Novel copper sulfide doped titania nanoparticles as a robust fiber coating for solid-phase microextraction for determination of polycyclic aromatic hydrocarbons

Mingguang Ma, Yunxia Wei*, Fang Liu

College of Chemistry and Chemical Engineering, Lanzhou City University, Lanzhou 730070, China

Abstract

Immobilized TiO_2 nanoparticles modified by nano scaled CuS (CuS@TiO_2NPs) were successfully synthesized and served as the fiber of solid-phase microextraction (SPME) for the determination of some polycyclic aromatic hydrocarbon (PAHs) in water samples. A novel fiber has been developed by postprecipitation of CuS coated the titania nanoparticles in situ grown on the titanium wire annealed at 550 ^{o}C in a nitrogen ambient atmosphere. Its morphology and surface properties were characterized by scanning electron microscopy and energy dispersive X-ray spectrometry. It was connected into high performance liquid chromatography-ultraviolet detector (HPLC-UV) equipment by replacing the sample loop of six-port injection valve, building the online SPME-HPLC-UV system. Variables affecting extraction procedures, including desorption time, stirring speed, extraction temperature, extraction time and ionic strength were investigated and the parameters were optimized. The SPME fiber exhibits

* Corresponding author at: College of Chemistry and Chemical Engineering, Lanzhou City University, Lanzhou 730070, China.
E-mail address: weiyx07@lzu.edu.cn.

high selectivity for the five PAHs studied. The linear ranges varied between 0.15 μg·L^{-1} and 200 μg·L^{-1} with correlation coefficients ranging from 0.9913 to 0.9985. LODs and LOQs ranged from 0.02-0.04 μg·L^{-1} and 0.07-0.13 μg·L^{-1}. RSDs for one fiber and fiber-to-fiber were in the range of 3.2%-4.3% and 4.6%-6.8%, respectively. Additionally, the fiber possessed advantages such as resistance to organic solvent, high mechanical strength and uneasy breakage, making it have strong potential applications in the selective extraction of PAHs from complex water samples at trace levels.

Keywords: TiO_2 nanoparticles; CuS; Annealed; Solid-phase microextraction; Polycyclic aromatic hydrocarbon

3.8 Analytical performance of the CuS@TiO_2NPs/Ti fiber in the extraction of PAHs

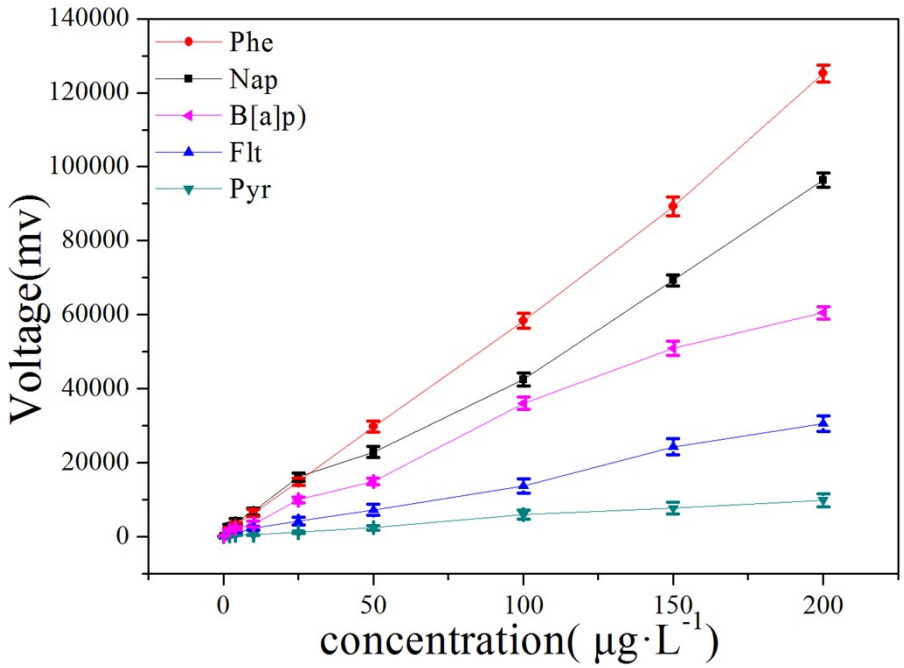

Fig. S1. The concentration of PAHs and standard curve of absorption peak area

The analytical performance of the developed method was investigated under the

optimized conditions by extracting a series of standard working solutions. Each experiment was repeated five times. The parameter of linearity was obtained from linear fitting of graphing software such as Origin.

3.10 Stability and durability

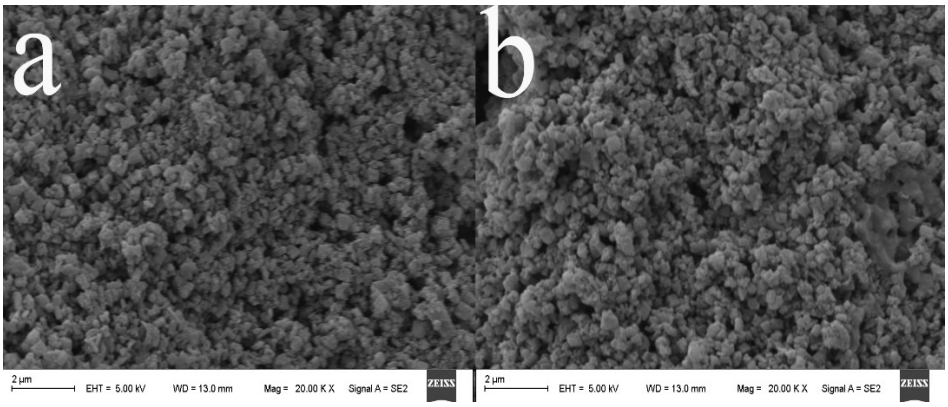

Fig. S2. SEM images of CuS@TiO_2NPs coating before (a) and after immersion in acid and alkali (b)

In order to examine its acid and alkali resistance, the fabricated fiber was allowed to be soaked in the solutions of 0.01 mol·L^{-1} H_2SO_4 and 0.1 mol·L^{-1} NaOH for 12h. Negligible morphological changes were observed from its SEM image, indicating that the composite coating was firmly immobilized onto the Ti substrate.