Supplementary Material

A Highly Sensitive and Selective Probe for the Colorimetric Detection of Mn(II) Based on the Antioxidative Selenium and Nitrogen Co-doped Carbon Quantum Dots and ABTS**

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S1. Experimental

S1.1. Materials and reagents

Citric acid (C₆H₈O₇), L-Histidine (C₆H₉N₃O₂), Cobalt chloride hexahydrate (CoCl₂·6H₂O), Iron sulfate heptahydrate (FeSO₄·7H₂O), Manganese chloride (MnCl₂·4H₂O), Nickel sulfate hexahydrate (NiSO₄·6H₂O), ABTS [2,2’-azinobis (3-ethylbenzothiazoline-6-sulphonic acid ammonium salt)], Dimethyl sulfoxide (C₂H₆SO) were purchased from Aladdin Industrial Corporation, (Shanghai, China). Sodium selenite anhydrous (Na₂SeO₃) was bought from Alfa Aesar (China) Chemical Co., Ltd., (Shanghai, China). Chromic chloride hexahydrate (CrCl₃·6H₂O) was purchased from Adamas Reagent Co., Ltd., (Shanghai, China). Quinine sulfate dihydrate was bought from Shanghai Titan Scientific Co., Ltd., (Shanghai, China). Trolox (6-hydroxy-2,5,7,8-tetramethylchro-man-2-carboxylic acid) was obtained from Sigma-Aldrich Co., Ltd., (Russian Fed). Calcium chloride anhydrous (CaCl₂), Magnesium chloride hexahydrate (MgCl₂·6H₂O), Sodium chloride (NaCl) were purchased from Sinopharm Chemical Reagent Co., Ltd., (Beijing, China). Na₂HPO₄·12H₂O, NaH₂PO₄·2H₂O, Potassium peroxydisulfate (K₂S₂O₈), Potassium dichromate (K₂Cr₂O₇), Potassium chloride (KCl), Sodium hydroxide (NaOH) and Zinc Chloride (ZnCl₂) were bought from Beijing Chemical Works (Beijing, China). Cupric sulfate, anhydrous (CuSO₄) was obtained from Beijing Yili Chemical Co., Ltd., (Beijing, China). Lead Chloride (PbCl₂) was purchased from Tianjin KERMEL Chemical Reagents Development Centre (Tianjin, China). The Ca(II), Co(II), Cr(VI), Cr(III), Cu(II), Fe(II), K(I), Mn(II), Mg(II), Na(I), Ni(II), Pb(II) and Zn(II)
solutions (1mM) were prepared in ultra-pure water from the salts of CaCl₂,
CoCl₂·6H₂O, K₂Cr₂O₇, CrCl₃·6H₂O, CuSO₄, FeSO₄·7H₂O, KCl, MnCl₂·4H₂O,
MgCl₂·6H₂O, NaCl, NiSO₄·6H₂O, PbCl₂ and ZnCl₂, respectively. All chemicals were
analytical grade and all solutions were prepared by ultra-pure water.

**S1.2. Apparatus**

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM)
were conducted with operating voltage of 300 kV on a TECNAI transmission electron
microscope. Atomic force microscope (AFM) images were collected by using a
Bruker Dimension Icon AFM equipped with Scanasyst in Air peak force
tapping mode AFM tips from Bruker. Raman spectroscopy measurement was
carried out using Raman spectroscopy with laser excitation of 532 nm at room
temperature (HORIBA Scientific, Xplora plus, France). X-ray photoelectron
spectroscopy (XPS) were obtained by a Thermo ESCALAB 250Xi spectrometer
(Setting parameters: monochromatic Al Kα (hv = 1486.6 eV), operated at 150 W, 500
μm beam spot, the binding energy was calibrated against the carbon 1s line at 284.8
eV, USA). Fourier-transformed infrared spectroscopy (FTIR) was taken on a
IRPrestige-21 (SHIMADZU, KBr wafer technique, Japan). Fluorescence spectra were
recorded on a fluorescence Spectrophotometer (HITACHI F-4600, Japan). The
lifetime of fluorescence was obtained by an Edinburgh FLS980 all functional
steady-state/transient fluorescence spectrometer (Edinburgh Instruments, UK).
UV-Vis spectrum was obtained a UV-3600 UV-VIS-NIR spectrophotometer
(SHIMADZU, Japan). Zeta potential was measured by using the Nano-ZS90
Thermogravimetric (TG) analysis was performed on a TA company TGA Q500 unit in N\textsubscript{2} at a heating rate of 10 °C min\textsuperscript{-1} from room temperature to 800 °C. XRD spectrum was measured by using the XRD-7000 X-RAY DIFFRACTOMETER (SHIMADZU, Japan). \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra were recorded on the Advance Bruker 400M NMR spectrometer. Ultra-pure water was obtained from a Millipore Mingche\textsuperscript{TM}-D 24\textsuperscript{UV} water purification system.

