Programmed dielectrophoretic assembly of Pd nanoparticles for conductance control in VO₂ nanowires

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ABSTRACT

Recently, hybrid nanodevices consisting of more than one type of nanomaterial, have been an intense research topic as far as science and advanced functionalities of such systems are concerned. However, lack of controlled, scalable and directed assembly techniques for these hybrid systems, particularly the accurate assembly of nanoparticles (NPs) on nanowires (NWs), has resulted in their limited applications. In the present work, a development has been reported using dielectrophoresis (DEP) technique through which a controlled assembly of palladium (Pd) NPs on VO₂ NWs has been deposited. Furthermore, modulation in conductivity of VO₂ NWs as a function of the NPs density is electrically measured and interpreted through work-function dependent surface doping effect of the Pd NPs on VO₂ NWs. This well-controlled and scalable approach to functionalize VO₂ NWs by assembling Pd NPs is significant in the view of a huge potential of Pd NPs like sensor applications thus adding functionalities to VO₂ NWs. Our approach can be generalized for the large-scale assembly of a variety of NP-NW combination to fabricate advanced functional hybrid devices.

1. Introduction

The large surface-to-volume ratio of the nanowires (NWs) and nanoparticles (NPs) offers advantages for a variety of device application including biochemical sensors, field effect transistors, light emitting diodes, lasers and photodetectors [1–5]. Further, additional functionalization or improvement in properties can be achieved using the assembly of nanomaterials like NPs on NWs. Such hybrid assembly of NPs on NW can modulate the basic functionality or can altogether add a new function to the hybrid assembly. In such hybrid systems, one of the constituent nanomaterials either assists or modulates the properties of the other nanomaterial such as Pd NPs on ZnO or VO₂ NWs, thus improving the sensitivity in such devices [6–9]. The Pd NPs on VO₂ NW systems exhibit potential applications in ultrafast optical switches, memristors, electronic and gas-sensing devices as VO₂ NWs possess unique metal-insulator-transition (MIT) property (at ~ 68 °C) while Pd shows strong potential for highly sensitive and selective hydrogen gas sensing, such hybrid assembly can be used continuously modulate the physical property like MIT point or to add new functionality like utilizing Pd NPs for gas sensing [8,10–12]. However, exploiting the full potential of these hybrid nanosystems has been limited by the inability of controlled assembly of NPs i.e., to spatially manipulate and address the constituent nano-entities, in particular, NPs on NWs, on a large scale. Therefore, a controlled, cost effective, and innocuous assembly technique is required for smart tuning of NPs on NWs which would eventually lead to a controlled variability in device performance. Non-lithographic manipulation utilizing electromagnetic fields is a promising technology to achieve the goal of fine-tuning self-assembly. In this direction, dielectrophoresis (DEP) technique offers an inexpensive and straightforward alternative to assemble nanostructures into nanodevices and nanosystems.

DEP is a simple and scalable technique to align or assemble dielectric nanomaterials including NPs, NWs and a wide range of bioparticles at room temperature [13–15]. In DEP process, the
motion of polarizable NPs suspended in a medium is easily controlled by the applied non-homogeneous electric field. Further, this technique is relatively safe as it requires no chemical treatment, unlike other assembly techniques viz. metal salt precursors and solution chemistry method [16]. DEP has been used successfully in many different fields like for the separation of metallic carbon nanotubes from semiconducting one and due to its non-destructive nature, the technique is employed to assemble nanoparticles such as Au and ZnO nano colloids and for trapping entities like cells, bacterial species, and various size of DNA in the nanogaps [13]. In this work, we demonstrated the controlled assembly of Pd NPs on VO2 NW by DEP to modulate the conductivity of the NW in a controlled fashion. We have also shown that the coalesced NPs on the NW can be dispersed uniformly on its surface by controlling the DEP time, thereby achieving uniform and enhanced covering over the NW’s surface.

