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This is certify that Mr./ Ms. *Sara Khadempir*

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Preparation and electrocatalytic application of novel Pd nanoparticle/polyoxometalate/Graphene nanohybrids

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Preparation and electrocatalytic application of novel Pd nanoparticle/polyoxometalate/Graphene nanohybrid

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Abstract: The easy, room temperature and environmentally friendly synthesis of Pd nanoparticle (Pd Nps) on graphene nanosheets (GNSs) was reported. Polyoxometalates (POMs) were used to serve as reducing, encapsulating and bridging molecules, which avoids the step of introducing other organic toxic molecules. Characterization using transmission electron microscopy, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction analysis (XRD), dynamic light scattering (DLS), cyclic voltammetry (CV), etc. was performed and verified the structure of the prepared nanohybrids of Pd NPs@POM-GNSs.

Keywords: Palladium nanoparticle; Graphene oxide; Polyoxometalates; Electrocatalytic activity.

Introduction

Fuel cells are widely considered to be an important power source due to their high energy conversion, efficiency and low pollution. The direct formic acid fuel cell has been proposed as a possible replacement for batteries and direct methanol fuel cell (DMFC) due to the high theoretical open circuit voltage and reduced fuel cross-over of formic acid compared to methanol, and the Pd-based catalysts toward formic acid oxidation exhibit a higher initial activity due to being free of CO poisoning compared to Pt, and also at a lower cost [1]. Furthermore, to maximize the electrocatalytic activity of NPs, a suitable carbon support is required to disperse these NPs. Graphene has received considerable attention due to its good chemical and physical properties [2]. There are various methods to load metal NPs on GNSs. Recently, polyoxometalates (POMs), the early transition metal oxygen anionic clusters with remarkably rich redox and photo-electrochemical properties [3], have been used as a sole agent to build metal NPs@POM [4-7]. Herein, we report an alternative, in situ, easy and green strategy for the synthesis of Pd NPs@POM-GNSs nanohybrids using solely polyoxometalates (POMs) as reducing, stabilizing and bridging molecules.

Materials and method

$PdCl_2$ and Graphite powder were purchased from merck Co., phosphomolybdic acid $H_3[PMo_{12}O_{40}]$ (PMo_{12}) was purchased from Aldrich Chemical Company.

Graphene oxide (GO) was oxidize from graphite powder by a modified Hummers method using H_2SO_4, $NaNO_3$ and $KMnO_4$ in an ice bath as reported in great detail elsewhere. For preparation of Pd NPs@POM-GNSs nanohybrids, PMo_{12} was firstly reduced by UV photo-reduction. In a typical synthesis PMo_{12}, isopropanol, $PdCl_2$ and GO were mixed under UV irradiation.

Results and discussion

Fig. 1. Represent the degree of oxidation by FT-IR. The bands around 1061, 1625, 1727, 3400 cm^{-1} could be attributed to oxygen-containing functional groups on GO. It indicates that the graphite have been oxidized to graphite oxide.

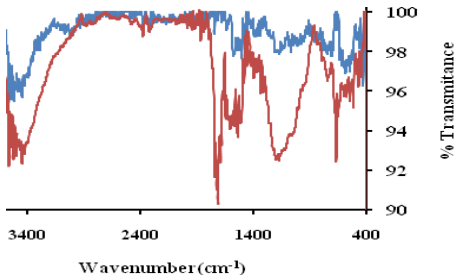

Fig. 1. FTIR spectra of Graphite powder (blue line), GO (red line).

Fig. 2. reveals the UV-Vis absorption spectrum of the suspended GO nanosheets. The main absorption peak at about 230 nm is attributed to the $\pi \rightarrow \pi^*$ transitions of aromatic C-C bond, and a shoulder at about 300 nm can be assigned to the $\pi \rightarrow \pi^*$ transitions of C=O bonds [2]. This result confirms the FTIR results on the existence of oxygen groups on GO nanosheets.

