Synthesis, physico-chemical characterization and field emission behaviour of 3D chrysanthemum like pristine ReS$_2$, and ReS$_2$-rGO nanocomposite

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Abstract

3D chrysanthemum like pristine ReS$_2$ and nanocomposite of ReS$_2$ with reduced graphene oxide (rGO) have been synthesized using facile one step hydrothermal method, followed by physico-chemical characterizations to reveal their phase, structural and electronic properties. Efforts have been made to reveal the influence of process parameters on morphology and growth of the as-synthesized products. From application point of view, field emission (FE) behavior of pristine ReS$_2$ and ReS$_2$-rGO nanocomposite emitters has been investigated at base pressure of $1 \times 10^{-8}$ torr. The ReS$_2$ and ReS$_2$-rGO nanocomposite emitters showed values of turn-on field (corresponding to emission current density of $1 \mu$A cm$^{-2}$) as 2.10 and 1.66 V $\mu$m$^{-1}$, and field enhancement factor ($\beta$) as $\sim$965 and 1176, respectively. Furthermore, the ReS$_2$-rGO nanocomposite emitter delivered maximum emission current density of $\sim$1472 $\mu$A cm$^{-2}$ at applied field of 3.1 V $\mu$m$^{-1}$. Both the emitters exhibited good emission current stability at pre-set value $\sim$5 $\mu$A over more than 3 h duration. The superior FE properties of the ReS$_2$-rGO nanocomposite emitter are attributed to optimized morphology offering high field enhancement factor coupled with modulation of electronic properties reflected as lowering of the work function. The value of work function of ReS$_2$-rGO nanocomposite, measured using a retarding field analyzer, is found to be 4.29, lower than that of the pristine sample (4.49 eV). The results signify that functionality of pristine nanostructures is greatly improved via formation of nanocomposites and desirable nanocomposites possessing unique morphology can be synthesized under optimized experimental conditions using a facile and inexpensive hydrothermal route.

Introduction

The two-dimensional transition metal dichalcogenides (TMDs) have attracted a great deal of attention of scientific community worldwide and are being recognized as promising materials for next generation electronic and optoelectronic devices [1–3]. Rhenium disulfide (ReS$_2$) is one of the TMDs possessing layered structure, in which S–Re–S atoms are joined by covalent bonds in a layer and the adjacent layers are coupled with weak van der Waals forces [4]. Furthermore, it has a unique distorted 1T structure, which is one of reasons for anisotropy in the fundamental properties [5]. Interestingly, it exhibits no indirect to direct band transition while thinning from bulk to monolayer. This makes ReS$_2$ a unique promising material for polarized light detection, in contrast to other TMDs [6]. In recent years, ReS$_2$ is being considered as potential candidate for fabrication of electronic and optoelectronic devices, such as thin film transistors [7], digital logic devices [8], and photo detectors [9].

Owing to their layered structures offering ‘high aspect ratio’, field emission (FE) characteristics of nanostructures and nanocomposites of various TMDs have been investigated. The early report on the FE studies on TMDs nanostructures, in particular Molybdenum disulphide, (MoS$_2$) nanoflowers was due to Li et al.
wherein the authors have observed turn-on field of 4.5 V μm⁻¹, corresponding to emission current density ~10 μA cm⁻² [10]. Our group has reported FE behavior of MoS₂ nanosheets synthesized using chemical and pulsed laser deposition [11, 12]. An attempt to improve the FE behavior of MoS₂ nanoflowers via synthesizing them on multi walled carbon nanotubes (MWCNTs) was carried out by Zhang et al [13]. Following this, our group has attempted hydrothermal synthesis of MoS₂ nanosheets on reduced graphene oxide (rGO) [14]. The physico-chemical characterization revealed that the rGO sheets act as potential substrate thereby facilitating vertically aligned growth of few layer MoS₂ nanosheets, and the MoS₂-rGO emitter has exhibited enhanced FE behavior. In addition to MoS₂, other TMDs nanostructures and nanocomposites have been characterized for their FE behavior [15–21]. Very recently, Antonio Di Bartolomeo et al have reported studies on field emission in ultrathin PdSe₂ back-gated transistors [21]. From the literature survey it is observed that, despite possessing unique properties, there are very few reports on FE studies of ReS₂ nanostructures and nanocomposites. FE characteristics of vertically aligned ReS₂ nanostructures deposited on Si wafer using RF sputtering method has been reported by Mohit Kumar et al [22] The authors have attributed the superior FE characteristics of the ReS₂ nanostructures emitter to the ‘optimized surface morphology’ offering high aspect ratio and less screening effect. Following this, we planned to perform systematic studies on growth and FE behaviour of pristine ReS₂ nanostructures and ReS-rGO nanocomposite owing to (i) in contrast to RF sputtering, hydrothermal method is facile and inexpensive, (ii) whether growth of ReS₂ nanostructures characterized by ‘optimized surface morphology’ (similar to that reported by Mohit Kumar) can be achieved on rGO sheets?, and (iii) very few reports of FE behaviour of ReS₂ nanostructures, demanding systemic studies in this respect. To the bets of our knowledge there is no report on hydrothermal growth of ReS₂-rGO nanocomposite and its FE study.

