Ultrasmall and Monolayered Tungsten Dichalcogenide Quantum Dots with Giant Spin–Valley Coupling and Purple Luminescence

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ABSTRACT: Monolayered tungsten dichalcogenide quantum dots (WS2 QDs) have various potential applications due to their large spin–valley coupling and excellent photoluminescence (PL) properties. What is expected is that with the decrease in lateral size of QDs, the stronger quantum confinement effect will dramatically strengthen the spin–valley coupling and widen the band gap. However, ultrasmall monolayered WS2 QDs prepared by ion intercalation unavoidably undergo the problem of structural defects, which will create defect levels and significantly change their properties. In this study, we report that by annealing defective monolayered WS2 QDs in sulfur vapor, pristine monolayered WS2 QDs with an ultrasmall lateral size of ca. 1.8–3.8 nm can be obtained. The results show that the ultrasmall monolayered WS2 QDs exhibit a giant spin–valley coupling of ca. 821 meV. Moreover, the pristine ultrasmall monolayered WS2 QDs show purple PL centered at 416 nm, and the defect PL peaks in defective WS2 QDs can be effectively removed by annealing. All of these results afford the ultrasmall monolayered QDs various applications such as in optoelectronics, spintronics, valleytronics, and so on.

INTRODUCTION

Two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDs) have aroused great interest recently due to a wide range of physical and chemical properties.1–6 The structure of monolayered TMDs is MX2 (M = Mo or W and X = S, Se, or Te), consisting of an intermediate layer of M atoms sandwiched between two layers of X atoms with strong ionic–covalent bonds.4 Recently, 2D TMDs with large spin–valley coupling, which will introduce a strong coupling interaction.5,6 Therefore, the large spin–valley coupling combined with the presence of direct band gap in monolayered WS2 sheets affords them different applications in optoelectronics, spintronics, valleytronics, and so on.7–19 By further reducing the lateral size of monolayered WS2 sheets, monolayered WS2 quantum dots (QDs) can be obtained. Normally, the WS2 sheets whose lateral size is under 100 nm can be named as WS2 quantum dots (QDs).20,21,22,23 The monolayered WS2 QDs can exhibit more striking properties than monolayered sheets due to the strong quantum confinement effect.20–24 In general, with the decrease in lateral size of QDs, the stronger quantum confinement effect will dramatically strengthen the spin–valley coupling and widen the band gap.20,21,25,26 Therefore, investigations of the spin–valley coupling and photoluminescence (PL) of ultrasmall monolayered WS2 QDs are favorable to both the fundamental study and their applications.

In this article, we show that the pristine monolayered WS2 QDs with the ultrasmall lateral size of ca. 1.8–3.8 nm and...
purely semiconducting phase can be obtained by annealing Li-intercalated WS$_2$ QDs in sulfur vapor. The results show that the pristine ultrasmall monolayered WS$_2$ QDs exhibit a giant spin–valley coupling of ca. 821 meV and two clear peaks at 416 and 342 nm in PL spectra. Compared with the monolayered WS$_2$ sheets and QDs with general lateral size, the ultrasmall monolayered WS$_2$ QDs show significant improvement in spin–valley coupling and a great blue shift.

Figure 1. TEM images of (a) a-WS$_2$ QDs and (b) annealed WS$_2$ QDs. The lower left insets show diameter distribution, and the upper right insets show HRTEM images. AFM images of (c) a-WS$_2$ QDs and (d) annealed WS$_2$ QDs. Insets are the corresponding height profiles of the white lines.

Figure 2. (a) XPS survey spectra over a range of binding energies (0–600 eV) and (b) high-resolution W 4f spectra of a-WS$_2$ QDs and annealed WS$_2$ QDs.
in PL, making them highly valuable for optoelectronics, spintronics, valleytronics, and so on.

Furthermore, it should be noted that so far the mass production of ultrasmall monolayered WS₂ QDs is mainly realized by Li-ion intercalation. However, the as-prepared QDs generally have plenty of structural defects such as high oxidation state and plenty of sulfur vacancies, which will unavoidably create defect levels in the electronic band. In addition, there are both metallic phase and semiconducting phase in these WS₂ QDs. The facts that the structural defects in our as-prepared QDs have been restored and the metallic phase has been discarded after annealing in sulfur vapor confirm the effectiveness of our method for the preparation of pristine WS₂ QDs with a purely semiconducting phase.

