

Modification of Graphene Oxide/ $V_2O_5 \cdot nH_2O$ Nanocomposite Films via Direct Laser Irradiation

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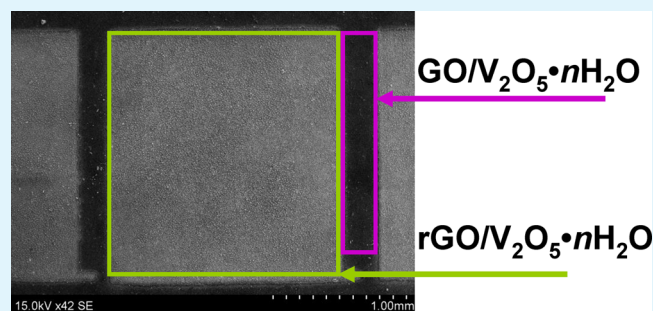
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ABSTRACT: Herein, photothermal modification of nanocomposite films consisting of hydrated vanadium pentoxide ($V_2O_5 \cdot nH_2O$) nanoribbons wrapped with graphene oxide (GO) flakes was performed via 405 nm direct laser irradiation. The combination of X-ray diffraction, X-ray photoelectron spectroscopy, Raman scattering, transmission electron microscopy, and scanning electron microscopy allowed comprehensive characterization of physical and chemical changes of $GO/V_2O_5 \cdot nH_2O$ nanocomposite films upon photothermal modification. The modified nanocomposite films exhibited porous surface morphology ($17.27 \text{ m}^2 \text{ g}^{-1}$) consisting of randomly distributed pillarlike protrusions. The photothermal modification process of $GO/V_2O_5 \cdot nH_2O$ enhanced the electrical conductivity of nanocomposite from 1.6 to 6.8 S/m. It was also determined that the direct laser irradiation of $GO/V_2O_5 \cdot nH_2O$ resulted in considerable decrease of C–O bounds as well as O–H functional groups with an increase of the laser power density.

KEYWORDS: graphene oxide, vanadium pentoxide, photothermal modification, laser, nanocomposite, functional



INTRODUCTION

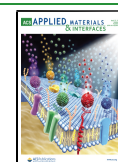
Vanadium pentoxide (V_2O_5) has gained substantial scientific interest due to its outstanding properties in many different applications, such as lithium-ion batteries (LIB),^{1,2} supercapacitors,^{3,4} field-effect transistors,⁵ sensors,^{6–8} electrochromic devices,^{9–11} and actuators.¹² This transition-metal oxide is highly valued because of its affordable cost and high energy density.^{13,14} It is almost unique electrode material that is capable of hosting monovalent as well as multivalent cations. In contrast to bulk V_2O_5 properties, enhanced device performances were reported via application of V_2O_5 nanostructures, such as nanowires,¹⁵ nanotubes,¹⁶ nanobelts,¹⁷ and nanorods.¹⁸ These crystalline V_2O_5 nanostructures can be synthesized via hydrothermal, solvothermal, or sol-gel methods. Another type of this transition-metal oxide is known as hydrated vanadium pentoxide (also known as “amorphous V_2O_5 ” or V_2O_5 xerogel) with general formula $V_2O_5 \cdot nH_2O$ (where n commonly falls in the range of 0–3). It can be characterized as a material having short-range order with an ordered stacking of VO_5 bilayers at nanoscale. In contrast to crystalline V_2O_5 nanoderivatives, $V_2O_5 \cdot nH_2O$ (as an electrode material) has been reported to exhibit higher electrochemical performance (e.g., discharge potential, energy density, and cyclic stability) owing to the fast heterogeneous charge-transfer reactions.^{19,20} It is also considered that amorphous or low-crystallinity electrode materials are less prone to mechanical stress during the large cation hosting and

release processes and thus can provide higher intercalation capacities than high-crystallinity ones.¹⁹ The $V_2O_5 \cdot nH_2O$ is also diversely used in other applications, such as chemical sensors,²¹ electrochromic devices,²² catalysis,²³ etc. Physical and chemical vapor deposition apart, $V_2O_5 \cdot nH_2O$ is commonly synthesized via solution-based routes, such as ionic exchange from $NaVO_3$,²⁴ hydrolysis and condensation from alkoxide,²⁵ crystalline V_2O_5 reaction with peroxides,²⁶ or melt-quenching²⁷ in H_2O . Like most metal oxides, both V_2O_5 and $V_2O_5 \cdot nH_2O$ suffer from low electrical conductivity, which limits implementation of these materials in LIB and supercapacitor applications.^{28–30} A common practice is to combine nanostructured metal oxides with carbonaceous nanoderivatives, such as carbon nanotubes,³¹ carbon nanofiber,³² mesoporous carbon,³³ and graphene³⁴ for the enhancement of the electronic conductivity and their structural stability.^{35–37} Specifically, the combination of reduced graphene oxide (rGO) with nanostructured V_2O_5 was reported to be an attractive protocol to achieve electrode materials with high electrochemical performance for supercapacitors due to

