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Low-Cost One-Pot Synthesis of WS₂ Quantum Dots with Wide Emission Spectrum for Light-Emitting Applications

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Keywords

WS₂; quantum dots; LEDs; white light

Tungsten disulfide (WS₂), a representative layered transition metal dichalcogenide (TMD) semiconductor consisting triatomic building blocks S-W-S, is promising for the next generation electronic and optoelectronic devices^[1] due to their unique electronic, optical, mechanical and chemical properties.^[2] The band gap structure of WS₂ is indirect except for monolayer,^[3] and that of WS₂ quantum dots (QDs) exhibits strongly layer-dependent properties^[4] and size-dependent quantum confinement effects.^[5] Besides, a surface defect related recombination processes is also contributed to the photoluminescence (PL) of TMD QDs. Thus, nontoxic few-layer WS₂ QDs with bright broadband visible emission fit well with the demand of lighting and display applications. However, due to the relatively low PL efficiency of TMD QDs, there is no study focusing on TMD QD based white-light-emitting diodes (WLEDs) to date.

The synthetic methods for TMD QDs can be divided into two classes: top-down and bottom-up. The top-down method can be purely physical (e.g., ultrasonication and mechanical exfoliation),^[6] chemically assisted (e.g., liquid exfoliation in a good solvent such as NMP),^[7] or purely chemical through intercalation with ions (e.g., lithium).^[8] The top-down method normally suffers from long preparation period with poor control over their shape, size, and edge properties. In contrast, the bottom-up strategy (including pyrolysis, hydrothermal and colloidal method) can be used to prepare QDs with good crystallinity,

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Conflict of Interest

The authors declare no conflict of interest.

monodispersity and control over the edges. However, existing synthetic methods use organic sulfur compounds which are costly, and toxic gas are released in the course of reaction. Hence, there is an urgent demand on developing a cost-effective and environment-friendly strategy to produce bright WS₂ QDs, which is important to explore the optical and electronic characteristics of WS₂ QDs. Here, we propose a low-cost, one-pot and environment-friendly synthesis for high-quality colloiddally stable WS₂ QDs with 7.8 nm, relying on activated elemental sulfur (S-TOP, S dissolved in tri-n-octylphosphine) instead of an organic S source. The as-prepared WS₂ QDs exhibit strong broad-band emission under UV light, with the PL quantum yield (QY) of 23%, which is the highest to date. The WS₂ QDs combine a blue chip and AgIn₅S₈ QDs for white LEDs (WLED) show a high color rendering index (CRI) value of 93. The Commission Internationale de l'Eclairage (CIE) coordinate of (0.34, 0.36) is close to the standard white emission.

Results and Discussion

The morphology of the as-prepared product was characterized by transmission electron microscopy (TEM). As shown in Figure 1a, the TEM image reveals that QDs are monodisperse crystalline with nearly spherical shape. The diameter distribution is mainly within a range from 5.4 to 10.3 nm with an average value of 7.8 ± 0.7 nm (Figure 1b). Figure 1c shows a high-resolution TEM (HRTEM) image of a QD. The lattice fringes of the QD are ~ 3.1 Å, which is corresponding to the (004) face of WS₂, suggesting a high crystallinity of the as-prepared WS₂ QDs. The presence of polycrystalline crystal structure is further revealed by the diffraction rings in the selected area electron diffraction (SAED) pattern of the WS₂ QDs (Figure 1d).

The standard Raman spectroscopy of the WS₂ QDs exhibited two phonon modes at Brillouin zone center, in-plane E_{2g}¹ (Γ) and out-of-plane A_{1g} (Γ), respectively.^[9] As we expected, there are two characterized peaks shown in Raman spectrum (Figure 2a), consisting with the high energy vibration A_{1g} (Γ) at 417.5 cm⁻¹ and the lower energy vibration E_{2g}¹ (Γ) at 353.7 cm⁻¹. The peaks located at 323.0 cm⁻¹ can be assigned to the acoustic phonon Raman active mode (2LA(M)).^[10] In comparison with monolayer WS₂ (E_{2g}¹ and A_{1g} located at 354.4 and 416.4 cm⁻¹, respectively), the E_{2g}¹ (Γ) phonon mode shows a slightly red-shift while the A_{1g} (Γ) phonon mode shows a more evident blue-shift with more layer number.^[11] We found the layer number of WS₂ QDs is 4–5, which is consistent with the results of Zhang and coworkers.^[11] X-ray diffraction (XRD) pattern of WS₂ QDs was given in Figure 2b. Three diffraction peaks are clearly observed, *i.e.* at 14.5°, 29.1° and 44.0°, which are corresponding to the (002), (004) and (006) planes of WS₂ (JCPDS no. 84–1398).^[12] The presence of perpendicular diffraction suggests that the QDs are multilayered, which is corresponded to the Raman result.

