

Thermal and plasma synthesis of metal oxide nanoparticles from MOFs with SERS characterization



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ARTICLE INFO

Article history:

Received 22 December 2015

Received in revised form 11 March 2016

Accepted 16 March 2016

Available online 17 March 2016

Keywords:

Aluminum oxide

Chromium oxide

PXRD

SERS

DFT

ABSTRACT

Aluminum oxide (Al_2O_3) and chromium oxide (Cr_2O_3) nanoparticles were synthesized by thermolysis of metal-organic frameworks (MOFs). Further O_2 plasma treatment is required to obtain high crystalline quality metal oxides. The composition and morphology of metal oxide nanoparticles were confirmed by powder X-ray diffraction and scanning electron microscopy characterization, respectively. The quality of synthesized metal oxides was also examined by observing the surface-enhanced Raman scattering (SERS) spectra of methyl orange adsorbed on Al_2O_3 and Cr_2O_3 . The observed SERS effect can be ascribed to charge-transfer (CT) resonance effect between methyl orange and metal oxide surfaces. UV–vis absorption spectra and DFT calculations of metal oxide–methyl orange complexes have confirmed that the observed SRS effect is due to CT resonance between the metal oxide nanoparticles and the adsorbed methyl orange molecules.

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1. Introduction

Plasmonic materials have attracted the attention of scientists and engineers for widespread applications in areas such as biomedicine, catalysis, electronics, and sensors [1–7]. Recent advances in nanomaterials synthesis have achieved new ways of controlling various properties of plasmonic materials. The development in nanotechnology and nanofabrication critically relies on the understanding of fundamental properties of materials.

Metal organic frameworks (MOFs) is a type of porous hybrid organic–inorganic crystalline materials providing versatile structures with adjustable chemical and physical properties suitable for many applications such as catalysis, energy, and sensing [8–11]. The study of the pyrolysis or thermolysis of MOFs prompts alternative synthetic routes to metal oxide nanoparticles (MONPs) [12] and porous nanocarbons [13]. Most of these research works have focused on the synthesis of porous carbon by sacrificing the metal oxide component. Residues and impurities are often found to be remained in the products. Traditionally, to obtain high purity MONPs from MOFs, multistep chemical oxidation/reduction [14]

and pyrolysis/thermolysis [15] procedures are required. Recently, Das et al. reported a generalized thermolysis approach for the synthesis of highly crystalline MONPs from MOFs. However, metal and MONPs are still dispersed in the porous carbon matrix.

Non-equilibrium oxygen plasma has been demonstrated to be a robust technique for the synthesis of nanomaterials [16–21]. By properly controlling plasma reactor parameters, such as flow rate, pressure, temperature, and discharge power, various products can be formed. Synthesis involving reactive oxygen plasma-based process usually can be classified into two categories. The first type is the direct participation of oxygen in the structure of the products, i.e. oxides. The second type is the removal of unwanted components to form new species. In this work, our oxygen plasma belongs to both types. The thermolysis of MOFs coupled with O_2 plasma treatment was used to produce MONPs. The carbon residue due to thermolysis can be removed by O_2 plasma treatment.

Typical substrate materials used for surface-enhanced Raman scattering (SERS) studies are noble metals such as Ag and Au. The energy levels of d–d transitions in these metals exhibit localized surface plasmon resonance (LSPR) around the visible spectral range [22]. Under the excitation of laser radiation, electrons on the metal surface are excited to a collective oscillation against the metal cores, i.e., surface plasmon resonance (SPR). It is associated with the electromagnetic mechanism (EM). Another SERS mechanism, called chemical enhancement (CE), is due to charge-transfer (CT) resonance or coupling between adsorbates and substrates

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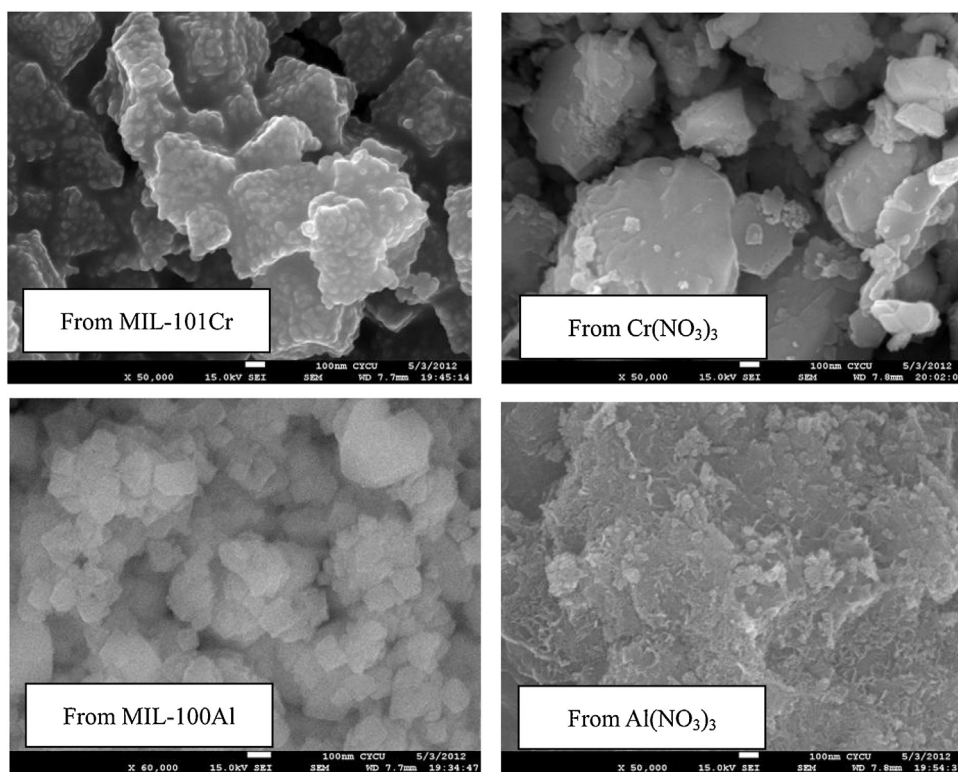