The electrochemical measurement was measured by using a AUTOLAB electrochemical workstation (Autolab PGSTAT302N, Metrohm, Switzerland) in a typical three electrode, a graphite rod as the counter electrode, a glassy carbon electrode coated with Se/N-CQDs as the working electrode and a saturated calomel electrode (SCE) as the reference electrode. The electrode was polished with polishing powder, washed with deionized water, and then dried with cold air. Then, 4 mg Se/N-CQDs powder, 4 mg carbon black were admixed in 750 μL deionized water, 250 μL ethanol, 30 μL 5 wt% Nafion solution, forming a mixed solution, which was ultrasound for at least 30 min, 5 μL the prepared solution was dropped onto the polished electrode eventually. The redox properties of Se/N-CQDs were investigated in phosphate buffer (pH = 7.20) with the loading of 0.5 mg cm\textsuperscript{-2} on a glassy carbon (GC) electrode. CV curve was performed at a potential range of -0.5 – 1.5 V vs RHE and at a scan rate of 100 mV/s.
S1.3. The measurement of quantum yield (QY) of Se/N-CQDs

The reference method was used to determine the quantum yield of Se/N-CQDs [S1]. Quinine sulfate in 0.1 M H₂SO₄ solution (quantum yield of 53.0% excited at 365 nm) was selected as a criterion by the following equation:

\[ \Phi = \Phi_s \left[ \frac{I}{I_s} \left( \frac{A_s}{A} \right) \frac{n^2}{n_s^2} \right] \]  

(1)

Where “\( \Phi \)” is the quantum yield, “\( I \)” is the fluorescence peak area at the maximum excitation wavelength, “\( A \)” is the UV-Vis absorbance intensity, the subscript “\( S \)” represents the reference quinine sulfate, “\( n \)” is the different refractive index of solvent, the superscript “\( 2 \)” means the square of “\( n \)”.

S1.4. Study on the fluorescence intensity of Se/N-CQDs

3 mL of Se/N-CQDs (1 mg/mL) were continuously measured for 20 counts to investigate the stability of the fluorescence intensity of Se/N-CQDs under the same conditions. In order to study the effect of concentration on the fluorescence intensity of Se/N-CQDs, the prepared Se/N-CQDs (1 mg/mL) were diluted to 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, 0.05 times with ultra-pure water. The effect of pH on the fluorescence intensity of Se/N-CQDs was further discussed. The aqueous solutions at different pH (2.60, 3.46, 4.23, 5.10, 6.03, 7.25, 8.36, 9.36, 10.35, 11.16, 12.03) were prepared by using sodium hydroxide and concentrated sulfuric acid. 3 mL of the aqueous solutions at different pH and 3 mL of ultra-pure water were added into 1 mL of Se/N-CQDs, respectively. The fluorescence intensities were recorded on the fluorescence spectrophotometer (HITACHI F-4600) at the excitation
wavelength of 370 nm. All solutions were prepared in ultra-pure water at room temperature.

S1.5. Effect of ionic strength on the ability of Se/N-CQDs to scavenge ABTS•+

To discuss the effect of ionic strength on the ability of Se/N-CQDs to scavenge ABTS•+, NaCl with the different orders of magnitude and the same order of magnitude were added into the ABTS•+ + Se/N-CQDs mixed solutions. 250 μL ultra-pure water and different concentrations of NaCl with the different orders of magnitude (0.000000001, 0.00000001, 0.0000001, 0.000001, 0.0001, 0.001, 0.01, 0.1, 1 M) were added into the 800 μL ABTS•+ + Se/N-CQDs mixed solutions S1 at 734 nm under the same conditions, respectively, and Se/N-CQDs + ABTS•+ mixed solutions S1 were composed of 40 mL ABTS•+ (A_{734 nm} = 0.70) and 500 μL Se/N-CQDs (1 mg/mL). In addition, 250 μL ultra-pure water and different concentrations of NaCl with the same order of magnitude (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 mM) were added into the 800 μL ABTS•+ + Se/N-CQDs mixed solutions S1, respectively. The UV-Vis absorption spectra were recorded by a UV-3600 UV-VIS-NIR spectrophotometer under the same conditions. All solutions were prepared in ultra-pure water at room temperature.

