学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Synthesis of mono-, bi-, and tri-metallic alloy nanoparticles by co-sputtering onto liquid substrate
(液体基板への同時スパッタによるモノ、バイ、およびトリメタリック合金ナノ粒子の合成)

Sputtering method is a widely used physical method to synthesize thin films and small nanoparticles (NPs) on solid or liquid substrates. Compared to traditional chemical reduction method for fabricating NPs, sputtering can synthesize NPs under room temperature. And this method does not use toxic reductants or produce by-products. Thus, it is a environmentally friendly fabricating approach. Synthesizing alloy NPs by co-sputtering onto liquids enables long time sputtering, breaks the limitations of miscibility gap in bulk phase diagram and makes the obtained NPs controllable by adjusting the sputtering parameters. The particle sizes and compositions can be controlled by adjusting the sputtering currents, sputtering times and so on. As a result, the alloy NPs can be used in various applications. Sputtered Pt NPs can be applied as catalysts in oxygen reduction reaction (ORR). Nevertheless, the high cost and sluggish kinetics of Pt impede the industrial application of Pt catalysts. Alloying Pt with other metals can not only cut the cost but also enhance the catalytic activity of the catalysts. Therefore, using sputtering method to prepare Pt-based alloy NPs is expected to optimize the compositions and maximize the catalytic activity of the catalysts. Furthermore, sputtering can also be used to prepare fluorescence NPs. Fluorescence Au alloy NPs synthesized by co-sputtering can pave the way for the study of diverse applications.

Chepter one is general introduction.

Chapter two firstly synthesized Pt/Ag solid solution alloy NPs smaller than 3 nm with composition in miscibility gap by co-sputtering onto liquid PEG. The sputtering currents did not affect particle sizes but have obvious impact on compositions and composition distributions of the alloy NPs. The sizes of NPs sputtered onto PEG were smaller than that on glass while the composition distributions of the NPs in PEG were broader than that on glass. This reveals that PEG hindered the combination of NPs and clusters, resulting in small particle sizes even for long time sputtering and broader composition distributions. Thus, the samples obtained in PEG have the compositions mainly determined by the random atom combination in the vacuum chamber and possibly in initial landing of atom/clusters on the PEG surface.

Chapter three reports about the synthesis of trimetallic CuPt/Ag alloy NPs prepared by co-sputtering onto PEG using a CuPt alloy target and an Ag target. The fine structure analysis reveals that the obtained NPs are trimetallic solid solution alloy. Ag compositions increased with the increase of sputtering currents applied to Ag target while keeping the sputtering currents applied to CuPt target constant. Moreover, it was found that the Cu:Pt atomic ratios of single NPs measured by energy dispersive spectroscopy (EDS) coupled with scanning transmission electron microscope (STEM) were lower than the average value of the sputtered NPs dispersed in PEG. This suggests that NPs which are big enough to be checked by STEM-EDS are mainly Pt-rich NPs. The Cu, Ag, and Pt compositions of trimetallic NPs varied in a wide range, indicating random alloy formation. The sputtered trimetallic CuPt/Ag NPs were studied as catalysts in oxygen reduction reaction (ORR), and the catalytic performance is compared with sputtered bimetallic alloy Cu/Pt and Ag/Pt NPs and monometallic Pt NPs. Trimetallic CuPt/Ag NPs showed higher ORR catalytic activities than bimetallic alloy Cu/Pt NPs owing to their better stability and dispersibility on carbon support. However, the trimetallic alloy NPs performed worse than bimetallic Ag/Pt NPs and Pt NPs. This is caused by Cu oxidation and dissolution of Pt and Cu. Comparable ORR catalytic performance of Ag/Pt NPs (40 atom% Ag) with Pt NPs is thought to come from the synergy between Pt and Ag in bimetallic alloy.

Chapter Four focus on the synthesis of fluorescence Au alloy NPs synthesized by co-sputtering onto PEG with MUA dispersed. The particle sizes and optical properties of the obtained bimetallic alloy NPs were checked and compared with the monometallic fluorescence NPs. For the alloy NPs composed of the same metals, the relationship between particle size and sputtering current applied to metal targets were investigated. And fluorescence wavelengths of the alloy NPs were also compared with their monometallic counterparts. It was found that the NPs with bigger sizes show longer fluorescence wavelength, however, for the alloy NPs with the same particle sizes, the sputtering currents didn’t show obvious impact on fluorescence peak position.

Chapter Five summarizes about the research findings and conclusions of the thesis.