ZnO nanowire arrays decorated with titanium nitride nanoparticles as surface-enhanced Raman scattering substrates

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Received: 11 January 2021 / Accepted: 8 March 2021 / Published online: 22 March 2021 © The Author(s), under exclusive licence to Springer-Verlag GmbH, DE part of Springer Nature 2021

Abstract
In this work, the potential of ZnO nanowire arrays decorated with titanium nitride (TiN) nanoparticles as surface-enhanced Raman scattering (SERS) substrates is demonstrated. ZnO nanowires were grown by hydrothermal synthesis while commercially obtained TiN powders were subjected to several hours of mechanical grinding to achieve 30–100 nm diameter nanoparticles. The nanoparticles were then dispersed in acetone and drop cast on the ZnO nanowire arrays for decoration. Scanning electron microscopy confirmed the presence of TiN nanoparticles on the ZnO nanowires. TiN nanoparticles exhibited multiple absorption features at 430, 520 and 600 nm. SERS experiments using Nile blue and methylene blue as the analyte molecules exhibited enhancement in the Raman signals. It is shown that the origin of the SERS effect is chemical in nature, with contribution from different interactions between the analyte molecule and the TiN nanoparticles. The current work, thus, represents a simple, cost-effective and facile method for the fabrication of TiN-based SERS substrates.

Keywords ZnO nanowires · TiN nanoparticles · Surface-enhanced Raman scattering · Sensor

1 Introduction
Surface-enhanced Raman scattering (SERS) and Surface-enhanced resonance Raman scattering (SERRS) have emerged as important tools for the detection of chemical and biological molecules. Enhancement of the Raman signals is generally achieved by decorating surfaces with Cu, Au, or Ag nanoparticles. It has been observed that most of the SERS enhancement occurs in the top layer of the nanostructured metals. Hence, the approach is to employ metal nanoparticle decorated surfaces where in plasmon resonances can be tuned by varying the shape, size and interparticle distance [1–11]. Recent work has shown that titanium nitride (TiN) thin films display a strong absorption peak related to plasmonic resonance at approximately 530 nm, which is very close to that of Au nanostructures [12, 13]. The electrical conductivity of TiN, which is almost the same as that of Au, also makes it an attractive alternative for many applications. As a result, TiN thin films and nanostructures can be used as SERS substrates. This has been demonstrated by the ability to detect molecules such as R6G [14–21]. However, complex processing techniques such as sputter deposition are required to produce the reported materials. It is quite well documented that TiN has several sub-stoichiometric compositions and the growth of the stoichiometric form requires precise process control [22]. Thus, although previous reports show the promise of TiN for SERS applications, they also point to the need for different strategies to expand the applicability. The aim of the current work is, therefore, to circumvent the problem of non-stoichiometry by producing nanoparticles from commercially available stoichiometric TiN powders and subjecting them to grinding for several hours. The produced nanoparticles are then dispersed in acetone and drop cast on hydrothermally synthesized ZnO nanowire arrays [23]. Decoration of the ZnO nanowire arrays with TiN nanoparticles takes place at room temperature. The proof-of-concept for application as SERS substrates is demonstrated using two molecules, Nile blue (NB) and methylene blue (MB). It is, therefore, a very facile
technique for the fabrication of SERS substrates. To the best of the authors knowledge there are no previous reports on TiN nanoparticles decorated ZnO nanowire arrays as SERS substrates.