S1.6. Effect of pH on the ability of Se/N-CQDs to scavenge ABTS•+

To reserach the effect of pH on the ability of Se/N-CQDs to scavenge ABTS•+, excess Se/N-CQDs were added into ABTS•+ firstly. 250 μL ultra-pure
water and various aqueous solutions with different pH (0.78, 1.82, 2.60, 3.46, 4.23, 5.10, 6.03, 7.25, 8.36, 9.36, 10.35, 11.16, 12.03, 12.95 and 13.55) were added into 800 μL ABTS$^{•+}$ ($A_{734\text{ nm}} = 0.70$) and 50 μL Se/N-CQDs (1 mg/mL) mixed solutions (Se/N-CQDs + ABTS$^{•+}$ mixed solutions S2), respectively.

Furthermore, when a small amount of Se/N-CQDs were added into ABTS$^{•+}$, the effect of pH on the ability of Se/N-CQDs to scavenge ABTS$^{•+}$ was also investigated. 250 μL ultra-pure water and various aqueous solutions with different pH (0.78, 1.82, 2.60, 3.46, 4.23, 5.10, 6.03, 7.25, 8.36, 9.36, 10.35, 11.16, 12.03, 12.95 and 13.55) were added into the 800 μL Se/N-CQDs + ABTS$^{•+}$ mixed solutions S1, respectively.

The influence of pH on absorbance of Se/N-CQDs or ABTS$^{•+}$ were further studied, respectively. 3 mL ultra-pure water and various aqueous solutions with different pH (0.78, 1.82, 2.60, 3.46, 4.23, 5.10, 6.03, 7.25, 8.36, 9.36, 10.35, 11.16, 12.03, 12.95 and 13.55) were added into the 1 mL Se/N-CQDs (1 mg/mL) solutions at 734 nm under the same conditions, respectively. 250 μL ultra-pure water and various aqueous solutions with different pH (0.78, 1.82, 2.60, 3.46, 4.23, 5.10, 6.03, 7.25, 8.36, 9.36, 10.35, 11.16, 12.03, 12.95 and 13.55) were added into the 800 μL ABTS$^{•+}$ ($A_{734\text{ nm}} = 0.70$) solutions, respectively.

The UV-Vis absorption spectra were recorded by a UV-3600 UV-VIS-NIR spectrophotometer under the same conditions. All solutions were prepared in ultra-pure water at room temperature.
S2. Results and discussion

S2.1. Figures and tables

**Fig. S1.** (A) High-resolution XPS spectrum of C\textsubscript{1s}. (B) High-resolution XPS spectrum of N\textsubscript{1s}. (C) High-resolution XPS spectrum of O\textsubscript{1s}. (D) High-resolution XPS spectrum of Na\textsubscript{1s}. (E) High-resolution XPS spectrum of Se\textsubscript{3d}. (F) EDS spectrum of Se/N-CQDs.
Fig. S2. (A) $^1$H NMR spectrum of Se/N-CQDs. (B) $^{13}$C NMR spectrum of Se/N-CQDs. (C) Raman spectrum of Se/N-CQDs.

Fig. S3. The CV curve of Se/N-CQDs in phosphate buffer (pH = 7.20) with the scan range of -0.5 – 1.5 V at the rate of 100 mV/s.
Fig. S4. (A) The UV-Vis absorption spectra of Se/N-CQDs + ABTS$^+$ mixed solutions (Mixed solutions) containing different concentrations of Mn(II) in tap water. (B) The UV-Vis absorbance of Mixed solutions containing different concentrations of Mn(II) in tap water from 0 to 130.40 μM at 734 nm. (C) The linear relationship between the UV-Vis absorbance of Mixed solutions and the concentrations of Mn(II) in tap water from 0 to 104.50 μM at 734 nm.
S2.2. Characterizations of Se/N-CQDs

Fig. S5. (A) FTIR spectrum of Se/N-CQDs. (B) UV-Vis spectrum of Se/N-CQDs.

The FTIR spectrum of Se/N-CQDs was shown in Fig. S5A. The band at 3410 cm\(^{-1}\) was the stretching vibration of O-H and N-H bonds [S2, S3]. The peak at 1580 cm\(^{-1}\) were attributed to stretching vibration of C=O bonds [S1, S2]. The band at 1400 cm\(^{-1}\) was ascribed to C-N stretching vibrations [S3]. The results of FTIR and XPS demonstrated that there were carbon-containing groups, oxygen-containing groups and nitrogen-containing groups on the surface of Se/N-CQDs, which were very important for the formation of CQDs and had an effect on the fluorescence intensity of Se/N-CQDs [S4]. Fig. S5B was the UV-Vis spectrum of Se/N-CQDs. The weak absorbance peak at 326 nm was attributed to the n-\(\pi^*\) transitions of the carboxyl groups (O-C=O) on the surface of Se/N-CQDs [S5].
Fig. S6. (A) TGA spectrum of Se/N-CQDs. (B) XRD pattern of Se/N-CQDs.

