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Carbon nanostructures as catalytic support for chemiluminescence of sulfur compounds in a molecular emission cavity analysis system

Afsaneh Safavi[a,b,*], Norouz Maleki[a,b], Mohammad Mahdi Doroodmand[a,b],
Mohammad Mehdi Koleini[a]

[a] Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran
[b] Nanotechnology Research Institute, Shiraz University, Shiraz, Iran

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ABSTRACT

The effect of different substrates including stainless steel, activated carbon, single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), fullerenes (C_{60}, C_{70}, etc.) and SWCNTs doped with iron and palladium nanoparticles were compared for catalytic chemiluminescence reaction of sulfur compounds in a flame-containing cavity of molecular emission cavity analysis (MECA) system. Different forms of CNT substrates were fabricated using electric arc-discharge method. The blue emission of excited S_2 was monitored using a CCD camera. The results demonstrate that, due to the high surface area, plenty of basal planes, high thermal conductivity, and high flexibility of the carbon nanostructure as appropriate support, carbon nanostructures play an important role in catalytic chemiluminescence emission of sulfur compounds in MECA. Moreover, the presence of metallic nanoparticles doped on carbon nanostructures enhances their catalytic effect. The results revealed that under similar conditions, SWCNTs/Pd doped nanoparticles, SWCNTs/Fe doped nanoparticles, SWCNTs, MWCNTs and fullerenes have the most catalytic effects on chemiluminescence of sulfur compounds, respectively.

1. Introduction

Catalysts have important roles in increasing the rate and controlling the selectivity of the chemical reactions involved. Today, much research is conducted in order to enhance the catalytic activity and selectivity and reduce the cost of catalyst preparation. Catalysts play an important role in the processing of several vital compounds in numerous fields such as fuel, pollutant abatement and chemical processes such as chemiluminescence. Catalytic processes account for more than 90% of the chemical manufacturing processes in use throughout the world [1–3]. In parallel with the development of new active phase formulations, intensive research has also been conducted both in academic and industrial groups in order to develop new catalyst supports which can modify the catalytic activity and selectivity of the existing active phases [2–5].

Carbon materials have been used for long time in heterogeneous catalysis, because they can act as direct catalysts or, more important, they can satisfy most of the desirable properties required for a suitable support [2,3,6–8]. Consecutive to the discovery of carbon nanotubes (CNTs), the carbon nanostructures such as CNTs, CNFs and fullerenes have received increasing interest during the last decade owing to their exceptional physical and chemical properties [9,10]. Theoretical calculations and experiments have predicted a large domain of applications for these nanostructures going from nanoelectronic components to biological applications [2,3,11]. Amongst these, catalysis seems to be the most direct and promising field according to the results published during recent years [12,13].

Carbon nanostructures generally exhibit catalytic performance higher than those encountered with traditional catalysts whatever the reaction is considered, i.e. gas phase or liquid phase. It is through that tailoring nanostructured catalyst such as CNTs, CNFs and fullerenes with a peculiar morphology, i.e. high length-to-diameter ratio (aspect ratio), tubular structure in the case of CNTs with possible confinement effect, high external surfaces and absence of 2D porosity, could lead to new electronic interactions. This results to the higher accessibility of the reactants to the deposited active phase. This phenomenon consequently, improves the catalytic properties of the carbon nanostructure-based catalysts when compared to those usually obtained up to now with traditional catalysts [2,3].

MECA is a spectroscopic technique in which a cool hydrogen flame is used to excite the analyte [14–19]. MECA process determines the elements (e.g. sulfur and nitrogen) having their atomic resonance lines in the vacuum ultraviolet (UV) region of the

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* Corresponding author at: Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran. Tel.: +98 711 6137351; fax: +98 711 2286008.
E-mail address: safavi@chem.susc.ac.ir (A. Safavi).

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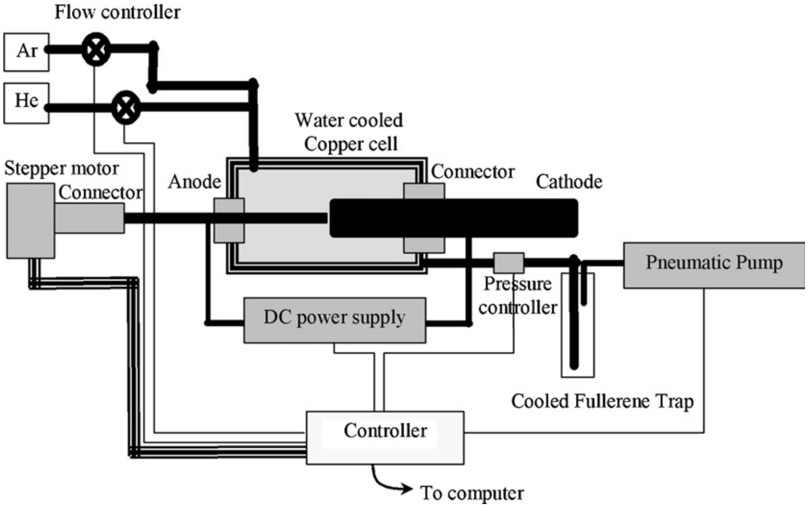

