



Strategy for controlling the morphology and work function of W₂C/WS₂ nanoflowers

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ABSTRACT

Recently, tungsten disulfide (WS₂) and tungsten carbide (W₂C) have been demonstrated as promising materials in energy conversion and storage applications. In this study, we describe the successful synthesis of W₂C and WS₂ alloy nanoflowers (W₂C/WS₂ NFs) via a simple hydrothermal method. Interestingly, the morphology of the W₂C/WS₂ alloy NFs and their work function can be precisely controlled by adjusting the precursor, reaction temperature, and reaction time. Specifically, the size of the W₂C/WS₂ alloy NFs was controlled from 100 nm to 1 μm by changing the reaction time from 2 to 12 h. The lattice constants of the materials calculated following the peak positions and Bragg's law indicate that the strain remained after the co-formation of W₂C and WS₂. In addition, the work function of the W₂C/WS₂ alloy NFs could be tuned from 4.31 to 4.95 eV by modulating the synthetic conditions. Therefore, this work provides a simple approach for the fabrication of W₂C/WS₂ alloy NFs whose morphology as well as work function can be controlled.

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1. Introduction

In recent decades, along with the development of graphene, two-dimensional (2D) transition metal dichalcogenides (TMDs) have been intensively investigated. In general, 2D TMDs have a layered structure consisting of a transition metal layer sandwiched between two layers of chalcogenide atoms. Layers are bonded to each other by weak van der Waals forces, making it easily to exfoliate sheets by physical and chemical methods. It has also been revealed that the nano size of thin-layer TMDs (single, few layers) bestows a number of advantages compared to bulk TMDs, including superior properties such as high thermal/electrical conductivity, stability, and a tunable band gap, which make these materials promising for applications in electronic and optoelectronic devices

[1–7]. Furthermore, their catalytic properties are also remarkable [8–13]. Among 2D TMDs, tungsten disulfide (WS₂) is one of the most attractive TMDs for scientists. WS₂ has been prepared and studied in various morphologies and sizes. For example, Voiry reported the efficient synthesis of WS₂ nanosheets via a lithium intercalation method for a hydrogen evolution reaction [14]. Le and coworkers have applied UV/ozone-treated WS₂ nanosheets as a hole-extraction layer in organic photovoltaic cells [15]. Yan et al. have grown vertically aligned WS₂ nanosheets on carbon cloth to exploit their catalytic properties in water splitting [16]. The Caruso group developed WS₂ microspheres for heavy metal ion sequestration [17]. In addition, WS₂ NFs have been grown on reduced graphene oxide for enhanced electrode performance in lithium-ion batteries [18]. Quantum dots of WS₂ have been used for antibody-free optical sensing of neurotransmitters [19]. Thus, it is believed that WS₂ plays an important role in catalytic, electronic, and optical applications.

In addition, transition metal carbides and nitrides, named as M-Xene, are also attractive to researchers [20]. M-Xenes have advantageous physical properties, including high electrical

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conductivity and chemical stability, which are beneficial for energy storage and conversion applications [21,22]. Furthermore, these materials have displayed excellent performance as electrochemical catalysts [23,24]. Among the M-Xenes, tungsten carbide (W_2C) has been well known since its historical appearance. The superconductivity and structure of this material were investigated by Morton and coworkers in the 70s for the first time [25]. In the years that followed, many experiments were conducted to understand its lattice structure and catalytic properties [25–29]. For example, Gong successfully synthesized W_2C nanoparticles on multi-walled carbon nanotubes which exhibited excellent properties in electrocatalytic and photoelectrochemical hydrogen evolution [30]. More recently, Li et al. fabricated a WS_2/W_2C composite by sulfurization and carburization using a hybrid zeolite imidazolate framework for enhanced hydrogen evolution catalysis [31]. All these research results indicate that W_2C and WS_2 are promising materials for catalytic, energy conversion, and energy storage applications.

The work function of a material is a minimum energy to remove the electrons held in the material to vacuum level or difference ($E_v - E_F$). It is similar to a semiconductor in that it determines the p-type or n-type when the position is close to the valence band or conduction band. To date, the graphene has been focused to find ways for tunable work function, which helps that materials could work in logical devices or could be a cathode or an anode with a suitable work function [32–34]. For TMD materials, Hu et al. reported the nitrogen doping in the MoS_2 monolayer, which led to the tunable work function ranging from 4.03 to 4.32 eV [35]. In addition, in order to obtain a good band alignment of organic photovoltaic cell, Le et al. have used the ozone treatment method to partially convert TMDs to oxide states. This illustrates that the controlling in the work function has been investigated for the efficient power conversion performance [15,36,37]. Furthermore, 2D materials with heterostructures have been reported for many applications such as memory, photodetector, organic light emitting diode, gas sensor and so on, due to the superior performance [38–42]. In recent publications, the W_2C/WS_2 material was also used to improve the catalytic properties for hydrogen evolution reactions [31,43]. Therefore, the insight view of the specific properties including the tunable band gap of this material is essential for future viable design and applications.

