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Detection of Cu(II) in water by using N,S co-doped carbon dots

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Abstract: Determination of Cu(II) ions in surface and drinking water is a high-priority issue both for the environment and human health. Here, we report on the preparation via a hydrothermal method of stable water suspensions of N and S co-doped carbon dots. This material demonstrated selective sensitivity to the presence of copper in water with the appearance of a characteristic absorption band at 658 nm resulting in a visual color variation from orange to dark brown. The colorimetric measurement, carried out by recording the difference between the absorbance at two wavelengths, showed a good linear dependence on the ion concentration from 1 to 100 μM with a lower limit of detection of 300 nM, significantly below the values set by health and environmental organizations. The sensing method is simply based on the addition of the contaminated sample to the carbon dot solution without any other reagents or previous treatment. Moreover, the sensing solution showed stability for at least 6 months after preparation.

1. Introduction

Copper, like some other heavy metals, is essential to life since it plays a fundamental role in many biochemical mechanisms, but too much can be dangerous for the environment and toxic for human beings. Excessive intake can produce sickness such as liver and kidney damage, Parkinson's or Alzheimer's diseases [1]–[3]. For this reason, health preservation requires that in drinking the copper ions must not exceed certain values of concentration set by the WHO to 30 μM (approximately equal to 2 mg/L) and by EPA to 20 μM (\cong 1.3 mg/L) [4]. This condition is increasingly jeopardized by growing industrialization. In fact, surface waters are contaminated by the massive use of copper in many industrial sectors such as electrical components, electrochemistry, batteries and fertilizers [5]. Therefore, it is important to develop advanced methods to evaluate Cu(II) levels efficiently in environments and biological systems.

Atomic absorption spectrometry (AAS), atomic fluorescence spectroscopy, high performance liquid spectroscopy (HPLC), are some of the established laboratory techniques that are currently used for the detecting and quantitatively determination of copper ions [6]–[13]. However, these reliable and accurate methods use sophisticated, expensive and bulky instrumentation, require well-trained personnel and complex, time-consuming preparation processes [14], [15]. Optical sensing, based on fluorescence



spectroscopy and colorimetric detection, has recently been investigated as a strategy for fast and easier procedures, using simple, portable, and low-cost methods. Nanomaterials, due to their large interaction surface and peculiar tunable properties, have further boosted the development of optical sensors by extending the range of possible techniques and analytes. In particular, carbon dots (CDs) have gathered considerable attentions as promising sensing nanomaterials because of the plentiful preparation methods, acceptable cytotoxicity, chemical inertness, low photobleaching, and lasting fluorescence properties [16], [17].

Most researchers have addressed the synthesis of luminescent CDs, including green materials as the precursors, for sensing, through variations of fluorescence signal. For instance, detection of metal ions such as silver [18], aluminum [19], copper/mercury [20] and nickel [21] has been reported. Differently, much fewer studies have investigated the variations of optical absorbance and thus of the perceived color. In fact, simple, selective, and sensitive colorimetric sensors for Cu(II) are still rare and need to be developed.

In this paper, we studied the sensing capability of N, S carbon dots (therein referred to as NS-CDs) prepared through a simple hydrothermal approach, based on o-Phenylenediamine and ammonium sulfate as the precursors and sources of nitrogen and sulfur atoms. NS-CDs selectively detected Cu(II) ions in water solution through variations of absorbance in the visible light spectral range, i.e., with the rising of an absorption structure at 658 nm. Since NS-CDs are transparent in that region, Cu(II) concentration could be accomplished based on a ratiometric measurement with a large range of linearity (1-100 μM) and a lower detection limit of 300 nM. The variation of absorption showed visually at concentrations exceeding 10 μM , with the test solution changing from an orange to a brown color. The sensing measurement can be performed in 5 min by the simply adding the water samples without other reactants, treatments, or use of pH buffer. Due to these peculiar features, the novel visual sensor material is a promising system in the field of water pollution detection.