2 Experimental

The ZnO nanowires are prepared on ZnO thin film coated glass substrates by hydrothermal synthesis, as described earlier [23]. Briefly, 100 nm thickness ZnO thin films are deposited on glass slides followed by annealing in air at 400 °C for 2 hr. ZnO nanowires are then grown on these films by hydrothermal synthesis at 120 °C for 3 hr in a 100 mL Teflon-lined stainless-steel autoclave. The precursors are aqueous solution of 25 mM each of Zinc acetate dehydrate [Zn(O2CCH3)2(H2O)2, 99.0%- ZnAcD] and 25 mM hexamethylenetetramine (HMTA) [(CH2)6N4, 99.0%]. TiN nanoparticles (NPs) were prepared by hand-milling commercially purchased powders that contained particles of 3–5 µm in diameter. After several hours of grinding, the particle size of the powders was reduced to 30–100 nm. The produced TiN nanoparticles are then dispersed in acetone and drop cast on the hydrothermally synthesized ZnO nanowire arrays to achieve decoration. Field-emission scanning electron microscopy (FE-SEM) images were acquired in a ModelUltra-55 microscope of Carl Zeiss equipped with a energy-dispersive X-ray (EDX) spectrum analyzer for chemical composition information. X-ray diffraction patterns were recorded in a PANalytical powder X-ray diffractometer using CuKα radiation of wavelength = 0.15408 nm. UV–visible-NIR spectra were recorded in a JASCO (Model V-670) spectrophotometer operating in the wavelength range of 190–2500 nm. Raman and SERS measurements were performed with a LabRAM-Horiba Jobin Yvon spectrometer. A wavelength of 532 nm was used to excite the light was focused via a 50 X, 0.5 NA microscope objective. The SERS spectra of two analyte molecules (MB and NB) were collected and each spectrum is a result of 3 accumulations (Averages) with an acquisition time of 8 s. An input power of ~ 20 mW was used in these measurements. The SERS substrates were prepared by simple drop casting 10 µL of MB/NB solution on the TiN–ZnO nanowire array samples.

3 Results and discussion

The top view of a typical ZnO nanowire array surface shown in Fig. 1a indicates that the nanowires are of diameter between 30 and 100 nm. The nanowires are fairly densely packed and cross-sectional microscopy analysis reported earlier showed that they are reasonably vertically aligned [23]. The as-received TiN powders were subjected to grinding for several hours. As a result, many of the particles which were initially 3–5 µm sized were reduced to ≤ 100 nm size after grinding as demonstrated in Fig. 1b. A closer examination of the nanoparticles, in Fig. 1c, indicates that there is agglomeration of the particles at some locations and the shapes are non-spherical. The ZnO nanowires underneath the nanoparticles are clearly visible in these images. This method is, thus, a facile and simple technique to produce TiN nanoparticles and decorate them on ZnO nanowire surfaces.

The X-ray diffraction pattern of pristine TiN nanoparticles is shown in Fig. 2a. It is evident that the nanoparticles crystallize in the FCC structure with crystallite size of the order of 35 nm. The highest intensity diffraction peak is from the {200} plane and the absence of XRD peaks from any sub-stoichiometric phase indicates that the nanoparticles are indeed stoichiometric. The XRD pattern of the TiN NP decorated surfaces is dominated by the peaks from ZnO nanowires. However, a low intensity peak from the {200} plane of FCC TiN is still visible. The Raman spectrum for the TiN nanoparticle decorated ZnO nanowire surface is displayed in Fig. 2b. Constable et al. [24] observed peaks at 215, 327, 566, and 609 cm⁻¹ in the Raman spectra of TiN films and these modes were assigned to the transverse acoustic(TA), longitudinal acoustic(LA), second-order acoustic (2A), and transverse optical (TO) modes, respectively. In a report by Subramanian and Jayachandran [25], the Raman peaks were observed at 320, 440 and 570 cm⁻¹ in the Raman spectra of TiN films and these modes were assigned to the transverse acoustic(TA), longitudinal acoustic(LA), second-order acoustic (2A), and transverse optical (TO) modes, respectively. Thus, in the present case, the peaks at 330, 559 and 662 cm⁻¹ are attributed to TiN nanoparticles while the peaks 374, 436 and 478 cm⁻¹ are assigned to ZnO. The most intense peak observed at 436 cm⁻¹ is the E₂ high mode of wurtzite ZnO [23]. The peaks at higher wave numbers may have contributions from both materials. It is evident from the data presented so far, that TiN nanoparticles are formed on
the surface of the ZnO nanowires and there is no chemical reaction between the two compounds.

The optical absorption spectrum of TiN nanoparticles dispersed on a glass slide in the form of a thin film was recorded on a UV–Vis-Near IR spectrophotometer and shown in Fig. 2c. The spectrum displays a strong absorption feature at 430 nm and low intensity features at 520–600 nm. In literature, this absorption peak has been attributed to plasmonic resonances [12, 13]. However, it can be plasmonic only under doping by extra Ti which is not the case in the present study. Hence, the main absorption peak in transmission spectrum of TiN could be related to fundamental
interband transitions, while the other additional peaks could occur from Mie-resonances in nanoparticles as observed in Si [26]. The EDX spectrum of the TiN particles in Fig. 2d indicates that they are nearly stoichiometric with no evidence for oxygen.

