Synthesis and catalytic property of urania-palladium-graphene nanohybrids

Li Ding, Zeyao Zhang and Yan Li*

ABSTRACT Urania-palladium-graphene nanohybrids were synthesized via a solvothermal process in ethylene glycol. With the solvothermal treatment, the Pd nanocrystals surrounded by well-crystallized urania supported on graphene oxide was obtained. This ternary hybrid showed considerably higher catalytic activity than palladium-graphene hybrids toward the reduction of 4-nitrophenol by NaBH₄. Besides the smaller sizes of palladium nanoparticles in the ternary hybrids, in which the aggregation of Pd nanoparticles was prevented by urania, the charge transfer between the nano-structured Pd and urania may also contribute to the enhancement of catalytic activity by offering more active sites for adsorption and reaction.

Keywords: uranium oxides, palladium, catalytic performance

INTRODUCTION

Uranium is one of the natural radioactive elements. Many current applications of uranium are based on its unique nuclear properties. The natural isotopes of uranium consist of ²³⁸U (99.275%), ²³⁵U (0.720%), and a very small amount of ²³⁴U (0.0050%) [1]. In the nuclear reactor, the fuel is normally enriched of ²³⁵U. Therefore, a large amount of ²³⁸U, which has an ultralong half-life period of ~4.5 billion years and hence is normally safe to be exploited conventionally, is abandoned from nuclear industry [1,2]. Therefore, developing applications of the residual ²³⁸U is of great importance.

Uranium is rich of 5f electrons which render it splendid chemical properties such as variable valence states and multiple oxide phases. The principal thermodynamically stable binary oxides are UO₂, U₄O₉, U₃O₈ and UO₃. Many other metastable oxides also exist [3,4]. Uranium oxide with flexible oxidation states, has wide applications in

catalysis [5–7]. For instance, mix-valence uranium oxide U₃O₈ is efficient for destroying a range of hydrocarbon and chlorine-containing pollutants under mild condition [8,9]. Uranium dioxide (urania) shows a hydrogen evolution electrocatalytic activity when combined with graphene [10]. Nevertheless, uranium oxides were seldom tested as the promoter in catalytic reaction, comparing to the conventional metal oxides [11,12]. However, the unique redox property may endow uranium oxides special advantage in serving as a catalyst promoter.

Palladium nanoparticles have very important applications in catalysis, for instance, as catalyst in Suzuki-Coupling reaction [13–16], low temperature CO oxidation, 4-nitrophenol reduction and so on [17–22]. In particular, the reduction of 4-nitrophenol to 4-aminophenol over Pd catalysts in the presence of NaBH₄ is of interest, because the product is a key intermediate compound for pharmaceuticals, agrochemicals, dyes, and pigments [23]. The combination of Pd and uranium oxides may bring about enhanced catalytic properties.

In order to maintain the nano-scaled morphology and structure of both Pd and uranium oxide, which are normally important to ensure the higher catalytic activity, the third component may need to be introduced as a supportive and/or dispersive agent. Graphene oxide (GO) is an ideal catalyst support due to its extraordinarily high specific surface area and numerous hydrophilic functional groups on its surface, which can facilitate the nucleation of nanocrystals [24–27].

Herein, we synthesized the ternary nanohybrids of palladium and urania supported on GO (Scheme 1). The nanohybrids show remarkably improved catalytic performance. A possible synergetic mechanism between urania

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Scheme 1 Schematic illustration of the compositional and morphological evolution process of urania-palladium-graphene nanohybrids by solvothermal treatment.

and Pd was proposed.

EXPERIMENTAL SECTION

Materials

Graphite flakes (Sigma-Aldrich, cat #332461), KMnO_4 (guaranteed reagent (GR), Sinopharm Chemical Reagent), ethylene glycol (EG) (analytical reagent (AR), Sinopharm Chemical Reagent), H_2SO_4 (AR, Xilong Chemical), HNO_3 (AR, Xilong Chemical), H_3PO_4 (GR, Beijing TongGuang Fine Chemical), U_3O_8 (AR, China National Nuclear), 20 wt.% aqueous solution of poly(diallyldimethylammonium chloride) (PDDA) (Sigma-Aldrich), KOH (GR, Xilong Chemical), and PdCl_2 (AR, Beijing TongGuang Fine Chemical) were used as received.

Preparation of Pd/ UO_2 /GO hybrids

Typically, 20 mL of PDDA-modified GO (1 mg mL^{-1}) [28,29] was dispersed in 80 mL of EG and sonicated for 5 min. Then 4 mL K_2PdCl_4 (0.1 mol L^{-1}) was added. After the mixture was stirred overnight, its pH was adjusted to 12 with 1 mol L^{-1} KOH. Immediately, 2 mL of UO_2^{2+} (0.2 mol L^{-1}) was added. The mixture was held at 140°C for 4 h under N_2 atmosphere and then transferred into a Teflon-lined stainless steel autoclave to carry out a solvothermal reaction at 200°C for 4, 12, and 24 h, respectively. The product was collected by centrifugation, washed with water, frozen by liquid nitrogen and lyophilized overnight.