2. Materials and Methods

Ammonium sulphate and O-phenylenediamine (OPD) were used for the synthesis of carbon dots as the N and S source, respectively. $\text{Cl}_2\text{Cu}\cdot 2\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, and AgNO_3 were used for the sensitivity experiments. All chemicals were provided by Merck Sigma Aldrich and used as they were received. Salt solutions of each metal were prepared in de-ionized ((18.25 M Ω cm), DI) water and diluted to the prescribed concentration immediately before the experiment.

The synthesis of NS-CDs was carried out starting from a solution of o-Phenylenediamine (400 μM) in 0.012 L of ethanol and a solution of Ammonium sulphate (400 μM) in 0.012 L of DI-water. The two solutions were combined and transferred to a sealed Teflon lined container and heated at 220 $^\circ\text{C}$ for 8 h. The reactor was then let cool down naturally. The resulting brown liquid product was filtered with a 220 nm polyethersulphone filter and then dialyzed through a of 3500 Da dialysis bag with deionized water. Finally, a dilution with DI water ($V_{\text{NS-CDs}}/V_{\text{DI}}$: 1/2) was performed to obtain the NS-CDs sensing solution.

The Fourier transform infrared spectra (FTIR) were acquired in the range from 400 to 4000 cm^{-1} on a FT-IR spectrometer (Perkin Elmer Spectrum 100) using KBr cells after drying the sample solutions at 40 $^\circ\text{C}$ under nitrogen flux. The spectra were acquired at room temperature.

The samples for TEM analysis were obtained from a droplet evaporated on carbon film. The dried-out NS-CDs were fixed into the carbon film by infrared radiation for a duration varying from 30 seconds to 2 minutes. TEM inspections were performed through a PhilipsTM CM-20[®] working at 0.2 MV. Three samples of NS-CDs were inspected. Due to the high volatility of the NS-CDs under high-voltage converged electron beam, the exposure times used to acquire the TEM images were kept to a maximum of 15 s. The quality of the TEM images is thus not optimal due to this experimental constraint and limit.

Optical absorbance spectra were measured on liquid samples contained in optical cuvettes with 10 mm thickness using a UV vis spectrophotometer (Cary 50 Varian Inc.). PL spectra were measured on a setup for fluorescence characterization based on a continuous discharge Hg-Xe lamp (Oriel Corp.) with

a 25-cm monochromator (PMI) as excitation light source. Emitted light was dispersed by an emission Cornerstone 260 1/4 m monochromator (Oriel) and detected by R3896 photomultiplier (Hamamatsu Corp.).

The sensing experiments for colorimetric detection of heavy metal (HM) ions were carried out by addition of 1000 μL of HM DI water solution to 1000 μL of NS-CDs sensing dispersion. After stirring for 15 seconds and waiting for 5-minutes, the UV-vis spectra were recorded. Measurements compared to a reference solution that was prepared by adding 1000 μL of NS-CDs to 1000 μL of DI water sensing solution.

3. Results and Discussion

3.1. Characterization of NS-CDs

Figure 1 shows the FTIR spectra for reference NS-CD (blue curve) and for NS-CD after reaction with Cu(II) ions (black). In the spectrum before reaction some arrows indicate peaks that are assigned to the variety of nitrogen groups introduced into the carbon structure by the preparation method [17]. Specifically, the peaks at 1113 cm^{-1} and 1400 cm^{-1} can be attributed to S=O bonds and C-S bonds, respectively, which thus indicates the presence of sulphur [22]. Remarkable differences are observed after the interaction with copper since all those peaks are strongly reduced. This strongly suggests the occurrence of coordination of copper to NS-CD mainly via the amino groups, as will be discussed in par. 3.2.