Two molecules, Nile blue (NB) and methylene blue (MB), were selected as prototypes to investigate the efficacy of the TiN nanoparticles decorated ZnO nanowire arrays for SERS applications. The Raman spectrum of NB, recorded by dispersing it in the form of a film on a glass slide and displayed in Fig. 3a, consisted of low intensity modes at 382, 472, 553 and 653 cm$^{-1}$, and all of them matched with previous reports. The most significant feature occurs at 592 cm$^{-1}$, which is assigned to C–C–C and C–N–C deformations [27]. In contrast, the Raman spectrum of MB in Fig. 3b exhibits several low intensity features at 450, 664, 716, 1038, 1154, 1390, 1430 and 1500 cm$^{-1}$. The signature peak which occurs at 1622 cm$^{-1}$, in this case, is assigned to ring stretching of C–C mode. All the characteristic peaks were well matched with previous reports [28]. Thus, when these spectra are compared with the Raman spectra of TiN nanoparticle decorated ZnO nanowires presented in Fig. 2b, it is evident that the signature peaks of both molecules (NB and MB) are clearly distinct from those of ZnO and TiN. As a consequence, the SERS effect can be unambiguously studied.

The control experiment to investigate the SERS effect was carried out at 5 μM NB and MB concentrations, directly on ZnO nanowires (ZNW). The Raman spectra of the NB and MB molecules were recorded at 10 different, random locations on the ZnO nanowire arrays. However, the spectra did not exhibit any signatures of either the NB or MB molecule at any of these locations. The only peak observed, as shown in a typical Raman spectrum in Fig. 4, appeared at 436 cm$^{-1}$ corresponding to wurtzite ZnO. Evidently, the pristine ZNW surface is not suitable as a SERS substrate.

The threshold concentration below which the analyte molecule, NB, is not detected by the TiN nanoparticles decorated ZnO nanowires (termed as T-ZNW) is determined by recording the SERS spectra for different concentrations, as shown in Fig. 5. It is observed that at a high concentration of 5 μM, there is decrease in the intensity of the ZnO peak at 438 cm$^{-1}$ and this is accompanied by an increase in

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**Fig. 3** Raman spectra of a Nile blue and b Methylene blue on glass slides

**Fig. 4** Raman spectra of Nile blue (NB) and Methylene Blue (MB) adsorbed directly on ZnO nanowires at 5 μM concentration

**Fig. 5** SERS spectra of Nile Blue adsorbed on TiN nanoparticles decorated ZnO nanowires at 1 and 5 μM concentration. The red curve corresponds to the Raman spectrum of 0.5 mM NB dispersed directly on glass, for comparison
the intensity of the NB signature at 592 cm\(^{-1}\), compared to the intensities on ZNW. At a NB concentration of 1\(\mu\)M, on T-ZNW, there is complete quenching of the Raman modes relating to it and only one high intensity peak at 438 cm\(^{-1}\), attributed to wurtzite ZnO is visible. The Raman spectrum of 0.5 mM NB dispersed on glass slide, presented earlier in Fig. 3 is also displayed for comparison.

The results of a similar experiment performed for MB adsorbed on T-ZNW at different concentrations are shown in Fig. 6. At 5 \(\mu\)M concentration of MB, the intensity of the peak at 1622 cm\(^{-1}\) is significantly increased. Furthermore, there is decrease in the intensity of the wurtzite ZnO mode which now occurs at 443 cm\(^{-1}\) as compared to the intensity on ZNW shown in Fig. 4. Further decrease in MB concentration to 1 \(\mu\)M, results in suppression of the Raman modes of MB and only the wurtzite ZnO peak at 443 cm\(^{-1}\) is visible. In both cases (i.e., NB and MB), there is enhancement at 5 \(\mu\)M concentration while the Raman signals of the analyte molecules are quenched at 1 \(\mu\)M concentration. It is also evident that even at a high concentration of 0.5 mM, there is no enhancement of the Raman signals when the analyte molecules are adsorbed directly on the ZnO nanowires. Another interesting aspect is the shift of the most intense peak of ZnO to higher wavenumbers.

