Synthesis of platinum based catalyst for methanol oxidation reaction using nano-GO as capping agent by femtosecond laser pulse irradiation

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It is well known that platinum nanoparticles (NPs) show excellent catalytic performance for methanol oxidation reaction (MOR). The negative effect of CO poisoning on the Pt-NPs surface during the reaction, which reduces their catalytic performance, can be reduced by combining Pt with other noble metals, such as ruthenium (Ru) or gold (Au). On the other hand, catalytic performance is significantly influenced by reactive surface area and dispersion state on a supporting material. One of the proposed methods is using a capping agent to control not only the size but also the dispersion state of NPs. However, utilization of the capping agent or sacrificial substance needs other purification steps causing a complicated synthesis protocol[1]. In this work, we propose the use of nano-GO as a particle stabilizer in the integration process of metal or alloy NPs on reduced graphene (rGO) through two steps: Firstly, nano-GO was simultaneously produced with metal or alloy NPs by fragmentation of GO through highly intense femtosecond laser irradiation of metal ion solution containing small amount of GO. Fabricated NPs seemed to be immediately modified with nano-GO in the solution and then stabilized through steric effect. Secondly, the colloidal solution of synthesized metal or alloy NPs capped with nano-GO was mixed with GO solution, and it was then irradiated with moderate laser power to produce NPs/rGO composite material. The optimal condition for the formation of NPs/rGO was laser energy of 5-6 mJ and repetition rate of 100 Hz for 45 minutes irradiation time while the metal ion solution was 2.5×10^{-4} M in concentration with 10% $^{v}/_{v}$ of GO solution (7.5×10^{-6} g·mL^{-1}). As a result, the size distribution profile obtained from TEM pictures showed well dispersed small particles with the mean size of less than 6.5 nm on the rGO. Catalytic activity of those composite catalysts in MOR process was evaluated using cyclic voltammetry. In acidic solution (H_2SO_4/CH_3OH 1M), the catalyst had no response during the measurement, but current peaks were observed in alkali solution especially with the alloy NPs catalyst. Even though the number of particles was tiny, 4.52×10^{17} particles in 27 mL of water, catalytic effect in MOR was observed as a clear peak of 3.5 μA at -0.14V (Fig. 1(b)). From these results, nano-GO was effective not only for controlling particle size but also for improving particle distribution on the rGO.

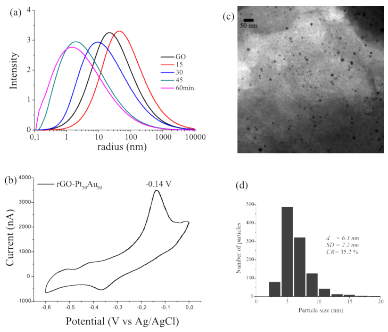

Fig. 1. (a) Size distribution of GO with different irradiation time, (b) cyclic voltammetry of $Pt_{50}Au_{50}$/rGO in alkali solution, (c) TEM image of $Pt_{50}Au_{50}$/rGO and (d) their particle size distribution.

Reference

1. Y. Chen, *J. Am. Chem. Soc.* **35**, 106 (2015).