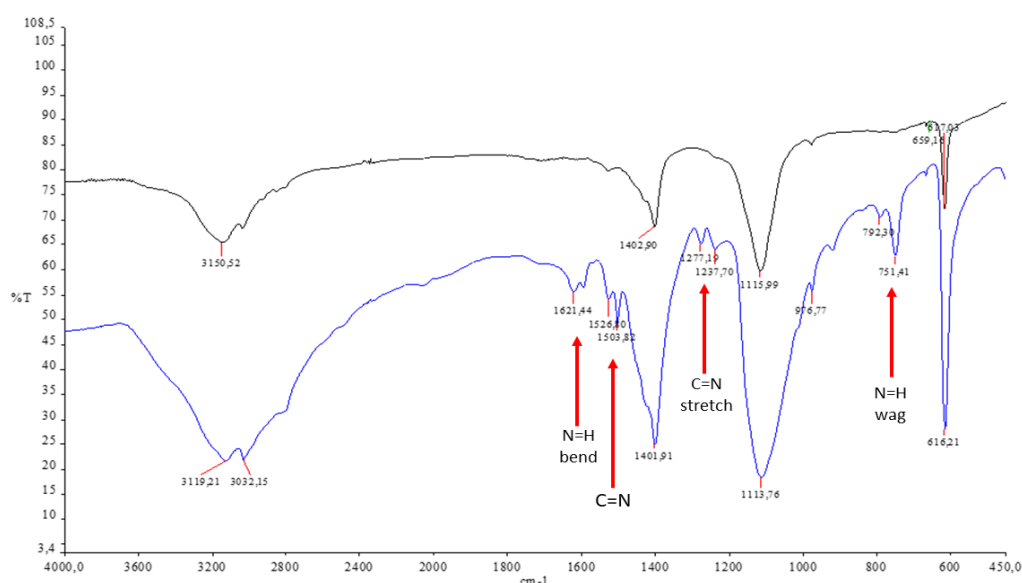


Figure 1. FTIR spectral curves of NS-CDs (blue) and NS-CDs upon interaction with Cu(II) (black).

Figure 2a displays a TEM image of pure NS-CDs sample with the typical population of NS-CDs while in Figure 2b a representative single NS-CD is displayed. Figure 2c reports the statistical size distribution of the detected NS-CDs. It appeared that the mean diameter of the NS-CDs was 2.3 ± 0.4 nm. The size distribution was quite narrow, and this in turn shows a full formation stability (Figure 2c).

