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Single-Crystalline Tungsten Oxide Quantum Dots for Fast Pseudocapacitor and Electrochromic Applications

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The research and development of devices regarding energy conversion, storage, and saving including fuel cells, lithium batteries, supercapacitors, and smart windows have attracted a great deal of interest due to the rapid economic expansion, increase in world population, and ever-increasing human reliance on energy-based appliances. A fast electrochemistry with efficient electron and ion transport sits at the heart, the success of which would not only create high rate capability for batteries and capacitors but also bring fast response for electrochromic devices and therefore achieve many exciting performances for energy-related devices.^[1] To this end, considerable attempts have been made to innovate upon the design of the energyrelated electrochemical devices from many aspects such as electrolyte, current collector, and electrode material,^[1a,2] among which reforming the electrode material was particularly actively explored through surface modification, tailoring pore structure, doping and making hybrid composites, etc..^[3] Nanoparticulate materials are usually desired, aiming at improving electrolyte accessibility and shortening ion diffusion length, which is beneficial to accelerate electrochemical process to a certain extent.^[4] Therefore, downsizing electrode material to extremely small, for example, zero-dimensional quantum dots (QDs) may represent a promising but challenging strategy. QDs materials possess several striking advantageous features desirable for this purpose: 1) the small size would greatly shorten the diffusion paths of intercalation ions in the solid phase, which would help to realize fast charge/mass transfer, 2) the large surface-tovolume ratio of QDs would facilitate intimate contacts between electrode materials and electrolyte/current collector, thereby providing fast charge-transport and electron-transfer kinetics, and 3) the significantly high proportion of surface atoms makes QD electrode more active for electrochemical reactions, and thus significantly improving reaction rates. However, although ODs have been documented to be utilized in several state-of-art applications including photocatalysis, solar cells, light-emitting devices and bio-imaging sensors,^[5] their utilization as electrode

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materials in electrochemical reactions remains a formidable challenge, which may be related with the poor conductivity of most available QD materials due to the detrimental insulation of organic ligands capped on QDs and the interparticle resistance raising with the increasing grain boundaries. Thus, it is highly desired to develop a strategy to overcome the deficiency and effectively utilize QDs as electrochemical electrode materials, which would be of great significance both to basic understanding of electrochemical processes and advanced design of electrochemical devices.

Meanwhile, tungsten oxide, WO_{3-x} , a typical electrode material with charge storage/delivery property engendered by the valence change between W^{6+} and W^{5+} , has been actively pursued because of its superior electrochemical performances in both electrochromic devices^[6] and supercapacitors,^[7] with attractive applications ranging from smart window to energy storage media. The structure of dehydrated tungsten oxide typically consists of stacking of infinite corner-sharing WO₆ octahedra layers, leading to the formation of tunnels between the octahedras, which provide sites for ion intercalation and transport. However, limited by the sluggish electrochemical kinetics, most currently available tungsten oxide materials suffer from poor rate capability as supercapacitors and slow response times for electrochromic uses, which closely relates to the time-consuming electrochemical double injection of positive ions (H⁺, Li⁺, Na⁺) and electrons into the host lattice of tungsten oxide electrodes.^[8] The slow Faradaic electrochemical process has become a bottleneck in achieving desirable performance for tungsten oxide-based capacitive and electrochromic devices. As ions transport in the lattice is diffusion-controlled, downsizing all the three dimensions to an extremely small size and making QDs stands a great chance to accelerate the Faradaic process. However, the creation of QDs for tungsten oxide analogues without any template is rather difficult, and attempts on structure-tailoring usually lead to the generation of twodimensional sheet or one-dimensional wire morphologies due to the unequal growth rate in the plane and normal to the plane direction.^[9]

Here we report developing of tungsten oxide QDs with aliphatic amines anchoring on the surface to diminish the anisotropic growth habit and a subsequent exchange of amine ligand with conductive molecule to endow the QDs with excellent conductivities, with the premise of which a very fast electrochemistry was ultimately realized, schematically illustrated in **Figure 1**. The obtained material manifested excellent electrochemical and electrochromic behaviors, surprisingly robust to be charged and discharged without significant distortion in CV profile shape, well keeping the fine structures even at a scan rate up to 500 mV s⁻¹, and fast response with both coloration and bleaching within 1 s.