The thermal stability of Se/N-CQDs was demonstrated by the TGA curve in Fig. S6A. The thermogram exhibited a two-step degradation pattern. Due to the elimination of water molecules or the moisture associated with Se/N-CQDs, the initial quality was reduced by 2% at 100 °C, illustrating that the thermal stability of Se/N-CQDs was up to 100 °C. A jump was attributed to the expansion of Se/N-CQDs between 350 and 390 °C. Owing to the gradual degradation of the surface functional groups of Se/N-CQDs, the final degradation step resulted in a significant weight loss (70%) in the range of 100–560 °C [S6]. The curve tended to be stable beyond 560 °C. Fig. S6B was XRD pattern of Se/N-CQDs. It could be seen that the broad X-ray diffraction peak at about 2θ = 24.9 was the characteristic graphitic carbon peak (PDF#74-2329), which further demonstrated the formation of Se/N-CQDs [S7].

Fig. S7. The chemical structures of (A) citric acid and (B) L-Histidine.
Fig. S8. (A) $^1$H NMR spectrum of citric acid. (B) $^{13}$C NMR spectrum of citric acid. (C) $^1$H NMR spectrum of L-Histidine. (D) $^{13}$C NMR spectrum of L-Histidine. (E) $^1$H NMR spectrum of Se/N-CQDs. (F) $^{13}$C NMR spectrum of Se/N-CQDs.

$^1$H NMR and $^{13}$C NMR spectra of citric acid, L-Histidine and Se/N-CQDs were recorded using a Bruker 600 MHz, the chemical shifts were reported as the delta scale in ppm relative to D2O ($\delta = 4.79$ ppm) for $^1$H NMR. In the $^1$H
NMR spectra, sp² hybridized carbon atoms signals were found in the range of 7–9 ppm, suggesting the aromatic structures in CQDs [S8, S9]. In the ¹³C NMR spectra, signals detected in the range of 15–70 ppm and 100–185 ppm correspond to aliphatic (sp³) carbon atoms and sp² hybridized carbon atoms, respectively. Signals between 170–185 ppm should correspond to carboxyl/amide groups on the surface of CQDs [S8–S12]. Fig. S8E was the ¹H NMR spectrum of Se/N-CQDs. Signals between 6 ppm and 9 ppm belong to sp² hybridized carbon atoms, illustrating the aromatic structures of Se/N-CQDs [S9]. ¹³C NMR spectrum of Se/N-CQDs was shown in Fig. S8F, signals between 25 ppm and 70 ppm were attributable to aliphatic (sp³) carbon atoms. Signals between 100 ppm and 180 ppm were ascribed to sp² hybridized carbon atoms [S9, S13]. Especially, signals between 160 ppm and 180 ppm should be put down to carboxy/amide groups on the surface of Se/N-CQDs [S9]. From the ¹H NMR and ¹³C NMR of spectra in Fig S7 and S8, compared with citric acid and L-Histidine, aliphatic (sp³) carbon atoms, sp² hybridized carbon atoms and carboxyl/amide groups were retained in the Se/N-CQDs. Compared with other reported CQDs[S8–S18], the NMR results of Se/N-CQDs had almost no change. There were also aliphatic (sp³) carbon atoms, sp² hybridized carbon atoms and carboxyl/amide groups in the CQDs [S8–S18].
Fig. S9. The size distribution of Se/N-CQDs by DLS intensity.

The Zeta-potential and size distribution of Se/N-CQDs were measured by using the Nano-ZS90 zetasizer (Malvern Instruments Corp, UK.). The Zeta potential of Se/N-CQDs was -13.8 mV in phosphate buffer (pH = 7.4, 0.01 M). As shown in Fig. S9, the size distribution of Se/N-CQDs was about 6 ± 2 nm.

**Tab. S5.** XRF analysis of Se/N-CQDs.

| Formula | Concentration (%) |
|---------|-------------------|
| CO₂     | 81.3              |
| Na₂O    | 18.2              |
| SeO₂    | 0.471             |
| SiO₂    | 0.0074            |
| SO₃     | 0.0108            |
| K₂O     | 0.0129            |
| ZnO     | 0.0022            |

The concentration (%) of Se in the powder sample was analyzed by X-ray fluorescence (XRF, Rigaku, XRF primus-2, Japan) and summarized in Tab. R1. The concentration (%) of Se as SeO₂ in the powder sample was 0.471%. It was
characterized by elemental analyzer (Elementar, vario El cube, German), the content of N was 9.32% in the 2.359 g powder sample (Se/N-CQDs).