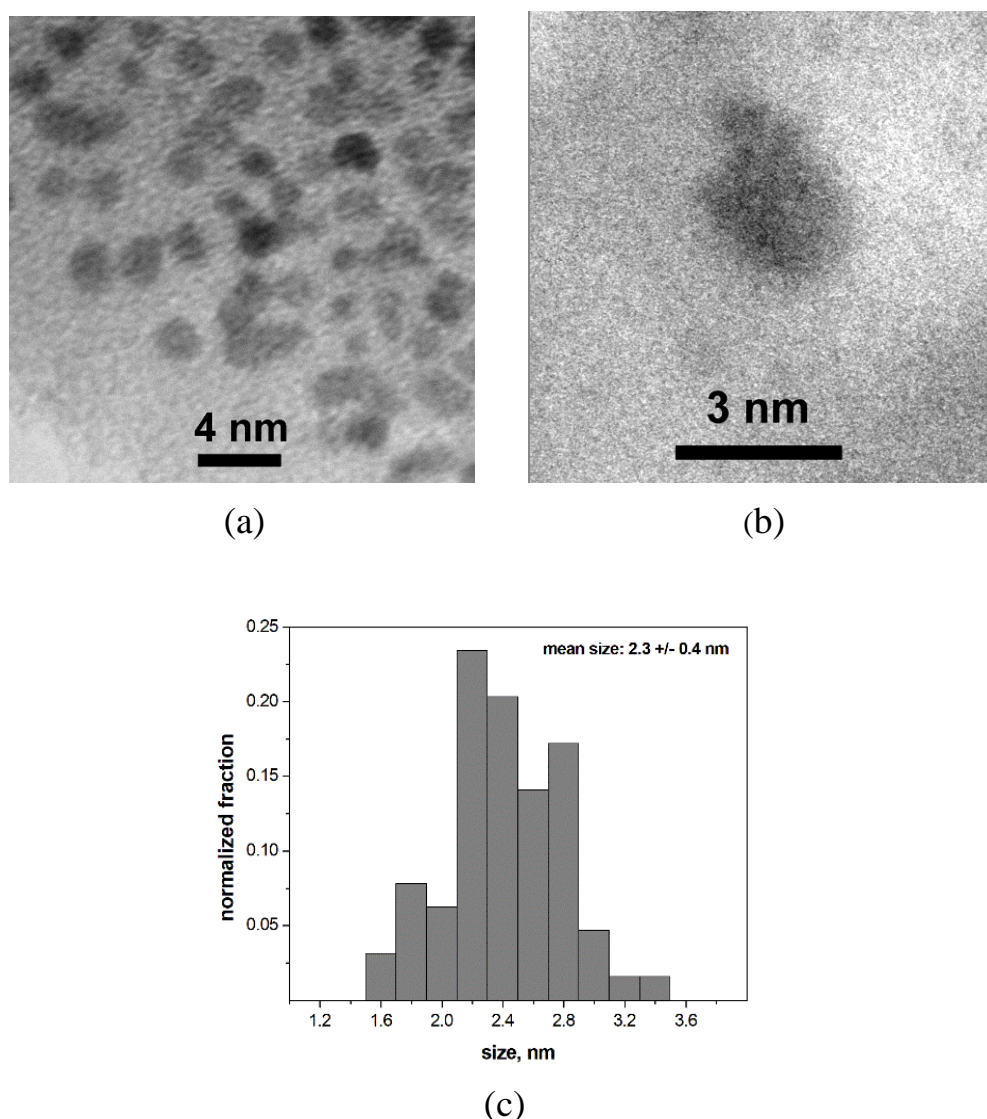


Figure 2. TEM micrographs and distribution of size of NS-CDs. In a) a typical population of NS-CDs is reported; b) shows a representative NS-CD; c) reports the statistical size distribution of the detected NS-CDs.

The UV-vis absorption spectrum of the reference solution is displayed in Figure 3 (black continuous line). The short-wavelength side of the spectrum is characterized by the presence of the higher-energy optical π - π^* transitions due to isolated residual sp^2 -carbon areas in the graphene-like defective structure of carbon backbone. The visible range is dominated by a strong absorption band at 460 nm that lays in a spectral range generally assigned to the n - π^* transition of nitrogen groups added by doping into the carbon structure [23], as confirmed by FTIR data. In the present case, however, the presence of an appreciable shoulder at 430 nm indicates the possible contribution coming from residues of oxidized o-Phenylenediamine (OPD_{ox}) [24], as will be discussed in par. 3.2. In fact, Figure 3 also shows that the photoluminescence spectrum obtained with excitation at 430 nm (see the red squares) encompasses the typical emission range of OPD_{ox} that is from 550 to 580 nm.

