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Salt template-assisted in situ construction of Ru nanoclusters and porous carbon: Excellent catalysts toward hydrogen evolution, ammonia-borane hydrolysis, and 4-nitrophenol reduction

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Sustainable yet effective manufacture of supported metal nanoclusters (NCs) with high performance for catalytic applications is worthwhile but remains a big challenge. Here, we report a salt template-assisted approach through direct calcination of the mixture of ruthenium oleate precursor and sodium sulfate for one-step synthesis of Ru NCs solidly loaded on the simultaneously formed porous carbon (Ru/PC). In this case, both the salt template of sodium sulfate and one-step approach play key roles in forming surface-clean Ru NCs with a good dispersion to supply abundant accessible active sites, and constructing three-dimensional architecture to boost the mass and/or electron transport during the applications. Taking advantages of these features, Ru/PC as the catalyst shows excellent activities for electrocatalytic hydrogen evolution with an overpotential of 21 mV at 10 mA cm⁻² in 1.0 M KOH, ammonia-borane hydrolysis with a high turnover frequency of 744 min⁻¹, and a high activity for 4-nitrophenol reduction with a reaction rate of 1.29 min⁻¹ at room temperature. The catalyst also shows high stability and reusability for the investigated reactions. This study presents a green yet sustainable method to produce supported NCs for versatile catalytic applications.

Introduction

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Supported metal nanoclusters (SMNCs) with metal size less than 2 nm have received continuous interest for catalytic applications because of their abundant surface active sites originated from the increased atom utilization compared with their counterpart of supported metal nanoparticles (NPs).¹⁻³ Owing to the high surface energy, however, the aggregation and heterogeneous distribution of metal nanoclusters (NCs) are generally unavoidable during synthetic procedure, which considerably prohibit their practical applications. Thus, stabilizing molecules and/or surface capping agents are employed for prohibiting the aggregation and controlling the size of metal NCs. However, these used agents also cover the active sites, resulting in the decline of catalytic activity. Moreover, the extra operation for removal of the organic species unavoidably causes the sintering of metal NCs, leading to the loss of active surface areas.⁴ In contrast, the introduction of heteroatoms on solid substrates has been demonstrated as an efficient strategy for synthesis of metal NCs due to the supplement of an appropriate coordination environment from the doped-heteroatoms.5-7 However, the generation of hazardous gases attributing to the application of heteroatom containing functional agents arouses seriously environmental problems.^{8, 9} Furthermore, most of previous developed synthetic methods for SMNCs generally need large amount of solvents and aggressive reduction atmosphere (H₂) or chemical agents (e.g. NaBH₄, hydrazine hydrate, alcohols), both of which are cost-ineffectiveness and environmental-friendlessness.¹⁰ Therefore, developing green and sustainable strategy to produce SMNCs in a good distribution is of considerable importance.

Notably, carbon materials with the features of large specific surface areas (SSAs), tunable physicochemical properties and cost-effective scaled-up synthesis as the catalyst supports to prepare SMNCs have sparked a surge of interest.^{11, 12} To increase the SSAs for a good load of metal NCs in a fine size/distribution and construct a three-dimensional (3D) architecture for an efficient mass and/or electron transport during the applications, hard templates, such as porous silica, layered metal oxide, etc., have been widely introduced in the fabrication procedure of nanostructured carbon materials.13 Though many types of porous carbon materials have been obtained successfully through such route, however, the operation procedures are relatively complex and timeconsuming, especially the template elimination which involves in the use of corrosive chemicals and rigorous washing. Despite much effort has been devoted to etching the templates, few template residues still present in the product, which will pollute the after synthesized catalysts, thus disturbing the expression of intrinsic activity of catalysts. One of class of hard templates, inorganic salts have drown many attentions in recent years because they not only show a similar function as other hard templates for synthesis of porous carbon materials but also