S2.3. Study on the fluorescence intensity of Se/N-CQDs

**Fig. S10** The 3-D fluorescence spectrum of Se/N-CQDs.

The 3-D fluorescence spectrum of Se/N-CQDs was shown in Fig. S10. The excitation wavelength of Se/N-CQDs was about 250 to 550 nm. The emission wavelength of Se/N-CQDs was about 380 to 650 nm.
Fig. S11. (A) The maximum fluorescence intensity obtained by continuously measuring the fluorescence intensity of Se/N-CQDs, \( \lambda_{ex} = 370 \) nm. (B) The maximum fluorescence intensity of Se/N-CQDs (1 mg/mL) diluted by PBS (pH = 7.40, 0.01 M) with different dilutions (0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1 and 0.05). (C) The maximum fluorescence intensity of Se/N-CQDs containing aqueous solutions at different pH (2.60, 3.46, 4.23, 5.10, 6.03, 7.25, 8.36, 9.36, 10.35, 11.16, 12.03).

The fluorescence intensity of Se/N-CQDs were continuously measured for 20 counts when the excitation wavelength was 370 nm. As shown in Fig. S11A, the maximum fluorescence intensities were almost the same (RSD = 8.51%), showing that the fluorescent probe based on Se/N-CQDs had good stability. When Se/N-CQDs (1 mg/mL) were diluted to 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1 and 0.05 times, it can be seen from Fig. S11B that the fluorescence intensities increased slowly at the beginning, the fluorescence intensity was maximum when Se/N-CQDs (1 mg/mL) were diluted to 0.5 time. Then, the fluorescence intensities decreased gradually. This phenomenon in fluorescence intensities might be related to self-quenching which occurred at high concentration due to the aggregation quenching effect. The effect of pH (2.60, 3.46, 4.23, 5.10, 6.03, 7.25, 8.36, 9.36, 10.35, 11.16 and 12.03) on the fluorescence intensity of Se/N-CQDs was further discussed. As shown in Fig. S11C, the fluorescence intensities of mixed solutions at different pH were almost unchanged, indicating that pH has no effect on the fluorescence intensity of Se/N-CQDs.
S2.4. Effect of ionic strength on the ability of Se/N-CQDs to scavenge ABTS$^{+}$

**Fig. S12.** (A) The relationship between $A/A_0$ and the concentration of NaCl, when different concentrations of NaCl with the different orders of magnitude were added into the Se/N-CQDs + ABTS$^{+}$ mixed solutions S1 at 734 nm. (B) The relationship between $A/A_0$ and the concentration of NaCl at 734 nm, when different concentrations of NaCl with the same order of magnitude were added into the ABTS$^{+}$ + Se/N-CQDs mixed solutions S1 at 734 nm.

To confirm the ability of Se/N-CQDs to scavenge ABTS$^{+}$ free radical under ionic strength environments, different concentrations of NaCl with the different orders of magnitude and the same order of magnitude were added into the Se/N-CQDs + ABTS$^{+}$ mixed solutions S1 at 734 nm under the same conditions. It could be seen from Fig. S12A and S9B that the lines were almost straight, some concentrations of NaCl caused slight changes in the absorbance of Se/N-CQDs + ABTS$^{+}$, but these effects might be negligible, showing that ionic strength had almost no effect on the ability of Se/N-CQDs to scavenge ABTS$^{+}$. 

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S2.5. Effect of pH on the ability of Se/N-CQDs to scavenge ABTS$^{++}$

Fig. S13. (A) Photographs of ABTS$^+$ and Se/N-CQDs + ABTS$^{++}$ mixed solutions S2 (excess Se/N-CQDs were added) containing water and various aqueous solutions at different pH. (B) The relationship between 1-A/A0 and pH at 734 nm. A was the UV-Vis absorbance of Se/N-CQDs + ABTS$^{++}$ mixed solutions S2 (excess Se/N-CQDs were added) containing water and various aqueous solutions at different pH. A0 was the UV-Vis absorbance of ABTS$^+$. (C) Photographs of ABTS$^{++}$ and Se/N-CQDs + ABTS$^{++}$ mixed solutions S1 (a
small amount of Se/N-CQDs were added) which containing water and various aqueous solutions at different pH. (D) The relationship between \( 1-A/A_0 \) and pH at 734 nm. A was the UV-Vis absorbance of Se/N-CQDs + ABTS\(^{++}\) mixed solutions S1 (a small amount of Se/N-CQDs were added) containing water and various aqueous solutions at different pH. \( A_0 \) was the UV-Vis absorbance of ABTS\(^{++}\). (E) The UV-Vis absorbance of Se/N-CQDs containing aqueous solutions at different pH at 734 nm. (F) The relationship between \( 1-A/A_0 \) and pH at 734 nm. A was the UV-Vis absorbance of ABTS\(^{++}\) solutions containing various aqueous solutions at different pH. \( A_0 \) was the UV-Vis absorbance of ABTS\(^{++}\) solutions containing water.

