Electrochemically induced Fenton reaction of few-layer MoS$_2$ nanosheets: preparation of luminescent quantum dots via a transition of nanoporous morphology†

Bang Lin Li, Ling Xiao Chen, Hao Lin Zou, Jing Lei Lei, Hong Qun Luo* and Nian Bing Li*

Electrochemically induced Fenton (electro-Fenton) reaction was used for efficient and controllable preparation of hydroxyl radicals, leading to the generation of luminescent quantum dots through etching of as-exfoliated MoS$_2$ nanosheets. Morphologic changes of MoS$_2$ nanosheets during the electro-Fenton reaction were monitored using transmission electron microscopy, showing that etching of MoS$_2$ nanosheets induced by hydroxyl radicals resulted in rapid homogeneous fracturing of the sheets into small dots via a transition of nanoporous morphology. The as-generated dots with vertical dimensional thickness of ca. 0.7 nm and plane size of ca. 5 nm were demonstrated to be MoS$_2$ quantum dots (MoS$_2$-QDs), and their photoluminescence properties were explored based on quantum confinement, edge effect, and intrinsic characteristics. Moreover, the degree of etching and the concomitant porosity of MoS$_2$ nanosheets could be conveniently tuned via the electro-Fenton reaction time, resulting in a new morphology of nanoporous MoS$_2$ nanosheets, with potential new applications in various significant areas.

Introduction

There is a great deal of interest in two-dimensional (2D) nano-materials derived from layered bulk crystals analogous to graphite, because of their unusual properties associated with ultra-thin thickness and 2D morphology.1–4 These developments have been led by research on graphene, a 2D nanomaterial with a unique combination of thermal, electronic, optical, and mechanical properties.5–10 As a result of the interest in graphene, other 2D materials with nano-layered structures, such as hexagonal boron nitride, transition metal dichalcogenides, and metal halides, have also attracted interest.11–15 In particular, MoS$_2$ nanosheets, 2D transition metal dichalcogenides, have been obtained through efficient exfoliation of three-dimensional crystals and breaking of van der Waals interactions between nanosheets.16–18 Owing to the specific 2D confinement of electron motion and absence of interlayer perturbation, MoS$_2$ nanosheets possess a direct band gap and show some remarkable properties, offering new opportunities for various areas, such as sensors,19–22 single-layer transistors,23 integrated circuits,24 phototransistors,24 nanometer thick photovoltaics,25 and materials for batteries.26–27 Recently, MoS$_2$ nanosheets were found to be promising materials for hydrogenation catalysis, attributed to active sites located along the edges of their layered crystal structures.28–31 However, as the potential applications of MoS$_2$ nanosheets are limited by insufficient active sites, then some novel morphologies of MoS$_2$ nanosheets have been presented, namely defect-rich MoS$_2$ nanosheets,32 oxygen-incorporated MoS$_2$ nanosheets,33 and metallic MoS$_2$ nanosheets.34

Following research into 2D and 1D materials, zero-dimensional materials have attracted more interest. Compared with graphene sheets, zero-dimensional graphene quantum dots (GQDs) possess strong quantum confinement and edge effects, resulting in new physical properties.35 As a result of their excellent properties and ongoing applications, there is great demand for the preparation of GQDs. Several strategies have been developed for preparation so far, including the hydrothermal route,36 the wave-assisted hydrothermal method,34 ultrasonication breaking,35 enzymatic oxidations,36 steam etching,37 and size fractionation.38 However, mass scale manufacture of GQDs is limited by the harsh conditions, time consumption, low yield, and damage to the aromatic carbon framework. To develop effective strategies for GQD preparation, a Fenton reaction with assistance of ultraviolet light irradiation (photo-Fenton reaction) was proposed based on the etching of graphene oxide (GO).39 However, regardless of whether the
reaction is conventional Fenton or photo-Fenton, the initial addition of numerous Fe$^{2+}$ and H$_2$O$_2$ causes an over-fast reaction at the beginning. Following this, the consumption of Fenton reagent slows the reaction down, which is detrimental to control of the reaction rate and effective preparation of GQDs. Decades ago, an electrochemically induced Fenton (electro-Fenton) reaction, an important advanced oxidation technology, was proposed and mainly used for the available degradation of pollutants in the environment via generation of highly powerful chemical oxidant hydroxyl radicals. The electro-Fenton process is an attractive method owing to its high effectiveness, fast treatment rate, and environmental compatibility in which hydrogen peroxide is generated in situ, and the addition of ferrous ions allows enhancement of the oxidation activity through formation of ·OH. Meanwhile, the ferrous ions are regenerated at the cathode, resulting in production of hydroxyl radicals in a catalytic and controlled mode, tuned by the electrochemical process.