Preparation of Pd/GO hybrid

All steps were the same as the preparation of Pd/ UO_2 /GO composite except for adding UO_2^{2+} .

Characterization

X-ray diffraction (XRD) measurements were performed on a Rigaku Dmax-2400 diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) with an accelerating voltage of 40 kV and current of 100 mA or a Panalytical X'Pert 3 Powder diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) with an accelerating voltage of 40 kV and a current of 40 mA. The transmission electron microscopy (TEM) study was

performed on a FEI Tecnai F20 electron microscope. X-ray photoelectron spectroscopy (XPS) was measured on an AXIS Ultra X-ray photoelectron spectroscope with Al-K α radiation ($h\nu = 1486.71 \text{ eV}$). X-ray source was operated at 225 W with 15 kV acceleration voltage. The C 1s line at 284.8 eV was used to calibrate the binding energies. The UV-vis spectra were performed on a PerkinElmer Lambda 750. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was conducted on a Profile Spec ICP-AES spectrometer (Leeman, USA). The X-ray absorption fine structure (XAFS) in X-ray absorption spectra of Pd K-edge ($E_0 = 24,350 \text{ eV}$) for Pd nanoparticles and $\text{L}_{3\text{-edge}}$ ($E_0 = 17,166 \text{ eV}$) for uranium were collected at BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF). The energy was calibrated according to the absorption edge of pure Pd foil and Zr foil at K-edge ($17,998 \text{ eV}$).

Catalytic reduction of 4-nitrophenol

4-Nitrophenol ($25 \mu\text{L}$, 10 mmol L^{-1}) was dissolved in 2.425 mL water in a cuvette and bubbled with N_2 for 60 s to remove the oxygen. Then NaBH_4 aqueous solution ($500 \mu\text{L}$, 0.1 mol L^{-1}) was added. After the solution showed yellow color, $50 \mu\text{L}$ (0.2 mg mL^{-1}) catalyst solution was added to ignite the reaction. The reaction progress was monitored by measuring the UV-vis absorption spectra of the reaction solutions.

RESULTS AND DISCUSSION

Characterization of Pd/ UO_2 /GO nanohybrids

As shown in Fig. 1a, c and e, there are nanoscaled materials loaded on GO. The high-resolution TEM (HRTEM) image in Fig. 1b shows fringes with an inter-distance of 0.22 nm, which is in accordance to (111) plane of Pd. This indicates that Pd nanocrystals were formed after the solvothermal treatment of 4 h. The typical particle size is around $\sim 6 \text{ nm}$. In the sample of 12 h solvothermal treatment, weak fringes with the inter-distance of 0.27 nm were observed (Fig. 1d), which is assigned to the (200) plane of UO_2 . This indicates

Figure 1 TEM and HRTEM images of Pd/VO₂/GO hybrids with the solvothermal time of 4 h (a, b), 12 h (c, d), and 24 h (e, f).

that the crystallized VO₂ appeared. In the HRTEM image of the sample treated for 24 h, very clear fringes with the space of 0.32 nm corresponding to (111) plane of VO₂ were observed. It is obviously seen that the Pd nanoparticle was surrounded by VO₂.

Fig. 2a shows the XRD patterns of the samples prepared at different conditions. All peaks are broadened due to the small grain size, which is consistent with the TEM images in Fig. 1. All the samples show characteristic peaks of Pd at $2\theta = 40.12^\circ$, 46.66° , and 68.12° , which are indexed to (111), (200), and (220) plane, respectively. In the sample with 24 h solvothermal process, the peaks of crystal VO₂ are clearly observed at $2\theta = 28.28^\circ$, 32.74° , and 55.75° , which are indexed to (111), (200), and (311) plane, respectively. The very broad peak at $27\text{--}28^\circ$ appears in the samples with 4 and 12 h solvothermal treatment may be attributed to uranium oxide with poor crystallinity, which is in consistency with

the HRTEM results. The XPS spectrum (Fig. 2b) shows that the sample contains Pd, U, O, and C elements. The two peaks at 336 and 341 eV can be respectively assigned to the binding energy of Pd 3d_{5/2} and 3d_{3/2}, while the peaks at 382 and 393 eV are assigned to U 4f_{7/2} and U 4f_{5/2}.

From the above discussion, the ternary nanohybrids were prepared with Pd nanoparticles attached to nano-structured VO₂. We estimated the grain size of Pd nanoparticles from the XRD results according to the Debye-Scherrer equation [30] (Table 1). The results are in good agreement with what we observed in TEM measurements. When comparing the samples with relative long solvothermal treatment, it is obvious that those with VO₂ possess smaller Pd nanoparticles (<5 nm vs. >20 nm) because the presence of VO₂ may help to prevent the Pd particles from aggregation.