2. Experiment

2.1. Growth procedure of VO2 nanowires and device fabrication

The VO2 NWs were grown by physical vapor deposition method at atmospheric pressure without the use of a catalyst. In the beginning, 0.1 g of fine mesh VO2 (99.9%, Aldrich) powder was placed at the center of a 10 cm long quartz boat, where a pre-cleaned SiO2/Si substrate was located approximately 5 mm from the VO2 powder. This was followed by placing the quartz boat at the center of a quartz tube furnace, in which high-purity He carrier gas (99.999%) was injected at 300 sccm. The temperature of the furnace was increased to approximately 700 °C and the sample growth was allowed to proceed for 2 h. After the growth, the furnace was allowed to cool down to room temperature before removing the substrate. The length of most of the NWs falls in the range of 20–150 μm with a rectangular cross-section, randomly oriented in the plane of Si substrate. Raman measurements confirm that the nanowires are single crystalline monoclinic VO2 nanowires [10]. Scanning electron microscopy (SEM) image of a number of nanowires leads to an average width and height as 100–400 (±10) nm and 50–200 (±5) nm, respectively.

For device fabrication, the as-grown VO2 NWs were detached from the SiO2 substrate by ultra-sonication in isopropyl alcohol and dispersed onto another 300 nm SiO2/Si substrate. The metallic contacts were defined by using optical lithography and lift-off technique for Ti/Au (10/200 nm) electrodes. The samples were annealed subsequently in nitrogen for 1 min at 200 °C to improve the ohmic contact between the NW and metallic contacts. Fig. 1 illustrates the microscopy images of fabricated NW devices. Fig. 1(a) shows the optical microscopy image of the chip showing 20 electrodes connected by metal pads, while Fig. 1(b) and (c) show SEM images of the 4 μm gap patterned electrodes and a VO2 nanowire of 120 nm width, respectively. The separation between two consecutive electrodes is 4 μm with 20 electrodes on a single chip.

2.2. DEP method

The schematic of the experimental setup used for an a.c. DEP assembly is shown in Fig. 2(a). A function generator is connected directly to the chip electrode on one side and an oscilloscope to the other end. Prior to the DEP assembling, the chip was cleaned with acetone/IPA, while Pd NPs varying in diameter from 2 nm to 4 nm were suspended in de-ionized water and ultrasonicated to ensure for a uniform dispersion. One microliter of aqueous Pd NPs solution was taken in a micro-pipette for DEP processing in ambient temperature and relative humidity conditions set at 23 °C and 33%, respectively, in a controlled chamber.

In general, the assembly of NPs using DEP depends on frequency $f$ of the applied a.c. signal, peak-to-peak voltage $V_{pp}$ and duration of the DEP process [17–19]. Therefore, it is important to optimize the DEP parameters for successful assembly of Pd NPs on VO2 NWs.

During DEP, the spherical Pd NPs floating in deionized water get electrically polarized when a $V_{pp}$ was applied between a pair of coplanar Au electrodes separated by 4 μm. The spatial field profile near VO2 NW is inhomogeneous (higher intensity in the NW vicinity, unlike uniform field between the parallel electrodes) which results in an unbalanced force acting on Pd NPs. This unbalanced force propels the NPs towards the NW where they are finally assembled. In the presence of nonzero electric field gradient, the DEP force acting on the polarized NPs (having time-dependent dipole moment $\mu(t)$ in an a.c. field) is written as

$$ F(t) = \langle \mu(t).E(t) \rangle $$

where $E(t)$ is a time-dependent electric field. The ‘classical’ time-averaged DEP force due to nonuniformity of the electric field acting on a particle floating in a medium of dielectric permittivity $\varepsilon_m$ is given by Ref. [11].

$$ F_{DEP} = 2\pi a^3 \varepsilon_m Re[K(\omega)] |E_{rms}|^2 $$

Here $a$ is the radius of the NP, $K(\omega)$ is the Clausius–Mossotti factor and $E_{rms}$ is the rms value of the electric field. The Clausius–Mossotti factor is defined by Ref. [11].
120 nm VO2 NW after DEP of Pd NPs was carried out at fixed frequency of 1 MHz for a time duration of 180 s and at different peak-to-peak voltages of (b) 1 V, (c) 2 V, (d) 3 V, and (e) 4 V.