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enhanced power and energy densities.^{38,39} However, common methods employed to produce rGO-containing nanocomposite materials, such as hydrothermal⁴⁰ and solvothermal³⁴ synthesis routes are not applicable to large-scale process and lack selectivity. Therefore, exploration and development of novel strategies is meaningful in this context. Photothermal modification via direct laser irradiation is one of the most attractive protocols due to its flexible, economical, selective, and reliable patterning characteristics.⁴¹ Importantly, it was shown that this protocol allows to obtain the graphene-like materials with high sp^2 content.⁴² Furthermore, the direct laser irradiation process is highly tunable and allows one to achieve different physical and chemical characteristics of the material.⁴³ Based on the above, photothermal modification via direct laser irradiation is a promising strategy to prepare rGO/ V_2O_5 or rGO/ $V_2O_5 \cdot nH_2O$ nanocomposite materials.⁴⁴

Hereby, we reported on the photothermal modification of nanocomposite films consisting of hydrated vanadium pentoxide ($V_2O_5 \cdot nH_2O$) wrapped with graphene oxide (GO) flakes through 405 nm direct laser irradiation. The laser modified areas in the GO/ $V_2O_5 \cdot nH_2O$ films are defined as rGO/ $V_2O_5 \cdot nH_2O$. We have demonstrated that the method applied produces porous surface morphology of rGO/ $V_2O_5 \cdot nH_2O$. As it will be shown below, the morphological evolution of surface features is dependent on laser power density (LPD). The combination of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman scattering, transmission electron microscopy (TEM), and scanning electron microscopy (SEM) analytical techniques allowed comprehensive characterization of physical and chemical changes of GO/ $V_2O_5 \cdot nH_2O$ nanocomposite films upon photothermal modification. General tendencies of changes in the functional groups depending on LPD were revealed.

RESULTS AND DISCUSSION

Characterization of Crystalline V_2O_5 and $V_2O_5 \cdot nH_2O$.

The diffraction patterns of the crystalline V_2O_5 and $V_2O_5 \cdot nH_2O$ powders are shown in Figure S1. For the fitting procedure, the crystallographic information files (CIF) of crystalline V_2O_5 and $V_2O_5 \cdot nH_2O$ were assembled from refs 45 and 27, respectively. The V_2O_5 (Figure S1a) has a typical orthorhombic lattice (Crystallography Open Database (COD) ID 9012220), space group $Pmn\ 21$ (group number = 31) with a cell parameters $a = 11.503 \text{ \AA}$, $b = 4.368 \text{ \AA}$, $c = 3.561 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ and the $(-2\ 0\ 0)$, $(0\ -1\ 0)$, $(-1\ -1\ 0)$, $(-2\ -1\ 0)$, $(-1\ 0\ -1)$, $(-3\ -1\ 0)$, $(0\ -1\ -1)$, $(-1\ -1\ -1)$, $(-3\ 0\ -1)$, $(-2\ -1\ -1)$, $(-4\ -1\ 0)$, $(0\ -2\ 0)$, $(-1\ -2\ 0)$, $(-2\ -2\ 0)$, $(-4\ -1\ -1)$, $(-6\ 0\ 0)$, $(-3\ -2\ 0)$, $(-1\ -2\ -1)$ reflexes observable in the range of $3.0\text{--}50.0^\circ$. The melt-quenching process of crystalline V_2O_5 resulted in formation of $V_2O_5 \cdot nH_2O$ (Figure S1b) with a monoclinic lattice (COD ID 4124512), space group $C12/m1$ (group number = 12) with a cell parameters $a = 11.700 \text{ \AA}$, $b = 3.617 \text{ \AA}$, $c = 11.447 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 88.07^\circ$ and the $(0\ 0\ 1)$, $(1\ 1\ 0)$ reflexes observable. The broad and pronounced $(0\ 0\ 1)$ reflex of $V_2O_5 \cdot nH_2O$ indicates lamellar ordering (albeit turbostatic) and is consistent with those reported elsewhere.²⁷ The crystallite size for the corresponding reflex was determined to be 51.2 \AA . The interplanar spacing (d -spacing) of the $(0\ 0\ 1)$ reflex was determined to be 11.7 \AA . It is known that the d -spacing in $V_2O_5 \cdot nH_2O$ varies depending on the amount of H_2O intercalated between V_2O_5 layers.^{46,47} The amount of H_2O molecules, n , evaluated from d -spacing of the $(0\ 0\ 1)$ reflex was