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b Bulk QDs а tunnel 2² Ligand exchange OD

Figure 1. Scheme of our strategy for realizing fast electrochemical process through extreme downsizing to QDs region with the assistance of conductive ligand exchange. (a) Efficient ion diffusion and charge transfer in QDs material in comparison with blocking in bulk materials. (b) The replacement of pristine aliphatic amine ligand formed during QDs growth (left) with conductive pyridine (right), through which reduced diffusion path and improved conductivity are achieved. Each QD is represented by layer structure of tungsten oxide viewing along the tunnel direction. The tunnels provide convenience for ion intercalations.

The synthesis of tungsten oxide ODs was achieved through a two-step procedure, reacting tungsten chloride (WCl₆) and phenol (C₆H₅OH) to yield tungsten aryloxide precursor $(W(OC_6H_5)_6)$ followed by thermal heating in octylamine at 180 °C. To avoid possible agglomerations and attain good dispersions in characterizations, the as-prepared samples were

redispersed in hexane after collecting by centrifugation. As shown in the inset of Figure 2a, the dispersion exhibited a uniform pale-blue color, typical of tungsten oxide of nonstoichiometric composition. The phase purity and crystal structure of the as-prepared product was examined by X-ray diffraction studies (Supporting Information), which showed reflections

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Figure 2. (a) Low-magnification and (b) high-resolution TEM images of as-prepared tungsten oxide materials confirming the successful achievement of monodispersed spherical QDs with average sizes of 1.6 nm. Inset in (a), an optical photo of the dispersion in hexane showing pale-blue color, which suggests the nonstoichiometric nature of the material. Inset in (b), SAED pattern composed of individual reflected spots supporting the single crystalline nature of the QDs. (c) XPS and (d) FT-IR spectra for the tungsten oxide QDs, suggesting the wrapping of octylamine ligand over the surface of QDs.

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closely matching (110), (200), and (102) of a tetragonal (P4/nmm) phase of nonstoichiometric WO3-x with lattice parameters of a (=b) = 5.31 Å, c = 3.93 Å. The obvious broadening of reflections implies ultrasmall crystalline sizes for the particles, which were roughly estimated with the Scherrer equation, giving a value as small as 1.8 nm.^[10] Figure 2a is a typical low-magnification transmission electron microscope (TEM) image for the product, showing monodispersed crystals with nearly spherical shapes possessing an average diameter of 1.6 nm, in good consistency with XRD estimations. Notably, the crystal sizes are even below the exciton Bohr radius for tungsten oxide materials, which was reported to be 3 nm,^[11] suggesting the possible occurrence of strong quantum confinement effect. The corresponding highresolution TEM image in Figure 2b manifests clear fringes in each individual nanocrystal, suggesting the single-crystalline nature of the QDs. The distances between the adjacent lattice fringes was measured to be 2.6 Å, corresponding to the lattice spacing of (200) or (020) planes. The high crystallinity was supported by the selected area electron diffraction (SAED) pattern (inset in Figure 2b), which shows a strong diffraction ring composed of several individual spots indexed as (200) or (020).