So far, attention has focused on the preparation, application, and property studies of MoS$_2$ nanosheets, with relevant exploration of MoS$_2$ quantum dots (MoS$_2$-QDs) being ignored. Zero-dimensional MoS$_2$-QDs, with smaller plane size than MoS$_2$ nanosheets, possess strong quantum confinement and edge effects, which can induce numerous unique and outstanding properties. After the successful preparation of graphene quantum dots (GQDs) from morphologic change of 2D graphene sheets, preparation of MoS$_2$-QDs was considered from MoS$_2$ nanosheets, owing to their specific 2D structure similar to graphene. Herein, a simple, cost-effective, efficient, and controllable method for production of hydroxyl radicals was used to cut GO into GQDs based on the electro-Fenton reaction. Reaction between MoS$_2$ nanosheets and hydroxyl radicals was explored, showing generation of zero-dimensional MoS$_2$-QDs from etching of MoS$_2$ nanosheets (Scheme 1). The whole reaction process was monitored by transmission electron microscopy (TEM) and a new morphology of MoS$_2$ nanosheets, nanoporous MoS$_2$ nanosheets, was obtained via tuning reaction time to control the degree of etching and concomitant porosity. Compared with MoS$_2$ nanosheets, both MoS$_2$-QDs and nanoporous MoS$_2$ nanosheets provide many more active sites at the edge of plane, important for application of MoS$_2$ nanomaterials in various areas.

**Experimental section**

**Materials**

Molybdenum(IV) sulfide (MoS$_2$ crystalline powder, <2 μm, 99%) was purchased from Sigma-Aldrich Co. (USA). Graphite powder (99.85%) was obtained from Shanghai Huayuan Chemical Engineering Co., Ltd. (Shanghai, China). Sodium cholate (98%) and iron(II) sulfate heptahydrate (FeSO$_4$·7H$_2$O) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Other chemicals employed in this work were of analytical reagent grade and were purchased from Kelong Chemical Reagent Co., Ltd. (Chengdu, China).

**Experimental instrumentations**

All electrochemical processes were conducted using a CHI 660B electrochemical workstation (CHEN HUA Instruments Co., China). A three-electrode system consisting of a 5 cm$^2$ graphite sheet working electrode, a saturated calomel electrode (SCE), and an auxiliary electrode made of platinum was adopted. All potentials were given with respect to the SCE. The KQ-250B ultrasonic bath (250 W, Kun Shan Ultrasonic Instruments Co., Ltd, China) was adopted to exfoliate MoS$_2$ powder. TEM, high resolution TEM (HRTEM), and high-angle annular dark-field scanning TEM (HAADF-STEM) measurements were performed on a Tecnai G2 F20 S-TWIN transmission electron microscope (FEI, USA) operated at 200 kV. The samples were prepared by dropping aqueous suspension of GQDs and MoS$_2$ nanomaterials onto the carbon grids and drying under ambient conditions. Scanning electron microscope (SEM) images were obtained using an S-4800 field emission scanning electron microscope (Hitachi, Japan). Atomic force microscope (AFM) data were obtained on a Dimension Icon atomic force microscope (Bruker, Germany). X-ray diffraction (XRD) patterns were obtained with a D8 DISCOVER X-ray diffractometer (Bruker, Germany). UV-visible spectra were recorded on a UV-2450 UV-vis spectrophotometer (Shimadzu, Japan) at room temperature. The
photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded on a F-2700 fluorescence spectrophotometer (Hitachi, Japan) with a Xe lamp as an excitation source; slit: 10 nm; PMT voltage: 400 V. Centrifugation was carried out using a TGL-16M high-speed refrigerated centrifuge (Xiangyi, China).

