Au nanoparticles. The etching of the ZnO nanowires after a longer period of Au nano-

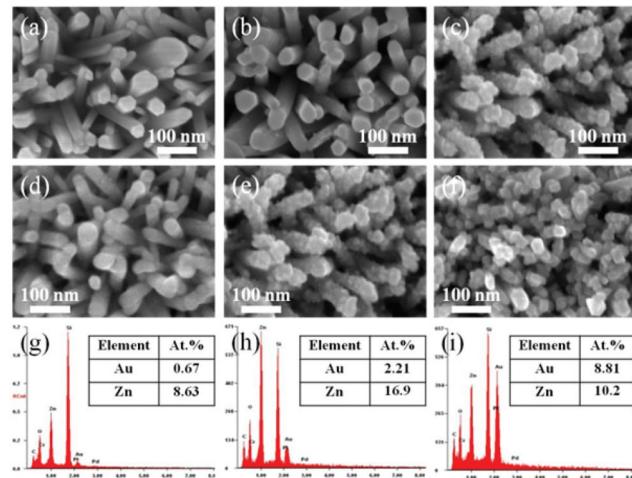


Fig. 3 The effects of electrical bias on the Au nanoparticle coating of ZnO nanowires: (a) SEM image of pristine ZnO nanowires before surface modification; (b–c) SEM images of the Au nanoparticles after coating at an electrical bias of 0.46 V (b) and 0.50 V (c), both for time periods of 60 s; effect of synthesis time period: (d–f) SEM images and (g–i) EDS results of the Au nanoparticle coating on ZnO nanowires at the electrical bias of 0.50 V for (d, g) 30 s, (e, h) 60 s and (f, i) 120 s.

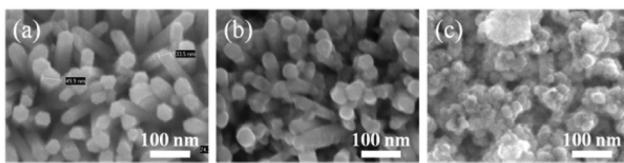


Fig. 4 SEM images obtained after the synthesis of Pd nanoparticles on ZnO nanowires using different electrical bias across the nanowire heater: (a) 0.45 V, (b) 0.49 V and (c) 0.53 V; same heating period of 60 s.

particle formation can also be verified by the decreased atomic percentage of Zn in the EDS analysis (see Fig. 3(h) and (i)). This etching phenomenon may be due to a decrease in the pH of the Au precursor solution, which is caused by the consumption of OH⁻ ions during the reduction of AuCl₄¹⁻. It is known that ZnO can be dissolved through reaction with H⁺ ions in an acidic aqueous solution²² as follows:



However, the decomposition of ZnO nanowires can be suppressed by controlling the concentration of the Au precursor, the heating temperature and the time period. Therefore, the coating of ZnO nanowires with a required amount of Au nanoparticles can be successfully achieved without damaging the integrity of ZnO nanowires.

Fig. 4 shows SEM images of Pd nanoparticle coated ZnO nanowires after different voltages were applied across the nanowire heater, for the same time period. Being similar to the results of Au nanoparticle coating, the synthesis rate of Pd nanoparticles was increased at higher reaction temperature by applying a higher electrical bias across the nanowire heater. Pd nanoparticles cannot be easily observed when a bias of 0.45 V had been applied across the nanowire heater. (Fig. 4(a)) Although Pd nanoparticles could be found on the surface of ZnO nanowires after a bias of 0.49 V, the size and surface density of the synthesized Pd nanoparticles were small (Fig. 4(b)). When the applied voltage was 0.53 V, fast reduction of the Pd nanoparticle precursor occurred due to the high reaction temperature and a dense layer of Pd nanoparticles covered the entire surface of the ZnO nanowires (see Fig. 4(c) and S5†).

The application of a nanowire heater array can be further extended to the fabrication of a multiplexed array of heterogeneous nanostructures. As mentioned earlier, a top-down fabrication approach allows accurate alignment, arbitrary geometry definition and individual electrical addressing of multiple nanowires in an array configuration. Electrical control of individual nanowire heaters realizes parallel or serial synthesis of heterogeneous nanostructures in the configuration of a highly integrated array. We have demonstrated two examples as a proof-of-concept for this technology: (a) array I: Au coated ZnO nanowires and Pd coated ZnO nanowires, and (b) array II: ZnO nanowires, CuO nanospikes and ZnO nanowires. In array I, ZnO nanowires were selectively synthesized along two neighboring nanowire heaters and then

