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Materials Research Bulletin



journal homepage: www.elsevier.com/locate/matresbu

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



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ARTICLE INFO

Article history: Received 14 June 2014 Received in revised form 13 October 2014 Accepted 17 October 2014 Available online 18 October 2014

Keywords: A. Nanostructures D. Catalytic properties

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.

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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 NaBH₄, 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 M Ω , 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 2h at room temperature. Subsequently, 30 mg EGCG dissolved in 5 mL H₂O was added and then the mixture was heated to 65 °C. After reaction for $6 \sim 7 \text{ h}$, 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 NaBH₄ 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 $0.22 \,\mu\text{m}$, 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 K α 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) K α source (1486.6 eV). The aluminum K α 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).

3. Results and discussion

3.1. Morphology, characteristics of HNTs, and functionalization of HNTs using AEAPTMS

The structure and morphology of HNTs were observed by TEM and FE-SEM. Fig. 1 a and b is the typical FE-SEM images of the purified HNTs at different magnification, which display the cylinder-shaped nanostructure and polydispersity in length. The TEM image in Fig. 1 c shows the hollow tubular structure of HNTs with the inner and outer diameter of about 15–20 nm and 40–70 nm, respectively. What is more, Fig. 1 d shows the XRD patterns of the HNTs, revealing the silicate nature of the clay mineral.

The FT-IR spectra of the HNTs, N-HNTs, Rh-N-HNTs were used to investigate the composition and structure of the resultant samples. The characteristic peaks of HNTs occurred at 3698 cm⁻¹, 3623 cm^{-1} , and 1635 cm^{-1} are attributed to O–H stretching of inner-surface hydroxyl groups, O–H stretching of inner hydroxyl groups, and deformation of water, respectively. Another two characteristic peaks at 1107 and 1033 cm⁻¹ correspond to in-plane stretching of Si-O in HNTs. Compared with the curves of N-HNTs in Fig. 2b and Rh-N-HNTs in Fig. 2c, most of the peaks for HNTs maintained, which indicates that the main crystal structures of HNTs are preserved in N-HNTs and Rh-N-HNTs after modification and loading of Rh NPs. The newly emerged peaks at 2927 cm⁻¹, 2860 cm⁻¹ appear in curve b and curve c are attributed to C–H asymmetric and symmetric stretching vibration, respectively. Besides, a broad band with a maximum at 3440 cm⁻¹ occurred in sample b and sample c, which is assigned to the N-H stretching vibration, indicating that silane coupling agent (AEPTMS), the sole source for C–H and N–H, has been successfully grafted onto HNTs. What's more, the intensity of Si-O in-plane stretching in curve b and curve c become relatively narrow and increase, implying the Si-O groups in AEAPTMS have been successfully grafted onto the HNTs. The above FT-IR results demonstrate that HNTs are easily modified by AEPTMS and the amine groups $(-NH_2, -NH_-)$ designed as the functional group are successfully detected in N-HNTs and Rh-N-HNTs.

3.2. In situ synthesis of noble metallic nanoparticles on N-HNTs

Since HNTs are functionalized with amino groups by APTEMS, they are expected to serve as substrates for complexation of noble metallic NPs, in which amino groups are the active sites [33]. Amino groups can electrostatically complex with aqueous negative-charged ions (RhCl₆^{2–}, PtCl₆^{2–}, and PdCl₄^{2–}), especially when they are exposed in acid condition that can promote the protonation of amino groups and exhibit adsorption ability for metallic ions. Subsequently, NPs are in-situ formed by chemical reduction process. In this work, we chose EGCG as both a mild and environment-friendly reducing agent and stabilizer. RhCl₃ solution was first selected as an example due to the excellent physical and chemical properties in various catalytic reactions [34].

FE-SEM images in Fig. 3a show that the morphology and structure of Rh–N-HNTs do not get noticeable change, indicating the main crystal structure of HNTs are preserved after loading Rh nanoparticles (Rh NPs). As shown in Fig. 3c,d, and f, ultrafine dots are found to exist both on the inside and outside surface of N-HNTs, and these Rh NPs distribute densely and uniformly. The chemical analysis by energy-dispersive X-ray spectroscopy (EDS, inset in Fig. 3b) confirms that these small dots are Rh NPs. Fig 3f shows the HRTEM image of Rh–N-HNTs, the lattice finger of an interplanar spacing of 0.21 nm is according with the (111) plane of Rh NPs. In addition, the sample appearance changed from oyster white to field gray during reducing process, which is believed to be caused by plasmon resonance on Rh nanoparticle surface. The average diameter of Rh NPs is calculated about 1.2 nm and the particle distribution is shown in the inset in Fig. 3b. XRD pattern of Rh-N-HNTs exhibited no Bragg reflection can be obviously detected. which can be ascribed to the ultrafine particle size and low content of Rh NPs on N-HNT (not shown).