**Preparation of MoS2 nanosheets and graphene oxide**

MoS2 nanosheets were prepared through sonication-assisted exfoliation of MoS2 crystal in aqueous surfactant solution. A mixed water solution, containing 5 mg mL\(^{-1}\) MoS2 powder and 1.5 mg mL\(^{-1}\) sodium cholate, was sonicated (KQ-250B 250 W) at normal temperature for 10 h, resulting in a preparation of black dispersion. The dispersion was centrifuged at 3000 rpm for 30 min, followed by separation of the yellow-green supernatant to remove bulk MoS2 powder. The separated supernatant was centrifuged at 12 000 rpm for 30 min, resulting in as-exfoliated MoS2 nanosheets. To remove sodium cholate, the MoS2 nanosheets were dispersed in ultrapure water with the assistance of sonication. Similarly, the regenerated dispersion was centrifuged at 12 000 rpm for 30 min, followed by the collection of sediments to complete the washing process. The washing process was repeated a further two times to remove sodium cholate completely. Ultimately, the sediments were dispersed in a certain amount of ultrapure water to prepare uniform MoS2 nanosheet dispersion. Graphene oxide was synthesized by oxidation of graphite powder according to the Hummers method, as characterized in our previous work.

**Electro-Fenton reaction**

Electro-Fenton reaction of MoS2 nanosheets (or graphene oxide) was conducted in an electrolytic cell equipped with an electrochemical workstation. A three-electrode system was adopted to connect the electrolytic cell with the electrochemical workstation. A portion of 50 mL mixed solution containing 0.3 mg mL\(^{-1}\) MoS2 powder and 0.05 M FeSO\(_4\) was added into the electrolytic cell. The initial pH of the mixture was adjusted to 3 by dropwise addition of 0.5 M H\(_2\)SO\(_4\) solution, and this remained almost constant over the whole reaction. A potential of \(-0.5\) V was applied and continuous saturation of the solution by O\(_2\) at atmospheric pressure was ensured through bubbling of compressed air. Solutions were continuously stirred using a magnetic bar (500 rpm) to allow mass transfer. After various reaction times, the products were collected and dialyzed (\(M_w = 3500\)) in H\(_2\)SO\(_4\) solution (pH = 3) for 1 day to remove iron ions and some other impurities, avoiding production of sediments induced by hydrolysis of iron, and in ultrapure water for another day to remove H\(^+\) and SO\(_4^{2-}\) ions.

**Results and discussion**

**Electro-Fenton process of graphene oxide**

In the electro-Fenton process, electrochemical generation of H\(_2\)O\(_2\) takes place at the cathode as in eqn (1), and with addition of a certain amount of ferrous ions, the Fenton reagent thus formed leads to formation of hydroxyl radicals according to eqn (2).

\[
\begin{align*}
O_2 + 2e^- + 2H^+ & \rightarrow H_2O_2 \quad (1) \\
Fe^{2+} + H_2O_2 + H^+ & \rightarrow Fe^{3+} + 'OH + H_2O \quad (2)
\end{align*}
\]

Meanwhile, O\(_2\) is fed into the electrochemical system, keeping the concentration of H\(_2\)O\(_2\) almost constant (Fig. S1†). The regeneration of Fe\(^{2+}\) can occur by a direct cathodic reaction (eqn (3)) under the conditions of electro-generation of H\(_2\)O\(_2\), and contribute to further production of a great number of hydroxyl radicals.

\[
Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)
\]

Compared with conventional Fenton and photo-Fenton reactions, electro-Fenton reaction can be conveniently controlled by tuning the electrochemical process, making the generation of hydroxyl radicals more efficient and controllable. The controllability of this electro-Fenton process was confirmed by conducting an experiment on degradation of rhodamine B (Fig. S2†). Meanwhile, when specific conditions for the electro-Fenton process were confirmed, the impact of 'OH on the substrate depended only on the reaction time.