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display a high solubility in water.¹⁴⁻¹⁹ These advantages guarantee the subsequent procedure of template elimination is environment-friendly and simultaneously ensure the inorganic salt could be removed rapidly and fully, thus, achieving satisfactory porous carbon materials to produce SMNCs with an excellently catalytic activity.²⁰ It should be noted that most of the carbon-based SMNCs were mainly prepared through carbon support synthesis and subsequent load of metal NCs. Compared with the two-step strategy, the in-situ pyrolysis of metal-organic molecule or polymer for one-step synthesis of carbon-based SMNCs without use of organic solvents, stabilizing and reducing agents is relatively convenient and low-cost. For instance, Lin et al. employed salt microcrystal as salt template for successful synthesis of Rh NCs deposited on carbon nanosheets, which showed high electrocatalytic activities for oxygen reduction and hydrogenation reactions.²¹ Based on the assistance of salt template, the developed Ni₃Fe/N-C as the electrocatalyst showed boosted activities for both oxygen reduction and evolution reactions.²² Despite these advances, the following shortages of salt template method need to be overcome. First, the roles of salt template in the synthetic process were not well studied. Second, it is still difficult to control the dispersion and the size of metal NCs during high temperature pyrolysis. Third, there still have room to optimize the synthesis technologies of carbon-based SMNCs for multiple catalytic applications. Based on above, developing efficient one-step synthesis strategy that is capable of largely improving the SSAs and constructing a welldefined nanostructure is a desirable but challenging goal.

Here, we report a simple yet efficient salt template-assisted approach through direct pyrolyzing the mixture of ruthenium oleate precursor and sodium sulfate for one-step synthesis of SMNCs, in which Ru NCs in a diameter of 1.50 nm are highly distributed on the simultaneously produced porous carbon (Ru/PC). It is discovered that sodium sulfate dominated the generation of mesopores, enlarged the pore structure, and thus promoted the formation of 3D architecture. The achieved Ru/PC displayed excellent activities toward electrochemical hydrogen evolution with an overpotential of 21 mV at 10 mA cm⁻² in 1.0 M KOH, ammonia-borane (AB) hydrolysis with a high turnover frequency of 744 min⁻¹, and a high activity for 4nitrophenol reduction with a reaction rate of 1.29 min⁻¹ at room temperature. The catalyst also shows high stability and reusability for the reactions. Compared with prior reported strategies for synthesis of the carbon-based SMNCs, this developed method stands out for the following features. a) The entire procedure avoids the use of a large amount of surfactant and reducing agents, thus saving cost and reducing environmental pollution. b) The salt template can be removed by washing with the green solvent of water, thus overcomes the shortcomings of soft template-based method and especially the hard template-based method which generally requires strong acid or alkali to remove the templates; Moreover, the sodium sulfate can be easily reused through recrystallization, making the synthesis cost-saving and sustainable. c) The highly efficient Ru/PC as the catalyst with an excellent activity and a strong durability can be applied in various catalytic reactions, i.e., electrocatalytic hydrogen evolution, AB hydrolysis, riend niffer nitrophenol reduction. Overall, this reported safe template assisted approach for the synthesis of SMNCs is convenient, economical, and environmental-friendly, which coincides with many of the principles of green chemistry and sustainability, such as a) the wide available starting materials, b) atom economy from the multiple roles of the achieved catalysts in catalytic applications, c) the entire process not involving the

catalytic applications, c) the entire process not involving the organic species (organic solvent, surfactants, and surface capping agents), and d) economic for the simplified synthetic process without using reducing agents for reducing the metal precursor and chemic agents for the template elimination, and the recycled salt template of sodium sulfate.

Results and discussion



Scheme 1. Synthetic illustration for synthesis of Ru/PC.

The preparation procedure for Ru/PC through one-step strategy by a green and sustainable salt template-assisted pathway is illustrated in Scheme 1. First, potassium oleate and ruthenium (III) chloride were reacted to form the ruthenium oleate complex, which could be applied as metal precursor and carbon source of SMNCs. Then, appropriate amount of ruthenium oleate was introduced into the large quantity to form a uniform mixture. When this mixture pyrolysis under Ar atmosphere, the ligand of ruthenium oleate gradually carbonized to form the PC under the assistance of salt template of sodium sulfate. At the same time, Ru ions were reduced to Ru NCs by the just generated PC and then loaded on this PC matrix. Ultrafine, surface-clean and uniformly dispersed Ru NCs decorated on PC matrix were easily obtained after removal of the sodium sulfate by water rinsing. The Ru loading in Ru/PC was 3.49 wt%, as determined by inductively coupled plasma-optical emission spectrometry (ICP-OES), which is very close to that measured by thermal gravimetric analysis (TGA) (3.20 wt%) (Fig. S1).