In this report, we demonstrate the facile synthesis of W_2C and WS_2 alloy NFs by a simple hydrothermal method based on common precursors. The formation of the materials is discussed in terms of a complex hydrothermal reduction reaction. The morphology of the W_2C/WS_2 alloy NFs can be precisely controlled by simply changing the reaction time and reaction temperature. In addition, the change in the lattice constant during the formation of the alloy due to the lattice mismatch was calculated based on X-ray diffraction (XRD) patterns. The crystal structures of the materials were fully studied and discussed. It was also discovered that the work function of the W_2C/WS_2 alloy NFs can be controlled by adjusting the synthetic conditions, which resulted in changes in the precursor crystal size. Based on these results, a strategy for controlling the size, morphology, composition, and work function of W_2C/WS_2 alloy is established.

2. Experimental

2.1. Chemical materials

Tungsten (VI) chloride (WCl_6 , 99.9% trace metals basis) and thioacetamide (C_2H_5NS , 99%) were purchased from Sigma Aldrich. Absolute ethanol was provided by Alpha Aesar. De-ionized (DI) water was obtained from Millipore Milli-Q, at $18.3 \text{ M}\Omega \text{ cm}^{-1}$.

2.2. Co-synthesis W_2C/WS_2 NFs

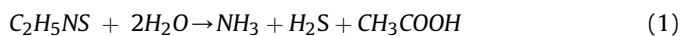
Tungsten (VI) chloride was used as a W source. To avoid any unexpected reactions due to its humidity sensitivity, this powder should be handled in an Ar/N_2 filled glove box. WCl_6 powder was kept in a 20-mL tube with a cap, and then the synthesis process was conducted inside of a fume hood. Materials were fabricated using a hydrothermal method. In brief, 0.6 g WCl_6 and 1.2 g thioacetamide were mixed separately in two 20-mL tubes with 4 mL of absolute ethanol each, via stirring at a warm temperature (40°C). Higher temperatures are not suggested due to the hydrolysis of thioacetamide. Then, the WCl_6 solution was quickly mixed with the thioacetamide solution during the stirring process. The color of the mixture immediately changed from yellow to black. To complete the pre-treated solution, 20 mL of DI water was added, and the solution was stirred for 10 min. The solution was transferred to a 100-mL Teflon-lined autoclave and put into the oven at 250°C for 8 h. The black precipitate which remained at the bottom of the Teflon liner was collected and washed several times with ethanol and DI water. W_2C/WS_2 powder was obtained after drying at 60°C . The effects of different conditions, such as temperature, ratio of WCl_6 :thioacetamide, and reaction time were also investigated.

2.3. Characterization

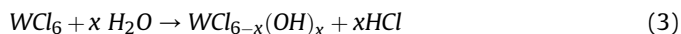
XRD (D8–Advance/Bruker-AXS) was used to confirm the structure of the materials. The morphology and composition of the materials were examined by field-emission scanning electron microscopy (FESEM, SIGMA/Carl Zeiss) and energy dispersive spectroscopy (EDS) at 20 kV using an EDS detector (Thermo NORAN System 7) integrated into the FESEM machine. Raman spectroscopy (Lab RAM HR, Horiba JobinYvon) and transmission electron microscopy (TEM, JEOL JEM–2100F) were used to determine the material structures and sizes. X-ray photoelectron spectroscopy (XPS, KRATOS AXIS Ultra DLD model) in advanced in situ surface analysis system (AISAS, KBSI, Korea) operated at a base pressure of 1.6×10^{-10} mbar at 300 K was also performed to discover material chemical compositions, binding energies and the ultraviolet photoelectron spectroscopic (UPS) measurement.

3. Results and discussion

Recent research has shown that the hydrothermal reduction of WCl_6 and C_2H_5NS follows two major reactions: hydrolysis of C_2H_5NS and the reduction of WCl_6 by hydro sulfur, as described in Equations (1) and (2) [18,44,45]:



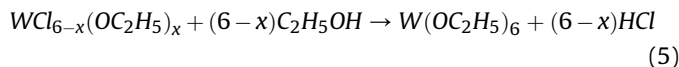
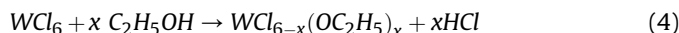
However, the WCl_6 is highly sensitive to humidity, and was therefore required to be processed in a glove box with controlled humidity. Equation (3) describes the reaction of WCl_6 with moisture:



The partial oxidation of the W precursor may cause the fast aggregation of tungsten oxide in solution during the stirring process. Without any modification, the as-prepared solution of WCl_6 and C_2H_5NS appeared to contain small precipitates owing to these phenomena.

Ethanol and other alcohols have been employed to prevent the oxidation of the W source during the fabrication of WO_3 particles and thin films [46–49]. The reaction of absolute ethanol and

tungsten oxide is described by Equations (4) and (5):



After reaction (4), the WCl_6 solution in ethanol had a yellow color which then turned blue while kept in air. If the ethanol continuously reacts with $\text{WCl}_{6-x}(\text{OC}_2\text{H}_5)_x$, the solution will become transparent in color. In this study, a thioacetamide/ethanol solution was added to the WCl_6 /ethanol solution while it was yellow. This process may prevent the complete reaction of ethanol with tungsten chloride and protect the precursor from humidity. The appearance of H_2S and NH_3 , which are reducing agents formed as hydrolysis products of thioacetamide in water, may have a specific role in the carburization process.

