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Synthesis of self-assembled and hierarchical palladium-CNTs-reduced graphene oxide composites for enhanced field emission properties

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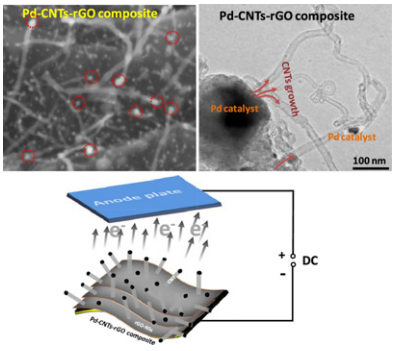
HIGHLIGHTS

- Microwave assisted synthesis of hierarchical palladium-CNTs-reduced graphene oxide composite.
- Pd catalyst assisted growth of CNTs on rGO nanosheets surfaces.
- The hierarchical structure shows enhanced field emission properties with good stability.
- The mechanisms for the enhanced field emission are proposed and discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

We report the synthesis of palladium-graphene oxide based (Pd-rGO) composite and its enhanced electron field emission studies. The palladium nanoparticles decorated reduced graphene oxide (Pd-NPs-rGO) and Pd catalyst assisted grown CNTs on reduced graphene oxide (Pd-CNTs-rGO) composite have been synthesized employing microwave. The hierarchical Pd-CNTs-rGO composite shows enhanced field emission performance due to the synergestic effect of Pd catalyst assisted grown CNTs on rGO nanosheets (rGO-NSs) and its proper contact on rGO surfaces. The enhanced field emission behavior of Pd-CNTs-rGO composite is attributed to the easy electron tunneling from the one-dimensional CNTs, which increases the emission sites and hence the field emission current density. The Pd-CNTs-rGO composite exhibits lower turn-on field, lower threshold field, larger field enhancement factor and high emission current stability as compared to Pd-NPs-rGO composite.

1. Introduction

The high impact of different carbon nanostructures like 1D carbon nanotubes (CNTs) and graphite nano-plates are well known and are promising candidate as a potential field emitter [1–4]. The recently discovered 2D carbon nanostructure, graphene containing

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a single atomic sheet of graphite, is currently one of the most widely studied materials in nearly every area of the natural sciences due to its remarkable physical properties like high specific surface area, excellent mechanical strength, excellent electrical properties, thermal conductivity and a high electron mobility [5–8]. Also, its ballistic transport of charges and metallic character possessing zero band gap, makes it one of the potential materials for field emission applications [5,9,10]. Graphene as field emitters exhibits high density of effective emission sites, high emission current, low turn-on/threshold electric field and large field enhancement factor. Besides graphene, one particular branch deals with graphene oxide and its reduced form known as reduced graphene oxide (rGO), derived from graphite, is also an extremely good and novel candidate for field emission [11,12].

Nowadays, the combination of rGO with different metal oxide forming composites has attracted attention for the improvement in the field emission properties. These rGO-metal oxide composites exhibit enhanced performance compared to the pristine graphene oxide [13–15]. It has been reported that the work function can be tuned and consequently the field emission properties can be improved by decorating/coating the carbon nanostructure (CNTs and graphene/graphene oxide) with metal/metal oxide nanoparticles (NPs) [14,16–19]. The metal/metal oxides NPs decorated graphene modifies the electronic structures through orbital hybridization as well as the work function and density of state [20]. Voggu et al. [21] reported the modification in the electronic structure of single-walled CNTs through Coulomb charge transfer by coating a thin layer of Au and Pt NPs. Also, theoretical calculations confirms that the interaction between metal atoms with carbon nanostructure depends mainly on the hybridization between carbon p_z and the *d* orbital of the metal atoms [22]. Up to now, in order to improve the field emission properties, several research groups have synthesized graphene/CNTs -metal NPs using various methods such as graphene-metal NPs (Ti, Pd, Ag, Au) via thermal evaporation [23], graphene-MgO via radio frequency magnetron sputtering [24], graphene-CsI by drop coating [25], graphene-Sn NPs via a chemical vapor deposition [26], CNTs-Ru metal nanoparticle via a chemical procedure [27], CNT-LaB_6 via sputtering coating [28], CNT-Hf coated via annealing [29],CNT-Ni/Ag metal NPs via electroless plating technique [30] and CNT-Al/Cu-NPs via annealing in Ar gas [31] etc.