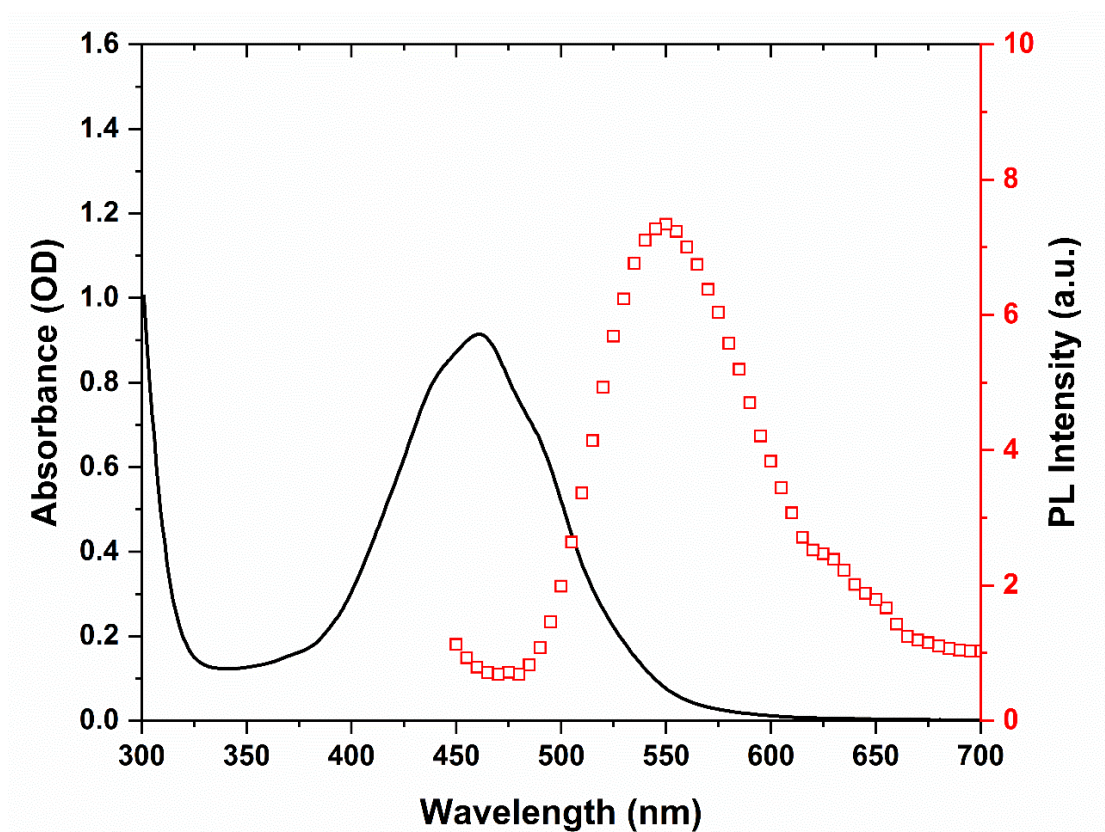


Figure 3. UV-vis absorption (black curve) and fluorescence (red squares) spectra of NS-CD sensing solution excited at $\lambda_{exc} = 430$ nm.

3.2 Colorimetric response towards Cu(II) ions

Figure 4 shows the effects on the absorption spectrum of the interaction of NS-CDs with some common heavy metals: Pb(II), Fe(III), Cu(II), Fe(II), Cr(III), Ag(I), Cd(II), Ni(II), and Co(II) at a concentration of 100 μ M. As can be clearly seen, the interaction with Cu(II) gave rise to enhancement of absorbance at 460 nm and, more significantly, the onset of a clear peak at 658 nm, approximately. As shown in the inset of Figure 4, the rise of this peak caused a visual colour variation from yellowish-orange to a sort of dark brown. At variance, the addition of all the other HMs did not cause significant changes, except for Fe(III) and Fe(II) that produced an increase of the absorbance at 460 nm. The band appearing at 658 nm in the presence of copper can be assigned to the amino groups of the CDs chelating the Cu(II) ions to form cuprammonium-like complexes that are known to exhibit absorption bands in the range 600 – 700 nm [25], [26]. This hypothesis is in agreement with the great reduction of FTIR signals coming from N containing groups observed after interaction with copper, as reported in paragraph 3.1. Similar mechanisms for formation of metal-CD complexes are usually observed in CDs synthesized with a range of different top-down strategies [27] as well as in fluorescent metallic nanoparticles [28]. We believe that the enhancement of the structure around 460 nm might be attributed to the effect of further oxidation of OPD to OPD_{ox} produced by copper and iron ions already described in literature [24].