Trigonal prismatic WS₂ (semiconductor, 2H-WS₂) is stable in nature, while octahedral WS₂ (metallic, 1T-WS₂) is instable in the bulk form.^[13] We find both of them in our products, which are identified by X-ray photoelectron spectroscopic (XPS). We distinguished 1T structure from 2H structure via the position of the binding energies of the W4f_{7/2} and W4f_{5/2} core level peaks, because tungsten signal is sensitive to its oxidation state and coordination geometry.^[2] As shown in Figure 2c, five peaks were found in the W4f spectrum of WS₂

QDs. The two located at 32.9 and 34.9 eV are assigned to $W4f_{7/2}$ and $W4f_{5/2}$ of 2H- WS_2 , respectively. The two peaked at 32.1 and 34.1 eV are associated with $W4f_{7/2}$ and $W4f_{5/2}$ of 1T- WS_2 , respectively. The one around 38 eV belongs to $W5p_{5/2}$. Similarly, the XPS measurement was also carried out for S2p (Figure 2d). The peaks at 162.5 and 163.6 eV correspond to $S2p_{3/2}$ and $S2p_{1/2}$ of 2H- WS_2 , respectively. Two additional signatures at 161.8 and 162.9 eV appearing by the 2H- WS_2 peaks are associated with 1T- WS_2 . In short, the XPS analyses clearly suggest that the QDs contain a small amount of 1T- WS_2 . Using the peak areas and the atomic sensitivity factors of W4f and S2p, the content ratio of 2H- and 1T- WS_2 was extracted to be 17:3. Note that the 1T- WS_2 do not emit any PL originated from metallic properties.^[14]

The WS_2 QDs show a pale-yellow color under sunlight and emit cyan PL with 365 nm excitation (the inset of Figure 3a). Only an acromion peak around 300 nm is exhibited, which is ascribe to the excitonic energy level.^[15] Figure 3b is the PL emission spectra of WS_2 QDs at various excitation wavelengths from 320 to 460 nm. It is obviously that the emission peak red-shifted with the increase of the excitation wavelength. The excitation-dependent PL feature of WS_2 QDs is in good agreement with those previously reported studies,^[15–16] which is originated from the different defect states of WS_2 QDs and the polydispersity.^[14,17] The PL QY of WS_2 QDs measured using Edinburgh was 23%, which is higher than the other WS_2 QDs synthesized through hydrothermal methods.^[16a] A possibility for the improved QY is that the surface is restructured to reduce the sulfur vacancies through highly active S-TOP as reactant. In addition, WS_2 QDs show a PL average lifetime of 4.8 ns (Figure 3c) when excited by a radiation of 360 nm.

For applications in WLEDs, the WS_2 QD powder was mixed with $AgIn_5S_8$ QD powder,^[18] and the mixture was coated onto the chips of 400 nm LEDs. Figure 4a shows the WLED fabrication process, with a photograph of a working WLED operated at 3.2 V. In order to verify the optical stability of WS_2 QDs, the EL spectra of WS_2 QD based LEDs are given in Figure 4b. With increased working bias, the EL intensity obvious increased but the EL spectra shape nearly unchanged (the inset of Figure 4b), demonstrating that WS_2 QDs have great optical stability. A WLED was obtained by adding nontoxic $AgIn_5S_8$ QDs with broadband emission, and the EL spectra under different forward bias are shown in Figure 3c. The broad peak at 500 nm is assigned to the emission of WS_2 QDs, while the other located at 620 nm is attributed to the emission of $AgIn_5S_8$ QDs (Figure S1). As the forward bias increases from 3.0 to 3.5 V, the emission peak intensity of WLED increases and peak positions have no shift (Figure 4c). Simultaneously, it is interesting to see that the ratio of cyan emission from WS_2 QDs to red emission from $AgIn_5S_8$ QDs slightly decreases as the forward bias increases from 3.0 to 3.2 V, leading to the fact that the CIE coordinates of the device change from (0.34, 0.38) to (0.34,0.36), which is very close to standard white emission (0.33,0.33). The spectrum containing two peaks is broad, which is in favor of white lighting. A high CRI value of 93 is obtained (Table S1). The brightness and power efficiency vs current density are exhibited in Figure 4d. The maximum brightness and power efficiencies of the WLED were 11600 cd/m² and 3 lmW⁻¹, respectively. The stability of the WLEDs is good. Under a voltage of 3.2 V, the brightness dropped to its half after 41 hours.

