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Room-temperature synthesis and characterization of carbon-encapsulated molybdenum nanoparticles

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ABSTRACT

Carbon-encapsulated molybdenum nanoparticles were synthesized by laser-assisted photolysis of gaseous precursors. In the proposed method, gas mixtures containing various hydrocarbons and molybdenum hexacarbonyl vapor diluted in argon were irradiated with a nanosecond pulsed UV laser at room temperature. Particle samples were analyzed by transmission electron microscopy (TEM), electron microdiffraction (EMD), energy-dispersive X-ray spectroscopy (EDS), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) techniques to observe the morphology and composition of the Mo/C nanoparticles. The influence of the type of hydrocarbon, its mole fraction, and the number of UV laser pulses on the resulting nanoparticles was investigated. The nanoparticles were heavily aggregated and consisted of Mo-based cores surrounded by carbon. The type of hydrocarbon did not have any visible effects on the nanoparticle structure and the size of the Mo-based cores or aggregates. Increasing the hydrocarbon mole fraction in the precursor mixture led to an increase in the carbon content and decrease of the Mo-based core size. Increasing the number of UV laser pulses led to larger Mo cores.

1. Introduction

Molybdenum-based nanomaterials have gained much attention recently because of their unique optical, electronic, catalytic, and mechanical properties. Molybdenum nanowires have been shown to be suitable for the inner interconnects of nanoelectronic devices due to their high current density [1]. Devices based on molybdenum oxide nanoparticles are recommended for use in electrochromic and photochromic displays, electrochromic mirrors, and gas sensors [2–4]. Molybdenum nanoparticle powder is used as an additive in different alloys to improve the friction and wear characteristics [5,6].

Molybdenum nanoparticles can be used as effective catalysts in various chemical processes to intensify reactions or reduce energy consumption. The presence of Mo nanopowder in catalysts has been reported to be very important for fabricating nanotubes. For example, molybdenum particles were used as catalysts for single-walled carbon nanotube growth [7–9]. Mo-based nanocatalyst was also successfully used in the synthesis of multi-walled carbon nanotubes [10]. Another promising application of molybdenum nano-materials as catalysts is sunlight-driven water splitting to convert and store solar energy. However, it requires active catalysts for the hydrogen evolution reaction (HER) [11,12]. Molybdenum-based nanoparticles also exhibit high HER activity [13–15].

Recently, molybdenum-based nanomaterials have been intensively investigated in regard to their human health impact. For example, potential anti-cytotoxicity effects have been reported for molybdenum nanoparticles in human breast and fibrosarcoma cells compromised with oxidant exposure [16]. However, several studies show that Mo nanoparticles can have negative effects on living cells [17,18]. Therefore, the influence of Mo particles on human health is currently ambiguous. However, it is evident that the high surface reactivity of pure metal nanoparticles such as Mo make them potentially toxic.

The aggregation and oxidation of Mo nanoparticles may aggravate their catalytic performance, which depends on the morphology, structure, and conductivity of the catalyst [19]. Most of the techniques used to synthesize Mo nanoparticles do not prevent nanoparticle aggregation and oxidation. However, synthesis in liquids can produce pure Mo nanoparticles and supress aggregation [20]. Nevertheless, such methods require the use of special materials and conditions. Therefore, there is a need to develop other techniques to prevent the aggregation and oxidation of Mo nanoparticles.

A common solution is to cover Mo nanoparticles with a carbon shell or to embed them in a carbon matrix. This makes the Mo nanoparticles resistant to oxidation and aggregation, resulting in more exposed active sites and hence improvement of the overall catalytic activity [19]. Additionally, carbon encapsulated MoO_2 nanoparticles were applied as

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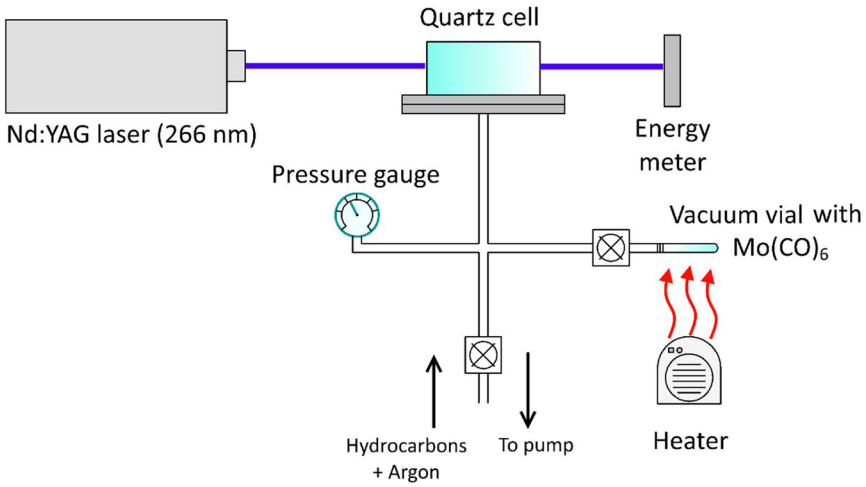

Fig. 1. Schematic of the experimental setup used for the synthesis of carbon-encapsulated molybdenum nanoparticles.

an electrode in lithium ion batteries and showed significantly improved electrochemical performance [21,22]. Furthermore, carbon is non-toxic and allows nanoparticles to be introduced to biological systems, such as human cells.