**RESULTS AND DISCUSSION**

Figure 1a shows the transmission electron microscopy (TEM) image of as-prepared WS₂ QDs (a-WS₂ QDs). Particle size analysis shows that the diameter distribution of these dots is approximately 2-4 nm with an average lateral size of ca. 3.2 nm (inset of Figure 1a). The lattice spacing is 0.22 nm (inset of Figure 1a), stemming from the (103) plane. After annealing, the diameter distribution is approximately 1.8-3.8 nm with an ultrasmall average lateral size ca. 2.9 nm (inset of Figure 1b). The high-resolution transmission electron microscopy (HRTEM) image presents a clear lattice fringe of Figure 1a), stemming from the (103) plane. After annealing, the diameter distribution is approximately 1.8-3.8 nm with an ultrasmall average lateral size ca. 2.9 nm (inset of Figure 1b).

X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the chemical environment of a-WS₂ QDs and annealed WS₂ QDs. Shown in Figure 2a are the XPS survey spectra over a range of binding energies of a-WS₂ QDs and annealed WS₂ QDs. The topographic heights of a-WS₂ QDs and annealed WS₂ QDs are ca. 0.5 and 0.4 nm, respectively (insets of Figure 1c,d), indicating that all of these quantum dots are monolayered. All of the results imply that annealing did not significantly change the size and thickness of a-WS₂ QDs.

Raman measurements were performed on the as-prepared and annealed samples. Considering that the Raman signals of WS₂ QDs are much weaker than those of bulk WS₂, 532 nm excitation wavelength was used to enrich the spectra, which would reveal many second-order peaks. As shown in Figure 3, the first-order modes LA(M) and A₁g(Γ) are located at 176 and 418 cm⁻¹, respectively. The strongest peak at 352.5 cm⁻¹ is attributed to the second-order mode 2LA(M) at 351.5 cm⁻¹ and the first-order mode E₂g(Γ) at 355.8 cm⁻¹. It is found that the A₁g(Γ) mode weakened after annealing. Therefore, we carried out the Gaussian–Lorentzian fitting to separate their individual contributions and calculate the relative intensity I_{2LA}/I_{A1g}. The intensity ratios of a-WS₂ QDs and annealed WS₂ QDs, respectively, are 1.5 and 2.3,
which further indicate that both of the samples are monolayered. One can find that the increase in the intensity ratio from 1.5 to 2.3 attributes to the small reduction of the $A_{1g}(\Gamma)$ mode. Considering the existence of high content of oxygen groups in a-WS$_2$ QDs, those oxygen groups bonded to tungsten or sulfur atoms are more likely to increase the out-of-plane phonon restoring force, which will lead to the enhancement of the $A_{1g}(\Gamma)$ mode. After annealing, oxygen groups are wiped off and thus the $A_{1g}(\Gamma)$ mode decreases. All of these results indicate that by annealing of defective a-WS$_2$ QDs, one can (i) restore their structural defects and (ii) discard the residual metallic 1T phase. Our monolayered WS$_2$ QDs with an ultrasmall lateral size of ca. 1.8–3.8 nm are favorable to investigate the intrinsic properties of pristine, ultrasmall, and monolayered WS$_2$ QDs with a purely semiconducting phase.

To investigate the optical properties of WS$_2$ QDs before and after annealing, we measured the UV–vis extinction spectra. As known, there are in general three absorption peaks at A (625 nm), B (550 nm), and C (450 nm) in monolayered WS$_2$ sheets. The A and B peaks were considered to originated from two kinds of transitions from the spin-splitting valence band to the conduction band at the K point of the Brillouin zone, whereas the absorption peak C may be attributed to the optical transitions between the density-of-state peaks in the valence and conduction bands. Figure 4a shows the UV–vis extinction spectra of a-WS$_2$ QDs and annealed WS$_2$ QDs.

Figure 4. (a) UV–vis extinction spectra of a-WS$_2$ QDs and annealed WS$_2$ QDs. (b) Diagram of the band structure of pristine monolayered WS$_2$ QDs near the K point.

Figure 5. PL spectra of (a) a-WS$_2$ QDs and (b) annealed WS$_2$ QDs with various excitation wavelengths. (c) Normalized PLE spectra with the detection wavelength of 416 nm and (d) normalized PL spectra at the excitation wavelength of 315 nm of a-WS$_2$ QDs and annealed WS$_2$ QDs.
The PL properties of monolayered WS2 sheets and WS2 QDs with the general lateral size have been well investigated. As reported, there is one strong emission peak A at ca. 638 nm and a weak emission peak B at ca. 530 nm for WS2 sheets,18,40 and one strong emission peak A at ca. 461 nm and a weak emission peak B at ca. 369 nm for WS2 QDs with the general lateral size of 8–15 nm.20 Figure Sd shows the normalized PL spectra of a-WS2 QDs and annealed WS2 QDs using the excitation wavelength of 315 nm. For the case of a-WS2 QDs, the highest emission peak A is located at ca. 420 nm. It is found that there are only two distinct emission peaks at 416 and 342 nm for the annealed WS2 QDs, corresponding to A and B emission peaks. It is clear that compared with the general WS2 QDs our ultrasmall QDs show a great blue shift in both A and B emission peaks, respectively, of ca. 45 and 27 nm in the PL spectrum.