The morphology and microstructure of Ru/PC were firstly characterized by TEM technique. It can be clearly seen in Fig. 1a, b that NCs are uniformly anchored on the PC matrix. The average size of NCs was determined to be 1.50 nm with a narrow size distribution ranging from 0.50 to 2.50 nm (Fig. 1a inset). High-resolution TEM (HRTEM) was used to verify the crystal structure of detected NCs (Fig. 1b inset). It was found that the NCs are highly crystalline with typical interplanar spacing of 0.20 nm, corresponding well to the characteristic feature of the (101) facet of the metallic Ru (JCPDS No. 06-0663).²³ This result clearly illustrate that these NCs are metal nanocrystals. Scanning TEM-energy dispersive X-ray (STEM-EDX) elemental mapping images demonstrate that Ru, C and O are homogeneously distributed across matrix without visible S signal (Fig. 1c-f). The selected area electron diffraction (SAED)

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pattern shows an obvious diffraction ring which can be indexed to the Ru (101) plane (Fig. 1g). To demonstrate the superiority of this developed synthetic strategy, two contrast samples were carefully designed, in which one was synthesized in parallel by the same approach as that for Ru/PC except for no addition of sodium sulfate (Ru/C) and another was prepared by impregnation method using pre-synthesized PC as the carbon matrix (Ru/PC-IM). From the TEM images, Ru NPs in the diameters of 3.10 (Fig. 2a, b) and 5.78 nm (Fig. 2c, d) with a wide size distribution were clearly observed in Ru/C and Ru/PC-IM, respectively, suggesting that both of sodium sulfate and onestep approach are very key for the formation of ultrafine and uniformly dispersed Ru NCs in this work.



Fig. 1 (a, b) TEM images, (c-f) STEM-EDX mapping images, and (g) SAED pattern for Ru/PC. Inset in (a) is the size distribution of NCs but that in (b) is the HRTEM image of NCs.

The crystal structures of samples were further studied by Xray diffraction (XRD). The diffraction pattern for PC has two broad peaks at 24 and 43°, which were characteristic of the (002) and (101) planes of graphitic carbon, respectively (Fig. 3a). Only one weak but broad diffraction peak at 44° attributing to the Ru (101) plane (JCPDS No. 06-0663) was observed in both Ru/PC and Ru/C samples, which should be ascribed to the low loading and/or small-size of Ru NCs in the samples. For Ru/PC-IM, distinct and sharp diffraction peaks of metallic Ru are detected, indicating the existence of large Ru NPs in this sample. These results are consistent of the TEM observations.

Brunauer-Emmett-Teller (BET) gas sorptometry measurement was performed to study the textural structure of Ru/PC. Fig. 3b depicts the N₂ adsorption/desorption isotherm and the pore-size distribution (inset) of Ru/PC. The BET surface area of Ru/PC determined from N₂ isotherm at -197 $^{\circ}$ C was found to be 575.16 m² g⁻¹. The isotherm was identified as type II , which was characteristic of mesoporous material. The pore-

size distribution derived from the isotherm discovers the sample with abundant mesopores in an average size of 7.38% fm. The single point total volume of pores at P/P₀= 0.99 is 0.73 cm³ g⁻¹. The large SSAs and pore volume of Ru/PC should be attributed to the assistance of salt template of sodium sulfate, which are expected to facilitate not only the load of metal NCs in a ultrafine size and good dispersion but also the mass transport for catalytic applications.²⁴



Fig. 2 TEM images for (a, b) Ru/C and (c, d) Ru/PC-IM. Insets in (a, c) are the size distributions of Ru NPs.