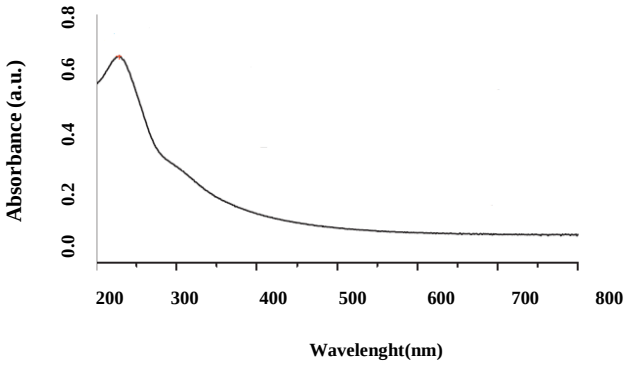

Fig. 2. UV-Vis absorption spectrum of GO

Metals that give a distinct surface plasmon peak, such as Au, Ag, Cu and Co, are relatively easy to monitor. The problem is that many transition metals do not show distinct surface plasmon peaks; several transition metals, including Pd, do not show pronounced surface plasmon peaks due to d-d interband transitions. Since there is no peak characteristic of palladium nanoparticles, their formation can be monitored by following the decrease in precursor ion concentration or the increase in absorbance at higher wavelengths. The increase in absorbance indicates an increase in the number and size of the particles formed [1]. Because of the noise at the maximum, we chose the latter method. Accordingly, we characterized particle formation by the increase in absorbance values measured at λ = 500nm in UV-Vis spectroscopy (Fig. 3.).

Conclusion

The surface methodology of novel Pd NPs@POM-GNSs tri-component nanohybrids have been examined by different analysis. This synthesis is simple and environmentally friendly. The reaction can be performed at room temperature without any other organic templates or surfactants, which is beneficial for its electro-catalytic activities. The obtained nanohybrids exhibited exciting electrocatalytic activity towards formic acid oxidation reaction.

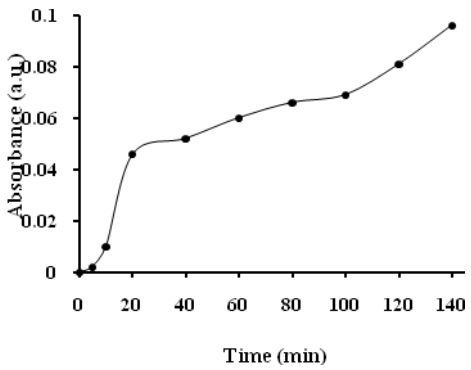

Fig. 3. Absorbance (λ = 500nm) by UV-Vis *vs.* time curves of Pd NPs.

References

[1] O. Winjobi, Z. Zhang, C. Liang, W. Li, "Carbon nanotube supported platinum–palladium nanoparticles for formic acid oxidation", Electrochimica Acta 55 (2010) 4217-4221.

[2] R. Liu, S. Li, X. Yu, G. Zhang, S. Zhang, J. Yao, B. Keita, L. Nadjo, L. Zhi, "Facile synthesis of Au-nanoparticle/polyoxometalate/graphene tricomponent nanohybrids: An enzyme-free electrochemical biosensor for hydrogen peroxide", Small 8 (2012) 1398-1406.

[3] F.F. Bamoharram, A. Ahmadpour, M.M. Heravi, A. Ayati, H. Rashidi, B. Tanhaei, "Recent advances in application of polyoxometalates for the synthesis of nanoparticles", Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry 42 (2012) 209-230

[4] A. Troupis, A. Hiskia, E. Papaconstantinou, "Synthesis of metal nanoparticles by using polyoxometalates as photocatalysts and stabilizers", Angewandte Chemie - International Edition 41 (2002) 1911-1914.

[5] M. Sun, J. Zhang, Q. Zhang, Y. Wang, H. Wan, "Polyoxometalate-supported Pd nanoparticles as efficient catalysts for the direct synthesis of hydrogen peroxide in the absence of acid or halide promoters", Chemical Communications (2009) 5174-5176.

[6] S. Li, X. Yu, G. Zhang, Y. Ma, J. Yao, B. Keita, N. Louis, H. Zhao, "Green chemical decoration of

multiwalled carbon nanotubes with polyoxometalate-encapsulated gold nanoparticles: Visible light photocatalytic activities", Journal of Materials Chemistry 21 (2011) 2282-2287.
[7] S. Park, J.H. Choi, T.J. Kim, Y.-M. Chung, S.-H. Oh, I.K. Song, "Direct synthesis of H2O2 from H2 and O2 over Pd catalyst supported on Cs2.5H0.5PW12O40-MCF silica", Catalysis Today 185 (2012) 162-167.