determined to be $n = 1.7$, which was found to be higher than $V_2O_5 \cdot nH_2O$ prepared using ion exchange⁴⁸ with thermal treatment at 150°C ($n = 1.1$) or alkoxide sol-gel⁴⁹ routes ($n = 0.9$, for sample subjected to atmospheric hydrolysis; $n = 1.5$, for sample prepared with $\text{pH} = 1$) reported previously. Several works reported that the amount of H_2O can considerably change the structural properties of $V_2O_5 \cdot nH_2O$.^{8,17,50,51} It is known that up to 250°C H_2O loss is reversible, while between 250°C and $320\text{--}350^\circ\text{C}$, H_2O molecules are removed from the lattice without a chance to be absorbed afterward at room temperature conditions, resulting in $V_2O_5 \cdot 0.1H_2O$; at 350°C and above, V_2O_5 crystallizes into Shcherbinaite with the orthorhombic structure.^{52,53}

The structure information on crystalline V_2O_5 and $V_2O_5 \cdot nH_2O$ was further obtained via Raman scattering, as depicted in Figure S2. The Raman spectrum of crystalline V_2O_5 (Figure S2a) exhibits a number of bands among which the band located at 994 cm^{-1} is attributed to the $V=O$ stretching vibration.⁵⁴ The $V-O$ stretching vibration is located at 702 cm^{-1} .⁵⁵ The band at 528 cm^{-1} is attributed to the V_3-O stretching vibration.⁵⁶ The $V-O-V$ bending vibrations are observed at 482 , 405 , and 304 cm^{-1} .^{55,57} The band at 284 cm^{-1} is assigned to $V=O$ bending vibration.⁵⁶⁻⁵⁸ The $O-V-O$ bending vibration is observed at 197 cm^{-1} .⁵⁹ The $V-O-V$ skeleton bending vibration is observed at 145 cm^{-1} .^{55,59} Similar vibrational modes of functional groups can be observed in the Raman spectrum of $V_2O_5 \cdot nH_2O$ (Figure S2b). In contrast to V_2O_5 , the observed bands in $V_2O_5 \cdot nH_2O$ spectrum exhibit broadening and their positions are slightly shifted due to water intercalation.

The XPS was employed for the analysis of the chemical properties of crystalline V_2O_5 and $V_2O_5 \cdot nH_2O$. Figure S3 shows the XPS V 2p and O 1s high-resolution spectra with deconvoluted components. Because of the orbital splitting, the energy level of V 2p splits into the V $2p_{3/2}$ and V $2p_{1/2}$. The deconvoluted components in the XPS V $2p_{3/2}$ and V $2p_{1/2}$ high-resolution spectra of crystalline V_2O_5 and $V_2O_5 \cdot nH_2O$ were attributed to V^{3+} (515.05 and 521.69 eV ; 515.01 and 522.51 eV), V^{4+} (515.9 and 522.75 eV ; 515.84 and 523.34 eV), and V^{5+} (517.2 and 524.33 eV ; 517.11 and 524.61 eV) oxidation states.⁶⁰ It is evident that the major part of V 2p spectra consists of V^{5+} . The O 1s photoemission line was deconvoluted into three components. The two components of crystalline V_2O_5 located at 529.99 and 530.38 eV were attributed to the O^{2-} ions⁶¹ and $V-O$ linkage in the V_2O_5 while the component at 531.82 eV was assigned to the OH^- groups.⁶² These components of $V_2O_5 \cdot nH_2O$ in XPS O 1s spectra were located at 529.92 eV , 530.94 eV , and 532.36 eV . The OH^- group component is much more pronounced in the XPS O 1s spectra of $V_2O_5 \cdot nH_2O$ due to its hydrated state.

Further, the TEM analysis of $V_2O_5 \cdot nH_2O$ was performed for characterization of morphology. Figure S4 shows the TEM image of $V_2O_5 \cdot nH_2O$ nanostructures formed via the melt-quenching process. The obtained nanostructures exhibited ribbonlike particle morphology,^{46,63} which is in line with V. Petrikov et al.²⁷ The observed morphology of $V_2O_5 \cdot nH_2O$ nanoribbons (Figure S4) is in good agreement with XRD results.