There are a number of different techniques to synthesize metal nanoparticles embedded in carbon material. A primary method is the Huffman–Krätschmer carbon arc process with metal-carbon composite anodes. Scott and Majetich were among the first to apply the arc plasma method for binary metal-carbon particle synthesis [23]. Carbon-encapsulated iron nanoparticles were synthesized by the simultaneous decomposition of iron powder and different carbon precursors by a plasma jet [24,25]. However, arc plasma methods involve complicated equipment and require high amounts of energy consumption.

Another method for the synthesis of metal-carbon nanoparticles is pyrolysis of both carbonaceous and Me-containing species in a thermal reactor. Mo_2C nanoparticles embedded in graphitized carbon matrixes were synthesized by calcination in a tube furnace under Ar/H_2 atmosphere at 850-950 °C [19]. Ammonium molybdate ($(NH_4)_6Mo_7O_4{\cdot}4H_2O$) and glucose were used to produce Mo_2C nanoparticles, and corn stalks were used as a carbon matrix source. The porous graphitized carbon matrices supported Mo_2C nanoparticles and prevented aggregation. Moreover, the graphitized carbon efficiently enhanced the conductivity of the composite. The composite showed excellent properties for HER in acidic and basic media.

Li et al. [26] obtained molybdenum-core/graphite-shell nanoparticles by combining hydrothermal carbonization at 900 °C and temperature-programmed reduction. Ammonium molybdate and methane were used as Mo and C sources. The composite demonstrated good catalytic performance on highly selective conversion of guaiacol to phenolic compounds in methanol. The high temperature processes used in these studies resulted in the synthesis of nanoparticles that were mostly composed of molybdenum carbide Mo_2C. Nanocrystalline molybdenum carbide (Mo_2C) smaller than 10 nm were also synthesized by a solution route [27]. Bokhonov et al. reported a method of high-energy ball milling amorphous carbon and molybdenum mixtures followed by thermal annealing at 860 °C [28]. This resulted in the formation of nano-sized Mo_2C particles encapsulated in 5 to 20-nm thick carbon shells. The size of the encapsulated particles varied from 10 nm to several hundred nanometers.

Another group of synthesis methods involves the decomposition of gas-phase precursors followed by solid nanoparticle condensation, which is called chemical vapor synthesis (CSV). One of the CSV methods for binary metal-carbon nanoparticle formation involves the thermo-decomposition of metal carbonyls in the presence of hydrocarbons. Iron-carbon nanoparticles were synthesized behind the shock waves of a gaseous mixture of $Fe(CO)_5$ + C_3O_2 diluted in argon [29]. The idea was to condense atomic metal vapor, followed by thermal decomposition of $Fe(CO)_5$ behind incident shock waves at temperatures of 600-1000 K. Heterogeneous condensation was then used to apply carbon to the metal cores after hydrocarbon decomposition behind reflected shock waves at temperatures 1800–2400 K.

Another CVS method for metal-carbon nanoparticles is the UV photo-dissociation of gaseous precursors [30]. This technique does not require any complex equipment excepting a radiation source. Another advantage of this method is that it can be implemented at room temperature. Carbon-encapsulated iron nanoparticles were obtained by irradiating various gaseous precursors with a UV pulse laser [31–35]. The results of these studies showed the possibility of catalytic decomposition of gaseous carbon-bearing species on the surfaces of iron nanoparticles and subsequent carbon shell formation at room temperature. Pure Mo nanoparticles have been synthesized by laser UV photo-dissociation of $Mo(CO)_6$ without addition of carbon compounds [36,37]. Besides the laser irradiation, a convenient high-pressure Xe lamp could be used for nanoparticle formation. For example Emelianov et al. used a 150-W Xe lamp [38].

The goal of this study is to use the gas-phase UV photo-dissociation technique to synthesize carbon-encapsulated molybdenum nanoparticles from gaseous molybdenum hexacarbonyl ($Mo(CO)_6$) in a mixture with various hydrocarbons at room temperature. The secondary goal is to investigate the influence of several parameters, such as the type of hydrocarbon (CH_4, C_7H_8, C_4H_9OH, C_6H_6, C_2H_2), the hydrocarbon mole fraction, and the number of laser pulses (from 1 to 30) on the size and structure of the Mo/C nanoparticles.

2. Experiment procedure

Carbon-encapsulated molybdenum nanoparticles were prepared by laser-assisted photolysis of gas-phase precursors in a 1-cm^3 quartz reactor. A schematic of the experimental setup is presented in Fig. 1. Molybdenum hexacarbonyl (≥98%, Sigma-Aldrich) was used as a source of Mo atoms to form Mo nanoparticles, and several hydrocarbons were applied as carbon sources. Mixtures of hydrocarbons diluted in argon were manometrically prepared in a stainless-steel tank. The following hydrocarbons were used: CH_4 (≥99.9%), C_2H_2 (≥99.5%) (Linde Gas Rus), C_7H_8 (≥99.9%), C_4H_9OH (≥99.9%), and C_6H_6 (≥99.9%) (Component-Reaktiv). In the case of liquid hydrocarbons such as toluene (C_7H_8), benzene (C_6H_6), and 1-butanol (C_4H_9OH), the saturated vapors of these components were used.

The mixtures and experimental conditions investigated are presented in Table 1. Before each experiment, a quartz cell and vacuum vial were evacuated using a vacuum pump. The mixtures of hydrocarbon and argon at 1 bar were used to fill the pre-evacuated vial,