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Synthesis and deposition of ultrafine noble metallic nanoparticles on amino-functionalized halloysite nanotubes and their catalytic application

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ABSTRACT

Using epigallocatechin gallate (EGCG) as both a green reductant and stabilizer, ultrafine noble metal nanoparticles (Rh NPs, Pt NPs, Pd NPs) are synthesized and in situ deposited within amino-functionalized halloysite nanotubes (N-HNTs) via a facile and eco-friendly process. These noble metal nanoparticles with extremely small size (~1.5 nm) are dispersed densely and uniformly on both outside and inside surface of N-HNTs. Rh deposited N-HNTs (Rh–N-HNTs) was investigated as a model composite catalyst and applied in the catalytic reduction of 4-nitrophenol (4-NP), and it exhibited amazing activity and recycle stability. Due to the green and flexibility of the technique described here, noble metal nanoparticles, metal nanoalloy, or metal oxide nanoparticles with ultrafine particle size also can be loaded densely and uniformly on the surface of diverse amino-functionalized nanotubes, nanofibers or nanoporous, and these composites may be applicable in catalysis, photocatalysis, and electrochemical areas.

1. Introduction

With the fast development of nanoscience and nanotechnology, much attention has been paid to the synthesis of noble metal nanoparticles (NPs). Because of their remarkable chemical and physical properties compared to bulk metals, applications using noble metal NPs in a wide range of areas, including electronic and optical devices [1], energy generation and storage [2], chemical sensors [3–5], catalysis [6–10], hybrid material [11], and even biological materials [12–14], have all been explored. It has been realized that noble metal NPs show characteristic size-dependent properties (e.g., catalytic, electronic, optical, and thermodynamic property) with significant size-effect at 1–10 nm diameters [15–17]. For example, the position of plasmon band of metallic NPs and their bandwidth reflected from UV–vis spectra are greatly depended on the size of NPs.

From the view point of practical applications, it is of great value to find a facile method for the preparation of uniform small size noble metal NPs with high stability. There are already many methods for the preparation of noble metal NPs, but most are complex, time-consuming, or strict in synthetic conditions. However, the aggregation of small-sized noble metal NPs is always inevitable in catalytic reactions due to the high surface energy of the NPs, thus resulting in remarkable reduction of the catalytic activities and impossible reusability. To overcome these disadvantages, noble metal NPs are immobilized in/onto cheap solid supports, such as organic polymers [18], metal oxides [19,20], composites [21], various inorganic supports [22–24], and so on, aiming to prevent NPs from aggregation and enhance their stability. It has been proved as an effective way to combine the unique electronic and mechanical properties of the supports, including nanotubes, nanofibers, core–shell NPs, hollow nanospheres, etc., with the size- and shape-dependent physicochemical properties of metal NPs [25–27]. And these hybrid nanomaterials have presented promising application in catalysis, sensor, and surface enhanced Raman spectroscopy (SERS) [28].

Among those nanostructured supports, nanotube is one of the most interesting nanostructures, which is regarded as a potential

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candidate for catalyst supports due to its high surface area to volume ration. halloysite nanotubes (HNTs) are a promising catalyst support because of the inherent hollow nanotubular structure and different outside and inside chemistry essence, with about 15 nm lumen, 50 nm external diameter, and 1000–2000 nm in length. However, since HNTs are relatively chemically inert, activating their surface is an essential prerequisite for depositing NPs. Chemical functionalization is a convenient and widely used way to modify HNTs, as well as to improve the dispersibility [29–31].

Inspired by above considerations, in the present work we developed a facile functionalization of HNTs by *N*-β-aminoethyl-γ-aminopropyl trimethoxysilane (AEAPTMS), aimed at the preparation of chemically modified nanotube surface capable of binding noble metal NPs. The amino groups functionalized HNTs (N-HNTs) were then purified and used as catalyst carriers. An additional goal was to avoid the use of environmental intolerance reductant like $NaBH_4$, dimethylhydrazine, hydrazine, etc., thus, EGCG was accepted as a green reductant to reduce the noble metallic ions. Noble metal NPs (Rh NPs, Pt NPs, Pd NPs) with ultrafine size were successfully immobilized on the outside and inside surface of N-HNTs densely and uniformly via an in suit reduction approach under a mild condition. In general, the decrease of particle size can lead to an increase of the catalytic activity because of the large surface-to-volume of smaller NPs, finally, the catalytic activities and reusability of N-HNTs deposited with noble metal NPs were evaluated by the catalytic reduction of 4-nitrophenol (4-NP).

2. Experimental

2.1. Materials

Chloroplatinic acid ($H_2PtCl_6{\cdot}H_2O$), palladium chloride ($PdCl_2$), rhodium chloride ($RhCl_3$) were all obtained from Aladdin chemistry Co., Ltd. Epigallocatechin gallate (EGCG) was purchased from Xuancheng Baicao Plant Industry and Trade Company and used as received without further purification. AEAPTMS was acquired from Sinopharm Chemical Reagent Co., Ltd., China. Aqueous solutions were prepared using Milli-Q water of 18 MΩ, and other reagents were of ananlytic grade and used as supplied.