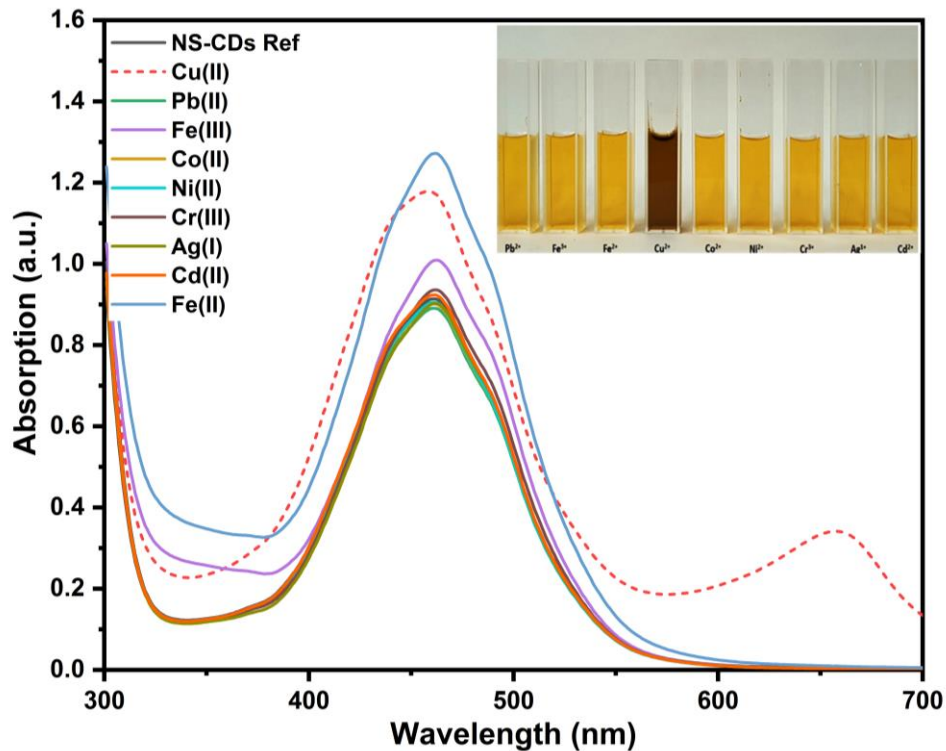


Figure 4. Selective response of the absorbance of NS-CDs sensing solution upon the interaction of HM ions with a concentration of 100 μM . The insert (on top right) is a photograph of the visual effect caused by the addition of copper.

As displayed in Figure 5 (a), the increase of Cu(II) concentration caused the progressive growth of the band at 658 nm. In particular, the behavior of absorbance vs. the copper ion concentration, i.e. the calibration curve, showed linear in the interval from 1 to 100 μM provided the difference between the absorption at 658 nm and that at 700 nm, defined as $\Delta A_{658/700}$, is plotted vs. the ion concentration and shown in Figure 5 (b).