Catalytic activities for 4-nitrophenol reduction

The ternary nanohybrids were used as catalysts for the reduction of 4-nitrophenol with an excess of NaBH₄ as reducing agent. During the reaction, the absorption of 4-nitrophenol at 400 nm showed significant decrease, accompanied with a successive increase of absorption of 4-aminophenol at 300 nm (Fig. 3a), which confirmed the catalytic activity of the ternary nanohybrids. Since the concentration of NaBH₄ was largely exceeded the concentration of 4-nitrophenol in our experiments, the catalytic reduction can be treated as first-order kinetics regarding to the 4-nitrophenol concentration as reported [31–32]. This is confirmed by the linear relationship between $\ln(A/A_0)$ and the reaction time t in Fig. 3b. The apparent rate constants (k_{app}) were calculated to be $6.1 \times 10^{-3} \text{ s}^{-1}$ for the Pd/VO₂/GO and $3.1 \times 10^{-3} \text{ s}^{-1}$ for the Pd/GO. As for the VO₂/GO hybrid, nearly no reduction of 4-nitrophenol is observed, indicating that VO₂ alone cannot catalyze the reduction reaction.

Figure 2 (a) XRD patterns of Pd/VO₂/GO hybrids with different solvothermal times (i, 4 h; ii, 12 h; iii, 24 h) and Pd/GO hybrid (iv) as comparison. (b) Typical XPS spectrum of the Pd/VO₂/GO hybrids with 24 h solvothermal treatment.

Table 1 Crystallite size of Pd in Pd/GO and Pd/VO₂/GO hybrids obtained at solvothermal time of 4 (S4), 12 (S12), and 24 (S24) h

Crystallite (nm)	(111)	(200)	(220)	Average
Pd/GO-S4	6.9	6.1	6.1	6.4
Pd/GO-S12	28	19.1	18.9	22.0
Pd/GO-S24	25.1	16.5	18.7	20.1
Pd/VO ₂ /GO-S4	5.9	5.3	8.3	6.5
Pd/VO ₂ /GO-S12	5.0	4.4	5.1	4.8
Pd/VO ₂ /GO-S24	5.0	3.7	5.1	4.6

To evaluate the performance of catalysts more precisely, we then calculated the rate constants of each catalyst based on the Pd quantity. The rate constants of Pd/VO₂/GO and Pd/GO hybrids with different solvothermal treatment times were compared in Fig. 3c. We find that the ternary nanohybrids always show higher activity than Pd/GO. Particle size is often a key factor affecting the activity of the catalysts because smaller particles present larger surface area and more active sites [33–37]. The smaller size of Pd nanoparticles in the ternary hybrids as shown in Table 1, contributes to higher catalytic activity. This is also valid for the comparison in the catalytic performance of the Pd/GO with different solvothermal treatment times. However,

the size effect cannot explain the difference in activity of the two samples with 4h's solvothermal treatment. Both samples show similar size of Pd nanoparticles, but the sample with VO₂ exhibits higher catalytic activity. This indicates that VO₂ should act more than just as a catalyst support. HRTEM and XRD characterizations shown in Figs 1 and 2a already reveal that longer solvothermal treatment benefits the formation of well crystallized VO₂. From Fig. 3c we also found that the catalytic activity of the Pd/VO₂/GO increases when prolonged the solvothermal time. This result gives further evidence indicating VO₂ acting as a promoter for Pd rather than only a support. In addition, we optimized the ratio between Pt and VO₂. As shown in Fig. 3d, the most suitable molar ratio is around 1:1. Higher content of VO₂ leads to a decline of activity, which is possibly caused by covering the active sites of Pd catalysts.

To analyze the mechanism of the superior activity of the Pd/VO₂/GO hybrids and the role of VO₂, we did XPS measurements (Fig. 4). Palladium does not show obvious valence change in different samples. But it is observed that uranium on the surface of Pd/VO₂/GO presents mix valence of +4 and +6 and the content of U(+6) component became lower when the solvothermal time was prolonged.

Figure 3 (a) Successive UV-vis spectra for the reduction of 4-nitrophenol catalyzed by the Pd/VO₂/GO hybrid with 24 h solvothermal treatment. (b) The kinetics study of the catalytic reaction of 4-nitrophenol over UO₂/GO, Pd/GO, and Pd/VO₂/GO. (c) Rate constants of catalysts with different solvothermal times, and Pd/VO₂/GO, Pd/GO. (d) Rate constants of catalysts with different UO₂:Pd ratio.