To verify the chelating effect of Rh NPs with amino groups, XPS survey was performed in order to get more detailed information of Rh atoms in Rh–N-HNTs. The chemical state of Rh NPs immobilized on the functionalized HNTs is presented in Fig. 4. As observed in Fig. 4a, the intense doublets emerged at 312.5 eV and 307.8 eV correspond well with Rh 3d₃ and Rh 3d₅ binding energies,



Fig. 1. (a) and (b) FE-SEM images of purified HNTs at different higher magnification; (c) TEM image of HNTs; (d) XRD patterns of HNTs (h: HNTs).



Fig. 2. FT-IR spectra of (a) HNTs, (b) N-HNTs, and (c) Rh-N-HNTs.

respectively. Compared with the zero valent Rh^0 (311.9 eV at Rh 3d₃, 307.2 eV at Rh 3d₅), the changes in binding energy indicate that there exist interaction between Rh NPs and surrounding chemicals, which is mainly caused by the chelating effect from amino groups. Because Rh NPs could be stabilized and firmly attached to the $-NH_2$ and -NH- through the strong metal/amine

coordination interactions between the empty d orbital of Rh atom and the free pair of electrons on the N atom of the amino groups. Hence, the N atoms for N-HNTs and Rh–N-HNTs were testified by XPS, and the results are shown in Fig. 4b and c. In Fig. 4b, two peaks occurred at 401.5 eV and 399.3 eV, standing for two types of N $(-NH_2, -NH-)$ in AEAPTMS grafted on HNTs. However, the binding energies of N 1 s observed in Fig. 4c shift to 402.1 eV and 400.1 eV, respectively, which can be attributed to the strong interaction between Rh NPs and amino groups. Overall, above results confirm the chelating effects between Rh NPs and amino groups. Therefore, the amino modified HNTs successfully act as supports for ultrafine Rh NPs which are in situ synthesized at the active sites provided by amino groups on N-HNTs.

Similarly, owing to the expected coordination between $PtCl_6^{2-}$, $PdCl_4^{2-}$, and $-NH_2$, the N-HNTs was exploited as scaffolds to prepare Pt NPs and Pd NPs with the reduction of EGCG. SEM studies of Pt–N-HNTs and Pd–N-HNTs (not shown) also revealed that the nanotubes were several micrometers in length and no metal nanoparticles can be clearly distinguished under the present resolution the same to Rh–N-HNTs sample, indicating that Pt NPs and Pd NPs are ultrafine too. TEM images of Pt–N-HNTs and Pd–N-HNTs show that Pt NPs, and Pd NPs are distributed on the surface of N-HNTs densely and uniformly, as evidenced in Fig. 5. As shown in Fig. 5a and b, an abundance of Pt NPs with an average diameter about 1.3 nm (inset in Fig. 5c) can be seen on both outside and



Fig. 3. (a) FE-SEM image of Rh–N-HNTs; (b) EDX spectrum of Rh–N-HNTs, the inset is the particle size distribution of Rh NPs on N-HNTs; (c)–(f) TEM images of Rh–N-HNTs under different magnifications, the inset in (d) shows the corresponding digital image of Rh–N-HNTs suspension.



Fig. 4. XPS spectra of (a) Rh 3d of Rh-HNTs; (b) N 1s of N-HNTs and (c) N 1s of Rh-N-HNTs.

inside surface of N-HNTs. In addition, the appearance of the N-HNTs suspension turned from oyster white to claybank with the reduction of $PtCl_6^{2-}$, suggesting the formation of Pt NPs, and it is in accordance with the EDS result in Fig. 5c.

For the preparation of Pd–N-HNTs, the synthetic process is a little different from the protocol of Rh–N-HNTs, and Pt–N-HNTs in temperature. In this work, H_2PdCl_4 solution was prepared by dissolving PdCl₂ powder in diluted hydrochloric acid (pH 2). It is believed that acid condition would promote the protonation of amino groups, so more dissociative $PdCl_4^{2-}$ will chelate with amino groups by electrostatic attraction. Furthermore, if the reduction is performed under relative high temperature, Pd crystal

nucleus would be synthesized in a very short time and are apt to aggregation to form large NPs. Therefore, the reduction temperature of $PdCl_4^{2-}$ in the present study was set at 35 °C. Subsequently, the precursor $PdCl_4^{2-}$ is reduced to Pd NPs with the addition of EGCG, giving rise to a clear-brown suspension (inset in Fig. 5e). The average Pd particle size is near 1.4 nm, which can be seen from the TEM images in Fig. 5d and e and the size distribution histogram in Fig. 5f. The EDS spectrum in Fig. 5f confirms the presence of Pd in Pd–N-HNTs.

According to above results, it is supposed that the chelating effects of noble metal ions with the amino groups grafted on HNTs and the phenolic hydroxyls in EGCG molecules play a crucial role in



Fig. 5. TEM images of (a) and (b) Pt–N-HNTs, (c) and (d) Pd–N-HNTs; EDX spectra of Pt–N-HNTs (e), Pd–N-HNTs (f). The insets in (b) and (e) show the corresponding digital image of the suspension of each sample. The insets in (c) and (f) are the size distribution histograms of Pt and Pd NPs, respectively.