Also the immense enhancement in field emission can be achieved by tuning the geometrical morphology of the emitter surface and thus it is important to control the surface morphologies for producing better field emitters [32,33]. Several research groups have already synthesized and studies the synergistic effects of three dimensional morphologies containing rGO and nanotubes/nanoparticles [34–37]. The combined structure in three dimensional morphologies containing graphene/rGO and CNTs with metal/metal oxide shows high performance field emission values [38–40]. The in-situ grown CNTs on graphene surface not only decrease the contact resistance between the CNTs and the substrate graphene, but also improve the joule heat transfer to achieve a stable emission current from CNTs [41].

In this article, we have reported the synthesis of rGO-NSs decorated Pd-NP (Pd-NPs-rGO) and catalyst (Pd) assisted CNTs grown on rGO-NSs (Pd-CNTs-rGO) composite materials via simple, fast and scalable microwave approach and its electron field emission properties. The comparative studies and analysis demonstrate the field-emission properties of Pd-CNTs-rGO composite which possess low turn-on electric field, low threshold field and high field-enhancement factor as compared to Pd-NPs-rGO composite. The formation of in-situ, Pd-CNTs-rGO shows the synergetic effect in the measurement of field emission properties. This confirms the better performance of the Pd-CNTs-rGO composite, as well as their promising application for large-area field emitters.

2. Experimental details

2.1. Synthesis of rGO-NSs

Graphite oxide was synthesized by chemical oxidation of graphite powder using modified Staudenmaier's method [42]. The graphite powder (10 g) was continuously stirred in the mixture of sulfuric acid (H_2SO_4) (180 ml) and nitric acid (HNO_3) (90 ml) solution at room temperature. After complete mixing, the solution container was then placed into an ice-water bath to ensure a constant temperature and potassium chlorate ($KClO_3$) (110 g) was slowly poured into solution to avoid explosion due to the exothermic reaction [43]. This solution was kept at room temperature for five days under continuous magnetic stirring for better oxidation of the graphite powder. After that, the solution containing graphite oxide was washed with DI water and 10% hydrochloric (HCl) solution to remove sulfate and other ion impurities. It was then washed several times with DI water to achieve its pH value of 7. Afterward the graphite oxide powder was dried at 70 °C under vacuum and exfoliated using microwave to partially exfoliate reduced graphene oxide nanosheets (rGO-NSs).

2.2. Synthesis of Pd-NPs-rGO and Pd-CNTs-rGO composites

Pd-NPs-rGO and Pd-CNTs-rGO composites were synthesized employing microwave irradiation. The graphite oxide powder was mixed with Pd containing precursors palladium(II) trifluoroacetate ($Pd(TFA)_2$) and palladium(II) acetate ($Pd(OAc)_2$) for the synthesis of Pd-NPs-rGO and Pd-CNTs-rGO composites, respectively. The graphite oxide powder (3 g) was dispersed into 200 ml of ethanol and sonicated for 15 min for dispersion. The dispersed graphite oxide powder in ethanol was divided into two parts for the synthesis of Pd-NPs-rGO and Pd-CNTs-rGO composites. Each part of (volume ~ 200 ml) was mixed separately with $Pd(TFA)_2$ (0.4 mol%) and $Pd(OAc)_2$ (0.4 mol%) and further stirred for 15 min at room temperature for homogeneous mixing of Pd containing precursors. During the continuous stirring, small amount (2 ml) of diluted ammonia ($NH_3 \cdot H_2O$) (2 M) solution was added and stirred for 10 min. Afterwards, the ethanol from the mixture was evaporated by drying at 35 °C in oven. The completely dried powder was washed several times with DI water for the removal of impurities. These two types of Pd salts modified powder were further separately treated with domestic microwave oven (Consul-CMW30AB) at fixed power (810 W) for 1.5 min and 3.0 min for the final formation of Pd-NPs-rGO and Pd-CNTs-rGO composites, respectively.

2.3. Materials characterization

The crystal phases of the as-prepared samples were determined using an X-ray diffractometer (XRD - D/MAX-2500/PC; Rigaku Co., Tokyo, Japan) over 2θ range 10 to 80°. The microstructural characterizations were investigated using scanning electron microscope (SEM - Dual Beam FIB/FEG model FEI Nova 200) and transmission electron microscope (TEM, FEI Tecnai G20). Raman measurements were carried out using a spectrometer with a 473 nm laser (NT-MDT NTEGRA Spectra). The field emission characteristics of all the samples have been investigated in a high vacuum field emission setup.

3. Result and discussions

3.1. Structural and microstructural analysis

The SEM images of rGO-NSs are presented in Fig. 1. The obtained rGO-NSs exhibits few-layered sheet-like structure as can be seen in Fig. 1a. It can be seen that rGO-NSs contains wrinkles on its top surfaces. Also, the surface morphology resembles strongly with folded curtain which indicates that rGO-NSs flakes are overlapped on each other rather