The Raman spectra were recorded at 10 different, random locations each for 5, 10, 15 and 25 \(\mu\)M concentration of MB and NB molecules on T-ZNW and typical spectra are shown in Fig. 7a, b, respectively. In both cases, there is enhancement of the signature peaks of the respective molecules, MB at 1622 cm\(^{-1}\) and NB at 590 m\(^{-1}\), with increase in concentration. The calculation of the relative standard deviation (RSD\%) is based on the Raman spectra recorded at 10 different locations on T-ZNW, for 5 \(\mu\)M concentration of MB and NB molecules (which is considered the threshold concentration for detection). The results for MB are shown in Fig. 8a, b while that for NB are shown in Fig. 9a, b. It is observed that the RSD\% for MB molecule is 14.22\% while the value is 24.87\% for NB.

The enhancement factors were calculated for both molecules using the expression [1, 2]

\[
E_f = \frac{I_{SERS}}{I_{Raman}} \times \frac{C_{Raman}}{C_{SERS}}
\]

where \(E_f\) is the enhancement factor, \(I_{SERS}\) is the SERS band intensity of probe molecules [MB (1622 cm\(^{-1}\)) and NB (592 cm\(^{-1}\))] using the synthesized TiN–ZnO substrate, \(I_{Raman}\) is the Raman intensity of a probe molecule on a glass slide (without using substrate), \(C_{SERS}\) represents the corresponding concentration of an probe molecule on a
TiN–ZnO substrate (10⁻⁶ M) and \( C_{\text{Raman}} \) is the concentration of an probe molecule on a glass slide (10⁻³ M, without substrate), which produces the Raman signal, \( I_{\text{Raman}} \).

The EF values obtained are summarized in Table 1 for different concentrations. It is observed that, as the concentration of the dye molecules on the T-ZNW surface is decreased, the \( E_f \) of their signature peak also decreases. This is attributed to the reduced adsorption on the T-ZNW surface. Nile blue has the chemical formula, C₂₀H₂₀ClN₃O and belongs to the family of phenoxazine and benzo-phenoxazine based dyes. Methylene blue has the chemical formula C₁₆H₁₈ClN₃S and is also known as methylthioninium chloride. Since in both compounds the chloride ions are present, it is hypothesized that the affinity of TiN to chloride ions might cause the binding of the dye molecules to the nanoparticles leading to a chemical SERS effect.

It is well established that there are two main mechanisms of surface enhancement of Raman signals [1–9]. They are either electromagnetic or chemical in nature. The electromagnetic enhancement of signals involves the coupling of the electric fields related to surface plasmons of the nanoparticles with incident radiation. The strength of coupling varies as fourth power of the local electric field. As a result, very small variation in the local field can cause very significant changes in the SERS signals. The chemical enhancement is, in contrast, a weaker effect relying on formation of complexes on the nanoparticle surface, charge

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**Table 1** Enhancement Factors for Methylene Blue and Nile Blue at different concentrations on TiN-ZnO nanowire array SERS substrates

| Concentration of analyte molecule (µM) | Enhancement factor for Methylene Blue | Enhancement factor for Nile Blue |
|---------------------------------------|--------------------------------------|----------------------------------|
| 1                                     | 0                                    | 0                                |
| 5                                     | 28                                   | 94                               |
| 10                                    | 33                                   | 110                              |
| 15                                    | 34                                   | 360                              |
| 25                                    | 36                                   | 369                              |

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**Fig. 8** SERS spectra of a Methylene Blue adsorbed on TiN nanoparticles decorated ZnO nanowires at 5 µM concentration at 10 different locations on the surface and b the calculated relative square deviation (RSD%) for the peak at 1620 cm⁻¹

**Fig. 9** SERS spectra of a Nile Blue adsorbed on TiN nanoparticles decorated ZnO nanowires at 5 µM concentration at 10 different locations on the surface and b the calculated relative square deviation (RSD%) for the peak at 590 cm⁻¹
transfer or charge transfer resonances induced by molecular adsorption. Due to the differences in their origins, the enhancement factors observed due to the EM effect are large in magnitude ($10^4$ or higher) whereas the chemical effect enhancement factors are of the order of $10^1$, at maximum. It would, thus, appear that in the present case the SERS effect is more chemical in nature. Interestingly, Wei et al. [18] have observed a combination of the electromagnetic and charge transfer effect in the TiN thin film-based SERS substrates that were used to detect R6G.

