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Synthesis of mono-, bi-, and tri-metallic alloy nanoparticles by co-sputtering onto liquid substrate

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1 General Introduction

Vacuum sputtering is a common fabricating method for synthesizing thin films on solid substrates. The energetic gas ions formed from Ar, O_2, N_2 or H_2 hit the metal targets, to make metal atoms/clusters ejected from the targets.[1-4] The ejected atoms or clusters finally deposit onto the substrate which has been placed in the vacuum sputtering chamber and the gas ions are generated by applying current or voltage to the sputtering chamber. During recent decades, sputtering has developed rapidly for some industrial applications, such as surface coating, functional films and so on.[1,4,5] It's also a traditional way of creating multilayer of metals, metal alloys, and metal oxides.[5-11] Therefore, the sputtering method has attracted much attention around the world due to its wide applications.

Except for the synthesis of thin films on solid substrates, the sputtering technique can also use liquids as substrates.[12] Traditionally, NPs were obtained by chemical methods, which was usually to be colloidal synthesis (CS).[2] This method is based on reactions in solution between reactants, so reaction conditions and stabilizing agents are used to control the size and shape of NPs.[13] In terms of managing NP size and permitting a range of applications, chemical synthesis is quite adaptable, which is one of the advantages of chemical methods. However, it generally produces toxic byproducts and low-purity NPs. Unlike chemical methods, sputtering, as a physical method, is a clean methodology to synthesize NPs with high purity. In this case, sputtering onto liquid substrates may offer an optimized method to control the sizes, shapes and purities of NPs.[14,15] And it allows for long time sputtering. As the development of sputtering technique over a liquid substrate, the choice of liquid also became diverse. Ionic liquids (ILs), silicon oil, vegetable oils and polymer liquids attracted much attention.[2,16-19]

Since after the development of sputtering onto liquid substrates in aspect of the synthesis of metal NPs, the synthesis of alloy NPs by sputtering had also begun to enter researchers' attention. 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 (such as the sputtering current and so on). 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.

2 Experimental Section

2.1 Preparation of Pt NPs and Pt-based alloy NPs

Before sputtering, PEG was stirred under vacuum at 650 rpm in a flask in an oil bath for 2 h to remove water and gases; the temperature of the oil bath was set at 90 °C. After that 10 mL of PEG was added into a petri dish with a diameter of 60 mm. The petri dish was then placed horizontally in the center of the sputtering vacuum chamber. A stirrer was put in the petri dish under the surface of PEG. To synthesize alloy NPs, the metal targets were co-sputtered. The elemental ratios of alloy NPs were controlled by adjusting the sputtering currents applied to the metal targets. When a glass slide was used as the substrate, it was placed in the center of the petri dish. The center of the petri dish was located at a distance of 110 mm from the two metal targets. PEG was stirred at 80 rpm. No stirring was carried out if glass slides were used. After several times of vacuum and purging with inert Ar to remove O_2, the pressure of the vacuum chamber was kept at 2 Pa. Cooling ethanol of 4 °C was used for cooling the metal targets during sputtering. Before collecting the NPs, the metal targets were sputtered for 10 min to clean the surfaces. During cleaning, removable shutters were located in front of the metal targets and above the petri dish to prevent contamination from falling onto the PEG. The sputtering time was 30 min for collecting NPs in PEG. The sputtering system was equipped with a thermocouple and a temperature-controlled system to keep the substrate temperature at 30 °C.