Hydroxyl radical-mediated oxidation of aromatic molecules has been established before. The initial attack by hydroxyl radicals produces an 'OH adduct or undergoes electron transfer to produce cation radicals, and continued attack by hydroxyl radicals causes complete oxidation of aromatic molecules to CO\(_2\) and water. Graphene and GO sheets could be considered as super aromatic molecules, and reaction between graphene sheets and hydroxyl radicals has been discussed. The hydroxyl radicals can make an impact on aromatic molecules and further break up parts of the hexatomic ring structure of GO sheets. Following this exploration into the electro-Fenton process, a route was proposed for using the electro-Fenton process to prepare GQDs from GO. Under optimal conditions (Fig. S3†), the electro-Fenton process of GO was conducted and progress was monitored using AFM. It observed (Fig. S4†) that bulk GO sheets turned into a great deal of small dots possessing a vertical dimensional thickness of ca. 0.8 nm after reaction for 60 min. These dots were demonstrated to be GQDs with great photoluminescence properties. As shown in the TEM image (Fig. 1a), the plane sizes of as-prepared GQDs range from 1.6 to 4.0 nm, with an average value of approximately 2.53 nm. The lattice spacing of the GQDs (plane size: ca. 2.60 nm) in the HRTEM image (Fig. 1b) is ca. 2.14 Å, similar to the hexagonal pattern of graphene with \(d_{1100}\). It was confirmed that hydroxyl radicals generated from the electro-Fenton process could break the 2D structure of GO and had a positive impact on conversion of GO to GQDs. In the electro-Fenton reaction, rates of hydroxyl radical production were influenced by the electrochemical process, making it effective to control the whole process of GQD preparation. The UV-vis spectra of GO before and after the electro-Fenton reaction were recorded. As shown in Fig. S5, the GO has two absorption peaks at 230 and 304 nm, corresponding to \(\pi^*\) to \(\pi^*\) transition of aromatic sp\(^2\) domains and n to \(\pi^*\) transition of C=O bond, respectively. Meanwhile, two UV-vis absorption peaks centered at 210 and 276 nm are observed after...
GO solution reacted with the electro-Fenton reagent (Fig. S5†). The origin of these absorptions can be ascribed to $p$ electron transition in oxygen-containing GQDs. The stronger absorption at 210 nm corresponds to a good deal of $p$ to $p^*$ transition of aromatic sp2 domains, and the absorption at 276 nm is a result of $n$ to $p^*$ transition of $C\equiv O$ bond, located in the edge of GQDs. The PL and PLE spectra of the GQDs solution were recorded (Fig. 1c). The GQDs were excited by a Xe lamp from the fluorescence spectrometer and an optimal emission peak centered at 401 nm was observed when the sample was excited at 320 nm with a Stokes shift of 81 nm. The PLE spectrum recorded with the optimal luminescence showed two peaks, one at 256 nm, which was regarded as a shoulder peak, and one at 320 nm. The theory used to account for this phenomenon was proposed by Pan et al.33 The PLE peaks at 256 and 320 nm correspond to the absorption from the transitions of $\pi$ to $\pi^*$ and $n$ to $\pi^*$, related to the absorption peaks at 210 and 276 nm in the absorption spectrum, respectively. Furthermore, the PLE spectrum demonstrates that the luminescence observed from GQDs is directly correlated with both kinds of transition rather than only transition of $\pi$ to $\pi^*$, which can be used to explain the unique optical properties of GQDs. The as-prepared GQDs also exhibit excitation-dependent PL behavior. When the excitation wavelength changes from 320 to 460 nm, the PL peak shifts to longer wavelengths and the PL intensity decreases significantly (Fig. 1d).