We herein report the FE studies of ReS₂-rGO nanocomposite synthesized by a single step facile hydrothermal route under optimized conditions. Attempts have been made to reveal the effect of rGO concentration on growth, overall morphology and FE behavior of the ReS₂-rGO nanocomposites. Interestingly, the as-prepared ReS₂-rGO nanocomposite emitter exhibits enhanced FE behavior, in terms of lower values of turn-on and threshold fields, along with good long-term emission current stability, as compared to the pristine ReS₂ emitter. Furthermore, work function measurement has been attempted using retarding field potential technique [23, 24] The improvement in the FE characteristics has been attributed to synergic effect due to unique morphology and modulation of the electronic properties i.e. reduction in the work function.

Method

Synthesis of ReS₂ microspheres

ReS₂ chrysanthemum like microspheres were synthesized using one pot hydrothermal method [25]. In a typical synthesis experiment, Ammonium perrhenate (NH₄ReO₄ Sigma Aldrich, purity 99.9%) molar concentration of 25 mM, Hydroxylamine hydrochloride (NH₂OHHCl, HPLC, purity 99.0%) 75 mM and Thiourea (CH₄N₂S, Sigma Aldrich, purity 99.0%) 100 mM were prepared in 15 ml of Deionized (DI) water and stirred for 30 min. This solution was then transferred in 25 ml capacity Teflon lined Stainless Steel autoclave. The hydrothermal reaction was carried out at 200 °C for 12 h. After completion of reaction duration, the autoclave was allowed to cool naturally. The reaction precipitate was harvested in powder form via filtration, followed rigorous washing using DI water and ethanol several times, and finally drying at 80 °C for 6 h under ambient conditions. In order to reveal the influence of process parameters on growth and overall morphology of the resultant product, hydrothermal synthesis was carried out by varying concentration of the precursors, reaction temperature (120, 150, 180, and 200 °C) and duration (6, 12, 18, 24, 30, and 48 h).

Synthesis of ReS₂-rGO microspheres

The ReS₂-rGO nanocomposite was synthesized using the same hydrothermal set up. First, graphene oxide (GO) was synthesized from graphite powder using modified Hummer’s method [26]. 3 mg of GO was added to 5 ml DI water and ultra-sonicated for 60 min. In a separate beaker, 10 ml of reaction mixture used for ReS₂ synthesis (as described in earlier section) was prepared. The GO solution was then added into the reaction mixture, followed by stirring for 15 min so as to form colloidal solution. This colloidal solution was transferred in 25 ml capacity Teflon lined autoclave. The nanocomposite was synthesized following the same procedure as adopted for synthesis of ReS₂ nanostructures. In this case too, in order to reveal the effect of amount of GO on overall morphology of the ReS₂-rGO nanocomposite, weight percent of GO with respect to ammonium perrhenate was varied as 3, 5, 10, and 20.
Characterizations