Chemical composition of the as-prepared samples was further examined. The presence of peaks belonging to W = O bond in Fourier Transform Infrared (FT-IR) and Raman spectra (Supporting Information) confirmed the nonstoichiometric nature of the as-synthesized QDs. The quantitative information on the relative number of W atoms in valence states different from +6 can be obtained from deconvolution analysis of W4f core-level spectrum (inset in Figure 2c), which was well fitted into two spin-orbit doublets. The main peaks at 35.4 and 37.6 eV correspond to W4f_{7/2} and W 4f_{5/2} lines of the W atoms in a +6 formal oxidation state, and the second doublet with a lower binding energy at 34.6 and 36.2 eV are originated from W4f5/2 and $W4f_{7/2}$ of the atoms in an oxidation state of +5. The relative percentage of W⁶⁺ and W⁵⁺ in the as-synthesized QDs was determined to be 87.5 and 12.5%, respectively. The O/W atomic ratio is therefore ~2.94. Additionally, the wide X-ray photoelectron spectrum (XPS) in Figure 2c identified signals from C, N along with W, O, and the FT-IR spectrum in Figure 2d displayed characteristic IR peaks derived from organic C-H, N-H, C-C, C-N bonds besides those from inorganic O-W-O bonds, implying the coexistence of tungsten oxide structures and organic amine moieties. Particularly, a broad peak centered at ~2028 cm⁻¹ was discerned, which arises from a combination of the bending vibration and torsional oscillation of -NH3+ group when it interacts with the apical oxygen of the W-O framework and forms R-NH₃⁺...⁻O–W bonds.^[12] Considering the WO_{3-x} QDs are produced in the solution of octylamine, probably the QDs are wrapped by a layer of octylamine molecules with amine end pointing inward and interacting with dangling bonds on the surface of QDs as illustrated in scheme Figure 1b. This also explains the good dispersibility in hexane.

The exciton Bohr radius of tungsten oxide materials was estimated to be 3 nm,^[11] and consequently the QDs with average crystalline sizes down to 1.6 nm are in the strong-quantumconfinement regime and would display clear features associated with size quantization effects such as a blue shift in absorption and near band edge emission. **Figure 3**a shows the UV-Vis optical absorption data, which detected a strong absorption peak in the ultraviolet window. For a sample behaving like a bulk indirect semiconductor, an estimate of the band gap can be obtained from the intercept of a function plotting $(\alpha hv)^{0.5}$ vs *hv*, where α represents the absorption coefficient and *hv* is the photon energy, as shown in inset of Figure 3a. A clear region of linearity was observed and the band gap was estimated to be $E_g \approx 4.19$ eV. In sharp contrast, the absorption for bulk material is broad and much red shifted, the band gap of which was determined to be 2.55 eV, agreeing well with the value in literature, which is 2.6 eV (Supporting Information).^[6,13] Meanwhile, the photoluminescence (PL) spectrum in Figure 3b featured a strong and sharp (fwhm = \sim 34 nm) UV emission at 299 nm (4.15 eV) under the excitation wavelength of λ_{ex} = 220 nm, which should be relevant to the band-to-band radiative recombination of photoexcited electrons and holes. With varying excitation wavelengths, no obvious shift in the emission peak was observed (Supporting Information). It should be mentioned that emission of bulk tungsten oxide materials is rarely observed, and even when compared with previously reported tungsten oxide nanostructures such as nanorods with a diameter of 4 nm, the emission of QDs discussed herein also shifts to lower numbers by nearly 50 nm.^[14] To determine the band electronic structure, the total densities of states of XPS valence band spectra for bulk tungsten oxide and as-synthesized QDs were measured (Figure 3c), which shows that the valence band edge for QDs shifts to the higher binding-energy side by 0.57 eV. The valence-band (VB) maximum for bulk tungsten oxide materials was documented to be 3.1 eV relative to a normal hydrogen electrode, $^{\left[13,15\right] }$ and accordingly the VB for QDs can be determined to be 3.67 eV. The conduction-band (CB) minimum was subsequently obtained by subtracting the band gap from VB maximum, yielding -0.51 and 0.5 eV for QDs and bulk materials, respectively. Therefore a simplified energy diagram comparison between bulk tungsten oxide and QDs is constructed and provided in Figure 3d. The upward shit of CB minimum, downward shift of VB maximum, and the resultant widened band gap unambiguously reveal a strong quantum confinement effect due to the ultrasmall dimensions of the QDs material and provide possibilities for unusual behaviors.