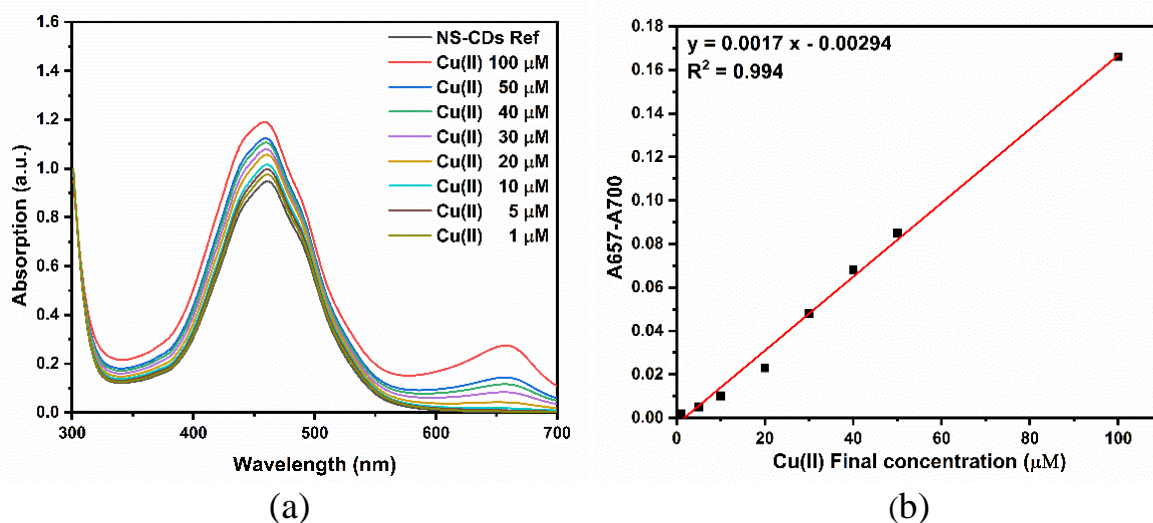


Figure 5. (a) Absorbance spectra of NS-CDs following the interaction with Cu(II) ions at different concentrations. (b) Calibration curve.

It should be pointed out that the measurement of $\Delta A_{658/700}$ enables a real colorimetric detection in that the method is less influenced by spurious alterations of absorbance due to other effects and turbidity of the real samples. The LOD estimated for the present system was calculated by the given Eq. (1)

$$\text{LOD} = 3\sigma/m \quad (1)$$

Where, the standard deviation σ refers to measurements at the lowest concentration data and m is the sensitivity, that is the slope of the above reported calibration curve. The LOD estimated for copper was 300 nM, which is well below the values set in drinking water by either the EPA (at $\sim 20 \mu\text{M}$, 1.3 mg/L) or the WHO ($\sim 30 \mu\text{M}$, 2 mg/L) or [4].

The colorimetric response of NS-CDs was also tested for the selectivity and interference effects. First, the metal ions that included Pb(II), Cd(II), Fe(II), Co(II), Cr(III), Fe(III), Ni(II), and Ag(I) were pre-incubated with NS-CDs. No significant changes were observed in absorbance spectra (blue bars in Figure 6b). Subsequent addition of 1 equivalent of Cu(II) to each of them caused an enhancement in the absorption intensity at 658 nm, as shown in Figure 6a and represented by cyan bars in Figure 6b, except for Fe(III), Fe(II) and Cr(III). For the iron ions, this behaviour can be attributed to their greater affinity for nitrogen and oxygen-containing groups and to the special coordinate interaction with the phenolic hydroxyl groups [29]. These factors lead to the formation of strong bonds with NS-CDs that the Cu(II) could not replace. On the other hand, further work is needed to understand the role of Cr(III).

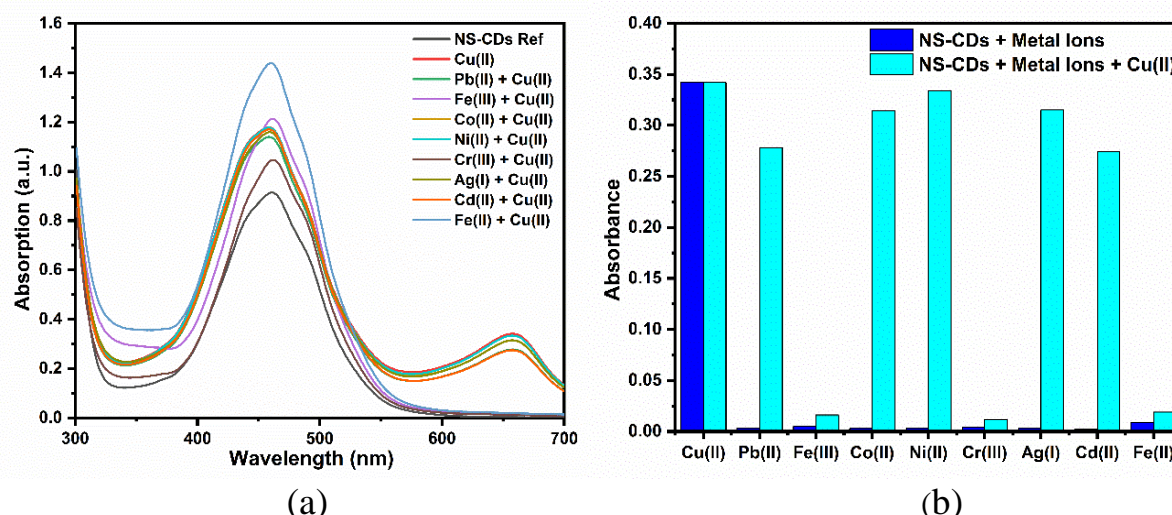


Figure 6. (a) The interference of the NS-CDs sensing solution (b) the corresponding intensity response of the Interference test of Cu(II) with respect to other heavy metals.

