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A fluorescence switching sensor based on graphene quantum dots decorated with Hg^{2+} and hydrolyzed thioacetamide for highly Ag^{+}-sensitive and selective detection

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A selective fluorescent sensor based on graphene quantum dots (GQDs) was developed for the determination of silver ions (Ag^{+}). The GQDs were prepared by the citric acid pyrolysis method. In the presence of mercury ions (Hg^{2+}), the fluorescence intensity of the GQDs decreased linearly and it was fully recovered by the hydrolysis of thioacetamide (TAA), giving hydrogen sulfide in the reaction system. This research study was aimed at using the fluorescence turn-off sensor for the selective determination of Ag^{+}. Upon the addition of Ag^{+}, the fluorescence intensity of the generated sulfide-(Hg^{2+} quenched GQDs) decreased as a linear function of the Ag^{+} concentration. Then, the acquired GQDs showed steady, selective, and highly sensitive detection of Ag^{+}. The experimental parameters affecting the fluorescence turn-on/off sensor were investigated and optimized. The optimum conditions included 4 μM Hg^{2+} concentration, 70 μM TAA concentration, solution pH of 7 and a 5 min reaction time. Under the optimized conditions, the working linear concentration range, limit of detection and limit of quantification for Ag^{+} were 0.5–10.0, 0.18 and 0.60 μM, respectively. The proposed method was successfully applied for the selective determination of trace amounts of Ag^{+} in five real water samples with satisfying levels of recovery (89.31–114.08%).

Introduction

Silver ions (Ag^{+}) are included in the list of heavy metal ions, and their potential toxicity for the environment and human body has drawn people's attention. Owing to their broad employment in many industries, such as electronics, photography, mirrors, and pharmacy, a large amount of silver is released into the environment annually from industrial waste and emissions, especially into sludge waste and even surface waters.[1,2] It has also been found that silver is toxic to humans at concentrations as high as 0.9 μM in drinking water.[3] Considering these facts, applying a simple, rapid and accurate method to monitor silver ions at trace levels in various samples is of great importance. Various techniques have been used for the determination of silver in real samples, such as the spectrophotometric method,[4] graphite furnace atomic absorption spectroscopy (GFAAS),[5] high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS),[6] inductively coupled plasma optical emission spectrometry (ICP-OES),[7] differential pulse anodic stripping voltammetry (DPASV),[8] and spectrofluorimetry.[9,10] Although these techniques are highly sensitive and selective, they require tedious sample preparation and preconcentration procedures, expensive instruments, and professional personnel.

Recently, nanomaterials have been used to build sensitive analytical sensors for the analysis of various inorganic and organic substances including trace amounts of hazardous substances in the environment. Such sensors possess certain advantages, *e.g.* high sensitivity, short analysis time, low cost, and simple preparation and treatment.[11] Graphene quantum dots (GQDs) have generated enormous excitement because of their superiority in a variety of advantageous properties. They were discovered very recently as a class of zero-dimensional graphitic nanomaterials with lateral dimensions less than 100 nm, and they have either a single layer, double layers, or a few layers (3 to <10).[12,13] Compared with organic dyes and semiconductive quantum dots (QDs), GQDs are superior in terms of their excellent properties, such as their high photostability against photobleaching and blinking, biocompatibility and low toxicity.[15] Moreover, similar to graphene, GQDs have

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