It could be seen directly from Fig. S13A and S10B, when water (blank) and various aqueous solutions at different pH (0.78, 1.82, 2.60, 3.46, 4.23, 5.10, 6.03, 7.25, 8.36, 9.36, 10.35, 11.16, 12.03, 12.95 and 13.55) were added into Se/N-CQDs + ABTS\(^{++}\) mixed solutions S2 which excess Se/N-CQDs were added. ABTS\(^{++}\) could be completely scavenged at pH 1.82, 2.60, 3.46, 4.23, 5.10, 6.03, 7.25, 8.36, 9.36, 10.35, 11.16, 12.03, 12.95 and 13.55. However, the content of ABTS\(^{++}\) increased under the strong acid condition at pH 0.78. Due to the positive charge of ABTS\(^{++}\), strong acidic conditions might be beneficial to the formation and stability of ABTS\(^{++}\). When water (blank) and various aqueous solutions at different pH (0.78, 1.82, 2.60, 3.46, 4.23, 5.10, 6.03, 7.25, 8.36, 9.36, 10.35, 11.16, 12.03, 12.95 and 13.55) were added into Se/N-CQDs + ABTS\(^{++}\) mixed solutions S1 which a small amount of Se/N-CQDs were added.
As shown in Fig. S13C and S10D, pH (1.82, 2.60, 3.46, 4.23, 5.10, 6.03, 7.25, 8.36, 9.36, 10.35, 11.16 and 12.03) could hardly affect the ability of Se/N-CQDs to scavenge ABTS$^{•+}$. However, the content of ABTS$^{•+}$ increased under the strong acid condition at pH 0.78, ABTS$^{•+}$ could be completely scavenged at pH 12.95 and 13.55. Therefore, pH affected the ability of Se/N-CQDs to scavenge ABTS$^{•+}$ under strong basic conditions and under the strong acid condition, and pH could hardly affect the ability of Se/N-CQDs to scavenge ABTS$^{•+}$ under mild conditions. As seen from the Fig. S13E, Se/N-CQDs had almost no absorbance when aqueous solutions with different pH were added into Se/N-CQDs at 734 nm, indicating that Se/N-CQDs might not affect the UV-Vis absorbance of ABTS$^{•+}$ at 734 nm. However, pH could affect the absorbance of ABTS$^{•+}$ at 734 nm in Fig. S13F. The results of pH affecting ABTS$^{•+}$ were consistent with the results of pH affecting the ability of Se/N-CQDs to scavenge ABTS$^{•+}$. In short, the impact of pH on the ability of Se/N-CQDs scavenging ABTS$^{•+}$ was due to the direct impact of pH on ABTS$^{•+}$. pH would not affect the ability of Se/N-CQDs scavenging ABTS$^{•+}$ in neutral, weak acid and weak alkaline environments. This was conducive to the application of Se/N-CQDs as an antioxidant in biomedicine and other fields.

S2.6. Stability of Se/N-CQDs + ABTS$^{•+}$ mixed solutions 1 for Mn(II) detection
Fig. S14. The absorbance of Se/N-CQDs + ABTS•+ mixed solutions 1 when it was continuously measured at 734 nm.

The absorbance of Se/N-CQDs + ABTS•+ mixed solutions 1 were continuously measured for 11 counts in 15 minutes. As shown in Fig. S14, the absorbance at 734 nm were almost the same (RSD = 0.808%), showing that Se/N-CQDs + ABTS•+ mixed solutions also had excellent stability.

S2.7. Experimental conditions of the colorimetric sensor based on Se/N-CQDs + ABTS•+ for the optimized assay for Mn(II) detection.

Some experimental conditions like the ratio of ABTS•+ and Se/N-CQDs, the reaction time between the colorimetric sensor and Mn(II) were investigated for the optimized assay for Mn(II) detection. Eight groups of experiments on the ratio of ABTS•+ and Se/N-CQDs were shown in Tab. S6. Two groups of experiments on the reaction time between the colorimetric sensor based on the ABTS•+ and Se/N-CQDs and Mn(II) were shown in Tab. S7. The UV-Vis absorption spectra of ABTS•+ (2 mL, A_{734 nm} = 0.7) + Se/N-CQDs (25 μL, 1 mg/mL) + Mn(II) (100 μL, 1 mM) and ABTS•+ (2 mL, A_{734 nm} = 0.7) + Se/N-CQDs (25 μL, 1 mg/mL) + Mn(II) (200 μL, 1 mM) were measured for 30
times in 3min.