Characterization of GO. Figure S5 shows XRD diffraction pattern of GO. In the XRD diffraction pattern, the broad and distinct $(0\ 0\ 1)$ reflex with a d -spacing of 7.9 \AA was observable, indicating the presence of GO, consistent with results reported elsewhere.^{64,65}

The Raman spectrum of GO is depicted in Figure S6. The deconvoluted G_1 and G_2 bands are located at 1596 cm^{-1} and 1545 cm^{-1} , while the D band is at 1350 cm^{-1} . The 2D and D+G bands are observed at 2697 and 2925 cm^{-1} , respectively. The statistical reliability factor (R^2) for fitting Gaussian components was found to be $R^2 \geq 0.97$. The D band arises from the defect-induced breathing modes of sp^2 rings.⁶⁶ The G_1 component is associated with the in-plane stretching vibration.⁶⁷ The G_2 component can be attributed to the bond angle disorder and surface functional groups (O–H).^{66,68} The I_D/I_{G1} ⁶⁹ and I_{G2}/I_{G1} ⁶⁶ intensity ratios were found to be 0.98 and 0.52 for GO. The second order overtone, 2D, is due to the two-phonon double resonance, while the D+G band is attributed to higher structure disorder of GO.⁷⁰

Chemical properties of GO were investigated using XPS. The XPS O 1s and C 1s high-resolution spectra are depicted in Figure S7. The first deconvoluted component at 531.2 eV in the O 1s spectrum (Figure S7a) is attributed to O=C=O, while the second and the third component at 532.4 and 533.6 eV to C–O and O–H chemical bonds.^{71,72} Five deconvoluted components in the C 1s photoemission line (Figure S7b) located at 283.6 eV, 284.8 eV, 285.6 eV, 286.7 eV, and 288.3 eV were assigned to the C=C/C–C, C–C, C–O/C–O–C, C–O, and C=O chemical bonds, respectively.^{64,72,73}

TEM image of GO is depicted in Figure S8. The GO flakes have a folded and corrugated sheet structure with numerous wrinkles. It can be observed, that the GO sheets are relatively large, indicating relatively low damage of the sheet structure produced by the mechanical stirring method.

Characterization of $GO/V_2O_5 \cdot nH_2O$ and $rGO/V_2O_5 \cdot nH_2O$ Nanocomposite Films. TEM inspection was performed for as prepared $GO/V_2O_5 \cdot nH_2O$ nanocomposite and is depicted in Figure 1. It can be seen that $V_2O_5 \cdot nH_2O$ nanoribbons are wrapped with GO sheets and are no longer easily distinguishable.

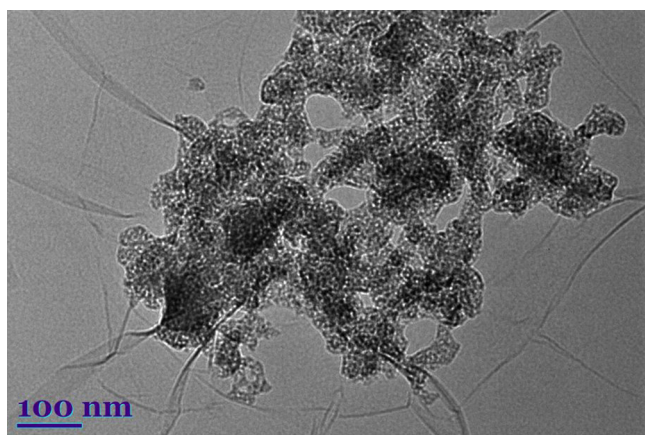


Figure 1. TEM micrograph of $GO/V_2O_5 \cdot nH_2O$ nanocomposite.

SEM analysis was performed to inspect the surface features of $GO/V_2O_5 \cdot nH_2O$ nanocomposite films. The SEM micrographs of $GO/V_2O_5 \cdot nH_2O$ nanocomposite surface are shown in Figure 2, indicating a uniform and wrinkled surface of the film. It is known that GO can have different surface morphologies, which can be highly influenced by the pH of the system⁷⁴ and the deposition method.⁷⁵ It can be observed from the SEM images that the intersection of wrinkles assembled into starlike microstructures. Similar microstructures

