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The use of $S_2O_8^{2-}$ and H_2O_2 as novel specific masking agents for highly selective "turn-on" fluorescent switching recognition of CN^- and I^- based on Hg^{2+}–graphene quantum dots

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In this study, we report that both CN^- and I^- can enhance the fluorescent intensity of Hg^{2+}–graphene quantum dots (Hg^{2+}–GQDs). However, the selectivity of the sensor was poor. Accordingly, simple specific masking agents can be directly used to solve this problem. Here, for the first time, we report the use of persulfate ion ($S_2O_8^{2-}$) as a turn-on fluorescent probe of Hg^{2+}–GQDs for selective CN^- detection, while hydrogen peroxide (H_2O_2) was selected for its sensing ability towards I^- ion detection. Interestingly, the signal was immediately measured after addition of the masking agent to Hg^{2+}–GQDs and the sample because its interaction was very fast and efficient. The method had a linear response in the concentration ranges of 0.5–8 μM (R^2 = 0.9994) and 1–12 μM (R^2 = 0.9998) with detection limits of 0.17 and 0.20 μM for CN^- and I^-, respectively. The sensor was successfully used for the dual detection of both CN^- and I^- in real water samples with satisfactory results. In conclusion, the specific masking agents in a Hg^{2+}–GQDs system appeared to be good candidates for fluorometric "turn-on" sensors for CN^- and I^- with excellent selectivity over other ions.

Introduction

Graphene quantum dots (GQDs) are single atom-thick graphene sheets with a size of less than 10 nm, similar to other graphene nanosheets.[1] They are the most commonly used optical sensing nanomaterials because of their high extinction coefficients and various alluring properties, such as high surface area, electrical conductivity, thermal conductivity and photostability, excellent chemical stability, environmental friendliness and good biocompatibility.[2,3] Moreover, their surface is versatile and can be easily immobilized with both various organic functional groups and metal nanomaterials, including glucose oxidase,[4] hyaluronic acid,[5] amino group,[6,7] carboxylic group and nitrite,[8] polyaniline,[9] gold nanoparticles,[10] platinum nanoparticles[11] and silver nanoparticles[12] through strong covalent bonding or physical adsorption. As a result, many GQDs-based fluorescent sensors have been developed to detect metal ions (*e.g.* chromium(VI),[1] mercury(II),[13] copper(II),[14] iron(III),[15]) biomolecules (*e.g.* dopamine,[16] microcystin-LR,[17] DNA,[18] doxorubicin[19] and biothiols[20]) and other analytes (*e.g.* phenol,[21] trinitrophenol[22] and uric acid[23]). However, the application of GQDs usually involves tedious processes for the dual detection of target analytes. Thus, the dual detection of GQDs sensors is needed urgently for the trace analysis of cations, anions, molecules and biomacromolecules.

The selective sensing of anions, such as fluoride (F^-), chloride (Cl^-), bromide (Br^-), iodide (I^-), acetate (AcO^-) and cyanide (CN^-) ions, is highly important because they are widely distributed and play important roles in biological, environmental and chemical industries.[24–26] In particular, iodide is an important microelement to humans, as it plays a key role in several biological activities, such as brain function, muscle tissue growth, neurological activity and thyroid function.[27] In addition, iodide helps to maintain the release of the thyroid hormone into the bloodstream. Either deficiency or excess of iodine intake would cause major health problems. For example, iodine deficiency in pregnancy will cause spontaneous abortion, fetal goitre, cretinism, anxiety and nervous agitation, intellectual impairment and neonatal hypothyroidism, while iodine excess will lead to hyperthyroidism. These disorders can be prevented by ensuring optimal iodide intake.[28,29] With regard to cyanide, it is the most threatening to the environment and human life. Various products are very high in cyanide due to their industrial uses, including the production of paper, textiles, plastics and nitriles, metals, electroplating and the extraction of gold and silver. In addition, cyanide is also released from biological processes of bacteria, fungi.[30] Due to

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