**Tab. S6.** Eight groups of experiments on the ratio of ABTS$^{+\circ}$ and Se/N-CQDs.

|    | ABTS$^{+\circ}$ | Se/N-CQDs | Water |
|----|----------------|-----------|-------|
|    | (A$_{734 \text{ nm}}$ = 0.7, $\mu$L) | (1 mg/mL, $\mu$L) | ($\mu$L) |
| 1  | 2000           | 0         | 400   |
| 2  | 2000           | 25        | 375   |
| 3  | 2000           | 50        | 350   |
| 4  | 2000           | 75        | 325   |
| 5  | 2000           | 100       | 300   |
| 6  | 2000           | 200       | 200   |
| 7  | 2000           | 300       | 100   |
| 8  | 2000           | 400       | 0     |

**Tab. S7.** Two groups of experiments on the reaction time between the colorimetric sensor and Mn(II).

|    | ABTS$^{+\circ}$ | Se/N-CQDs | Mn(II) | Water |
|----|----------------|-----------|--------|-------|
|    | (A$_{734 \text{ nm}}$ = 0.7, $\mu$L) | (1 mg/mL, $\mu$L) | (1 mM, $\mu$L) | ($\mu$L) |
| 1  | 2000           | 25        | 100    | 200   |
| 2  | 2000           | 25        | 200    | 100   |
**Fig. S15.** (A) The UV-Vis absorption spectra of ABTS$^{+*}$ (2 mL, $A_{734 \text{ nm}} = 0.7$) in the presence of different Volume of Se/N-CQDs (0, 25, 50, 75, 100, 200, 300 and 400 μL, 1 mg/mL). (B) The absorbance at 734 nm of ABTS$^{+*}$ (2 mL, $A_{734 \text{ nm}} = 0.7$) in the presence of different Volume of Se/N-CQDs (0, 25, 50, 75, 100, 200, 300 and 400 μL, 1 mg/mL).

**Fig. S16.** (A) The UV-Vis absorption spectra of ABTS$^{+*}$ (2 mL, $A_{734 \text{ nm}} = 0.7$) + Se/N-CQDs (25 μL, 1 mg/mL) + Mn$^{2+}$ (100 μL, 1 mM) for 30 times in 3 min. (A) The UV-Vis absorption spectra of ABTS$^{+*}$ (2 mL, $A_{734 \text{ nm}} = 0.7$) +
Se/N-CQDs (25 μL, 1 mg/mL) + Mn^{2+} (200 μL, 1 mM) for 30 times in 3min.

(C) The absorbance at 734 nm of ABTS^{+} (2 mL, A_{734 \text{ nm}} = 0.7) + Se/N-CQDs (25 μL, 1 mg/mL) + Mn^{2+} (100 μL, 1 mM) and ABTS^{+} (2 mL, A_{734 \text{ nm}} = 0.7) + Se/N-CQDs (25 μL, 1 mg/mL) + Mn^{2+} (200 μL, 1 mM) for 30 times in 3min.

As shown in Fig. S15, when the different volumes of Se/N-CQDs were added into ABTS^{+}, respectively, ABTS^{+} was scavenged with the increase of Se/N-CQDs. Moreover, based on the synergistic effect of Se/N-CQDs and Mn(II) on ABTS^{+}, Se/N-CQDs and ABTS^{+} as the colorimetric sensor was applied to the detection of Mn(II). Thereby, a small amount of Se/N-CQDs were added into ABTS^{+} to form a colorimetric sensor for detecting Mn(II). A part of ABTS^{+} was reserved and Se/N-CQDs and Mn(II) had the synergistic effect to scavenge ABTS^{+} for the Mn(II) detection. When 25 μL of Se/N-CQDs were added into 2 mL of ABTS^{+}, ABTS^{+} could be scavenged, so Se/N-CQDs + ABTS^{+} mixed solutions (Mixed solutions) were prepared by 40 mL ABTS^{+} (A_{734 \text{ nm}} = 0.70) and 500 μL Se/N-CQDs (1 mg/mL) in the manuscript.

As shown in Fig. S16, when the UV-Vis absorption spectra of ABTS^{+} (2 mL, A_{734 \text{ nm}} = 0.7) + Se/N-CQDs (25 μL, 1 mg/mL) + Mn(II) (100 μL, 1 mM) and ABTS^{+} (2 mL, A_{734 \text{ nm}} = 0.7) + Se/N-CQDs (25 μL, 1 mg/mL) + Mn(II) (200 μL, 1 mM) were measured for 30 times in 3min, the redox reaction occurred rapidly, with the increase of reaction time, the absorbance at 734 nm had a slight negligible decrease. Therefore, the absorbance was measured
immediately after the sample was prepared.