Figure 4 (a) XPS spectra of the Pd/UiO-66/GO hybrids with different solvothermal times (i, 4 h; ii, 12 h; iii, 24 h). The spectra were fitted with peaks of U(+4) and U(+6) (dash line). (b) XPS spectra of the Pd/UiO-66/GO hybrids with different solvothermal times (i, 4 h; ii, 12 h; iii, 24 h), and the Pd/GO hybrid (iv) with a solvothermal time of 4 h. The spectra were fitted with peaks of Pd(0) and Pd(+2) (dash line).

Figure 5 XAFS of U L3-edge of the Pd/UiO-66/GO hybrids with different solvothermal times (i, 4 h; ii, 12 h; iii, 24 h).

This phenomenon was also demonstrated by XAFS spectra in Fig. 5. The near edge absorption peak of the Pd/UiO-66/GO with 24 h solvothermal treatment is 0.3 eV lower than that of the sample with 4 h solvothermal treatment, which indicates the lower oxidation state of the uranium in the samples with longer solvothermal treatment. During the solvothermal process, the U(+6) was gradually reduced by EG. Longer solvothermal treatment should be propitious

to a thorough reduction of U(+6). However, this might not be the only reason why uranium shows lower oxidation state with longer solvothermal treatment. As we discussed previously, UiO-66 crystallized better when prolonging the solvothermal time, which generally should show greater resistance to oxidation when exposed to air [38,39]. This effect should also be taken into account.

It is known that the reduction of 4-nitrophenol with NaBH₄ follows the model of Langmuir Hinshelwood, that is, both reactants are adsorbed onto the surface to react [29,30]. Conventionally, Pd is regarded as the catalytic site to react with BH₄⁻ by accepting electrons which transfer to 4-nitrophenol subsequently. In our catalysts, an electron transfer from palladium to uranium may take place since that Pd (5.12 eV) has a lower work function than UiO-66 (6.68 eV) [40,41]. It is known that Fermi level alignment occurs whenever a metal and a semiconductor are placed in contact, resulting in charge redistribution and formation of a depletion layer surrounding the metal [42]. Therefore, electrons are partially transferred from Pd through a depleted region near the Pd/UiO-66 interface to UiO-66, forming an electron-rich region, which was suggested by the XAFS spectra of Pd shown in Fig. 6. The Pd near edge absorption

Figure 6 XAFS of the Pd K-edge of Pd foil (i), Pd/GO (ii) and Pd/VO₂/GO hybrids with different solvothermal times (iii, 4 h; iv, 12 h; v, 24 h).

Scheme 2 The proposed mechanism of the catalytic reduction of 4-nitrophenol with Pd/VO₂/GO hybrids.

peak of the Pd/VO₂/GO with 24 h solvothermal treatment is 1.1 eV higher than that of the sample with Pd/GO, indicating a slightly higher oxidation state of the Pd in the ternary hybrids. The shift of edge energy is tiny, so it might not be easily observed in the XPS profiles. Previous studies have shown that nitro groups can be easily adsorbed on the basic or reducible supports [43–45]. Hence, VO₂ tends to adsorb 4-nitrophenol, which then can be further reduced by the injected electrons on VO₂. Thus, VO₂ may contribute to the improvement of catalytic performance by offering more active sites for both adsorption and reaction of 4-nitrophenol. That may be one of the main reasons why our Pd/VO₂ catalyst exhibits enhanced catalytic activity toward the reduction of 4-nitrophenol as shown in Scheme 2.

CONCLUSIONS

In conclusion, we synthesized the Pd/VO₂/GO nanohybrids via a solvothermal process. The Pd nanoparticles (~4 nm) were loaded uniformly on GO and closely surrounded by nano-structured VO₂ with good crystallinity, which protected Pd from aggregation. A charge redistribution

at the Pd-VO₂ interface may take place and consequently VO₂ can act as the promoter by offering additional active sites for both adsorption and reduction of the reactant 4-nitrophenol. Therefore, the ternary hybrids present enhanced catalytic performance toward the reduction of 4-nitrophenol to 4-aminophenol.

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Conflict of interest The authors declare that they have no conflict of interest.

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二氧化铈-钯-石墨烯纳米复合材料的合成及其催化4-硝基苯酚还原反应的研究

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摘要 本文通过溶剂热方法合成了二氧化铈-钯-石墨烯纳米复合材料. 在这种复合材料中, 金属钯和二氧化铈的纳米晶负载在石墨烯氧化物上, 且钯纳米晶与二氧化铈纳米晶密切接触. 这一复合材料对4-硝基苯酚还原反应表现出良好的催化活性, 二氧化铈在其中发挥了关键作用. 二氧化铈有效地防止钯颗粒在溶剂热过程中团聚、长大; 此外, 在钯与二氧化铈界面处, 电子从钯转移至二氧化铈表面, 为催化还原反应提供了更多的吸附和反应位点, 从而有效地提高了催化剂活性.