Conclusion

In summary, a facile bottom-up hydrothermal method with high reproducibility was developed to synthesize WS₂ QDs, with the expensive organic sulfur sources was replaced by high activity and low-cost S-TOP. Our results show that as-prepared WS₂ QDs of 7.8 nm exhibit strong PL, which is due to the decrease of surface defects. The PL QY of WS₂ QDs is 23%, which is higher than previously results using the solvothermal method. The as-prepared QDs are integrated with GaN chip acting as a color-converter in white LEDs. Our WLEDs have shown excellent stability, with CIE coordinates of (0.34, 0.36) in the white region and a high CRI value of 93. Given those results, the as-prepared WS₂ QDs are promising candidates for lighting and displaying.

Experimental Section

Chemicals

Sodium tungstate (Na₂WO₄ · 2H₂O), sulfur (S), N-methylpyrrolidone (NMP), dodecanethiol (DDT) and oleylamine (OM) were purchased from Aladdin Industry. Tri-n-octylphosphine (TOP) was purchased from J&K Scientific Ltd. Octadecene (ODE) and silver nitrate (AgNO₃) were obtained from Alfa Aesar. Indium acetylacetonate (In(acac)₃) and oleic acid (OA) were purchased from Sigma-Aldrich. Ethanol and toluene were bought from Sinopharm. All chemicals were used directly.

Synthesis of WS₂ QDs

The WS₂ QDs were synthesized through a simple hydrothermal method. Typically, S-TOP (1 mmol S dissolved in 1 mL TOP) and Na₂WO₄ · 2H₂O (0.3 mmol) were mixed in a beaker containing 30 mL NMP. After stirred for 10 min, HCl (1 mmol, 20 μL) was added into the mixture. Subsequently, the mixture was transferred into a 50 mL quartz-lined stainless steel autoclave and heated at 210°C for 24 h. At the end, an orange-yellow suspension was separated by centrifugation at 13,000 rpm for 20 min and was re-dispersed in toluene.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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We report a facile and low-cost synthesis of WS₂ quantum dots with bright broad-band emission, which are suitable for lighting applications. The thus fabricated WS₂ light-emitting diodes (LEDs) exhibit voltage independent electroluminescence spectra, and the optimized white LEDs generate a high color rendering index of 93.

Figure 1.

(a) TEM image of WS₂ QDs; (b) size distribution histogram of WS₂ QDs; (c) high-resolution TEM image of a QD; (d) selected area electron diffraction (SAED) pattern of those QDs.

Figure 2. (a) Raman spectrum of WS₂ QDs; (b) XRD pattern of WS₂ QDs; High-resolution peak-fitting XPS spectra of the W4f and S2p region from WS₂ QDs are shown in (c) and (d), respectively.

Figure 3.

(a) Absorption spectrum of the as-prepared WS₂ QDs. Inset: digital photographs of QD solution under sunlight (left) and UV light (365 nm, right). (b) PL spectra of WS₂ QDs with different excitation wavelengths. (c) Time resolved PL decay of WS₂ QDs; inset is the fitting data.

Figure 4.

(a) Schematic illustration for the preparation of a WLED with the encapsulation of WS₂ QDs and AgIn₅S₈ QDs; inset: a photograph of the working device. (b) EL spectra of an LED with encapsulated WS₂ QDs; inset: the normalized EL spectra. (c) The EL spectra of a WLED based on WS₂ and AgIn₅S₈ QDs at different working biases; inset: the normalized EL spectra. (d) The brightness and power efficiency vs current density.