The as-synthesized products (pristine ReS$_2$ and ReS$_2$-rGO nanocomposites) were subjected to various characterizations to reveal their phase, morphological, structural, chemical, electronic and electrical properties. The x-ray Diffraction (XRD) analysis for phase identification was performed on x-ray Diffractometer (Bruker AXS D8 Advance) using Cu K$_\alpha$-radiation ($\lambda = 1.5418$ Å). The morphology and compositional analysis were carried out using Scanning Electron Microscope (SEM, JEOL JSM 6360 A, Japan) and Field Emission Scanning Electron Microscope (FESEM – Nova NanoSEM-450 and Zeiss Ultra Plus FESEM). Energy Dispersive Spectroscopy (EDS) measurement were carried out using Oxford X-ACT and Bruker XFlash 6130, attached to the SEM and FESEM systems, respectively. For in-depth morphological and structural studies, Transmission Electron Microscope (TEM, FEI Tecnai G2 200 KV) was used. The structural analysis was performed using Raman Spectrometer (RenishawinVia Raman Microscope). X-ray Photoelectron Spectroscopy (XPS) (Thermo scientific K-ALPHA$^+$ surface analysis) was employed to reveal the electronic and chemical characteristics of the as-synthesized materials. In addition, work function measurement was performed using retarding field technique, using a low electron beam collimated by an axial magnetic field, whereas electrical conductivity measurements were carried out using two-probe method (details given in Supporting Information, SI (available online at stacks.iop.org/NANOX/2/020018/mmedia)).

The FE studies were carried out in a planar diode configuration at base pressure of $1 \times 10^{-8}$ mbar. The emitter was prepared by sprinkling a small quantity of as-synthesized powder on a piece of conducting carbon tape ($0.25$ cm$^2$) and then pasted on a Copper rod of $5$ mm diameter (cathode holder). A phosphor coated Indium doped Tin Oxide (ITO) glass, circular disc of diameter $\sim 50$ mm, was used as an anode. All FE measurements were carried out at fixed anode–cathode separation of $\sim 2$ mm. Prior to the FE measurements, pre-conditioning of the cathode was carried out. For this, the cathode was held at $-500$ volts (with respect to anode) for $20$ min duration, so as to remove the surface asperities and/or contaminants by in situ ion bombardment. In order to ensure reputability and reproducibility, at least two emitters of each case were tested for their FE behavior.

Results

X-ray diffraction

A typical x-ray diffraction (XRD) pattern of as-synthesized ReS$_2$ powder specimen (reaction temperature $\sim 200^\circ$C, duration $\sim 12$ h) is depicted in figure 1. It exhibits well defined intensities at angles $(2\theta) \sim 13.5^\circ$, $16.9^\circ$, $25.8^\circ$, $32.7^\circ$, $35.1^\circ$, $39.2^\circ$, $41.8^\circ$, $43.8^\circ$, $49.6^\circ$, $51.4^\circ$, and $56.8^\circ$, which are indexed to (100), (010), (110), (002), (211), (222), (120), (0 32 ), (0 33 ), ( 2T3) and (024) planes of triclinic ReS$_2$ phase (JCPDF card no. 82-1379). The diffraction peak observed at $\sim 13.5^\circ$ indicates lower stacking, i.e. higher distorted packing [27]. Thus, the XRD analysis clearly indicates formation of crystalline phase of ReS$_2$ with stacking disorder.

The typical XRD pattern of ReS$_2$-rGO nanocomposite synthesized with GO $-10$ wt.%, temperature $\sim 200^\circ$C, and reaction duration $-12$ h is depicted in figure 1(b). At the outset it looks identical to the pattern of pristine sample exhibiting diffraction peak positions, which are characteristics of triclinic phase of ReS$_2$. In figure 1(b), absence of a characteristic diffraction peak of GO (typically observed around $\sim 11.00^\circ$) and

![Figure 1. Typical x-ray diffraction patterns of (a) pristine ReS$_2$ and (b) ReS$_2$-rGO nanocomposite samples.](image-url)
appearance of a noticeable peak at \( \sim 26^\circ \) (inset of figure 1(b)) along with a shallow humps around 44.00 and 60.00\(^\circ\) implies in situ reduction of GO to rGO during the hydrothermal reaction (JCPDS PDF\# 75-1621). The x-ray diffraction patterns of ReS\(_2\)-rGO nanocomposites synthesized with different wt.% of GO (3, 5, 10, and 20) are depicted in Supporting Information.