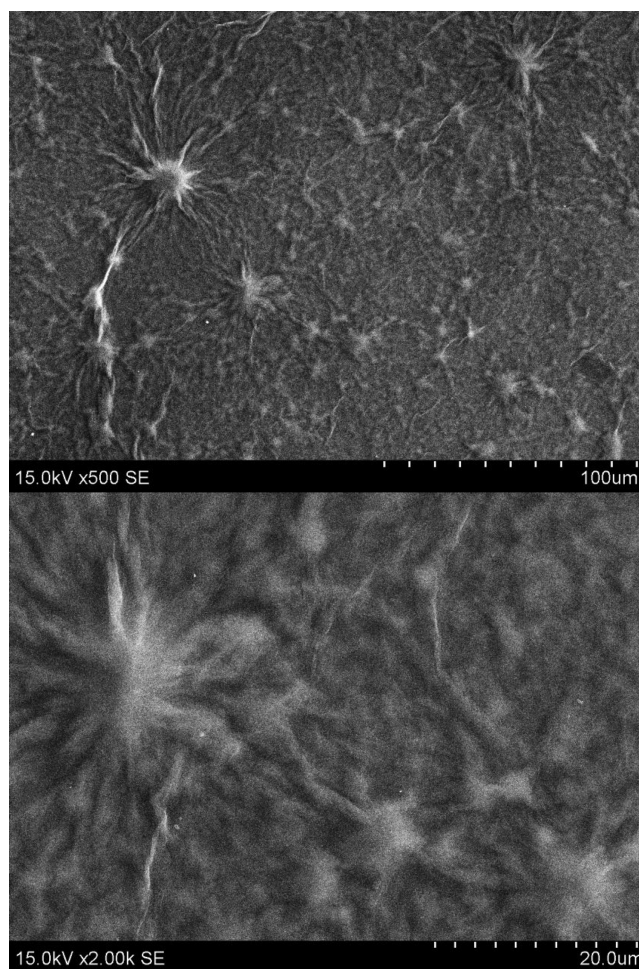


Figure 2. SEM micrographs at different magnification scale of $GO/V_2O_5 \cdot nH_2O$ nanocomposite films.

were observed in our previous work,⁴² where only GO films were studied. This is an indication that the resultant nanocomposite film morphology is mainly governed by GO sheets and $V_2O_5 \cdot nH_2O$ nanoribbons in the system have no observable influence at this point. Additionally, SEM observations also imply that $V_2O_5 \cdot nH_2O$ nanoribbons are not distinguishable from GO sheets on the surface of nanocomposite film, which is consistent with TEM results, that $V_2O_5 \cdot nH_2O$ nanoribbons are wrapped with GO sheets.

Figure 3 shows SEM micrographs of $rGO/V_2O_5 \cdot nH_2O$ nanocomposite films where direct laser irradiation took place in the grayish rectangle areas with LPD varied. In Figure 3a–d, LPD was varied in the range of $1.69\text{--}2.71 \times 10^5\text{ W/cm}^2$. The $rGO/V_2O_5 \cdot nH_2O$ areas in the SEM micrographs are easily distinguishable indicating that the photothermal modification process took place.

In contrast to $GO/V_2O_5 \cdot nH_2O$, the observed surface morphology of $rGO/V_2O_5 \cdot nH_2O$ is significantly different. In all cases, the surface of $rGO/V_2O_5 \cdot nH_2O$ is covered with randomly distributed pillarlike protrusions with the size in the range from several nanometers to tens of micrometers, exhibiting porous surface morphology. The specific surface area of $rGO/V_2O_5 \cdot nH_2O$ was determined to be $17.27\text{ m}^2\text{ g}^{-1}$, more than 4 times higher than that of $GO/V_2O_5 \cdot nH_2O$ ($3.84\text{ m}^2\text{ g}^{-1}$). This is a very promising result considering LIB, supercapacitor, and sensor applications as it can improve the