With successful preparation of GQDs from morphologic change of GO sheets induced by hydroxyl radicals in the electro-Fenton reaction, it was proposed that other 2D materials like graphene in structure also might react with hydroxyl radicals. Therefore, as a result of their unique and excellent properties, few-layer MoS2 nanosheets, originally obtained from exfoliation of MoS2 powder, were also considered. To the best of our knowledge, discussion of the reaction between MoS2 nanosheets and hydroxyl radicals has never been made before. Nevertheless, morphologic changes of MoS2 nanosheets under the influence of hydroxyl radicals generated from electro-Fenton reaction attracted our interest.

**Exfoliation of MoS2 in aqueous surfactant solution**

A more recent strategy for exfoliation is to expose the layered material to ultrasonic waves in a solvent.41,45 Such waves generate cavitation bubbles that collapse into high-energy jets, breaking up the layered crystallites and producing exfoliated nanosheets. Sonication has been used to exfoliate bulk MoS2 in water, so long as ionic surfactants are present to prevent rapid reaggregation of MoS2 nanosheets caused by van der Waals binding to the exfoliated sheets and subsequent electrostatic stabilization.41 In our experiment, MoS2 nanosheets were obtained through sonication-assisted exfoliation of MoS2 crystal in aqueous surfactant solution (Fig. 2a). MoS2 powder was added to sodium cholate aqueous solution for sonication-treatment, resulting in a preparation of dispersed solution. Centrifugation of dispersed solution at 3000 rpm was used to remove the bulk and thicker MoS2. The precipitation was collected at 12 000 rpm to obtain exfoliated MoS2 nanosheets. The surfactant adsorbed on the surface of MoS2 nanosheets was removed through re-dispersal of the precipitation in ultrapure water and collection of the new precipitation at 12 000 rpm centrifugation. Thermogravimetric analysis was used to verify the purification of MoS2 nanosheets through washing and

**Fig. 1** (a) TEM image of the GQDs prepared from electro-Fenton reaction and diameter distribution of as-prepared GQDs. (b) HRTEM image of an individual GQD shown in (a). (c) PLE spectra of GQDs with detection wavelength of 401 nm and PL spectra excited at 320 nm. (d) PL spectra of the GQDs excited by various wavelengths ranging from 320 to 460 nm.

**Fig. 2** (a) Schematic illustration of the exfoliation of bulk MoS2 for the preparation of MoS2 nanosheets. (b) UV-vis absorption spectrum and photograph (inset) of exfoliated MoS2 nanosheet aqueous solution. (c) SEM and (d) AFM images of a typical MoS2 nanosheet with the inset representing the height profile along the white line overlaid on the image. (e) The thickness distribution is based on 100 randomly selected MoS2 nanosheets.
centrifugation, exhibiting that most of the sodium cholate was removed (Fig. S6†). Optical absorption is a characteristic related to the band structure of a semiconductor. Bulk MoS2 is a semiconductor with an indirect bandgap of about 1.29 eV, and no characteristic absorption peak can be observed in the UV-vis absorption spectrum.16 However, theoretical calculations have predicted an indirect to direct bandgap transition in the d-electron system when the bulk MoS2 is thinned to a single layer, and a few angstrom-thin single-layered MoS2 has recently been reported to exhibit a significant energy bandgap of 1.8 eV, whereas those of double- and triple-layer MoS2 reduced to 1.65 and 1.35 eV, respectively.17 The as-exfoliated MoS2 nanosheet aqueous solution with yellow-green color has two characteristic absorption peaks at 610 and 672 nm (Fig. 2b), corresponding to B and A excitonic peaks, respectively, derived from the K point of the Brillouin zone in 2D MoS2 with large lateral dimensions.25,47 The sheet structure and morphology are shown on the SEM image (Fig. 2c), primarily showing the nanoscale of as-exfoliated MoS2. The AFM image of MoS2 nanosheets is shown in Fig. 2d, wherein the height of as-exfoliated MoS2 nanosheets was measured to be around 2.8 nm (inset of Fig. 2d), corresponding to about four monolayers of MoS2.25,47 Statistical analysis based on AFM measurements indicated that the MoS2 nanosheets prepared from sonication-assisted exfoliation of MoS2 powder had various thicknesses, with the majority in the range of three to five monolayers (Fig. 2e).