3.3 Comparison with Other Sensing Systems

In table 1, the linearity range and detection limit of the present method are compared to those of dye-based compounds and other nanomaterials that have investigated recently for their response to Cu(II) ions in water. Together with colorimetric methods also fluorometric detection is also reported for comparison. The present LOD ($0.3 \mu\text{M}$) is exceeded by those of some other colorimetric [30], [31], and also some fluorimetric ones [32], [33]. However, it is still well below the guideline limit suggested by the WHO (30 micromole). Moreover, the present method presents the broadest linearity range, with the exception of Si nanoparticles [34] which, however, show a much higher LOD. In fact, NS-CDs demonstrated the best trade-off between LOD and linearity range of all reported systems. In addition, in comparison with most colorimetric methods, the linear calibration curve of the present system demonstrated a zero baseline, due to the unimportant value of absorbance of the sensing solution. Finally, most of the reported methods require solutions of specific reactants that have to be prepared immediately before the sensing experiment and need quite complicated sensing algorithms. For example, for Cu(II) sensing in [31], 36 μL of a solution at 25.0 mM of TMB, 0.150 mL of the His-AuNCs stock solution,

90 microliters of 10 M solution of H₂O₂ had to be added into 2.694 mL of 200 mM pH 3.0 acetate buffer to measure the concentrations of copper ions in the 30 μ L sample. In [30] it was first required to mix 20 microliters of CdTe/CdS quantum dots (at 1 μ M), 0.02 mL of TMB (at 1500 mg/L), 160 μ L citrate buffer and =.2 ml of copper standard solution. Then the reaction had to be carried out under UV irradiation at a wavelength of 254 nm. Differently, the the NS-CDs preparations used in the present approach demonstrated long term stability (at least 6 months) and thus can be synthesized and stored for future tests. Finally, the present method just requires adding the water sample to the sensing NS-CD dispersion, without the needs for any other reactant and further procedures.

Table 1. Comparison of the performances of different methods and materials for Cu(II).

Materials	Method	Linear Range (nM)	Limit of Detection (nM)	Reference
Au Nanoclusters	Colorimetry	1 – 100	0.1	[31]
Si nanoparticles	Colorimetry	3 – 200	2000	[34]
Semicond. QDs	Colorimetry	25 – 2500	10	[30]
CDs	Fluor.	500 – 7000	150	[6]
Si nanoparticles	Fluor.	50 – 10000	30	[33]
Adenine CDs	Fluor.	1 – 750	0.3	[32]
NS-CDs	Colorimetry	1000 – 100000	300	Present work

Semicond.: Semiconductor; QDs: quantum dots.; Fluor: Fluorescence;

4. Conclusion

In summary, stable water dispersions of NS-CDs were prepared by a simple one-pot hydrothermal approach. this material showed response to copper in water by forming cuprammonium complexes with the onset of a distinct optical absorption structure at 658 nm, thus resulting in a visual colour change from orange to dark brown. This variation allowed a colorimetric measurement of absorbance at two different wavelengths that changed linearly in the relatively large range of 1–100 μ M with a LOD of 300 nM, significantly lower than that set by the WHO (30000 nM). More interestingly, at variance with most colorimetric methods, the preparation demonstrated stability for at least 6 months, while the assay experiment was simple and relatively quick, in that it is only required the mixing of the water sample to the sensing preparation. We believe that these characteristics make NS-CDs an interesting material for easy, onsite detection of copper in water.

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