**SEM analysis**

In the first set of synthesis experiments, keeping the reaction duration constant \( \sim 12 \) h, effect of reaction temperature on overall morphology of the pristine ReS\(_2\) microstructures was investigated using SEM analysis. The SEM image of sample synthesized at 120 \( ^\circ\)C (figure 2(a)) reveals growth of tiny lumps of sulphur. This is confirmed from the EDS analysis. It indicates that the reaction temperature is sufficient to utilize the available concentration of sulphur precursor (Thiourea) for formation of ReS\(_2\) but insufficient to utilized ammonium perrhenate (Re precursor). With increase in reaction temperature to 150 \( ^\circ\)C, formation of ReS\(_2\) pod-like structures (length \( \sim 1 \) \( \mu \)m, and diameter \( < 1 \) \( \mu \)m) with smooth surface was observed (figure 2(b)). Interestingly, presence of lumps due to un-reacted ammonium perrhenate were not observed, implying that this temperature is enough to consume total Re concentration for growth of ReS\(_2\).

With increase in reaction temperature to 180 \( ^\circ\)C, noticeable change in the surface morphology was observed, transformation of pod-like structures into nearly spherical particles with diameter more than 1 \( \mu \)m (figure 2(c)). A careful observation of the SEM image revealed that the surface of ReS\(_2\) microspheres is not smooth. It is concluded that, formation of ReS\(_2\) commences at 180\(^\circ\)C. Further increase in reaction temperature to 200 \( ^\circ\)C, growth of nearly mono-disperse spherical particles (average diameter \( \sim 1 \) \( \mu \)m) was observed (figure 2(d)). The surface morphology of these microspheres is characterized by networking of very tiny sheets. However, the details of network due to ultrathin petals/sheets, indicative of chrysanthemum like morphology, could not be resolved under the SEM.

To gain better morphological insight, FESEM analysis was performed. The FESEM image (figure 3(b)) revealed that the surface is characterized by presence of a criss-cross network of vertically oriented ReS\(_2\) nanometric petals/sheets. Thus, the microscopic analysis reveals formation of 3D chrysanthemum like microstructures of ReS\(_2\) under the optimized process parameters (reaction temperature \( \sim 200 \) \( ^\circ\)C, and duration \( \sim 12 \) h). The EDS analysis showed presence of Re and S, with atomic ratio \( \sim 1:2 \). (The EDS spectrum is presented in Supporting Information, figure S4).
In order to study the morphological progression during hydrothermal synthesis, reactions were carried out for different durations of 6, 12, 18, 24, 30 and 48 h, at fixed reaction temperature ∼200 °C, and the corresponding FESEM images are depicted in figure 3. For the reaction duration of 6 h, commencement of growth of petals on the surface of ReS₂ microspheres is observed (figure 3(a)). For 12 h duration, the FESEM image (figure 3(b)) clearly reveals formation of well-defined networking of vertically oriented petals exhibiting chrysanthemum like surface morphology. With increase in the reaction duration to 18 h, thickness of the petals is observed to increase (figure 3(c)), and overgrowth of petals is observed for reaction duration of 24 h (figure 3(d)). When the synthesis was carried out for 30 h and longer duration, chrysanthemum like morphology was completely destroyed and formation of horizontally lying submicron thick sheets is observed. Thus, the SEM and FESEM analysis clearly reveals that for formation of 3D chrysanthemum like ReS₂ microspheres, the optimized values of process parameters, reaction temperature and duration, are 200 °C and 12 h, respectively. Accordingly, the ReS₂-rGO nanocomposite synthesis was carried out under these optimized process variables and varying the GO weight percent.