While the octylamine wrapping outside of QDs is critical to keep the desirable dispersibility of QDs, such long-chain aliphatic molecules often impose a disastrous effect on the interparticle charge transport because of their electrical insulation.^[16] Therefore, before employing the WO_{3-x} QDs as electrode materials, the pristine octylamine ligand on QDs surface was exchanged with short-chained and conductive pyridine. This process can improve the conductivity of electrode material accompanied by changing surface to hydrophilic, which would greatly facilitate the infiltration of aqueous electrolytes into the electrode materials (schematic illustration in Figure 1b). The successful exchange of octylamine ligand with pyridine was evidenced by FT-IR characterizations with the appearance of a peak characteristic of C-N-C bonds for pyridine molecules at 1445 cm⁻¹ and the simultaneous disappearance of signals for octylamine formerly located at 2028 and 2920 cm^{-1} (Figure 4a). The QDs have excellent structural integrity and no significant morphological changes were found during the exchange process, as evidenced by the findings of monodispersed QDs of



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Figure 3. (a) UV-Vis absorbance spectrum of the QDs solution held in a quartz cell. Inset: plot of $(\alpha h \nu)^{0.5}$ against $h\nu$ to achieve the bandgap of 4.19 eV for QDs, greatly blueshifted compared to 2.6 eV for bulk materials. (b) PL emission spectrum under excitation wavelength of 220 nm showing an obvious and sharp UV emission peak at 299 nm. Even when compared with other nanostructured materials such as nanorods or nanofilms, the emission is shifted to high-energy regime. (c) Total densities of states of XPS valence band showing the higher-energy-shift of VB maximum for QDs by 0.57 eV. (d) A comparison of modulated CB and VB energy levels of as-synthesized QDs with bulk tungsten oxide materials. The numbers with asterisk are from previous reports.^[13,15]

comparable sizes in TEM (Figure 4b) and AFM (Supporting Information) observations. It is noted, however, after the exchange treatment the particle size distribution is slightly broadened with increased percentage of particles with slightly bigger sizes, which can be explained by some aggregations of nanoparticles due to the relatively thinner shell of pyridine

ligand and the resultant decreased interparticle distances. Electrochemical impedance spectroscopy characterizations confirmed that the QDs after pyridine exchange possess both fast ion diffusion and low charge transfer resistance, which may provide advantages for excellent electrochemical performances (Supporting Information).

The behavior of the QDs after pyridineligand exchange as electrode materials was first examined by electrochemical studies of cyclic voltammograms (CV) and galvanostatic charge/discharge measurements and compared with that of bulk tungsten oxide materials. The QDs samples after ligand exchange were coated onto FTO glasses as working electrode, followed by sintering at 140 °C to remove possible unbonded organics. Electrode of bulk materials was made similarly with the same mass loading. A comparison view of the CV profiles at an example scan rate of 80 mV s⁻¹ is shown in **Figure 5**a. For bulk tungsten oxide, one pair of weak and broad redox peaks is observed at the potentials of +0.13 and -0.12 V, which derives from the redox reactions



Figure 4. (a) FT-IR spectrum supporting the successful ligand exchange with the occurrence of peak corresponding to C-N-C of pyridine and disappearance of signals for octylamine. (b) a typical TEM image showing that ligand exchange did not bring obvious morphology changes.