Fig. 6. (a) Time-dependent UV-vis absorbance of 4-NP catalyzed by Rh–N-HNTs; (b) catalytic conversion of 4-NP by using Rh–N-HNTs for five cycles; (c) time-dependent conversion of 4-NP reduction catalyzed by Rh–N-HNTs, Pt–N-HNTs, N-HNTs, respectively; (d) $ln(C_t/C_0)$ versus reaction time.

the synthesis of ultrafine NPs. The N-HNTs possess a large amount of amino groups, which can "anchor" noble metal ions in the solution through chelating effect. With the addition of EGCG, multiple phenolic hydroxyls were introduced to the reaction system, resulting in increased binding sites for noble metal ions through chelating effect. The high density phenolic hydroxyls groups in EGCG acted as the reducing agent and reduced the noble metal ions to metal NP accompanying the oxidation of phenolic hydroxyls to quinones, finally, the synthesized noble metal NPs were firmly fixed on the N-HNTs with the stabilization effect caused by the quinones. Besides, mainly because of the space steric hindrance caused by the basal material (N-HNTs), the neighboring small NPs cannot easily collide with each other to aggregate to form large NPs.

3.3. Catalytic performance

The catalytic reduction of aromatic nitrocompounds using noble metal NPs in the presence of $NaBH_4$ has been widely investigated for the efficient preparation of aromatic



Fig. 7. TEM images of (a) Rh-N-HNTs, (b) Pt-N-HNTs, and (c) Pd-N-HNTs after catalytic reactions.

aminocompounds [35-40]. Therefore, the reduction of 4-NP-4-AP with an excess amount of NaBH₄ was used as a model system to evaluate the catalytic activity of the prepared nanocomposite catalysts. The results showed that the reaction did not proceed in the absence of nanocomposite catalysts during a long period of time. After the nanotubular catalyst, Rh-N-HNTs, was added, the color of the mixture changed from yellow to colorless within 600 s, indicating the complete conversion of 4-NP-4-AP. Fig. 6a shows the UV-vis spectra of the reaction mixture containing Rh-N-HNTs catalyst recorded at different time during the reaction process. The characteristic absorption peak of 4-NP at 400 nm gradually decreased. After reaction for a given time, the Rh-N-HNTs catalyst was separated by simple centrifugation from the mixture and washed several times by deionized water, then reused in the next cycle reaction. As shown in Fig. 6b, the Rh-N-HNTs catalyst was recycled for five times, and there is almost no decrease in reaction conversion. These results clearly indicate that Rh-N-HNTs catalyst has good catalytic efficiency and high stability.

The catalytic activities of Rh–N-HNTs, Pt–N-HNTs, and Pd–N-HNTs are compared in the reduction of 4-NP. As Fig. 6c shows, the reaction conversion is calculated from C_t/C_0 , where C_t is the 4-NP concentration at time t and C_0 is the initial 4-NP concentration, measured from the relative intensity of UV–vis absorbance (A_t/A_0) at 400 nm. In the presence of Pt–N-HNTs and Pd–N-HNTs catalyst, the reaction completed within 600 s, similar to Rh–N-HNTs in reaction efficiency. Fig. 7d shows the ln (C_t/C_0) versus reaction time for the reduction of 4-NP by using the three kind of catalysts, and the apparent rate constant were directly calculated from the slops of the straight lines. The reaction rate constant are calculated to be $k_{\rm Rh–N-HNTs} \sim 0.0069 \, {\rm s}^{-1}$, $k_{\rm Pt–N-HNTs} \sim 0.00727 \, {\rm s}^{-1}$, $k_{\rm Pd–N-HNTs} \sim 0.00642 \, {\rm s}_{-1}$, respectively.

In fact, the morphology and structure of the three catalysts, including the size and the density of noble metal NPs, did not show obvious change after five cycles of the catalytic reactions, as shown in Fig. 7. Above results exhibit that the noble metal NPs anchored on the outside and inside surface of HNTs with high specific surface area and chemical stability have perfect catalytic activity and efficiency, which can be applied to many other catalytic systems.

4. Conclusions

In summary, ultrafine noble metal NPs (Rh, Pt, and Pd) with the diameter less than 2 nm have been successfully synthesized by in situ green reduction. They are immobilized densely and uniformly on both the inside and outside surface of amino functionalized HNTs. The as-prepared Rh–N-HNTs, Pt–N-HNTs, and Pd–N-HNTs nanocomposite catalysts exhibited excellent catalytic activity in the reduction of 4-NP and Rh–N-HNTs showed satisfactory cycling stability. Considering the fact that amino groups can host a series of ions, the N-HNTs are anticipated to be exploited as a platform to synthesize different metal, metal alloy, or metal oxide nanoparticles, the resulting materials may have great use in catalysis and photoelectric conversion application due to their availability, formability, high specific surface area, and chemical stability.

Acknowledgements

This work was supported by the project of the National Natural Science Foundation of China (NSFC) (51373154), and the 521 Talent Project of Zhejiang Sci-Tech University.

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