As discussed above, the density of the Pd NPs assembled on VO2 NW can be controlled by varying three key parameters i.e., the amplitude of the applied voltage $V_{pp}$, applied frequency $f$ and DEP processing time $t$. The impact of these parameters on the controlled assembly of Pd NPs can be optimized by varying one parameter at a time while fixing the other two parameters. SEM images in Fig. 2 (b)-(e) show the variation in the NPs density by increasing the amplitude of the applied voltage at fixed frequency of 1 MHz for 180 s. As DEP force acting on NP is implicitly related to $V_{pp}$, the density of Pd NPs is increased with higher $V_{pp}$ as seen from Fig. 2. In the next step, the response of NPs assembly with frequency variations is analyzed at a fixed $V_{pp}$ of 4.0 V and time of 180 s. As seen from Fig. 3 (a)-(d), an increment from 500 KHz to 1 MHz led to increased assembly of NPs while further step increments to 1.5 MHz and 2.0 MHz consequently showed the reverse effect on the density of NPs. This physical observation also reflects in the electrical measurements as discussed in the next section. After optimizing two critical parameters of DEP process i.e., applied voltage and frequency, time variation effects on the Pd NPs assembly are also studied by fixing $V_{pp}$ = 4.0 V and $f$ = 1 MHz and varying DEP time. Fig. 4 shows SEM images of VO2 NW after DEP with Pd NPs was carried out for time varying from 30 s to 180 s. It is seen that a negligible NPs assembly occurred when DEP was carried for 30 s but an appreciable increment in the NPs assembly was observed when the time was increased to 60 s. However, Pd NPs on VO2 NW coalesce instead of having monodispersed particle

\[ F_{DEP} \] Can be positive or negative depending upon various factors like frequency of the a.c. signal and the relative permittivities and conductivities of the NPs and the aqueous medium respectively. Positive value of $Re[K(w)]$ leads to a positive time-averaged DEP force pulling NPs towards the strong electric field regions while negative value of $Re[K(w)]$ leads to a negative time-averaged DEP force that repels NPs from the strong electric field regions. For Pd NPs, conductivity ($\sigma_p$) and permittivity ($\varepsilon_p$) are $9.5 \times 10^{12}$ $\mu$S/m and 6.25$\varepsilon_0$, respectively, while for deionized water, the values of conductivity ($\sigma_m$) and permittivity ($\varepsilon_m$) are 100 $\mu$S/m and 78$\varepsilon_0$, respectively. Here $\varepsilon_0$ is the vacuum permittivity. In our previous works [18–20], the behavior of $Re[K(w)]$ indicates positive DEP for frequencies up to several MHz of the applied a.c. signal.