The origin of the enhancement effect has been deliberated in earlier works [1–9] and it is attributed to three mechanisms:

1. the existence of surface plasmon resonances
2. charge transfer between the metal and conduction band of the adsorbed molecule
3. resonances within the adsorbed molecule leading to single-molecule detection.

The charge transfer effect may be due to the differences in Fermi levels of the adsorbed molecule and TiN [3]. It is hypothesized that the chemical enhancement is induced by the interaction between the TiN nanoparticles and the adsorbed molecule leading to the formation of a charge transfer state. When this state is resonant with the laser wavelength an additional resonant—chemical effect enhances the SERS. This is possible due to the interaction between the Fermi level of the metal and the frontier orbitals of the molecule. Additional factors to be considered are postulated by Kudryashov et al. [29] in samples produced by mask-less micro-patterning of thin plasmonic films of Ag, Cu, Al and Au–Pd alloys for surface-enhanced IR spectroscopy application. The IR transmission response of micro-hole arrays with varying parameters were studied. In the case of R6G adsorbed on Ag substrates they find evidence for a donor-like chemical enhancement. This process is sensitive to bonding/vibration in analyte molecules and also has contribution from analyte-metal complexing via charge transfer. Thus, the effect of TiN dangling bonds and spectrally homogeneous Mie-type SERS enhancement in optically resonant TiN nanoparticles (either electric dipolar or magnetic dipolar/quadrupolar resonances) also need to be considered in the present case. A third point that needs consideration is that the observed SERS enhancement can be photoinduced in nature. This is inferred from literature wherein it has been shown that TiN is a good catalyst for photodegradation of molecules such as methylene blue [30]. The essential requirement is adsorption, of the molecule to be photodegraded, onto the catalyst material. In photodegradation, the molecule absorbs the incident radiation to generate electron–hole pairs, which is followed by separation of the excited charges and charge transfer to the surface of the photocatalyst. Finally, these charges are used for redox reactions [31]. It is assumed that the charge transfer process occurring in the present case is an amalgamation of the three mechanisms (non-photoinduced and photoinduced) as described above. However, the individual contributions cannot be isolated with the experimental set-up used in the present study.

The proof-of-concept study presented here indicates promise and that further enhancements will be possible with these substrates by optimizing size, shape, and interparticle distance of the TiN nanoparticles. The main advantages are the ease of preparing large-area substrates and the low costs involved. More detailed studies with different analyte molecules (including explosives and pesticides) are being carried out to test the efficacy of these substrates and will be reported elsewhere.

4 Conclusions

TiN nanoparticle decorated ZnO nanowires are synthesized by a simple process. The TiN nanoparticles are 30–100 nm in size and exhibit absorption-related features at wavelengths between 400 and 600 nm. The application of these substrates as surface-enhanced Raman scattering substrates is demonstrated by detecting Nile blue and methylene blue molecules on the nanoparticles. It is demonstrated that the origin of SERS in this system is chemical in nature. The facile approach to synthesis indicates promise for cost-effective scale-up.

Acknowledgements Y. Rajesh acknowledges a NFHE Ph.D. fellowship awarded by UGC. M.S.S. Bharati and S. Venugopal Rao acknowledge DRDO financial support through ACRHEM, University of Hyderabad. Center for Nanotechnology and School of Physics, University of Hyderabad, India are acknowledged for facilities. The support of DST-PURSE, UGC-DRS, UGC-NRC programmes is also acknowledged. S. Venugopal Rao acknowledges the University of Hyderabad for the IoE project [Ref. No. UOH/IOE/RC1/RC1-20-016]. The IoE scheme was sanctioned vide MHRD notification F1/19/2019-U3(A).

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