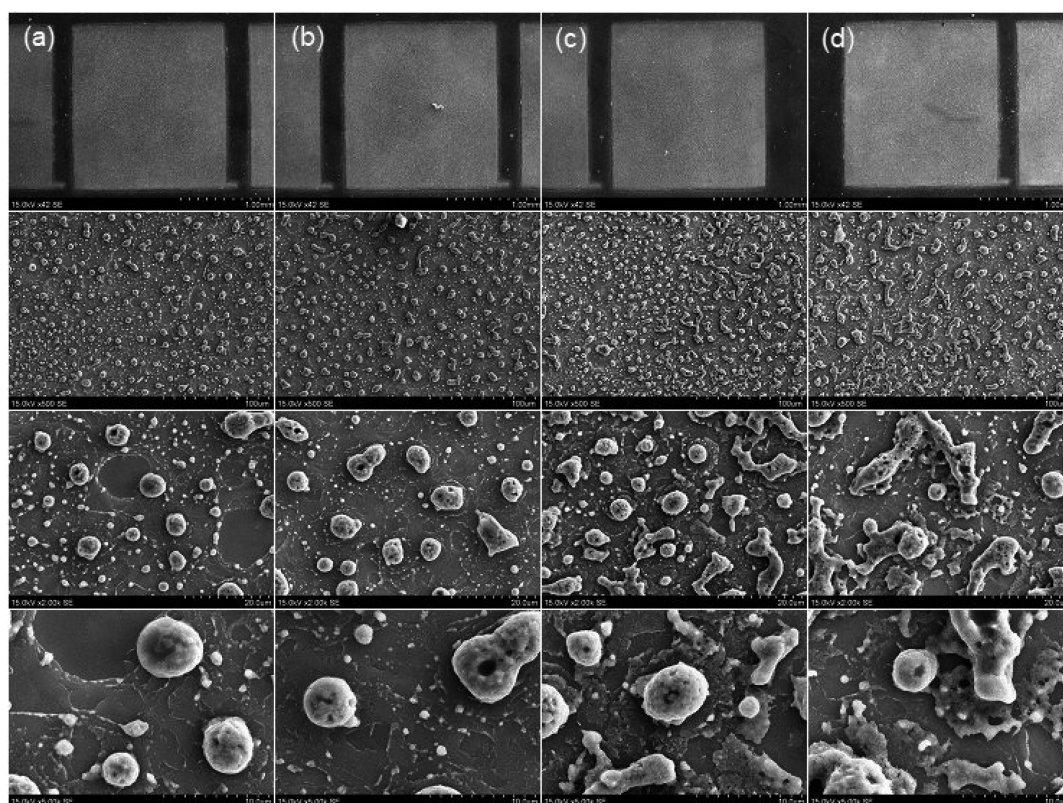


Figure 3. SEM micrographs at different magnification scales of rGO/V₂O₅·*n*H₂O nanocomposite films. The direct laser irradiation took place in the grayish rectangle areas. LPD (a) 1.69, (b) 2.03, (c) 2.37, and (d) 2.71 × 10⁵ W/cm² varied, respectively.

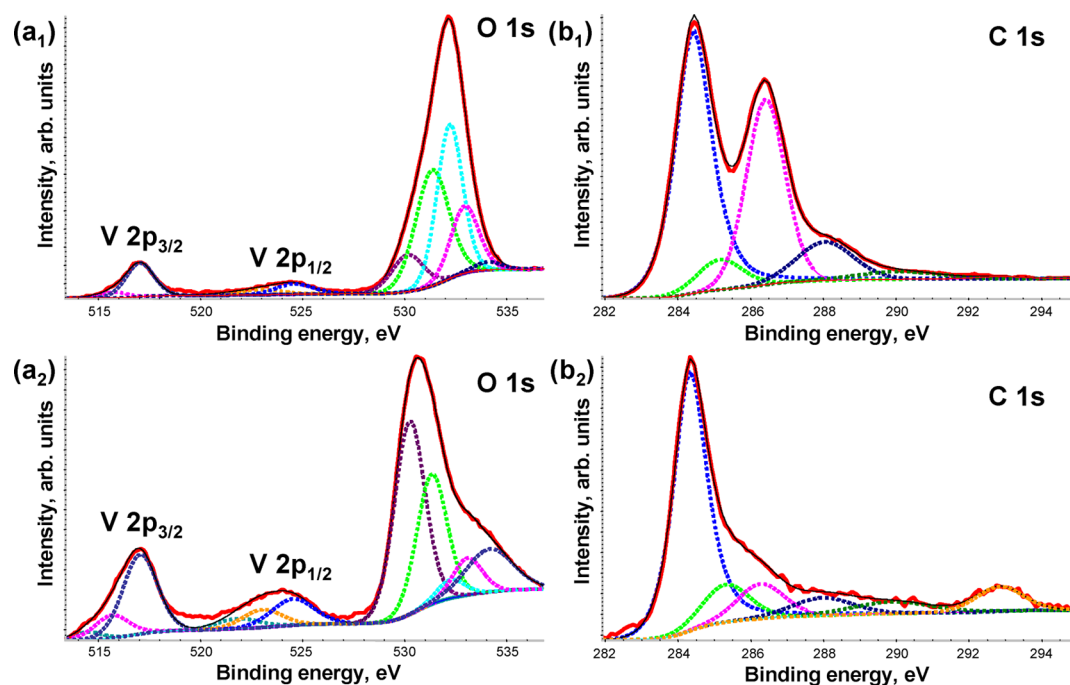


Figure 4. Deconvoluted high-resolution XPS: V 2p, O 1s, and C 1s spectra of (a₁ and b₁) GO/V₂O₅·*n*H₂O and (a₂ and b₂) rGO/V₂O₅·*n*H₂O nanocomposite films. Thick red lines show experimental data, thin black lines show the envelope, and thick dashed lines show the fitted components.

resultant energy storing capacity as well as sensor response with lower operating temperature and efficient detection characteristics. Importantly, SEM micrographs at 500× magnification (Figure 3) revealed morphological tendency,

which is dependent on the LPD: with the increase of LPD the pillarlike protrusions are prone to form clusters with increasing size. Quantitative data for morphological changes of cluster formation with LPD is depicted in Figure S9. Additionally, the

increase of LPD produced more nanometer-scale protrusions across the surface, e.g., from 2.37 to 2.71×10^5 W/cm² produced 12% more nanometer-scale protrusions. Fractional areas of all surface features constituted of 18.5 (1.69×10^5 W/cm²), 18.6 (2.03×10^5 W/cm²), 27.8 (2.37×10^5 W/cm²), and 26.5% (2.71×10^5 W/cm²). SEM observations suggest that photothermal modification of GO/V₂O₅·*n*H₂O results in formation of rGO/V₂O₅·*n*H₂O with heterogeneous surface morphology having a combination of micro- and nanoscale structural features.