In recent years, MoS2 based catalysts have been considered as promising alternatives for platinum because of their high abundance and low cost. Promising catalytic activity from MoS2 in the hydrogen evolution reaction (HER) is attributed to the active sites located along the edges of its two-dimensional layered crystal. If MoS2 based catalysts are to realize their potential, there is a need to design MoS2 nanostructures with more edge sites.28–31 On the basis of electro-Fenton reaction of GO turning 2D graphene sheets into small quantum dots, a protocol using electro-Fenton reaction to generate new morphologies of MoS2 sheets was proposed.

Electro-Fenton process of MoS2 nanosheets

The progress of electro-Fenton reaction of MoS2 nanosheets was monitored using TEM. The basal plane of MoS2 nanosheets is clearly observed in Fig. 3a, meanwhile, a number of ultrasmall nanoparticles, representing the fragments arising from sonication of bulk crystals, could also be found in the samples of as-obtained nanosheets. After 20 min of the reaction, a few small holes with a diameter of approximately 20 nm were observed on the basal plane of MoS2 nanosheets (Fig. 3b). Undergoing a short time of electro-Fenton reaction less than 20 min, the layered morphology of the MoS2 nanosheets is preserved, but exhibits the nanoporous facets. Herein, a new morphology of MoS2, nanoporous MoS2 nanosheets, was obtained through electro-Fenton treatment of exfoliated MoS2 nanosheets. Indeed, considerable focus has been placed on developing unique morphologies of 2D material, including graphene sheets with nanoporous facets that exhibit excellent performance as supercapacitor electrodes.48,49 By creating pores within the MoS2 nanosheets, the active edge sites at the surface of sheets can increase and improvements are realized in some unique properties of MoS2 nanosheets. Similar to the nanoporous graphene sheets, the nanoporous MoS2 nanosheets have potential uses in opto-electronic and renewable energy applications. Furthermore, increasing the reaction time to 40 min resulted in an increasing number of holes of various sizes on the MoS2 nanosheets, and a number of small nanosheets under the quantum scale were gradually obtained, which were derived from the spaces between holes (Fig. 3c). After 60 min of the electro-Fenton reaction, MoS2 nanosheets were completely cut into small dots (Fig. 3d), which were later demonstrated to be zero-dimensional MoS2-QDs using HRTEM, AFM, and PL. As a control experiment, the same electrochemical process was conducted for 60 min on MoS2 nanosheets aqueous solution without addition of Fe2+, and no apparent changes were found on basal planes. Meanwhile, the reaction of MoS2 nanosheets with conventional Fenton reagent was carried out, and no apparent holes or changes were observed. It was verified that the electrochemical process and pre-Fenton reagents (O2 and Fe2+) were essential for preparation of nanoporous MoS2 nanosheets and MoS2-QDs.

Characterization of MoS2 quantum dots

The as-prepared MoS2-QDs were subjected to TEM measurement (Fig. 4a), revealing that a few MoS2-QDs are uniformly distributed without agglomeration. The HRTEM image (Fig. 4b) shows an individual MoS2 quantum dot with length and width of approximately 11.5 and 5.3 nm, respectively, indicating that zero-dimensional MoS2-QDs have a different morphology compared with other one-dimensional nanomaterials, such as nanoribbon, nanotube, and nanowire.28 Moreover, as expected, the HRTEM illustrates that the MoS2-QDs have 2D hexagonal
symmetry crystalline structure with lattice spacing of 3.0 Å, which is similar to the hexagonal pattern of MoS2 monolayer. This result was further verified by the electron diffraction pattern of MoS2-QDs (Inset of Fig. 4a). To reveal the morphology feature of MoS2-QD, the HAADF-STEM image is shown clearly in Fig. 4c. Fig. 4d presents the AFM image of the MoS2-QDs on a fresh mica substrate and a few small dots with various scales of heights below 3 nm are observed. From the size distribution (Fig. 4e), we can see that the size of as-prepared MoS2-QDs ranged from 3 to 8 nm, with an average value of 5.43 nm. Meanwhile, combining the AFM image and height distribution (Fig. 4f), it was shown that the heights of most of the MoS2-QDs were below 2 nm, that is, around 1.4 nm representing the height of MoS2 bilayers and approximately 0.7 nm indicating the type of monolayer.