The FESEM images of ReS₂–rGO nanocomposites synthesized with different GO wt.% are depicted in figure 4. For 3 wt.% case, growth of vertically oriented ReS₂ nano-petals on rGO sheets is clearly noticed and the surface morphology resembles with 3D chrysanthemum like ReS₂ microspheres. With increase in the GO wt.%, the morphology shows noticeable change indicating complete demolition of the 3D chrysanthemum like morphology. This morphological transformation is attributed to simultaneous in situ reduction of GO into rGO and growth of ReS₂ nanostructures on the rGO flakes/sheets. In one of our earlier reports on synthesis of MoS₂-rGO nanocomposite, we have elucidated the growth mechanism MoS₂ nanostructures on rGO substrate, and in the present case, similar growth mechanism is speculated [14].

Since the presence rGO sheets are not well resolved in FESEM images, to gain better morphological and structural resolution of the ReS₂ nanocomposites, TEM analysis was performed.

**TEM analysis**

For TEM analysis, specimens synthesized in powder form were dispersed in iso-propyl alcohol (IPA) solution (separately), ultra-sonicated for more than 2 h, and then drop-cast on a formavar coated copper grid (200 mesh). The bright field TEM image (5(a)) of pristine ReS₂ microsphere shows presence of thin nano-petals protruding outside the surface. The high resolution (HRTEM) image (5(b)) depicts different orientation of petals and inter-planar spacing of ~0.64 nm, corresponding to (100) plane of ReS₂. Figure 5(c) depicts the selected area electron diffraction (SAED) pattern, indicative of polycrystalline nature of sample.

The TEM images of ReS₂–rGO nanocomposite are depicted in figure 6. In this case, presence of mircosphere (seen in figure 5(a) is not observed. In contrast, the ReS₂ nano-flakes are observed to be ultra-thin. In the HRTEM image, we could not resolve lattice, which may be due to presence of large number of randomly
Figure 4. (a) FESEM images of ReS$_2$-rGO nanocomposites synthesized with (a) 3% rGO (b) 5% rGO (c) 10% rGO (d) 20% rGO.

Figure 5. (a) TEM image (b) High resolution (HRTEM) and (c) SAED pattern of pristine ReS$_2$ specimen.

Figure 6. (d) TEM image, (e) High resolution (HRTEM), and (f) SAED pattern of ReS$_2$-rGO nanocomposite.
oriented ultrathin nano-flakes on rGO surface. The SAED pattern is similar to figure 5(c) indicative of polycrystalline nature.

Raman spectroscopy

For ReS$_2$, out of the 36 vibrational modes, only 18 modes are Raman active, which include 4 out of plane, 6 in-plane, and 8 coupled vibrational modes [5]. The Raman spectrum of ReS$_2$-rGO nanocomposite (10 wt.%) is depicted in figure 7.

The Raman spectrum of pristine ReS$_2$ shows characteristics peaks at 143.02, and 431.94 cm$^{-1}$, due to out-of-plane vibration of Re and S atoms, respectively. The peak observed at 305.79 cm$^{-1}$ represents the in-plane vibration of S atoms. The Raman spectrum of ReS$_2$-rGO nanocomposite (figure 7) exhibits well defined peaks at 1341.59, 1593.37, 2699.84 and 2926.33 cm$^{-1}$ representing D, G, 2 G and D + G bands of reduced graphene oxide, respectively. Also, the estimated value of I$_{D}$/I$_{G}$ to be 1.03 (greater than 1) indicates presence of fewer defects in rGO. Furthermore, in contrast to GO, the 2D band is insignificant to the D + G band [28]. Furthermore, the partial Raman spectrum (inset of figure 7) shows the characteristic signatures of ReS$_2$ phase. Thus, the Raman analysis clearly confirms presence of both ReS$_2$ and rGO phases in the nanocomposite.

XPS analysis

The XPS survey scans of ReS$_2$-rGO nanocomposite is depicted in figure 8(a). It shows presence of C and O at positions 285.08 and 532.08 eV, respectively with correction for specimen charging.