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Figure 5. (a) CV profiles at a scan rate of 80 my s⁻¹ with QDs material showing two pronounced redox pairs but bulk material having no clear features. CV profiles for (b) bulk and (c) QDs materials at various scan rates of 5, 10, 20, 50, 80, 150, 300, and 500 mV/s. Fine features for QDs are well maintained even at a high scan rate of 500 mV/s while those for bulk material are lost at increasing scan rates. (d) Galvanostatic charge/discharge profiles for QDs and bulk materials under different currents, 0.2, 0.5, 1, 2, 4, 6, and 8 mA, in the potential range of -0.5 to 0.2 V. With increase in applied current, the triangle shape for QDs electrode in both charge and discharge process is well maintained and only limited capacity sacrifice was found, supporting the fluent ion transport in QDs materials.

between W⁶⁺ and W⁵⁺ accompanied by H⁺ insertion/extraction $WO_{3-x} + e^- + H^+ \Leftrightarrow HWO_{3-x}$. Such nearly featureless CV profiles have been usually observed with various tungsten oxide analogues of both stoichiometric and nonstoichiometric compositions as well as other oxides, especially at high scan rates, which results from the difficult and long distance ion diffusion in the oxide lattice.^[17] In contrast, the profile for QDs possesses a richer structure, which features two well-resolved pairs of redox peaks with the anodic voltage peaks lying at -0.02 and -0.18 V and the cathodic ones at -0.14 and -0.30 V. Excluding the possibilities that the signals arise from existing organics or FTO substrate, they can be both ascribed to WO_{3-x} QDs, suggesting that the ion insertion probably occurs in two distinct stages, $WO_{3-x} + ne^- + nH^+ \Leftrightarrow H_nWO_{3-x}$ and $H_nWO_{3-x} + (1-n)$ $e^- + (1-n)H^+ \Leftrightarrow HWO_{3-x}$ (0 < n < 1). A similar split of redox peaks was observed in a nanostructured V₂O₅, reflecting the phase transformations from α -V₂O₅ to ϵ -V₂O₅ and from ϵ -V₂O₅ to δ -V₂O₅, which, however, did not occur to bulk materials except scanning at very low rate of 1 mV s^{-1.[18]} For tungsten oxide materials, the visibility of such fine structures is believed to be a great profit from the dimensional downsizing of electrode materials. Furthermore, the potential difference between the oxidation and reduction potential $(E_{O}-E_{R})$ is an important measure of the reversibility of the redox reaction, with 0.12 V for WO_{3-x} QDs but 0.25 V for bulk counterpart, suggesting the improved reversibility of QDs materials.^[19]

The charge storage/delivery capability was further examined by recording CV profiles at various sweep rates ranging from 2 to 500 mV/s (Figure 5b and c). At increasing scan rate, although both bulk and QDs materials exhibit current increase together with shift of oxidation peaks to a more positive position and reduction peaks to a more negative position due to an increase in the internal diffusion resistance within the pseudocapactive material, QDs material is robust enough to be charged and discharged without significant distortion in profile shape, well keeping the fine structures even at a scan rate up to 500 mV s^{-1} , in distinctive difference from the loss of reaction information at high scan rates for bulk counterpart, corroborating a low internal resistance and fast charge transfer in the QD materials. Figure 5d depicts the charge/discharge behaviors at various currents, with the downward lines corresponding to charging and upward ones for discharging. In obvious contrast from the unsymmetric curve shape for bulk tungsten oxide, the WO3-x QDs manifest typical pseudocapacitive triangular shapes over a wide range of applied currents, from 0.2 up to 8 mA, indicative of the reversible occurring of efficient and fast ion transport for QDs materials. Voltage change during current switching is known to be proportional to the resistance of electrode materials. Much smaller voltage drop is observed with QDs at the beginning of the discharge compared with those of bulk WO3 recorded at the same current, which is attributed to the fluent ion transport through the conducting surface. With an increase in applied