The chemical components and structures of the obtained materials were confirmed by XPS, Raman, XRD, FESEM, and TEM measurements. The hexagonal structures of W_2C and WS_2 are shown in Fig. 1. WS_2 has a layered structure consisting of W atoms between S atoms. W_2C has a hexagonal lattice with continuous bonding of W and C without a layered structure. It is believed that

the co-formation of these two materials will create a layer material consisting of sandwich structures of each material during hydrothermal reduction. First, the XPS spectrum in Fig. 2 (a) provides evidence that a W–S–C alloy was made, with clearly visible peaks from each element in the surface scan. The S 2p peaks located at about 160–170 eV indicate the formation of WS_2 materials. The tungsten W 4f peaks are sharp and show the doublet of W 4f_{7/2} and W 4f_{5/2} at about 32 and 34.2 eV, respectively, in Fig. 2 (b). These binding energies are consistent with the binding energies of W in WS_2 and W_2C . The close gap between the W 4f binding energies of these two materials prevents the clear deconvolution of the doublet peaks. Also, there are two weak peaks of W appearing in the range of 36–39 eV, which are attributed to the slight oxidation of materials on the surface. In Fig. 2 (c), the C 1s peaks have been deconvoluted into W–C/C–C bonding, C–O bonding, and C–OH bonding contributions at 284.7, 286.2, and 288.5 eV, respectively, following the normal deconvolution procedure described in previous reports [50,51]. The close binding energies of W–C and C–C bonding also limited the separation of these peaks. The Raman spectrum of $\text{W}_2\text{C}/\text{WS}_2$ in Fig. 2 (d) has two main peaks of WS_2 , which are related to the weak van der Waals interlayer interactions affecting the interlayer bonding and lattice vibrations of the stacked layer crystallites. These two peaks originated from the

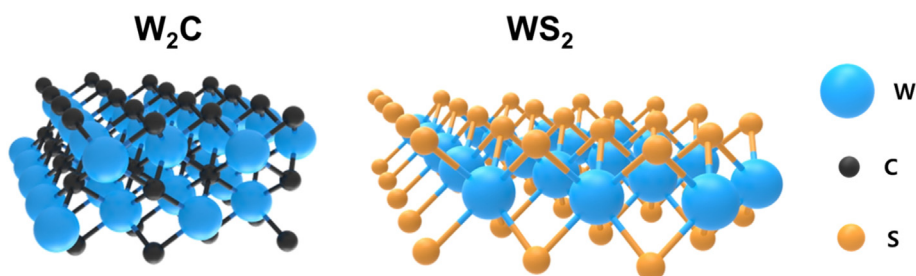


Fig. 1. Lattice structures of W_2C and WS_2 .

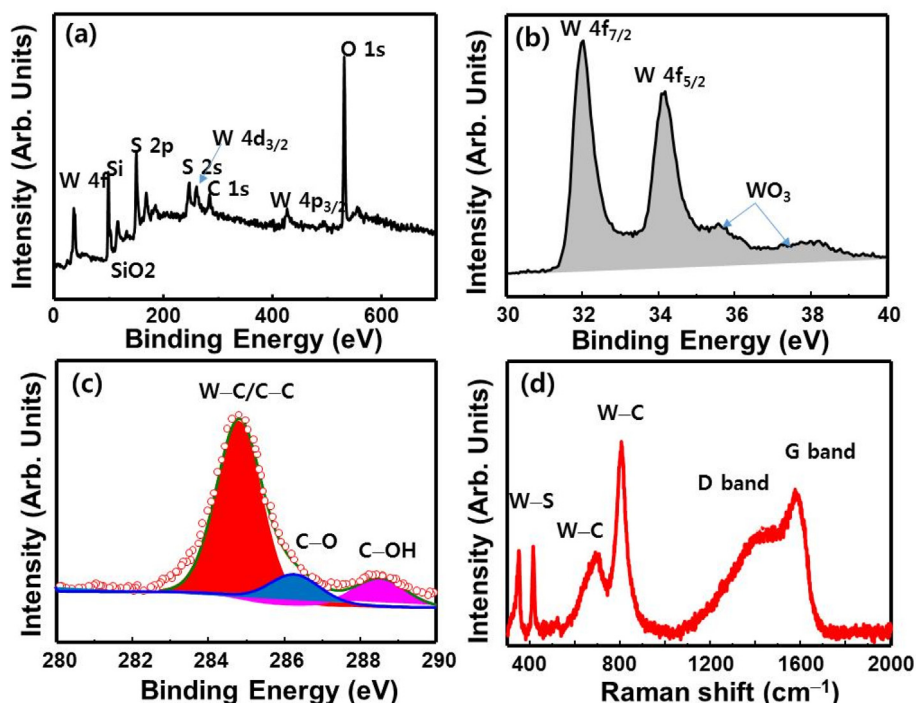


Fig. 2. XPS spectra of $\text{W}_2\text{C}/\text{WS}_2$ NFs: a) the survey scan from 0–700 eV, b) W 4f region, and c) C 1s region. d) Raman spectra of $\text{W}_2\text{C}/\text{WS}_2$ NFs under 532 nm laser beam excitation.