The survey scan is further resolved corresponding to C and O energy levels, as is depicted in figure 8(d). The deconvoluted spectrum for C-1s exhibits three well defined peaks at 284.78, 286.28 and 288.68 eV corresponding to C=C, C–C and C–O, respectively. The Carbon in C–O corresponds to SP$^2$ hybridized state [29]. The inset shows deconvoluted spectrum for oxygen. The figure 8(b) shows a Gaussian doublet positioned at 42.28 and 44.68 eV representing Re 4f$_{7/2}$ and 4f$_{5/2}$, respectively indicative of Re$^{4+}$ state [3]. The resolved spectrum of S, figure 8(c) shows signatures at 162.88 and 164.28 eV, representing energy levels 2P$_{3/2}$ and 2P$_{1/2}$, indicating S$^{2-}$ state [3].

Field emission

The field emission behavior of the pristine ReS$_2$ and ReS$_2$-rGO nanocomposite emitters, emission current density (J) as a function of applied field (E), is depicted in figure 9(a). It is observed that with the same incremental step in applied field, the emission current density initially increases slowly, then rapidly, exhibiting exponential nature over the entire range, as expected by the Fowler-Nordheim (F-N) [30], as stated below,

![Figure 7. Raman spectrum of ReS$_2$-rGO nanocomposite. Inset shows the sectional part of the spectrum corresponding to characteristic features of ReS$_2$.](image-url)
\[ J = a \varphi^{-1} E^2 \exp \left( -b \frac{\varphi^2}{\beta E} \right). \] (1)

Where, \( a \approx 1.541434 \text{ AeV}^{-2} \) and \( b \approx 6.830890 \text{ eV}^{-3/2} \text{ V } \text{nm}^{-2} \) are constants, \( E \) is applied electric field, \( \varphi \) is work function, and \( \beta \) is the field enhancement factor (also termed as geometric enhancement factor) of the emitter.

The values of turn-on field (corresponding to emission current density of 1 \( \mu \text{A cm}^{-2} \)) and threshold field (corresponding to 10 \( \mu \text{A cm}^{-2} \)) are observed to be 2.18 and 2.46 \( \text{V } \text{nm}^{-1} \) for pristine ReS\(_2\) and 1.66 and 1.86 \( \text{V } \text{nm}^{-1} \) for ReS\(_2\)-rGO nanocomposite emitters, respectively. Furthermore, maximum current density of \( \sim 850 \mu \text{A cm}^{-2} \) extracted at an applied field of 4 \( \text{V } \text{nm}^{-1} \) from the pristine ReS\(_2\) emitter, whereas the ReS\(_2\)-rGO nanocomposite emitter delivered current density of \( \sim 1472 \mu \text{A cm}^{-2} \) at applied field of 3.1 \( \text{V } \text{nm}^{-1} \). These values clearly indicate that the ReS\(_2\)-rGO nanocomposite emitter shows superior FE behaviour as compared to the pristine emitter.

The observed J-E characteristic was further analyzed by plotting graph of \( \ln(J/E^2) \) versus \( (1/E) \), termed as F-N plot. Figure 9(b) depicts the corresponding F-N plots, which show deviation from linearity, indicative of semiconducting nature of the emitters. In case of planar emitter comprised of semiconducting nanostructures, in addition of the field screening effect (amongst the closely grown/spaced nanostructures), field penetration and band bending effects are responsible for the observed nonlinear nature of the F-N plot. A careful observation of the F-N plots reveals that, for pristine sample noticeable change in the slope (two nearly linear sections with different slopes) is observed, in contrast to the nanocomposite emitter. This can be attributed to the difference in their electrical conductivities (explained in later section). From slope of the F-N plot, one can estimate the value of field enhancement factor \( \beta \), as stated in equation (2)

\[ \beta = \frac{2.97 \times 10^5 \varphi^{3/2}}{m}. \] (2)