The crystal structure of these as-generated MoS2-QDs was investigated using XRD system, with the MoS2 powder is used as a reference. From the XRD pattern shown in Fig. 5a, it can be observed that both MoS2-QDs and bulk powder are identified as 2H MoS2 with a dominant peak appearing at 14.4°, representing the (002) plane (ICDD card no. 77-1716). To explore the changes of chemical composition, XPS of MoS2 nanosheets were recorded before and after electro-Fenton reaction. XPS survey (Fig. 5b) shows that the proportion of oxygen element in the MoS2 nanosheets sample after electro-Fenton reaction increases because of the influence of hydroxyl radicals. Meanwhile, the atomic ratio of Mo : S increases from 1 : 2.30 (MoS2 nanosheets) to 1 : 2.42 (MoS2-QDs), ascribed to an increasing number of unsaturated sulfur atoms located at the external edge of MoS2-QDs. As shown in Fig. 5c and d, Mo3d3/2, Mo3d5/2, S2s, S2p1/2, and S2p3/2 peaks can be observed at 232.7, 229.5, 226.7, 163.6, and 162.3 eV, respectively, indicating the dominant 2H MoS2 phase in the crystal structure. Two characteristic peaks located at 229.5 and 232.7 eV arise from Mo3d5/2 and Mo3d3/2, suggesting dominance of the +4 oxidation state. In contrast, the S2p region (Fig. 5d) exhibits primarily a single doublet with the 2p3/2 peak at 162.3 eV, corresponding to the −2 oxidation state of sulfur. The semiconducting phase of as-prepared MoS2-QDs (2H MoS2) was further verified based on XPS analyses.

Photoluminescence properties of MoS2 quantum dots

Recent success in isolating MoS2 monolayer has allowed observation of strong photoluminescence, attributed to the direct gap electronic structure of monolayer MoS2. According to theoretical calculation, the MoS2 nanostructure has some unique photoluminescence properties because of the effect of quantum confinement and edge. Therefore, the optical properties of as-prepared MoS2-QDs were explored. Fig. 6a shows the PL spectra of exfoliated MoS2 nanosheet solutions at different reaction times in the electro-Fenton process when the excitation wavelength is 283 nm. It can be seen that before the electro-Fenton reaction the as-exfoliated MoS2 nanosheets are PL inactive, indicating the absence of MoS2-QDs in exfoliated MoS2 nanosheet samples. However, after 20 min of electro-Fenton reaction, the as-generated nanoporous MoS2 nanosheets (Fig. 3b) show a weak PL peak centered at 370 nm, which continues to increase when the reaction time increases to 60 min. Hence, the morphology of quantum dots (Fig. 3d) was demonstrated to exhibit great PL properties. The MoS2-QDs

Fig. 4  (a) TEM image of the as-prepared MoS2-QDs. The inset presents a typical electron diffraction pattern of MoS2-QDs. (b) HRTEM image of an individual MoS2-QD with measured lattice spacing. (c) HAADF-STEM image of the dots. (d) AFM image of the dots deposited on freshly cleaved mica substrates. (e) Size distribution and (f) height distribution of as-prepared MoS2-QDs in (d). Height: ca. 0.7 nm, one layer; ca. 1.4 nm, two layers.