The characteristic XRDGI pattern of rGO/V₂O₅·*n*H₂O nanocomposite film (LPD of 2.71×10^5 W/cm²) is shown at Figure S10. After direct laser irradiation of GO/V₂O₅·*n*H₂O, the *d*-spacing for the (0 0 1) reflex of V₂O₅·*n*H₂O was found to be 10.3 Å, indicating removal of water molecules from the lattice with *n* = 1.5 (before modification *n* = 1.7). The crystallite size for the (0 0 1) reflection was found to be 54.4 Å, consistent with TEM. Another peak in the XRDGI pattern corresponds to rGO (0 0 2) reflex with *d*-spacing of 3.5 Å. The broadening in the rGO (0 0 2) indicates poor ordering of the stacked layers.

Figure S11 shows baseline-corrected Raman spectrum of rGO/V₂O₅·*n*H₂O nanocomposite film (LPD of 2.71×10^5 W/cm²). It can be seen that Raman spectrum exhibits characteristic bands attributed to V₂O₅·*n*H₂O (104 – 1170 cm⁻¹) and rGO-deconvoluted bands by Gaussian components: G₁ (1600 cm⁻¹), G₂ (1535 cm⁻¹), D (1353 cm⁻¹), 2D (2714 cm⁻¹) and D+G (2936 cm⁻¹); *R*² ≥ 0.97. The highest laser power density produced rGO in the nanocomposite system with *I*_D/*I*_{G1} and *I*_{G2}/*I*_{G1} ratios of 0.98 and 0.36. In contrast to GO, the considerable decrease in *I*_{G2}/*I*_{G1} ratio was observed for rGO, which indicates more ordered structure⁶⁷ and removal of functional groups.⁶⁸

The *I*–*V* curves of GO/V₂O₅·*n*H₂O and rGO/V₂O₅·*n*H₂O (LPD of 2.71×10^5 W/cm²) nanocomposite films are depicted in Figure S12. The *I*–*V* curve of rGO/V₂O₅·*n*H₂O nanocomposite shows ohmic characteristics which demonstrates that the photothermal modification process of GO/V₂O₅·*n*H₂O enhanced the conductivity of nanocomposite film. The electrical conductivity values for GO/V₂O₅·*n*H₂O and rGO/V₂O₅·*n*H₂O were determined to be 1.6 and 6.8 S/m. In contrast, V₂O₅ was reported to suffer from low electrical conductivity, which is in the range of 10^{-2} – 10^{-3} S/cm.²⁸

The effect of photothermal modification on the chemical states of GO/V₂O₅·*n*H₂O was investigated via XPS. The deconvoluted XPS V 2p, O 1s, and C 1s high-resolution spectra of GO/V₂O₅·*n*H₂O and rGO/V₂O₅·*n*H₂O (LPD of 2.71×10^5 W/cm²) are shown in Figure 4. Similarly as in crystalline V₂O₅ and V₂O₅·*n*H₂O (Figure S3), the deconvoluted components of GO/V₂O₅·*n*H₂O and rGO/V₂O₅·*n*H₂O in the XPS V 2p_{3/2} and V 2p_{1/2} photoemission lines were assigned to V³⁺ (514.7 and 521.28 eV; 514.5 and 521.83 eV), V⁴⁺ (515.77 and 522.97 eV; 515.66 and 523.03 eV), and V⁵⁺ (517.02 and 524.58 eV; 517.03 and 523.03 eV) oxidation states.

The deconvoluted components of GO/V₂O₅·*n*H₂O and rGO/V₂O₅·*n*H₂O (LPD of 2.71×10^5 W/cm²) in XPS O 1s spectra were assigned to V–O linkage in the V₂O₅ (530.15 and 530.24 eV), O–C=O (531.35 and 531.33 eV), C–O (532.21 and 532.25 eV), and O–H (532.94 and 533.08 eV) chemical bonds.^{62,70,72} The intensity decrease of C–O component at 532.25 eV for rGO/V₂O₅·*n*H₂O (Figure 4a₂) indicates the removal of carbon–oxygen bounds. The additional component