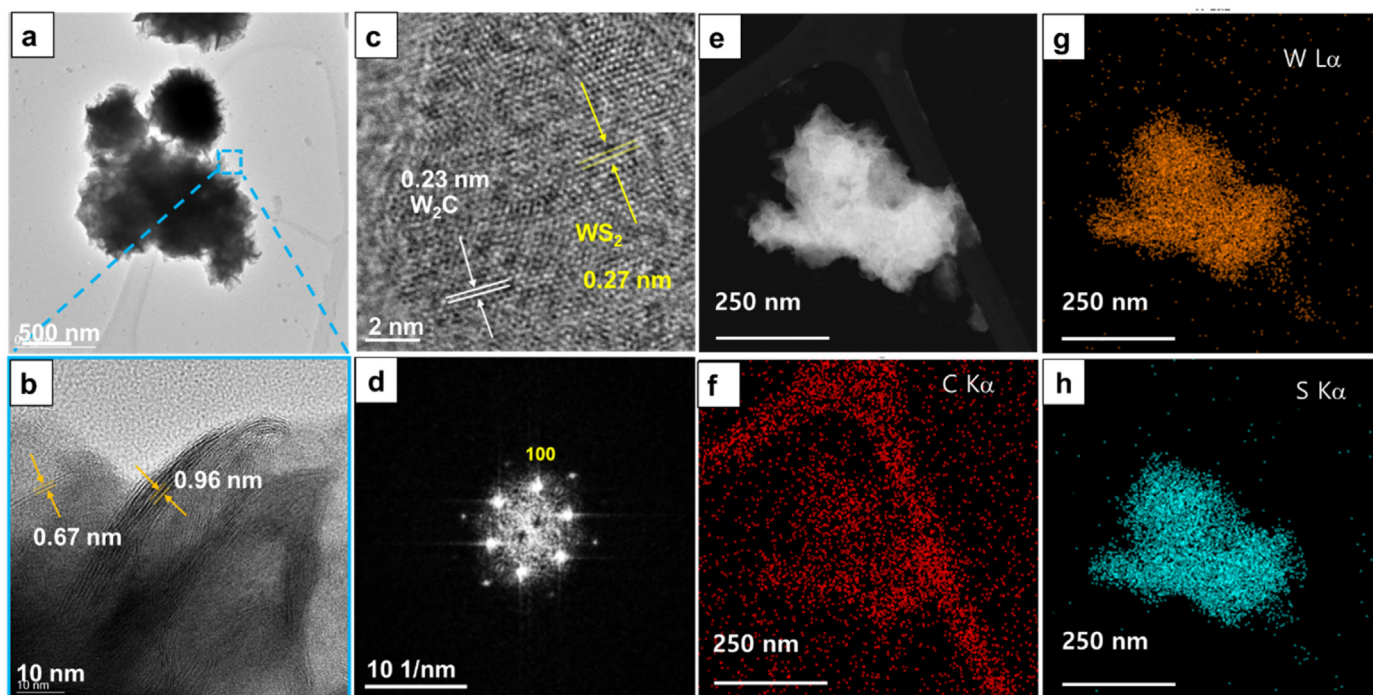


Fig. 3. TEM image (a, e), high resolution TEM images of a leaf (b, c), selected-area electron diffraction pattern (SAED) (d) and EDS elemental mapping of C K α (f), W L α (g) and S K α (h) of W₂C/WS₂ NFs synthesized at 250 °C.