Where, \( \varphi \) is work function and \( m \) is a slope of F-N plot. From slopes of the corresponding F-N plots and work function values as 4.49 and 4.29 eV (experimentally measured using retarding field analyzer), the value of \( \beta \) were estimated to be 965 and 1176 for pristine ReS\(_2\) and ReS\(_2\)-rGO nanocomposite emitters, respectively.
Figures 9(c) and (d) depict the emission current stability of the emitters tested at pre-set value of 5 μA for duration of more than 4 h. The pristine ReS₂ emitter exhibited good current stability with current fluctuations within ± 2.5% of an average value. The emitter exhibited relatively more fluctuations up to period of 60 min, followed by very good current stability. In contrast, the ReS₂-rGO nanocomposite emitter showed very good emission stability, characterized by fluctuations within ± 1.5% of an average value (figure 9(d)). The ‘spike’ type fluctuations are due to atomic scale processes (like adsorption, migration, and/or desorption of residual species) occurring on the emitter surface. Furthermore, the SEM image of the ReS₂-rGO nanocomposite emitter recorded after FE studies (Supporting information, figure S.5) shows very little change in the surface morphology, indicating its mechanical sturdiness against in situ ion bombardment.

The improved FE characteristics of the ReS₂-rGO nanocomposite emitter is attributed to synergic effects due to unique morphology and modulation of electronic properties via interface effects. As revealed from the microscopic characterization, presence of randomly oriented and nearly vertically aligned ultrathin nanoflakes possessing high aspect ratio act as potential emission sites, in addition to the protruding edges of the rGO sheets. Furthermore, use of rGO sheets as substrate for growth of ReS₂ noticeably modulates its electrical properties. We have carried out electrical conductivity measurement (details are described in Supporting Information) which revealed that the ReS₂-rGO nanocomposite has better electrical conductivity in contrast to the pristine ReS₂ sample. Furthermore, we have experimentally measured the work function values of both the emitters using a retarding field energy analyzer (details are described in Supporting Information). Interestingly, the ReS₂-rGO nanocomposite has lower value of work function (4.29 eV) than that of pristine ReS₂ emitter (4.49 eV). Thus, the improved electrical properties along with enhanced number of potential emission sites make the ReS₂-rGO nanocomposite emitter superior than the pristine one.

To justify the improved FE behavior of ReS₂-rGO nanocomposite emitter, table 1 depicts compilation of the values of turn-on fields, maximum emission density with corresponding applied fields of emitters due to TMDs nanostructures and nanocomposites.

**Conclusions**

The ReS₂-rGO nanocomposite emitter showed potential to deliver high emission current density of ~1.472 mA cm⁻² at relatively moderate applied field of 3.1 V μm⁻¹, and thus can be accepted for practical applications.
applications in vacuum micro-nano electronic devices. The observed results exhibiting enhancement in FE behaviour via formation of nanocomposite with rGO, indicate that functionality of semiconducting nanostructures can be efficiently improved by tailoring the morphology and modulation of electronic properties via formation of nanocomposites with suitable semiconducting nanomaterials. Furthermore, a simple synthesis route like hydrothermal can be efficiently used to fabricate various nanocomposites for potential applications.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Table 1. Comparison of FE characteristics of emitters due to TMDs and their composites.

| Sr No. | Field emitters | Turn on field (V μm−1) | Maximum current density (μA cm−2) | References |
|--------|----------------|------------------------|-----------------------------------|------------|
| 1      | CdS Nanocombs  | 0.26 at 0.1 μA cm−2    | 33 at 1.2 V μm−1                 | [15]       |
| 2      | MoS2 nanosheets| 3.5 at 10 μA cm−2      | —                                 | [12]       |
| 3      | MoS2 sheets    | 4.7 at 10 μA cm−2      | —                                 | [13]       |
| 4      | WS2            | 3.5 at 1 μA cm−2       | 220 at 6.3 V μm−1                | [16]       |
| 5      | WS2–rGO       | 2.0 at 1 μA cm−2       | 800 at 4.1 V μm−1                | [16]       |
| 6      | MoS2–rGO      | 2.6 at 10 μA cm−2      | 800 at 3.9 V μm−1                | [14]       |
| 7      | ReS2          | 2.10 at 1 μA cm−2      | 850 at 4.0 V μm−1                | Present work |
| 8      | ReS2–rGO      | 1.66 at 1 μA cm−2      | 1472 at 3.1 V μm−1               | Present work |
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