3. Results and discussion

As discussed above, the density of the Pd NPs assembled on VO2 NW can be controlled by varying three key parameters i.e., the amplitude of the applied voltage $V_{pp}$, applied frequency $f$ and DEP processing time $t$. The impact of these parameters on the controlled assembly of Pd NPs can be optimized by varying one parameter at a time while fixing the other two parameters. SEM images in Fig. 2 (b)-(e) show the variation in the NPs density by increasing the amplitude of the applied voltage at fixed frequency of 1 MHz for 180 s. As DEP force acting on NP is implicitly related to $V_{pp}$, the density of Pd NPs is increased with higher $V_{pp}$ as seen from Fig. 2. In the next step, the response of NPs assembly with frequency variations is analyzed at a fixed $V_{pp}$ of 4.0 V and time of 180 s. As seen from Fig. 3 (a)-(d), an increment from 500 KHz to 1 MHz led to increased assembly of NPs while further step increments to 1.5 MHz and 2.0 MHz consequently showed the reverse effect on the density of NPs. This physical observation also reflects in the electrical measurements as discussed in the next section. After optimizing two critical parameters of DEP process i.e., applied voltage and frequency, time variation effects on the Pd NPs assembly are also studied by fixing $V_{pp}$ = 4.0 V and $f$ = 1 MHz and varying DEP time. Fig. 4 shows SEM images of VO2 NW after DEP with Pd NPs was carried out for time varying from 30 s to 180 s. It is seen that a negligible NPs assembly occurred when DEP was carried for 30 s but an appreciable increment in the NPs assembly was observed when the time was increased to 60 s. However, Pd NPs on VO2 NW coalesce instead of having monodispersed particle
assembly; the cause for this observation, at this stage, may be attributed to the incomplete dispersion behavior of the solvent resulting in the formation of NPs drops, though the exact reasons can be the topic for further separate study. This behavior of aggregated NPs is observed continuously for higher DEP time along with a continuous increase in the density of NPs cluster, which saturates at 180 s. For DEP time longer than 180 s, the coalesced NPs dispersed uniformly on the NW for 210, 240 and 270 s (See Supporting information) The possible reasons for this dispersion may lie in the solvent induced adhesive forces holding many nanoparticles in droplets and the dispersion occurs when the solvent dried up in the longer DEP process time.

To explore the effects of Pd NPs DEP and the associated assembly parameters (voltage, frequency, and time) on the electrical properties of VO₂ NWs, I-V characterization was carried out for all sets of voltage, frequency and time variations. In Fig. 5 (a), electric current shows negligible variations when the applied bias for DEP processes is \( V_{pp} = 1 \text{ V}, 2 \text{ V} \) and \( 3 \text{ V} \) while keeping the other parameters fixed. But this scenario changes for \( V_{pp} = 4 \text{ V} \) assembly, where a considerable improvement in the I-V characteristics was observed. The resistivity and conductivity variation plotted in Fig. 5 (b) further illustrate the quantitative change due to DEP voltage variation. This enhanced conductivity can be linked to the high assembly density of Pd NPs which acts like surface dopants through electron transfer from Pd NPs to VO₂ NW on the account of work function difference between them \( (\phi_{VO_2} - \phi_{Pd} = 5.15 \text{eV} - 5.01 \text{ eV} = 0.14 \text{ eV}) \). This is illustrated in Fig. 6 (a) and (b), where the band alignments before and after NPs attachment is illustrated along with the band profile along the horizontal cut line in the NW. Although Pd NPs are well known for catalytic dissociation of H₂ to form lower work function palladium hydrates (PdHₓ), which can further enhance the NW conductivity,
but such lowering of Pd work function under atmospheric condition can be ruled out because of the following reactions [21].

\begin{align}
H_2 \text{ in air} & \leftrightarrow 2H_{\text{on Pd surface}} \leftrightarrow 2H_{\text{on Pd-VO}_2 \text{ interface}} \\
2H_{\text{on Pd surface}} + O_2 \text{ in air} & \leftrightarrow 2(\text{OH})_{\text{on Pd surface}} \\
H_{\text{on Pd surface}} + (\text{OH})_{\text{on Pd surface}} & \leftrightarrow H_2O \\
H_2O_{\text{in air}} & \leftrightarrow H^+ + (\text{OH})^- \\
\end{align}