Figure 6. (a) Transmittance spectra taken for electrodes of tungsten oxide QDs on deposited FTO in the colored (-0.8 V) and bleached (+0.2 V) states. The material has high transparency at bleached state, over 90% of transmittance, and large modulation window, >80%, which are very desirable for electrochromic devices. Inset: optical images of the electrode at bleached and colored states, appearing almost transparent and dark blue color, respectively. (b) Plot of optical density variation as a function of charge density monitored at wavelength of 633 nm, which gives coloration efficiency of 154 cm² C⁻¹. (c) Transmittance switching for bulk (green) and QDs (black) tungsten materials showing the significant fast response for QDs martials. (d) Enlarged in situ transmittance variation curve between the colored and bleached states for QDs. The switching time for QDs is within 1 s, whereas for bulk tungsten oxide even 50 s could not give complete coloring or bleaching.

current, the decrease in capacity for bulk material is much more severe than that of QDs, especially in cathodic capacity (downward direction), indicative of improved rate capability or better behaviors under high current charge/discharge conditions for QDs (estimated specific capacitance in Supporting Information).

Electrochromism is one most visualized phenomenon that reflects the on-going electrochemical process. The electrochromic optical modulation range for QDs was initially examined, and Figure 6a shows the obtained UV-Vis transmission spectra in its colored and bleached states at different potentials with the corresponding optical images in the inset. At bleached state under applied voltage of +0.2 V, the electrode is transparent with optical transmittance of ~94% at a wavelength of 633 nm, while it is in a deep blue color with transmittance at the same monitored wavelength decreased to 9.0% at the colored state under the voltage of -0.8 V. Therefore, the QDs material possesses both a high transparency over 90% under bleached state and an extremely large modulation range of visible light, up to 80%, which is very desirable in the electrochromic devices. Coloration efficiency (CE) is a very important parameter for electrochromic materials, which is defined as the change in optical density (OD) per unit of inserted charge, i.e., $CE = \Delta OD/\Delta Q = \log(T_b/T_c)/\Delta Q$, where ΔQ is the inserted charge that promotes the $\triangle OD$ change in the optical

absorbance, $T_{\rm b}$ and $T_{\rm c}$ refer to the bleached and colored transmittance at a certain wavelength, respectively. The relative chronoamperometric transient for ΔQ is provided in Supporting Information. A high CE gives a large optical modulation at small charge insertion or extraction, which can desirably induce long-term cycling stability.^[8] Figure 6b plots the relation of OD with current density and the CE can be calculated from the slope of the linear region of this curve, yielding 154 cm² C⁻¹ for tungsten oxide QDs. The value is much larger than that for bulk tungsten oxide and reported tungsten oxide nanomaterials, either amorphous or crystalline, which typically ranges from 10 to 108 cm² C⁻¹,^[8,20] suggesting the much improvement in charge utilization by the size quantization and conductive ligand wrapping. As a direct gauge parameter for electrochemical process speed, the switching time between coloration and bleach in electrochromism was tested. Figure 6c depicts the reversible switching between colored and bleached states monitored by transmittance changes at a wavelength of 633 nm with time over a range of 500 s. The switching time is defined as the spanning period required for 90% of the change between the steady bleached and colored states. The electrochromic response times of QDs is significantly faster compared with bulk counterpart. For bulk tungsten oxide material, even given 50 s, the plateau of coloration or bleaching could not be

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achieved. In contrast, a zoon-in view on one cycle in Figure 6d shows that the response time for both coloration and bleaching are surprisingly within 1 s. The stability with extended tests of 50 cycles is included in the Supporting Information. To the best of our knowledge, the new tungsten oxide QDs material herein is among the best in documented inorganic materials and even competitive with organic compounds in electrochromic performances. For reference, a table listing the performances of some typical materials is provided in the Supporting Information.