Surface analysis of Ru/PC was performed by X-ray photoelectron spectroscopy (XPS). XPS survey spectrum (Fig. 3c) evidence the coexistence of Ru, C and O elements in the sample, in agreement well with the result of EDX experiment. According to XPS analysis, the contents of Ru, C and O in Ru/PC were measured to be 6.82, 85.53 and 7.65 wt%, respectively (Table S1). It should be pointed out that Ru loading of Ru/PC from ICP-OES (3.49 wt%) and TGA (3.20 wt%) analysis is much lower than the outmost surface Ru content (6.82 wt%) measured by XPS. This result helps us to conclude that the tiny Ru NCs are anchored on the surface instead of embedded in the PC.²⁵ The high-resolution Ru spectrum was recorded to analyse the chemical state of Ru active component. In this work the Ru3p spectrum instead of Ru3d spectrum was used for further study since the Ru3d overlaps with C1s in the XPS detection (Fig. 3d). The Ru3p core level consists of the spin-orbit components of Ru3P_{3/2} and Ru3p_{1/2} with the binding energies of 462.5 and 484.8 eV, respectively. This observation suggests the formation of metallic Ru in the sample.⁶ Compared with the standard binding energy of Ru⁰, a shift of 0.3 eV was observed in Ru/PC, indicating a strong interaction between metal and carbon support.^{26, 27} The C1s and O1s spectra were further recorded to obtain more information about the oxygen-containing species. The C1s spectrum was fitted into three peaks with binding energy of 284.7, 286.1, and 289.2 eV, which are accounted for

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C-C, C-O and O=C-O bonds, respectively (Fig. 3e).²⁸ The O1s spectrum was deconvoluted into two components with binding energy of 531.8 and 533.2 eV,²⁹ which are ascribed to bridging hydroxyls and physically absorbed water, respectively (Fig. 3f).³⁰⁻³⁴ These results demonstrate the presence of massive oxygen-containing groups on the surface of catalyst, which enables a good dispersion of Ru NCs on PC matrix.



Fig. 3 (a) XRD patterns of PC, Ru/PC, Ru/C and Ru/PC-IM. (b) N₂ sorption isotherm curve of Ru/PC (Inset is the pore size distribution). (c) XPS survey and high-resolution XPS spectra of (d) Ru 3p, (e) C 1s and (f) O 1s for Ru/PC.

Above characterization results suggest that Ru NCs in an ultrafine size and good dispersion with a clean surface loaded on the PC matrix have been successfully prepared via our developed one-step approach. It is well-documented that the catalytic reaction over a metal catalyst is commonly sizedependance.^{35, 36} One can thus expect that the small-sized Ru NCs with narrow size distribution and clean surface in Ru/PC can provide an abundance of accessible active sites, leading to a distinct performance for catalytic applications.³⁶

Note that the Ru NPs in control sample of Ru/C prepared without the sodium sulphate template are relatively large with size of 3.10 nm, indicating the vital role of sodium sulphate template in maintaining the small size of Ru NCs during the synthetic process. Except for as template, sodium sulfate has been reported to be act as sulfur source for the synthesis of molybdenum disulphide.³⁷ However, the observations from EDX and XPS suggest the undetectable S element in the Ru/PC sample, suggesting that in this case sodium sulfate may not serve as the S source for doping in Ru/PC. This was further confirmed by a control experiment conducted via direct calcination of conductive carbon/sodium sulfate, in which no any S signal was detected (Fig. S2). Nevertheless, as demonstrated by N₂ sorption measurements, this operation decreases the SSAs but enlarge the pore volume and pore size (Fig. S3 and Table S2, S3). According to these results, the roles of sodium sulfate for Ru/PC synthesis can be concluded as follows: a) as a soluble template to produce nanostructured hybrid of Ru/PC; b) acting as a pore-extending agent to enlarge the pore volume and pore size. Additionally, it should be pointed out that in this work the size and dispersion of Ru NCs is still correlated to the synthetic methods. For a

demonstration, a control sample (Ru/PC-IM) was done through impregnation method using PC as the matrix. Note that the RU NPs in Ru/PC-IM show a size of 5.78 nm, much larger than that of Ru/C (3.10 nm) and the NCs of Ru/PC (1.50 nm), which strongly demonstrates the superiority of our developed salt template-assisted strategy through one-step pyrolysis of the mixture of ruthenium oleate and sodium sulfate.