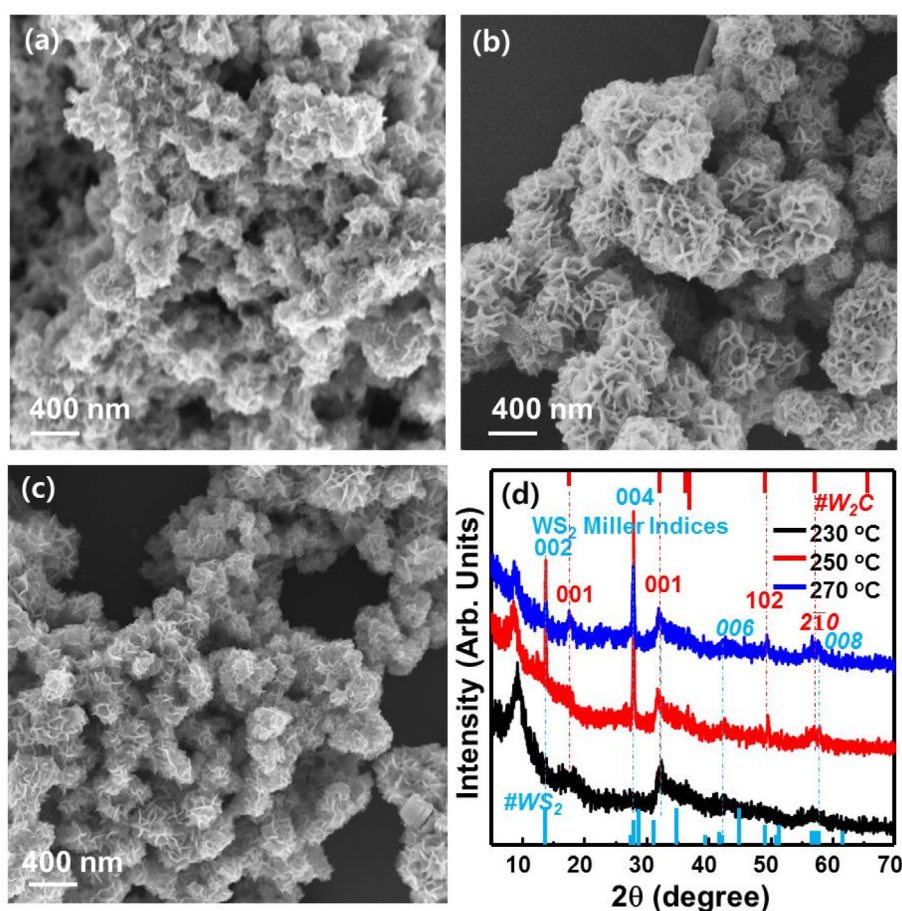


Fig. 4. FESEM images of (a) W₂C/WS₂_4h_230, (b) W₂C/WS₂_4h_250, (c) W₂C/WS₂_4h_270 synthesized at 230, 250, 270 °C, respectively, and (d) their XRD patterns.

optical phonon modes (E_{2g}^1 and A_{1g}). The E_{2g}^1 mode is an in-plane optical mode, whereas the A_{1g} mode corresponds to the out-of-plane vibrations of the sulfur atoms [52]. In the recorded data, the E_{2g}^1 and A_{1g} Raman peaks are located at 351.5 cm^{-1} and 415.2 cm^{-1} , respectively. Tungsten carbide vibration modes were detected at 700 and 805 cm^{-1} , which are consistent with the values previously reported in the literature [53]. Also, the sp^3 and sp^2 C atoms in carbide materials resulted in D band and G band peaks that are located in the range of $1200\text{--}1700\text{ cm}^{-1}$. Thus, this suggests that the W_2C/WS_2 alloy was successfully obtained. TEM images and EDS elemental mapping of the W_2C/WS_2 alloy is shown in Fig. 3(a–h). The flower shape of the particles at about $300\text{--}500\text{ nm}$ consists of many nanosheet layers. It clearly shows some Moiré patterns as seen in Fig. 3(b). Moreover, the high resolution TEM images show the appearances of distance spacing of WS_2 (100) and W_2C (101) planes are 0.27 and 0.23 nm , respectively. Notably, the selected-area electron diffraction pattern (SAED) pattern as shown in Fig. 3(d) indicated the high crystalline of the materials with hexagonal structure. Fig. 3(e–h) confirmed the material components of W, C, and S atoms in the composite. Therefore, it can be concluded that the layered W_2C/WS_2 NFs are formed well with hexagonal structure.

For controlling the size and composition of W_2C/WS_2 , a series of experiments were carried out. At first, the reaction temperature was varied from 230 to 270°C . The FESEM images and XRD patterns of the W_2C/WS_2 alloys fabricated at different synthetic temperatures of 230°C , 250°C , and 270°C are shown in Fig. 4. These samples were produced following the standard preparation procedure with a WCl_6 concentration of 12 mg mL^{-1} and a 4-h

hydrothermal treatment. At 230°C , there were no peaks of WS_2 observed, but only W_2C peaks. The peaks appearing at $\sim 9.5^\circ$ can be assigned to an interlayer spacing of about $9.5\text{--}10\text{ \AA}$. At 250 and 270°C , sharp WS_2 peaks appeared, which indicated the reduction of H_2S to form WS_2 hexagonal crystals. Thus, these results suggest that the carburization reaction occurred at lower temperature, and the co-formation of WS_2/W_2C NFs occurred above 250°C .

The effect of the WCl_6 concentration was also investigated. Fig. 5(a–d) shows FESEM images and XRD patterns of the materials synthesized at a fixed temperature of 250°C for 4 h. Samples are designated $W_2C/WS_2\text{-}4/8/12$, as the concentrations of WCl_6 were 4, 8, and 12 mg mL^{-1} . At a low concentration of 4 mg mL^{-1} of WCl_6 , the formation of WS_2 and nanorods of triclinic WO_3 were observed, as shown in Fig. 5(a). Increasing the concentration of WCl_6 to 8 mg mL^{-1} led to the appearance of W_2C peaks at a 2θ of about $\sim 36^\circ$. In this sample, hexagonal WO_3 was also formed, contributing some peaks together with triclinic WO_3 and hexagonal WS_2 . In usual, these types of structures of WO_3 including the cubic, rod, plate or wire can be easily formed as shown in Fig. 5(b). To obtain the pure W_2C/WS_2 alloy, the concentration of WCl_6 was adjusted to 12 mg mL^{-1} . In this condition, the W_2C/WS_2 showed flower shapes as shown in Fig. 5(c). This phenomenon could be due to the introduction of 2D materials such as MoS_2 and WS_2 , which would be easier to form the flower shape resulting from the formation of layered structure via hydrothermal method [18,54–56]. The formation of WO_3 and the WCl_6 concentration effect can be explained as follows. First, the hydrolysis of thioacetamide produces an amount of NH_3 proportional to H_2S . This NH_3 can be hydrolyzed in water to form OH^- , which may lead to an increase in pH and to form