While QDs with the ligand exchanged with pyridine manifest unparalleled electrochemical and electrochromic behaviors, the performances exhibited by pristine QDs with long-chain octyalmine as capping ligand are much inferior. Significantly different from the good behaviors of QDs with pyridine ligand, such as occurrence of fine features in CV scans, consistent keeping of the fine structures even at a very high scan rate of 500 mV/s, the CV profiles of pristine QDs were almost featureless, and severe distortion was found with increased scan rates. which can be explained by the larger internal resistance and slower charge transfer of pristine QDs compared with pyridineexchanged QDs. With regard to electrochromic behaviors, the pristine QDs showed obviously prolonged coloration/bleaching time (7.4/6.4 s) compared with pyridine-exchanged sample (both <1 s) under the same conditions (Supporting Information). Therefore, the superior performance of pyridine-exchanged QDs can mainly be accounted by two important factors, 1) fast and efficient diffusion of the electrolyte ions to the active material due to the conducting and hydrophilic surface, and 2) excellent mass transport within the lattice because of the size quantization.

In summary, QDs of a nonstoichiometric tungsten oxide, WO_{3-x} (3- $x \approx 2.94$), with an average crystalline size of 1.6 nm are successfully synthesized via a simple colloid process using tungsten aryloxide as the precursor. The QDs are stabilized with a surface layer of octyalmine ligand, the exchange of which to pyridine brings about excellent hydrophilicity and conductivity, providing possibilities for superior electrochemical behaviors. Electrochemical investigations revealed the reversible occurrence of efficient and fast ion transport in charging and discharging for QDs electrodes, and consequently an extremely excellent electrochromic performance was achieved, with coloration/bleaching time within 1 s and coloration efficiency up to 154 cm² C⁻¹, which is much superior to inorganic analogues and even competitive to organic related materials. We believe the unusually good behaviors benefit from the size quantization and the deliberately wrapped conductive pyridine ligand on the surface, which would create short diffusion path length and greatly facilitate the mass/charge transfer both at the contact interfaces and within the electrode materials during the electrochemical process, leading to an enhanced mass/energy utility especially at high current densities. The findings here are exciting because they demonstrate the zero-dimensionaldownsizing of normal materials greatly facilitates fast electrochemical kinetics, and further pave the way for applications of QDs materials into ultrafast-response electrochemical devices.

Experimental Section

Materials: Tungsten hexachloride (WCl₆, 99%), octylamine (OA, 99%) and phenol were purchased from Aladdin Chemicals, pyridine

and hexane were from Sinopharm Chemicals. All reagents were used as received without further purifications. The substrate for making electrode was commercial SnO₂: F-coated glass provided by NSG, the sheet resistance for which was 15 Ω square⁻¹.

Synthesis of Tungsten Aryloxide $(W(OC_6H_5)_6)$ Precursor. Tungsten aryloxide $(W(OC_6H_5)_6)$ was synthesized through a modified approach on a previously reported method.^[21] In a typical synthesis route, phenol (15 g) was added to tungsten chloride (3.6 g) under nitrogen atmosphere in the absence of any solvent, and the system was put to refluxing under continuous magnetic stir for 6 h. After reactions the resultant dark red mixture was extracted with 100 mL ether and washed with ~5% NaOH solution for several times to ensure complete removal of excess phenol. The ether was finally removed in vacuum to give a dark red solid of tungsten aryloxide with yields estimated to be of ca. 35%.

Synthesis of Tungsten Oxide (WO_{3-x}) QDs: Tungsten aryloxide precursor (0.2 g) was melted in a flask under 180 °C under N₂ flow, followed by immediate injection of octylamine (3 mL). After performing the reaction at this temperature for 5 min, the QDs appearing in pale blue color were precipitated by addition of ethanol, collected by centrifugation, and thoroughly washed with ethanol to remove unreacted raw materials. The surface of QDs was covered by a layer octylamine ligand to keep the unusual QD morphology, and therefore the product was redispersed in hexane to achieve monodispersity.

Pyridine-Exchange for the QDs: To exchange the surface octylamine ligand to pyridine, the QDs were dissolved in pyridine and heated in an oil bath for 3 h at 70 °C and a subsequent extended exchange reaction was performed overnight at room temperature while keeping stirring. After the exchange was completed, hexane was added to the solution to precipitate the pyridine-exchanged QDs, which was isolated by centrifugation and redispersed in pyridine.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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