**S2.8.** The reproducibility of the colorimetric sensor based on ABTS$^{++}$ + Se/N-CQDs for the detection of Mn(II).

**Tab. S8.** Three groups of experiments on the reproducibility of the colorimetric sensor based on ABTS$^{++}$ + Se/N-CQDs for the Mn(II) detection.

| ABTS$^{++}$ (μL) | Se/N-CQDs (μL) | Mn(II) (μL) | K2S2O8(μL) | Water (μL) |
|------------------|----------------|-------------|------------|------------|
| 2000             | 0              | 0           | 0          | 1500       |
| 2000             | 100            | 400         | 0          | 1000       |
| 2000             | 100            | 400         | 1000       | 0          |

**Fig. S17.** (A) The UV-Vis absorption spectra of ABTS$^{+}$, ABTS$^{++}$ + Se/N-CQDs + Mn$^{2+}$, ABTS$^{+}$ + Se/N-CQDs + Mn$^{2+}$ + K$_2$S$_2$O$_8$. (B) The absorbance at 734 nm of ABTS$^{++}$, ABTS$^{++}$ + Se/N-CQDs + Mn$^{2+}$, ABTS$^{++}$ + Se/N-CQDs + Mn$^{2+}$ + K$_2$S$_2$O$_8$.

To study the reproducibility of the colorimetric sensor based on ABTS$^{+}$ + Se/N-CQDs for the detection of Mn(II), K$_2$S$_2$O$_8$ was used to investigate the reproducibility of the colorimetric sensor based on ABTS$^{++}$ + Se/N-CQDs. Three groups of experiments on the reproducibility of the colorimetric sensor based on
ABTS⁺⁺ + Se/N-CQDs for the Mn(II) detection were shown in Tab. S8. As shown in Fig. S17, when K₂S₂O₈ was added into ABTS⁺⁺ + Se/N-CQDs + Mn(II), the absorbance at 734 nm increased significantly and was similar to that of ABTS⁺⁺, showing that ABTS⁺⁺ increased and recovered in ABTS⁺⁺ + Se/N-CQDs + Mn(II) + K₂S₂O₈ solutions. Therefore, when moderate Se-CQDs were added into the ABTS⁺⁺ + Se/N-CQDs + Mn(II) + K₂S₂O₈ solutions again, the mixed solutions might be used for the Mn(II) detection again. The colorimetric sensor based on ABTS⁺⁺ and Se/N-CQDs could be recycled for the Mn(II) detection and be a reproducible colorimetric sensor.
### S2.8. Tables

**Tab. S1.** Four groups of the synergy of Mn(II) and Se/N-CQDs.

| ABTS\(^{\bullet+}\) (mL) | Water (μL) | Mn(II) (1 mM, μL) | Se/N-CQDs (1 mg/mL, μL) |
|---------------------------|------------|--------------------|------------------------|
| 1                         | 2          | 300                | 0                      |
| 2                         | 2          | 50                 | 250                    |
| 3                         | 2          | 250                | 0                      |
| 4                         | 2          | 0                  | 250                    |

**Tab. S2.** Comparison of different probes for the detection of Mn(II).

| Detection probe            | LOD (μM) | Ref.            |
|----------------------------|----------|-----------------|
| Multifunctional sensor     | 6.03     | Lee et al. [S19]|
| Silver nanoparticles       | 1.70     | Mehta et al. [S20]|
| Schiff base chemosensor    | 5.0      | Harihara et al. [S21]|
| Schiff base                | 7.11     | Kim et al. [S22]|
| Copper nanoclusters        | 10       | Han et al. [S23]|
| Se/N-CQDs                  | 1.69     | This work       |
**Tab. S3.** Analysis of Mn(II) in ultra-pure water determined by the colorimetric probe based on Se/N-CQDs + ABTS•+ method.

| Sample | Added Mn(II) (μM) | Found (μM) | Recovery (%; n = 3) | RSD/% |
|--------|------------------|------------|---------------------|-------|
| 1      | 62.50            | 66.00      | 105.60              | 8.27  |
| 2      | 90.90            | 95.90      | 105.50              | 5.95  |
| 3      | 117.60           | 122.00     | 103.70              | 3.15  |
| 4      | 142.90           | 138.00     | 96.60               | 7.52  |

**Tab. S4.** Analysis of Mn(II) in tap water determined by the colorimetric probe based on ABTS•+ + Se/N-CQDs and ICP-OES methods.

| Sample | Added Mn(II) (μM) | ABTS•+ + Se/N-CQDs (%) (n = 3) | ICP-OES Found (μM) | Recovery (%) (n = 3) | RSD/% |
|--------|------------------|--------------------------------|-------------------|---------------------|-------|
| 1      | 32.20            | 33.30                          | 31.87             | 98.98               | 2.20  |
| 2      | 47.60            | 49.44                          | 48.27             | 101.41              | 1.25  |
| 3      | 62.50            | 63.00                          | 62.13             | 99.41               | 1.61  |
| 4      | 76.90            | 76.42                          | 76.43             | 99.39               | 0.89  |
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