Fig. 1. Schematic diagram of electric arc-discharge system.

spectrum, by the formation of molecules which emit in the visible and UV region [20]. In this method the sample is introduced to a cool hydrogen flame via using a cavity. Various designs of cavity have been used for different types of samples [21–23]. A simple system of a MECA–VAP (MECA using a vapor generating system) has been used for the chemiluminescence emission of sulfur compounds. Here, the sulfurous dioxide evolved upon acidification of the sulfurous sample within the generation system, is combusted in hydrogen flame to give excited sulfur dimer, which returns to the ground state with the emission of light. The radiation occurs in the blue region with a peak at 384 nm. Its intensity is proportional to the concentration of excited sulfur dimer [24].

Although there are numerous MECA–VAP procedures for detection and determination of sulfurous species, the systematic studies on the catalysts in the S_2 molecular emissions within hydrogen flames are rare. It has been found that the materials used for cavities are also effective in obtaining emission within the cavity. Cavities are usually constructed using materials such as stainless steel, quartz, silica, carbon, etc. Depending on the influence of temperature and pressure applied to the cavity body; it has been found that, the carbon cavities give higher emission intensity than stainless steel [25]. The surface of the cavity has also an important effect on the response of the S_2 emission [26]. This effect has been attributed to the roughness of the surface [26]. It has been reported that, the roughness of the surface results in aggregation of the excited S_2 products and also enhances good dispersion and volatility of the sulfurous samples and suppresses peak splitting [26]. Therefore, the lined cavities with high specific surface are considered as suitable support for molecular emission. In the hydrogen flames, as hydrogen radicals play an important role in the mechanism of the formation of excited species such as S_2, it is expected that, carbon nanostructures with high surface area, high thermal conductivity, and high flexibility of the carbon nanostructure, could act as suitable catalytic supports for the molecular emission of sulfurous compounds.

In this paper, the effect of different substrates including stainless steel, and carbon nanostructures are compared for the catalytic chemiluminescence reaction of sulfur compounds in a flame-containing cavity of MECA.

2. Reagents and solutions

A stock solution of 100 $\mu g\,mL^{-1}$ sulfite was prepared by dissolving 0.0197 g of anhydrous Na_2SO_3, 0.0184 g of the sodium salt of EDTA (ethylene diamine tetra acetic acid), and 0.02 g of NaOH in a 50 mL volumetric flask and diluting to the mark with triply distilled water. Standard solutions were prepared daily by successive dilution of the stock solution.

MWCNTs and fullerenes were synthesized by a home-made arc-discharge system using highly pure graphite rods. SWCNTs were also synthesized by electric arc-discharge method using ferrocene (Merck, Darmstadt, Germany) and palladium acetate (Merck, Darmstadt, Germany) as source of metal nanocatalysts.

Solutions of 1.0, 2.0, 3.0 and 4.0 M of different acids were prepared by dilution of concentrated H_3PO_4 (35%, Merck), HCl (37%, Merck), HNO_3 (64%, Merck) and pure HIO_4 (Merck, Darmstadt, Germany).

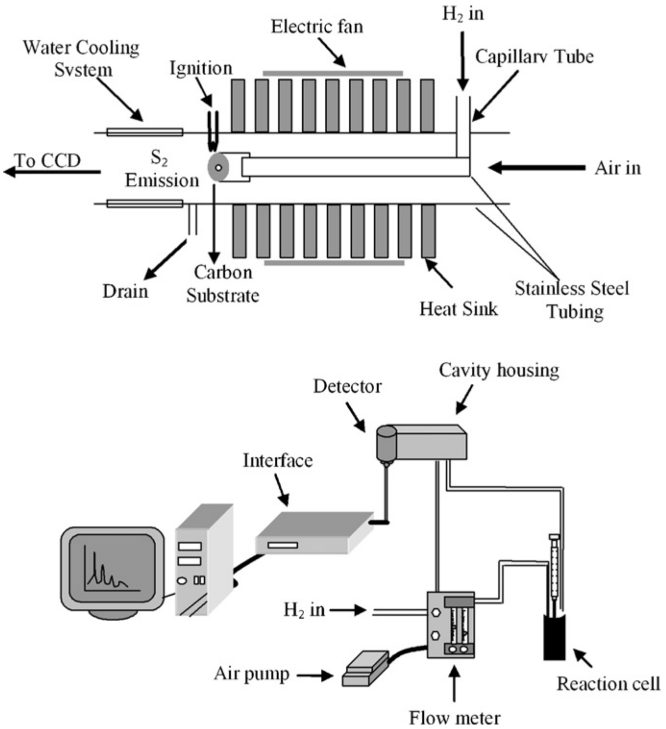

Fig. 2. Schematic of the stainless steel cavity, and the assembly for MECA-VAP.