Hydrogen evolution from water splitting



Fig. 4 (a) Polarization curves of PC, 20 wt% Pt/C, Ru/C, Ru/PC-IM, and Ru/PC in 1.0 M KOH. (b) Comparison of overpotential (η_{10}) with Ru/PC, Ru/C, Ru/PC-IM and previous Ru based nanocatalysts. (c) TOF values, mass activity, and tafel slopes for Ru/C, Ru/PC-IM, and Ru/PC. (d) Tafel plots and (e) capacitive current at middle potential of CV curves as function of scan rates for Ru/C, Ru/PC-IM and Ru/PC. (f) Polarization curves of Ru/PC before and after 1000 cycles (inset: V-t curve at 10 mA cm⁻² for Ru/PC).

Hydrogen evolution through electrocatalyic water dissociation has been regarded as green and sustainable route in comparison with traditional methods.³⁸⁻⁴¹ Pt has been demonstrated as the sate-of-the-art electrocatalyst for HER as it shows highly intrinsic activity. Considering the high-cost and low reserve of Pt, however, non-Pt metals (Ru,⁴²⁻⁴⁶ Rh,^{8, 47-52} and lr^{7,} ⁵³⁻⁵⁵) have been explored as alternatives for HER electrocatalysis. Among the metals, Ru is cost-effective with about ~4% price of Pt, which enables its widespread used as electrocatalyst for HER.56, 57 Here, our developed Ru/PC was firstly employed for HER in alkaline solution. For comparison, control experiments using PC, Ru/C, Ru/PC-IM and commercial

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Pt/C as electrocatalysts for HER were also performed. As shown in Fig. 4a, Ru/PC displays the best electrolytic activity with low overpotential of 21 mV at 10 mA cm⁻², which is lower than that of Ru/C (η_{10} =46 mV), Ru/PC-IM (η_{10} =86 mV) and Pt/C (η_{10} =23 mV). It is noteworthy that Ru/PC also displays a higher activity than many recently reported Ru-based nanocatalysts, including Ru@CN (η_{10} =32 mV)⁵⁶, NiO/Ru@Ni (η_{10} =39 mV)⁵⁸, Ru/CoO $(\eta_{10}=55 \text{ mV})^{59}$, Ru_2P $(\eta_{10}=50 \text{ mV})^{60}$, Pd@Ru $(\eta_{10}=30 \text{ mV})^{61}$, $\text{RuP}_{x} @\text{NPC} ~(\eta_{10} \text{=} 74 \text{ mV})^{62}$ (Fig. 4b and Table S4). For exact comparison, the catalytic activity of HER was normalized based on the metal loading of each catalyst. Notably, Ru/PC still presents the highest mass activity (884.8 A g⁻¹) for HER at only an overpotential of 30 mV, much higher than that of Ru/C (242.3 A g⁻¹) and Ru/PC-IM (97.2 A g⁻¹) (Fig. 4c). The TOF values for three samples were also calculated according to the method illustrated in Supporting Information. As shown in Fig. 4c, Ru/PC exhibits the higest TOF of 0.20 s⁻¹, while Ru/PC-IM shows the lowest TOF of 0.019 s⁻¹, indicating the superior intrinsic activity of Ru/PC for HER.