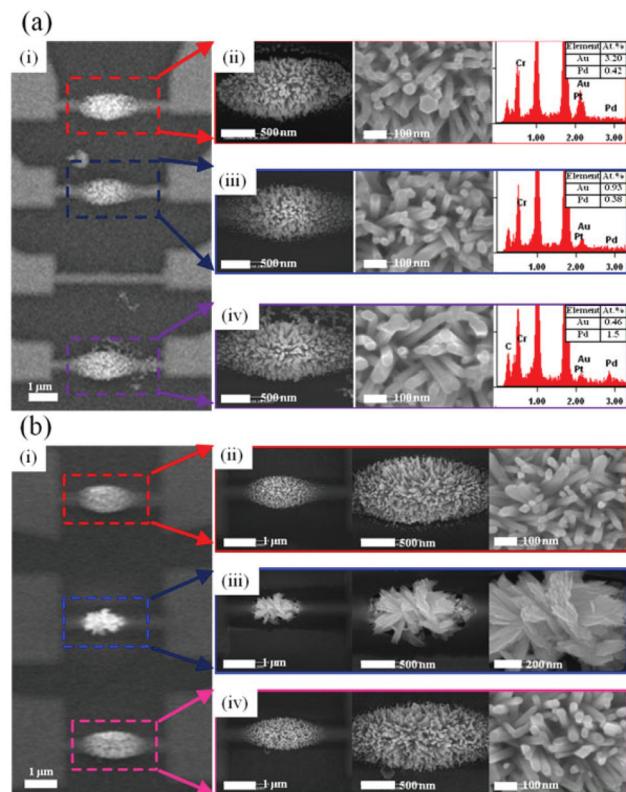


Fig. 5 Multiplexed array of heterogeneous nanostructures synthesized on a nanowire heater array: (a) SEM images and EDS results of an array of Au coated ZnO nanowires and Pd coated ZnO nanowires, (i) array of nanowire heaters with synthesized nanostructures on heater #1, #2 and #4, (ii) Au coated ZnO nanowires on heater #1, (iii) pristine ZnO nanowires on heater #2 and (iv) Pd coated ZnO nanowires on heater #4; (complete scans for the EDS results are shown in Fig. S3†) (b) SEM images of an array of ZnO nanowires, CuO nanospikes and ZnO nanowires: (i) array of nanowire heaters with synthesized nanostructures on heater #1, #2 and #3, (ii) ZnO nanowires on heater #1, (iii) CuO nanospikes on heater #2 and (iv) ZnO nanowires on heater #3.

functionalized with different metal nanoparticles. First, the ZnO nanowires were synthesized by localized hydrothermal reaction on three nanowire heaters (heater #1, #2 and #4 from top to bottom, see Fig. 5a). Then, ZnO nanowires on heater #1 were first decorated with Au nanoparticles by applying a voltage across nanowire heater #1 in the presence of the precursor solution for Au nanoparticle synthesis. After rinsing the surface of the device sample with DI water, the ZnO nanowires on heater #4 were decorated with Pd nanoparticles by Joule heating of nanowire heater #4 in the presence of the precursor solution for Pd nanoparticle synthesis. Here, 0.49 V was applied across nanowire heater #1 for 60 s to decorate the wire with Au nanoparticles and 0.54 V was applied across nanowire heater #4 for 30 s to decorate the wire with Pd nanoparticles. As observed in Fig. 5a, locally synthesized ZnO nanowires were surface-functionalized with Au and Pd on nanowire heaters #1 and #4, respectively. Although visual observation of the metal nanoparticles was not possible due to the small quantity, EDS spectra revealed the existence of Au and Pd on the two ZnO

nanowire bundles. It should be noted that a small atomic percentage (<1%) of Au and Pd could either result from EDS instrument noise or from the underlying Au nanowire heater. However, larger atomic percentages of Au (3.20%) and Pd (1.50%) were measured from the Au coated ZnO nanowires (on nanowire heater #1) and the Pd coated ZnO nanowires (on nanowire heater #4), respectively. This indicates the presence of surface modification with Au and Pd on each ZnO nanowire bundle. From the experimental results, it can be concluded that selective surface functionalization of ZnO nanowires with different noble metal nanoparticles in a nanoscale region can be obtained by controlling the local thermal energy using a nanowire heater array.

Array II was fabricated by sequential synthetic steps, forming heterogeneous nanostructures on each nanowire heater. Firstly, ZnO nanowires were synthesized on nanowire heaters #1 and #3 by using the localized hydrothermal synthesis process explained above. Secondly, CuO nanostructures were synthesized on nanowire heater #2 by changing the ZnO precursor to the CuO precursor²³ within the PDMS based liquid container and applying the electrical bias across the nanowire heater for 300 s. ZnO nanowires were selectively grown on nanowire heaters #1 and #3 and CuO nanostructures were selectively grown on nanowire heater #2, as shown in Fig. 5b. The nanostructures were selectively synthesized on each nanowire heater without significant cross-contamination or damage to the other nanostructures.

In summary, we have developed a novel method for the fabrication of a multiplexed array of heterogeneous nanostructures in a highly integrated manner by using a top-down fabricated nanowire heater array. Individual electrical addressing and heating control of nanowire heaters in a controlled chemical environment enables the fabrication of highly integrated and multiplexed array of heterogeneous nanomaterials. We have demonstrated two types of arrays: (a) Au coated ZnO nanowires and Pd coated ZnO nanowires, and (b) ZnO nanowires, CuO nanospikes and ZnO nanowires. This method can be extended to the fabrication of arrays of various nanomaterials, which can be controlled by temperature modulation. It is expected that multiplexed nanostructure arrays fabricated by this method could be used for various multifunctional nanodevices such as chemical sensors, biosensors, photonic devices and energy storage systems.

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