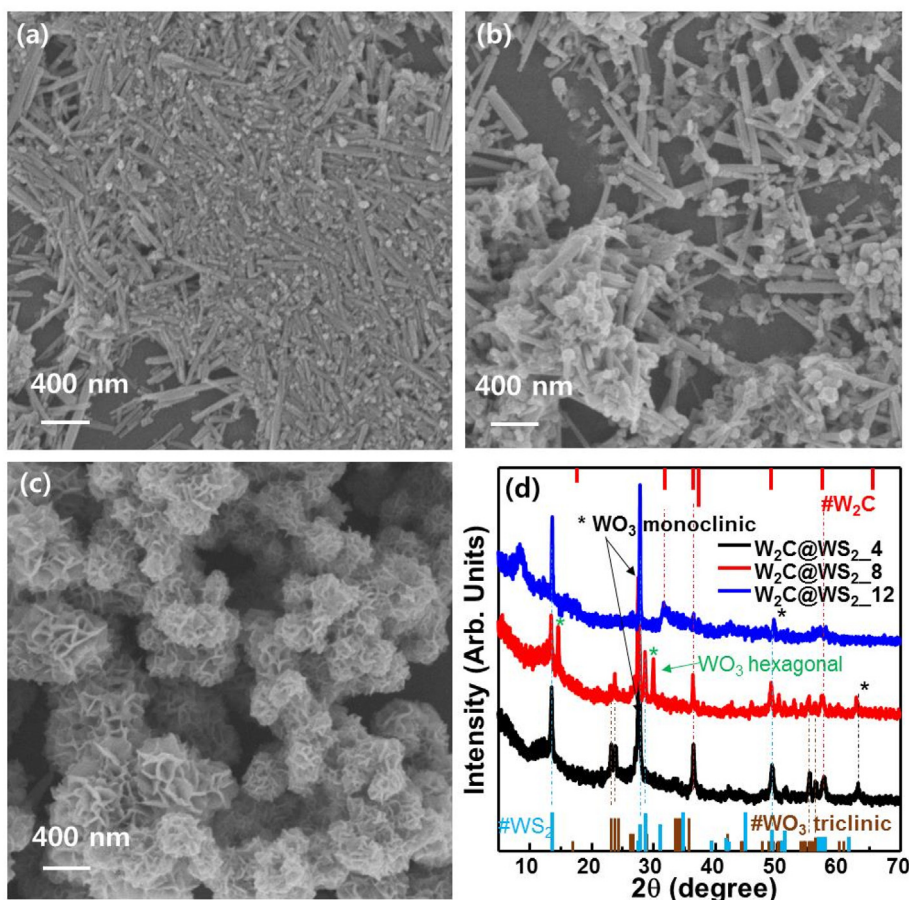


Fig. 5. FESEM images of (a) $W_2C/WS_2\text{-}4$, (b) $W_2C/WS_2\text{-}8$, (c) $W_2C/WS_2\text{-}12$ synthesized at different concentrations of WCl_6 of 4, 8, 12 mg mL^{-1} , and (d) their XRD patterns.

WO₃. According to the reactions shown in equations (3)–(5), the WCl₆ is able to react with H₂O or C₂H₅OH to produce HCl, which can neutralize increased pH and finally decrease the overall pH in the reaction medium. Therefore, it can be thought that the use of high concentration of WCl₆ can avoid the formation of WO₃. At 12 mg mL⁻¹ concentration, the XRD pattern of the resulting material showed peaks of W₂C and WS₂ as well as an interlayer peak at about 9.5°. It is believed that the co-formation of these two materials leads to a sandwich structure with an interlayer spacing of about 10 Å.

To confirm the role of ethanol, the same experiment was conducted; however, the ethanol was omitted. The results in Fig. S4 indicate that the product formed without using ethanol was composed only of WS₂ particles with random sizes due to the precipitation of tungsten oxide before the hydrothermal reduction. The use of ethanol not only prevents sedimentation but also supports the size control of W₂C/WS₂. Fig. 6(a–d) shows FESEM images of W₂C/WS₂ with different size distributions obtained by controlling the reaction time at 2, 4, 8, and 12 h at 250 °C. The size of the NFs increased as the reaction time was increased. At 2 h, the alloy flower size was about 100–200 nm. At 4 h, it was 200–400 nm. At 8 h, it increased to 500–600 nm, and for 12 h of reaction time, the size reached from 700 nm to 1 µm. The XRD patterns and UPS spectra of W₂C/WS₂ synthesized at different reaction times are shown in Fig. 7(a) and (b), respectively. It is evident that at 2 h of reaction time, the main peak is only W₂C. From reaction times of 4 h and above, peaks of W₂C and WS₂ can be observed in the patterns. This indicates that a reaction time of 2 h is sufficient for the hydrothermal system reach the critical pressure, hence, the reduction

to form W₂C occurs first, but the formation of WS₂ is not complete.

Note that the positions of the W₂C and WS₂ peaks in each sample are slightly different. We postulated that the materials remained strained due to the lattice mismatch. To calculate the lattice constants of these alloys, we have used a calculation method for determining Miller indices. The structures of W₂C and WS₂ are well-known to be hexagonal structures, models of which are shown in Fig. 1. Bragg's law is given in Equation (6):

$$\lambda = 2d \sin \theta \quad (6)$$

The mathematical equation for the d-spacing of a hexagonal structure is given by Equation (7):

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (7)$$

where h, k, l are the Miller indices of the plane (h k l), while a and c are lattice constants of the hexagonal structure.