2.2. Synthesis of amino-functionalized HNTs (N-HNTs)

N-HNTs were prepared in a facile approach using water and ethanol as solvents, AEAPTMS as functionalization agent according to the synthesis procedure in our previous work [32]. In a typical procedure, HNTs were firstly purified via washing/centrifugation process and dried at 80 °C in a vacuum oven for a whole night. 95 g ethanol water solution (95%) was adjusted to pH 5 with acetic acid, and then 5 g AEPTMS was dissolved in above mixture and 15 min was required for hydrolysis of AEAPTMS under vigorously stirring. Next, 10 g HNTs were added and the whole mixture was kept refluxing at 80 °C for 6 h. The product was purified via washing/centrifugation process with ethanol and deionized water to remove dissociative AEAPTMS or hydrolysis byproduct. Last, the functionalized HNTs were dried in vacuum oven under at 80 °C for 12 h and used for further experiments.

2.3. Loading of noble metal NPs (Rh, Pt, Pd) on N-HNTs

To prepare rhodium and platinum NPs decorated silanized HNTs (Rh–N-HNTs, Pt–N-HNTs), 100 mg of the purified N-HNTs powder was added in 50 mL deionized water, and the suspension was dispersed ultrasonically for 1 h at room temperature. Then 10 mL rhodium chloride (10 mM) or 10 mL chloroplatinic acid (10 mM) was added dropwise to the dispersion of N-HNTs, and the mixture was kept under vigorous stirring for 2 h at room temperature. Subsequently, 30 mg EGCG dissolved in 5 mL H_2O was added and then the mixture was heated to 65 °C. After reaction for 6 ~ 7 h, the color of the sample changed, suggesting the formation of noble metal NPs, and the products were purified and centrifuged for three times using ethanol and deionized water, respectively, to remove excess EGCG, meanwhile, the supernatant was tested by UV–vis spectrophotometer to make sure the catalysts are clean before evaluation of catalytic activity. To prepare palladium NPs decorated N-HNTs (Pd–N-HNTs), 35 °C was maintained during reduction process, and other synthesis steps were the same as mentioned above. According to the X-ray photoelectron spectra analysis, the relative ratio of metal NPs loaded on Rh–N-HNTs, Pt–N-HNTs, and Pd–N-HNTs is 1.41%, 1.37%, and 1.18%, respectively.

2.4. Evaluation of catalytic activity

The catalytic activity of the synthesized catalysts (Rh–N-HNTs, Pt–N-HNTs, Pd–N-HNTs) was measured under identical catalytic reduction reaction of 4-NP–4-AP. Typically, 5 mg catalyst was added into fresh made $NaBH_4$ solution (100 mL, 25 mM) under vigorous stirring for 20 min at room temperature to make sure the catalyst dispersed uniformly in the solution. Subsequently, 4-NP aqueous solution (5 mL, 1 mM) was added, and the yellow suspension became colorless within 10 min. Meanwhile, the absorption spectra of the supernatant, were recorded by UV–vis spectrophotometer with an interval of 60 s. Typically, about 3 mL of the solution was withdrawn from the reaction system using a syringe, and then the syringe was equipped with a one-off filter. Thus, the supernatant was obtained by injecting the solution through the filter to the cuvette for test, leaving the HNTs loaded with metal NPs on the filter. The aperture of the membrane in the filter is 0.22 μm, which is efficient for the filtration of the catalyst. The maximum values of the absorption peaks at 400 nm for the obtained supernatant in the UV–vis spectra were recorded in order to evaluate the efficiency of the catalyst. Rh–N-HNTs catalyst was selected as an example and used for five successive cycles. The catalysts were separated after reaction by centrifugation at 8000 rpm for 5 min. The sediment was purified and centrifuged for several times with deionized water, and reused for next cycle reaction and the yellow suspension became colorless within 10 min every time. As a control, another sample was carried out without catalyst under the same condition.

2.5. Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 5700 spectrophotometer. TEM images were obtained with a JSM-2100 transmission electron microscopy (JEOL, Japan) at an acceleration voltage of 200 kV. XRD patterns of the HNTs characterized with a SIEMENS Diffraktometer D5000 X-ray diffractometer using Cu Kα radiation source at 35 kV, with a scan rate of $2\theta\,s^{-1}$ in the 2θ range of 10–80°. The morphology of HNTs and N-HNTs were observed by a ULTRA-55 field-emission scanning electron microscopy (FE-SEM) at an acceleration voltage of 3 kV. X-ray photoelectron spectra of N-HNTs, Rh–N-HNTs, Pt–N-HNTs, and Pd–N-HNTs were recorded using an X-ray photoelectron spectrometer (Kratos Axis Ultra DLD) with an aluminum (mono) Kα source (1486.6 eV). The aluminum Kα source was operated at 15 kV and 10 mA. The catalytic reduction reaction of 4-NP–4-AP was recorded at the absorption band 300–500 nm in the UV–vis spectra using a U-3010 UV–vis spectrophotometer (Hitachi).