of GO/V₂O₅·*n*H₂O and rGO/V₂O₅·*n*H₂O observed in XPS O 1s spectra at 534.09 and 534.18 eV is related to water molecules.^{76–78} In the case of GO/V₂O₅·*n*H₂O, the latter component is significantly weaker as compared to rGO/V₂O₅·*n*H₂O, because H₂O molecules are tightly bound to their position in between GO and V₂O₅ layers. These XPS results are in line with the results reported in ref 79. Evolution of water molecules and changes in the O–H groups with LPD are summarized in Figure S13. The relative fraction of each component was calculated by dividing its area (*A_x*) by the total area (*A_{Tot}*) of all O 1s components. The deconvoluted components of GO/V₂O₅·*n*H₂O and rGO/V₂O₅·*n*H₂O in XPS C 1s spectra were assigned to C–C (284.41 and 284.31 eV), C–O/C–O–C (285.15 and 285.3 eV), C–O (286.41 and 286.26), C=O (288.03 and 287.95 eV), and O=C–OH (290.05 and 289.88 eV) bounds, and π – π^* shakeup transition (292.9 and 292.85 eV), respectively.^{80,81} Again, decreased intensity of the C–O component at 286.26 eV for rGO/V₂O₅·*n*H₂O (Figure 4b₂) indicates the removal of carbon–oxygen bounds. The summary of C–O chemical bond changes depending on the LPD for rGO/V₂O₅·*n*H₂O nanocomposite films is shown in Figure S14. Relative fraction of the C–O component was calculated by dividing the *A_x* by the *A_{Tot}* of all C 1s components. It is evident, that the removal of carbon–oxygen bounds took place up to the LPD of 2.03×10^5 W/cm². Afterward, the relative fraction of C–O chemical bonds remained steady at ~ 0.1 , indicating that no more breakup of carbon–oxygen bonds with increasing LPD. For GO/V₂O₅·*n*H₂O, the C–C/C–O ratio was determined to be 1.3, while after photothermal modification to rGO/V₂O₅·*n*H₂O with the LPD of 1.69×10^5 W/cm² it increased up to 5.0, indicating $\sim 83\%$ conversion of GO to rGO. The GO reduction with the LPD of 2.03×10^5 W/cm² resulted in nearly complete restoration of aromatic $\pi \rightarrow \pi$ system with the C–C/C–O ratio of 5.98 ($\sim 99\%$ conversion of GO to rGO) remained steady in the range of 5.98–6.0 for higher laser power densities.

CONCLUSIONS

The photothermal modification of GO/V₂O₅·*n*H₂O via 405 nm direct laser irradiation has been studied. The nanocomposite system consisted of nanoribbons wrapped with graphene oxide (GO) flakes. The melt-quenching process produced V₂O₅·*n*H₂O nanoribbons having a monoclinic lattice, space group C 1 2/m1 (group number = 12) with a cell parameters *a* = 11.700 Å, *b* = 3.617 Å, *c* = 11.447 Å, $\alpha = \gamma = 90^\circ$, $\beta = 88.07^\circ$ and the (0 0 1), (1 1 0) reflexes observable. After direct laser irradiation of GO/V₂O₅·*n*H₂O via the *d*-spacing for the (0 0 1) reflex of V₂O₅·*n*H₂O was found to be 10.3 Å (before modification, 11.7 Å), indicating removal of water molecules from the lattice with *n* = 1.5 (before modification, *n* = 1.7). The XRD and Raman analyses confirmed that photothermal modification reduced GO to rGO as evident from broad (0 0 2) reflex in XRDGI pattern and decrease of *I*_{G2}/*I*_{G1} intensity ratio from 0.52 to 0.36 in Raman spectra. The rGO/V₂O₅·*n*H₂O nanocomposite films exhibited porous surface morphology (17.27 m² g⁻¹) consisting of randomly distributed pillarlike protrusions with the size in the range from several nanometers to tens of micrometers. It was determined that with the increase of LPD, the pillar-like protrusions are prone to form clusters with increasing size. The direct laser irradiation of GO/V₂O₅·*n*H₂O enhanced the electrical conductivity of nanocomposite from

1.6 to 6.8 S/m. It was determined that the photothermal modification process results in considerable decrease of C–O bonds as well as O–H functional groups with increase of LPD. The GO/V₂O₅·nH₂O nanocomposite can be further used in lithium–ion batteries, supercapacitors, and sensor applications.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c02066>.

Materials and methods: formation of GO/V₂O₅·nH₂O nanocomposite films; photothermal modification of GO/V₂O₅·nH₂O nanocomposite films; characterization: XRD, Raman, XPS spectra as well as TEM images, and I–V curves; cluster formation dependence on LPD; evolution of water molecules and changes in O–H groups depending on LPD; and C–O chemical bond changes depending on the LPD (PDF)

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Notes

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