By comparing the XRD patterns with the positions of standard peaks of WS₂ and W₂C, we created a table to calculate lattice constants based on the positions of peaks. Each lattice constant was calculated from the (001), (100), (210), (105), etc. peaks and recalculated with the remaining peaks to obtain accurate results for the a and c constants. The calculation results are summarized in Table 1. The standard WS₂ has lattice constants of about a = 3.18 nm and c = 12.5 nm. In this calculation, the a lattice constant increased to approximately 3.2–3.25 nm and the c lattice constant increased to 12.7–12.9 nm. Notably, for the samples fabricated at a low

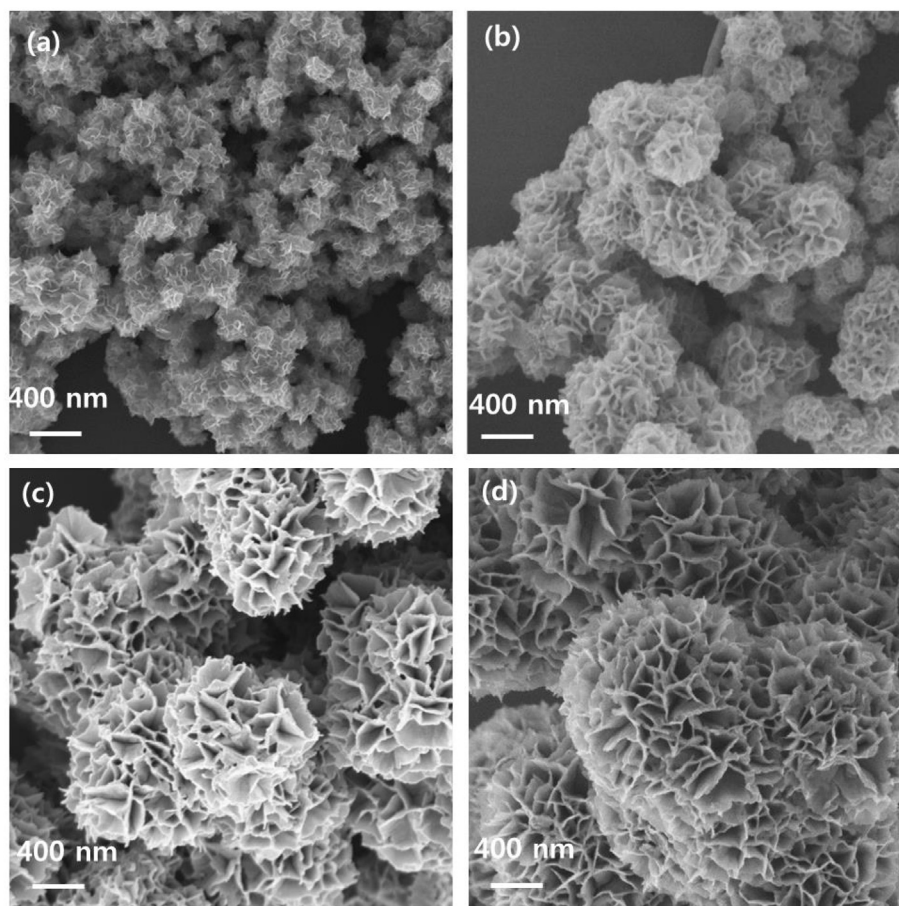


Fig. 6. FESEM images of W₂C/WS₂ synthesized at 250 °C with different reaction times of (a) 2 h, (b) 4 h, (c) 8 h, and (d) 12 h.

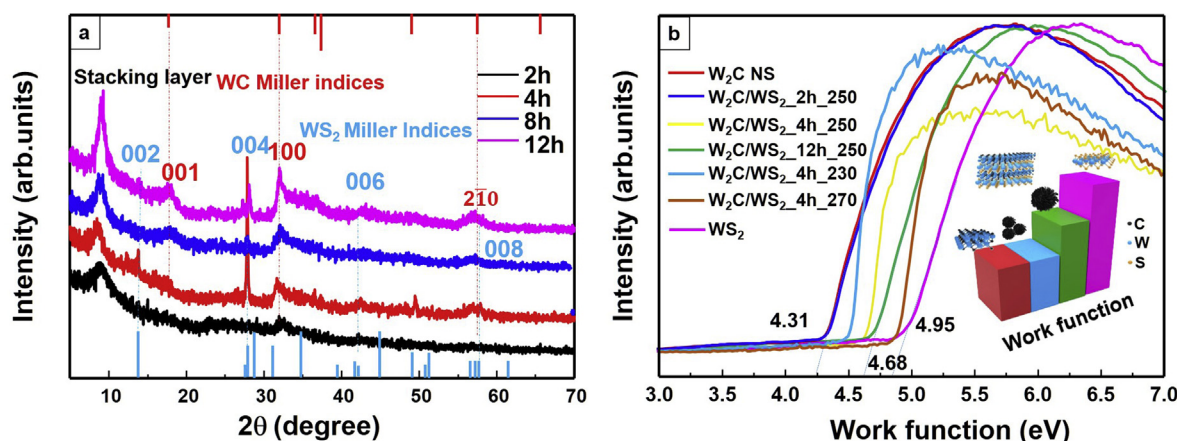


Fig. 7. (a) XRD patterns of W_2C/WS_2 synthesized at 250 °C with different reaction times, and (b) UPS spectra of W_2C NS, W_2C/WS_2 _2h_250, W_2C/WS_2 _4h_250, W_2C/WS_2 _12h_250, W_2C/WS_2 _4h_230, W_2C/WS_2 _4h_270 and WS_2 .