Fig. 5  (a) XRD patterns of MoS2-QDs prepared from electro-Fenton reaction and bulk MoS2 powder (peaks correspond to [002] 2H MoS2). (b) XPS survey of MoS2 nanosheets before electro-Fenton reaction and as-prepared MoS2-QDs. High resolution Mo3d (c) and S2p (d) spectra of MoS2-QDs.
Fig. 6 (a) PL spectra of exfoliated MoS$_2$ nanosheet suspensions before and after the electro-Fenton reaction for 20, 40, and 60 min using excitation wavelength of 283 nm. (b) UV-vis absorption, PL, and PLE spectra of MoS$_2$-QDs dispersed in water. (c) PL spectra of as-prepared MoS$_2$-QDs aqueous solution at different excitation wavelengths ranging from 260 to 310 nm. Inset: excitation wavelengths ranging from 310 to 390 nm. (d) pH-dependent PL spectra when pH is switched between 12 and 2. Inset: reversible switching of PL intensity through the change of pH between 12 and 2.

have an absorption band peaked at 276 nm (Fig. 6b), whereas the characteristic absorption peaks of exfoliated MoS$_2$ nanosheets at 610 and 672 nm disappeared, indicating the absence of 2D MoS$_2$ nanosheets with large lateral dimensions in as-prepared MoS$_2$-QDs. It was suggested that optical absorption of low-dimensional or quantum dot MoS$_2$ exhibited a strong blue shift when the lateral dimensions of the MoS$_2$ nanostructures were reduced to <50 nm, ascribed to the quantum size effect.\textsuperscript{32} Hence, for MoS$_2$-QDs with plane size of ca. 5 nm, the optical absorption peak centered at 276 nm can be assigned to blue-shifted convoluted Z, C, and D excitonic peaks.\textsuperscript{52,55} As we can see from the PL and PLE spectra (Fig. 6b), an optimal emission peak centered at 370 nm is observed when the sample is excited at 283 nm with a Stokes shift of 87 nm. The PLE spectrum recorded with the detection wavelength of 370 nm shows a peak at 283 nm, corresponding to the absorption peak at 276 nm in the UV-vis absorption spectrum. The PL spectra excited by different wavelengths ranging from 260 nm to 390 nm are shown in Fig. 6c, showing that MoS$_2$-QDs aqueous solution has an excitation-independent characteristic emission spectrum peak at 370 nm, and the PL intensity decreases with the excitation wavelengths changing from 270 to 310 nm. Meanwhile, there is another weaker emission spectrum. When the excitation wavelength changes from 270 to 390 nm, the PL peak shifts to longer wavelengths from 310 to 465 nm and the intensity decreases, showing the excitation-dependent characteristic. A pH-dependent PL with the peak at 370 nm is exhibited in MoS$_2$-QDs aqueous solution (Fig. 6d). Under alkaline conditions, the MoS$_2$-QDs emit strong PL, whereas, the PL is nearly completely quenched under acidic conditions. If pH is switched repeatedly between 12 and 2, the PL intensity varies reversibly. It has been suggested that a significant number of H$^+$ intercalate into the 2H MoS$_2$-QDs, transforming from the semiconducting 2H phase to the metallic MoS$_2$ (1T) phase, which eventually leads to loss of their PL properties.\textsuperscript{47}

Conclusion

In summary, a new route was proposed for effective and controllable preparation of GQDs from GO sheets using the electro-Fenton reaction. Meanwhile, it was demonstrated that exfoliated MoS$_2$ nanosheets could react with hydroxyl radicals induced by the electro-Fenton process, achieving generation of new morphologies, nanoporous MoS$_2$ nanosheets and zero-dimensional MoS$_2$-QDs, on a mass scale. The as-prepared MoS$_2$-QDs showed unique PL properties because of quantum confinement, the edge effect and their intrinsic characteristics, and are of great promise to as novel optical probes and for optoelectronic systems. Compared with MoS$_2$ nanosheets exhibiting excellent catalytic activity for the hydrogen evolution reaction, nanoporous MoS$_2$ sheets and MoS$_2$ quantum dots possessing much more active edge sites could enable new opportunities for enhancing properties in hydrogen evolution catalysis and other important technological applications.

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Notes and references

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