The superior electrocatalytic activity of Ru/PC for HER can be further verified by studying the Tafel slope and capacitance of double layer (C_{dl}), which is in line with ECSA. The Tafel slopes of the samples at an overpotential of 30 mV are shown in Fig. 4c, d. Ru/PC exhibits the lowest Tafel slope of 46.6 mV dec⁻¹, while Ru/PC-IM shows the highest Tafel slope of 72.8 mV dec⁻¹, indicating the superior kinetics of Ru/PC for HER in alkinline solution. Generally, three typical reaction steps are presented for alkaline HER. The first step refers to the Volmer reaction, where a discharge route occurs with the generation of adsorbed H*. Afterward, the H* must undergo two separated routes including Heyrovsky and Tafel reactions to generate hydrogen⁵⁶. Consequently, the Volmer-Heyrovsky pathway should be explored to explain the mechisam for HER using Ru/PC as the electrocatalyst. Furthermore, it can be clearly seen that the $C_{d\mathrm{l}}$ increases as the size of metal NPs decrease. Ru/PC with the smallest Ru NCs (1.50 nm) gives the largest C_{dl} of 35.90 mF cm⁻² while Ru/PC-IM with the largest Ru NPs (5.78 nm) has the smallest C_{dl} of 9.60 mF cm⁻² (Figs. 4e and S4). The largest C_{dl} of Ru/PC means that abundant active sites are available for HER, leading to the highest catalytic activity. The stability test of Ru/PC for HER indicates a negligible variation of electrochemical HER activity before and after 1000 cycles (Fig. 4f). Moreover, the stability test by performing the V-t curve with continuous electrolysis for 11 h shows that the overpotentail of Ru/PC only has a slight decrease in alkaline solution (Fig. 4f inset). However, significant acitive loss is oberved for Ru/C and Ru/PC-IM after 1000 cycles (Figs. S5 and S6). The results suggest that the Ru/PC prepared by salt-template assisted synthesis has the highest stability for HER in alkaline medium. The slight durability loss of Ru/PC was ascribed to the increase of the size (3.37 nm) of Ru NPs during stability testing, as demonstrated by the TEM image of recovered Ru/PC (Fig. S7).

Catalytic hydrogen generation from AB



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Fig. 5 (a) Plots of hydrogen generation versus time for AB hydrolysis with Ru/PC, Ru/C and Ru/PC-IM (inset: TOF values). (b) Plots of hydrogen generation versus time for AB hydrolysis with Ru/PC at varied temperatures (inset: Arrhenius plot). (c) Plots of hydrogen generation versus time for reusability tests. (d) TOF values for each cycle.

AB is regarded as a potential and eco-friendly hydrogen source and has been widespread investigated for hydrogen production by various kinds of strategies including hydrolysis, thermolysis, and methanolysis.63 To study the catalytic performance of Ru/PC, Ru/C and Ru/PC-IM, AB hydrolysis to release hydrogen was chosen as the model reaction. Control experiments by using PC matrix showed negligible hydrogen evolution, whereas large amount of hydrogen was produced by Ru/PC, suggesting that Ru was the catalytic active sites for this reaction (Figs. 5a and S8). Note that the highest TOF value of 744 min⁻¹ was observed with AB and Ru concentrations of 200 and 0.6 mM, respectively, better than that of Ru/C (532 min⁻¹), Ru/PC-IM (217 min⁻¹), and many recently reported Ru based catalytic results (Fig. 5a and Table S5). The kinetic studies on hydrogen generation from AB catalyzed by Ru/PC were performed at varied Ru and AB concentrations. Figs. S9 and S10 show the hydrogen generation versus reaction time for AB hydrolysis over Ru/PC at varied AB and Ru concentrations. The hydrogen generation rate (HGR) versus Ru and AB concentrations both in logarithmic scales were constructed, respectively. The slope of 0.46 of ln rate versus In [AB] indicates the less much correlation between HGR and AB concentration for hydrolytic decompositon of AB with Ru/PC, but it does not follow a zero-order kinetic in accordance with previous results.⁶⁴ The slope of 0.94 of ln rate versus ln [Ru] leads to the conclusion that the hydrolytic decomposition of AB on Ru/PC is regarded as first-order with Ru concentration.⁵⁸

The time dependences of hydrogen evolution from AB hydrolysis at varied temperatures were conducted (Fig. 5b), from which the activation energy (E_a) was calculated by Arrhenius plot. The E_a value of AB hydrolysis over Ru/PC was 39.11 kJ/mol (Fig. 5b inset), lower than many previous Ru nanocatlysts (Table S5). The reusability of Ru/PC for AB

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hydrolysis was further explored. As illustrated in Fig. 5c, d, the Ru/PC still can completely catalyze AB hydrolysis to generate sufficient hydrogen after six reusability tests, whereas the TOF values decreased with increasing reusability tests, with 53.90% remained catalytic activity of initial run. However, the present Ru/PC still preserves comparable reusability for AB hydrolysis, compared with previous results of Ru nanocatalysts (Table S5). To clarify the activity loss, the recycled catalyst was characterized by TEM and XRD. As shown in Fig. S11, no visible characteristic peaks relative to Ru species were detected in the XRD pattern of reused Ru/PC. The TEM image of spent catalyst indicates the slight increase of the size of Ru NPs from 1.50 to 2.14 nm, which must be accounted for the activity loss.