concentration WCl_6 where the W_2C peaks were not well recorded, the lattice constants of WS_2 were also increased. However, the WS_2 that was synthesized via the same procedure without using ethanol had an XRD pattern that matched well with the standard powder pattern of WS_2 found in the literature (Fig. S4). The calculated *a* and *c* lattice constants of as-prepared WS_2 NFs are 3.19 and 12.4 nm, respectively. In previous reports, W_2C was found to have *a* and *c* constants of about 0.29 and 4.72 nm, respectively [26,57]. Their *a* and *c* constants were found to be about 3.08 and 5.04–5.12 nm, respectively. The interlayer spacings calculated for each sample were around 9.57 to 10.20 Å. The XRD pattern of W_2C nanosheets obtained by sonicating W_2C NFs showed that the strain in the lattice was released, with a single peak at a 2θ of 18.78°. This can be attributed to the *c* lattice with a lattice constant of 4.73 nm, which agrees with standard W_2C . The work functions of the materials were investigated, and the results are shown in Fig. 7 (b). As can be seen from the graph, W_2C nanosheets exhibited a work function of 4.31 eV, which is in good agreement with a recent report [28]. The W_2C/WS_2 NFs synthesized for more than 2 h showed a similar work function to that of bare W_2C and W_2C nanosheets. However, the work function increased to 4.51, 4.68 and 4.82 eV with sample W_2C/WS_2 _4h_230, W_2C/WS_2 _12h_250 and W_2C/WS_2 _4h_270, respectively. Thus, the work function was changed as the increase in time or temperature. As shown in Figs. 4 and 6, the sizes of W_2C/WS_2 were dependent on the time and temperature as well. It is worth noting that this enhancement in work function can be attributed to the increase of NFs size and the formation of WS_2 in the composite. Bare WS_2 NFs showed the highest work function of 4.95 eV. It is

reported that band energy of WS_2 is changed when changing the number of layers or the thickness of nanosheets [58–60]. The nanoflower was assembled by nanosheets consisting of WS_2 and W_2C materials. Therefore, the thickness of these layered structures will affect the characteristics of nanoflowers. The crystal size (*D*) can be calculated by Scherrer equation, $D = \frac{0.9\lambda}{\beta \cos \theta}$, where λ is x-ray wavelength, θ is the Bragg angle and β is the full width at half maximum of the peak. Therefore, in a certain measurement condition, the sharpening of the peak is proportional to the crystal size. Based on this information, the increase in work function when increasing the size of materials is well matched with XRD results of samples prepared at high temperature or long reaction time, where the peaks of WS_2 become sharper, indicating the enhanced crystallinity and illustrating that the 2D WS_2 layer is thicker. Furthermore, the tungsten carbide has a low work function of 4.3 eV which is in good agreement with our results that the major XRD peaks belongs to the synthesized W_2C prepared at the low temperature or short reaction time. Moreover, the defects resulting from the heterostructure would contribute to the change of work function as well. Based on the aforementioned information, it is believed that the change in size based on the different reaction conditions leads to the change of work function in W_2C/WS_2 alloy materials. Therefore, by controlling the size distribution of the materials in W_2C/WS_2 alloy NFs, we can tune the work function of the composite from 4.31 to 4.95 eV.

4. Conclusion

In this report, we introduced a facile method for the synthesis of W_2C and WS_2 alloy NFs based on common precursors. The morphology of the W_2C/WS_2 alloy NFs can be precisely controlled from 100 nm to 1 μm by changing the reaction time from 2 to 12 h, accordingly. The changes in the lattice constants during the formation of the alloy due to the lattice mismatch was calculated based on XRD patterns and discussed. In addition, we discovered that the work function of the W_2C/WS_2 alloy nanoflowers can be controlled by size distribution. Therefore, this work offers a facile route for designing W_2C/WS_2 alloys for use in energy generation and storage devices.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have

Table 1
Calculated lattice constants of W_2C and WS_2 via XRD patterns.

Samples	W_2C		WS_2		Interlayer spacing
	<i>a</i> (Å)	<i>c</i> (Å)	<i>a</i> (Å)	<i>c</i> (Å)	
W_2C/WS_2 _4	—	—	3.24	12.9	—
W_2C/WS_2 _8	—	—	3.20	12.8	—
W_2C/WS_2 _12	3.08	5.09	3.21	12.9	10.20
W_2C/WS_2 _4h_230	3.08	5.09	—	—	9.57
W_2C/WS_2 _4h_250	3.07	5.05	3.25	12.8	10.24
W_2C/WS_2 _4h_270	3.08	5.06	3.21	12.9	10.05
W_2C/WS_2 _2h_250	3.08	5.02	—	—	9.65
W_2C/WS_2 _4h_250	3.08	5.12	3.20	12.9	10.16
W_2C/WS_2 _8h_250	3.08	5.04	3.20	12.8	9.93
W_2C/WS_2 _12h_250	3.08	5.04	3.21	12.7	9.72
W_2C nanosheets	—	4.73	—	—	—
WS_2 NFs	—	—	3.19	12.4	—

appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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