As it is clear from the above reactions that the effect of atmospheric H\textsubscript{2} on Pd NPs got canceled by the humidity in air through additional OH\textsuperscript{-} ions which react with adsorbed atomic hydrogen in Pd NPs to form water vapor, thus canceling any doping due to PdH\textsubscript{x} formation. A similar counter mechanism of water molecules also rule out any contribution due to a possible 'spill-over' of atomic hydrogen from Pd NPs to VO\textsubscript{2} NWs, which may have resulted in electron-phonon and electron-electron coupling induced conductivity modulation [8]. Though, at this point, contribution to overall conductivity by Pd NPs induced localized strain effect in VO\textsubscript{2} NW cannot be ruled out, but such effect can be neglected as the contact area between the Pd NPs and NW is negligibly small. It may be noted that the variation in the resistance of VO\textsubscript{2} NW due to the doping effect of Pd NPs can also affect its MIT properties like shift in MIT voltage or temperature. As the present work focus on the optimization of DEP parameters, therefore NPs induced variation in MIT properties of VO\textsubscript{2} NWs is beyond the scope of this study. However, the observed variation in the NW resistance is not an indication of MIT itself as an insulator-metal transition in VO\textsubscript{2} NWs usually involves an abrupt three-four order jump in the resistance whereas the variation in the resistance due to the DEP of PD NPs is below a single order of magnitude.

The effect of frequency variation on I-V characteristics is plotted in Fig. 5 (c) and (d), where the current characteristics follow NPs assembly density and peaked at 1 MHz. The increase in the current can also be explained through the doping effect of Pd NPs, whereas a fall in the conductivity enhancement beyond 1 MHz is observed. This is in good consistency with the physical observation in Fig. 3, where a relatively lesser NPs attachment to the NW was observed beyond 1 MHz. This variation is conjectured to be a reflection of the behavior of loss tangent (\tan\phi = \varepsilon''/\varepsilon'\text{, ratio of imaginary and real components of complex dielectric permittivity}) of the DEP medium.
(in our case, DI water, which passes its minimum value ~ $5 \times 10^{-3}$ at the frequency of ~1 MHz due to strong polar behavior of water molecules [22]. At higher frequencies, orientational degree of polarization for dipolar molecules sets in the dielectric loss giving rise to the reduction in the medium dielectric constant $\varepsilon_m$, which reduces the DEP assembly force and resulting in the lesser NPs attaching to NW.

After optimizing voltage and frequency, the time variation, which is also a critical parameter for controlling the assembly density, was carried out. Fig. 5 (e) and (f) show the current and conductivity variations with the DEP time. The time variations are accurately reflected in the electrical characteristics, showing a continuous increase in the conductivity with DEP time. This shows that once the basics parameters of voltage and frequency are optimized then a continuous and controlled NPs assembly density can be obtained using DEP time duration. This control of NPs assembly on the NW can have potential applications to add various functionalities related to the interaction of NPs with NWs in the hybrid device. Further, in the present case, the doping effect of NPs on the conductivity of NW can be enhanced further if the coalesced NPs are dispersed on the NW. This is shown in detail in the supporting information, where the variation in resistance almost doubled when the NPs are dispersed for the DEP time longer than 180 s.

In order to test the repeatability of this process, DEP has been carried out on more than 30 devices for all DEP parameters. Although an exact repeatability of the assembly for a given set of DEP parameters was not achieved, possibly due to slight variation in the NWs dimensions, topology and its aspect ratio which can affect the spatial distribution and local build-up of DEP force, thus affecting the distribution and density of NPs assembly. However, the variations observed in the NPs density and conductivity follow a reproducible pattern, thus confirming the reproducibility and scalable application of the current process. One such full set of variations in the DEP parameters is illustrated in the supplementary information demonstrating the repeatability of this technique.

4. Conclusion

In conclusion, we have in principle, illustrated an inexpensive, scalable and controlled process of assembling hybrid nanosystems, in particular, Pd NPs on VO$_2$ NWs system. This controlled assembly of NPs was first optimized through voltage and frequency variations and then the density of NPs was controlled by DEP time. In the case of Pd NWs assembled on VO$_2$ NWs system, the conductivity of the NW was found to be a function of NPs density, which can be utilized for various applications including electronic and biosensors, bioelectronics applications besides serving as an ideal platform to study advanced fundamental sciences. Using this technique, various other nanomaterial combinations can also be devised depending upon the functionalities requirements of the application covering the diverse field of electronics, sensors, optical and medical sciences.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.cap.2016.12.018.

References