Notably, it is found that there is an obvious peak at 466 nm (2.66 eV) and several other shoulder emission peaks at greater than 420 nm in the as-prepared QDs, similar to the results reported in ref 20. These shoulder emission peaks were considered to originate from the transitions from the conduction band to the new defect levels above the valence band (as illustrated in Figure 4b).20 It is clear that defect-related emission peaks in a-WS2 QDs were eliminated due to the restoration of an intrinsic band structure. Moreover, one can find that broad peaks in a-WS2 QDs were narrowed after restoration (Figure Sd). All of these results indicate further the structural restoration of a-WS2 QDs after annealing, leading to the perfect structure with an intrinsic electronic band.

As mentioned above, the strong quantum confinement effect will dramatically strengthen the spin–valley coupling and increase the band gap of QDs.20,21,25,26 Therefore, one can propose that both the giant energy difference (ΔE0) and the purple PL in our annealed WS2 QDs may be attributed to the ultrasmall lateral size. We should note that there is no clear spin–orbit splitting observed in a-WS2 QDs. As reported, structural defects in monolayered TMDs would induce intervalley electronic scattering and defects are the common limiting factors that can provide the required momentum for intervalley scattering due to their short-range nature.45 Therefore, even if the giant spin–valley coupling is in pristine WS2 QDs due to the suppression in the intervalley scattering, the features expected from the valence band may be absent due to the high-density defects in defective a-WS2 QDs. As we noted, the defect PL peaks have been removed completely, which may lead to the shift of the highest main PL emission position. Compared with WS2 QDs with the general lateral size, our WS2 QDs with the ultrasmall lateral size have stronger spin–valley coupling and greatly blue-shifted emission, which afford them high potential for various applications.

## CONCLUSIONS

In conclusion, we have synthesized pristine, monolayered, and semiconducting WS2 QDs with an ultrasmall lateral size of ca. 1.8–3.8 nm by annealing defective WS2 QDs in sulfur vapor. The results showed that after annealing (i) a giant spin–valley coupling up to ca. 821 meV appeared; (ii) the ultrasmall monolayered WS2 QDs showed purple PL centered at 416 nm, and the defect-related areas in PL spectra of defective WS2 QDs disappeared. The fact that the excellent properties of pristine QDs are absent in the as-prepared ones suggests the necessity of sulfur annealing. Compared with the general WS2 sheets or QDs reported, the ultrasmall monolayered WS2 QDs
show a significant improvement in spin–valley coupling and a great blue shift in PL. The spin–valley coupling and purple PL are obtained with the ultrasmall lateral size of our pristine WS₂ QDs. All of the results afford these ultrasmall monolayered QDs various applications in optoelectronics, spintronics, valleytronics, and so on.

**METHODS**

**Materials.** a-WS₂ QDs were purchased from Nanjing XFNANO Materials Tech Co., Ltd. Sulfur powder (99.998% purity) was purchased from Sigma-Aldrich. N-Methyl-2-pyrrolidone (NMP) was purchased from Nanjing Chemical Reagent Co., Ltd. XFNANO Materials Tech Co., Ltd. Sulfur powder (99.998%) was purchased from Sigma-Aldrich.

**Sample Preparation.** a-WS₂ QDs (100 mg) and 1 g of sulfur powder were put in two quartz boats, respectively. They were then placed inside a quartz tube in sequence with sulfur powder on the upstream of the gas flow. Before heating in a tubular furnace, the tube was emptied by a vacuum pump and fed with Ar several times to ensure that there is no residual oxygen. After that, the restoration process was performed at 450 °C for 30 min with Ar flow at 20 sccm. Finally, annealed WS₂ QDs were collected after cooling down to room temperature.

**Sample Characterizations.** The morphologies were investigated by transmission electron microscopy (TEM, FEI Tecnai-F20) and atomic force microscopy (AFM, Veeco). X-ray photoelectron spectroscopy (XPS) measurements were performed on PHI-5000 VersaProbe using Al Ka radiation. Raman spectra were obtained by a confocal Raman microscope (LabRAM Aramis, Japan) using a laser excitation of 532 nm. The extinction and PL spectra were recorded at ambient conditions by an ultraviolet spectrophotometer (Shimadzu UV-3600, Japan) and fluorescence spectrophotometer (Shimadzu RF-5301PC, Japan), respectively. For optical spectrum investigation, samples were prepared at a concentration of 0.1 mg/mL using NMP and were ultrasonically dispersed for 1 h.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01125.

PL spectra of sonicated NMP and PL spectra of annealed WS₂ QDs and sonicated NMP (PDF)

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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