2.2 Characterization

UV-Vis spectra were collected immediately after sputtering deposition using a JASCO V-630 spectrophotometer and a quartz cuvette with an optical path of 1 mm. The baseline was collected using an empty quartz cuvette. The size and shape of the NPs were analyzed using TEM (JEOL JEM-2000FX, 200 kV) and scanning TEM (STEM, JEOL JEM-ARM200F, 200 kV and FEI Titan3 G2 60-300, 300 kV). Samples for TEM and STEM analysis were prepared by immersing TEM grids into NPs/PEG dispersions for 10 s, then immediately immersing the grids into ethanol for at least 20 min to remove excess PEG, and finally drying in air at room temperature for a few minutes. The size distributions were collected from TEM and STEM images by measuring approximately 150 particles in at least three different regions of the grid using ImageJ software. The crystal structure of NPs was evaluated using STEM high-angle annular dark-field (HAADF) images. The samples sputtered on glass slides were analyzed with X-ray diffraction (XRD, Rigaku Mini Flex II, Cu Kα radiation, λ = 1.5418 Å, scanning speed of 0.5° min^{-1}). The X-ray diffraction intensities for all samples were plotted as a function of 2 theta. Area analysis using energy-dispersive X-ray spectroscopy (EDS) coupled with STEM (JEOL JEM-ARM200F) was carried out to verify the existence of CuPt/Ag alloy NPs and their compositions. The metal compositions of NPs/PEG dispersions and metal loading on carbon of the catalysts were obtained by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-OES, Shimadzu ICPE-9000). For preparing the samples, aqua regia or nitric acid was added into 1 mL of NPs/PEG dispersion or 10 mg catalyst powders. Aqua regia was used to prepare samples for measuring Pt and Cu, and nitric acid was used to prepare samples for measuring Ag. The mixtures were then kept for at least 30 min. After the metals were entirely dissolved, the mixtures were centrifuged, the precipitates were discarded, and the supernatants were diluted to 10 mL for ICP-OES measurements. The durability of the catalysts after electrochemical tests were analyzed by X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9200, Mg Ka source). The catalysts before and after electrochemical tests were collected and XPS was performed using 20 eV pass energy, and scanned 300 times.

3 Results and Discussion

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 didn't 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 miscroscope (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.

4 Conclusions

Sputtering is a conventional physical method for fabricating thin films on solid substrates. During decades, sputtering has been developed for wider applications, and not limited in the generation of thin films. The sputtering substrates have also realized the development from solid to liquid. Therefore, synthesizing metal NPs through sputtering onto liquid substrates has become a common and facile approach without using of toxic reductants and free of production of by-products. The synthesized NPs can also be utilized in variety of applications. The key results and conclusions can be summarized as follows:

(1) Pt/Ag alloy NPs could be synthesized by co-sputtering of Pt and Ag metal targets. And the compositions of alloy NPs could be controlled by changing the sputtering currents. PEG hindered NPs from growing to larger sizes, which led to the broader size distributions of the NPs sputtered onto PEG. Moreover, the alloy NPs formed at the beginning of sputtering, and they continue to grow and combine with other

atoms/clusters after deposition. The interaction between PEG and the NPs also contributed to the broader composition distributions of the NPs sputtered onto PEG than that on glass slides.

(2) CuPt/Ag trimetallic alloy NPs were synthesized by co-sputtering of Cu/Pt alloy target and Ag target. Although the sputtering current applied to Cu/Pt alloy target was fixed, the adjustment of the Ag sputtering current could control the compositions of the trimetallic alloy NPs. Ag compositions of the NPs increased with the increase of Ag sputtering currents, however, the Cu:Pt molar ratios in the NPs were lower than that in Cu/Pt alloy target. Possible reason could be the small particle sizes of the alloy NPs with higher Cu compositions that were no able to be detected by STEM-EDS area analysis, or some sputtered Cu didn’t combine with Ag and Pt. The co-sputtered trimetallic CuPt/Ag alloy NPs were applied as catalyst in ORR and compared with monometallic Pt NPs, bimetallic Pt/Ag and Pt/Cu alloy NPs. It was found that the oxidation of Cu and dissolution of Pt and Cu decreased catalytic performance of samples (CuPt)50Ag0 and (CuPt)50Ag30. However, the synergy between Pt and Ag in samples (CuPt)50Ag30 and Pt50Ag50 was confirmed to enhance the catalytic activity of the alloy NPs.

(3) Au, Pt, Ag monometallic NPs and Au/Pt, Au/Ag bimetallic alloy NPs were prepared by sputtering onto PEG with MUA dispersed. This method successfully synthesized fluorescent mono- and bimetallic alloy NPs. By checking the optical properties of resulted NPs, it was found that the fluorescence wavelengths of the Au alloy NPs were longer than their monometallic counterparts. Within the same alloy

NPs, the fluorescence wavelength can be dependent by the particle size, but when the particle sizes of the alloy NPs are the same, the sputtering currents applied to the targets didn't have obvious impact on the fluorescence wavelength.

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