Catalytic reduction of 4-NP

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Removal of 4-nitrophenol (4-NP) from wastewater is of significant importance in view of environment protection since 4-NP is a prevalent contaminant produced in industry and agriculture.^{65, 66} Therefore, the reduction of 4-NP toward 4-aminophenol (4-AP) in the presence of NaBH₄ was selected as a model reaction to further confirm the generality of Ru/PC. The conversion of 4-NP at different intervals was detected via



ultraviolet-visible spectroscopy (UV-Vis). A shift of absorption peak from 317 to 400 nm is observed when NaBH₄ solution is added because of the transformation of 4-NP into 4nitrophenolate ion (Fig. S12). When Ru/PC catalyst was added, the intensity of characteristic peak at 400 nm quickly declined. The reduction of 4-NP was completed within 5 min (Figs. 6a and S13). The rate constant (k) was calculated according to the pseudo-first-order kinetic equation (ln (C_t/C_0)=-kt), in which C_0 and C_t referred to the initial and residual concentration of substrate at the time intervals, respectively. A good linear correlation of ln (C_t/C_0) versus time was observed ($R^2 = 0.992$), further confirming the pseudo-first-order kinetic ADE & ADE reduction catalysed by Ru/PC. Consequently, the RU/PC has a very high reaction rate of 1.29 min⁻¹ for 4-NP reaction (Fig. 6a inset), which is higher than that of Ru/C (0.034 min⁻¹) and Ru/PC-IM (0.198 min⁻¹) under ambient conditions (Figs. 6b, c and S13), suggesting the generality and superiority of Ru/PC for the reaction. The reusability testing results for 4-NP reduction toward 4-AP show that Ru/PC was reusable for seven successive runs. Note that the conversion of 4-NP is still higher than 95% in the seventh recycling test compared with the initial one (99%), suggesting a good reusability of Ru/PC for 4-NP reduction (Fig. 6d). The slight decrease in 4-NP conversion with increasing recycling runs should be ascribed to the increased size of Ru NPs from 1.50 to 2.93 nm in the reused Ru/PC catalyst, which leads to the partial loss of active surface area (Fig. S14).

The excellent catalytic performances of Ru/PC for the hydrogen evolution, AB hydrolysis, and 4-nitrophenol reduction can be contributed to the following featured advantages. a) The salt-template assisted synthesis of PC with large SSAs and porous structure boosts the in-situ formed ultrafine and surface-clean Ru NCs homogenously dispersed on the surface of simultaneously formed PC matrix, instead of embedded in PC matrix. b) The in-situ transformation of ruthenium oleate complex into Ru NCs and PC matrix via carbothermal approach ensures the strong interaction between Ru NCs and PC matrix, significantly improving the stability of Ru/PC. These features make the Ru/PC with the enlarged atom utilization and boosted stability, thus, showing excellent catalytic properties for the investigated reactions.

Conclusions

In summary, a salt template-assisted strategy via direct pyrolyzing the mixture of ruthenium oleate precursor and sodium sulfate was delicately developed for one-step synthesis of Ru/PC, in which Ru NCs in a diameter of 1.50 nm are highly distributed on the simultaneously generated porous carbon. The resultant Ru/PC as the catalyst showed excellent activities for electrocatalytic HER (η_{10} =21 mV), AB hydrolysis (TOF=744 min⁻¹) and 4-NP reduction (reaction rate of 1.29 min⁻¹) under ambient conditions. The Ru/PC also displayed good durability and reusability for the catalytic reactions. The excellent catalytic properties of Ru/PC should be attributed to the one-step approach and the salt template of sodium sulfate, which ensures that the in-situ formed Ru NCs with an ultrafine size, a clean surface and a good dispersion are solidly loaded on the simultaneously produced PC matrix. This work may offer a new opportunity to produce supported NCs in an ultrafine size and a good dispersion for widespread catalytic applications.

Conflicts of interest

There are no conflicts to declare.

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Porous carbon supported Ru nanoclusters developed by a salt template-assisted strategy show excellent performances for multiple catalytic applications.