Fig. 1. SEM photos of MONPs synthesized from MOFs and nitrate salts (scale bar: 100 nm). Experimental conditions: MIL-101 (Cr): He/O₂ plasma = 1 Torr, 500 °C; Cr(NO₃)₃: He flow = 1 Torr, 700 °C; MIL-100 (Al): He/O₂ plasma = 1 Torr, 750 °C; Al(NO₃)₃: He flow = 1 Torr, 900 °C.

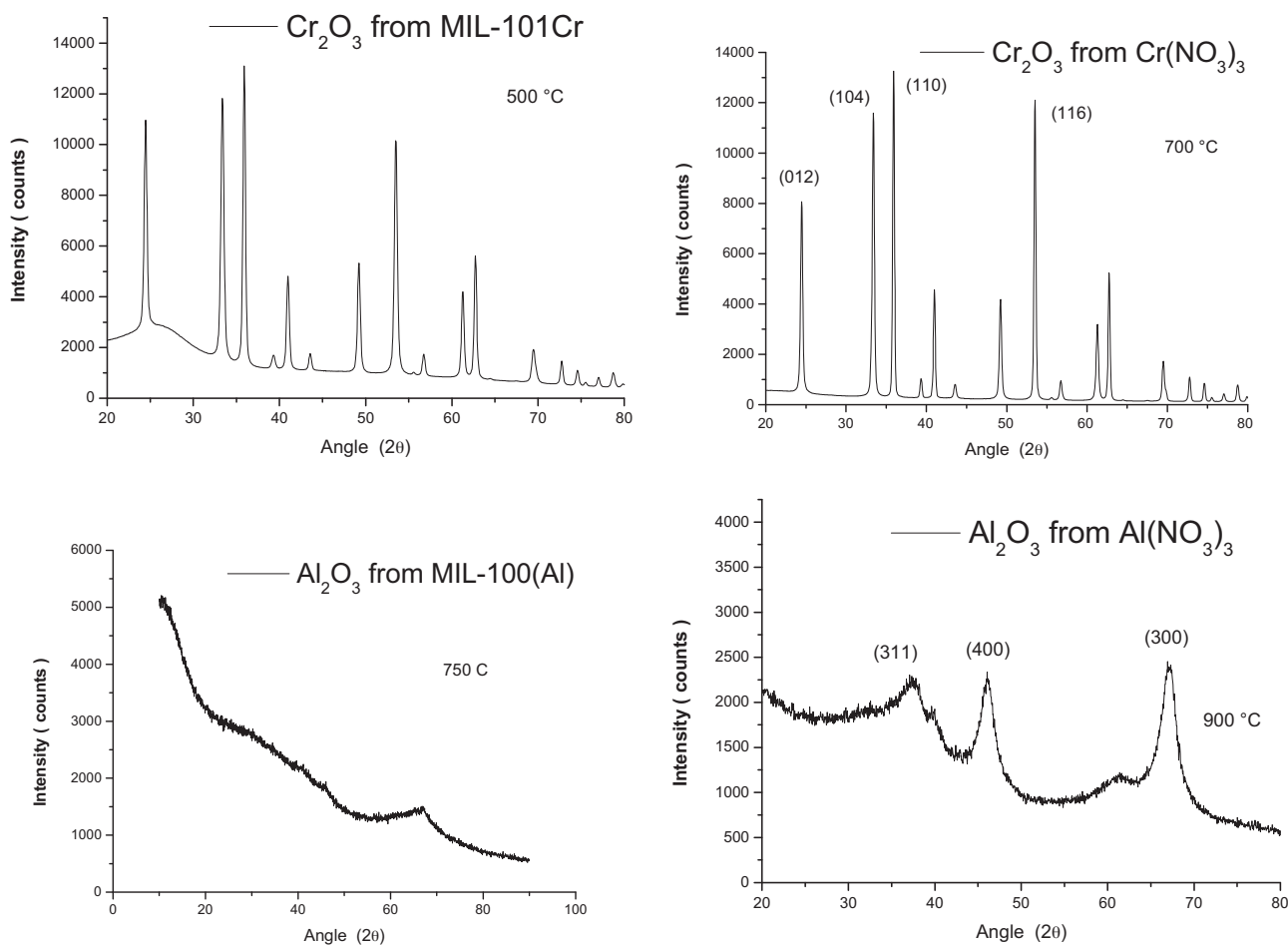


Fig. 2. Comparison of PXRD patterns of MONPs synthesized from MOFs and nitrate salts with calcination temperature below 900 °C.

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