Tunable preparation of ruthenium nanoparticles with superior size-dependent catalytic hydrogenation properties

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HIGHLIGHTS

- A facile and efficient strategy is firstly developed for the synthesis of Ru NPs.
- Ru NPs are stable and uniform with the controllable sizes from 2.6 to 51.5 nm.
- Ru NPs exhibit size-dependent and superior catalytic hydrogenation activity.

GRAPHICAL ABSTRACT
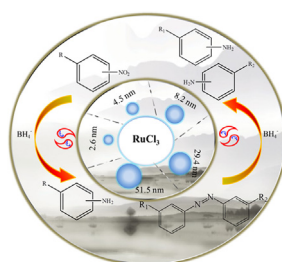
ABSTRACT

Ruthenium (Ru) featured with an unusual catalytic behavior is of great significance in several heterogeneous and electro-catalytic reactions. The preparation of tractable Ru nanocatalysts and the building of highly active catalytic system at ambient temperature remains a grand challenge. Herein, a facile strategy is developed for the controllable preparation of Ru nanoparticles (NPs) with the sizes ranging from 2.6 to 51.5 nm. Ru NPs show superior size-dependent catalytic performance with the best kinetic rate constant as high as $-1.52\,\mathrm{min}^{-1}$, which could far surpass the other traditional noble metals. Ru NPs exert exceedingly efficient low-temperature catalytic activity and good recyclability in the catalytic reduction of nitroaromatic compounds (NACs) and azo dyes. The developed catalytic system provides a distinguishing insight for the artificial preparation of Ru NPs with desired sizes, and allows for the development of rational design rules for exploring catalysts with superior catalytic performances, potentially broadening the applications of metallic NP-enabled catalytic analysis.

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1. Introduction

Nanocatalysts featured with superior catalytic performances are critical for in situ monitoring the kinetics and mechanism of heterogeneous reaction [1–4]. Persist efforts were devoted to enhance the catalytic action of nanocatalysts through the selection of the composition and the regulation of the morphology of nanocatalysts [5–14]. However, poor accessibility and poisoning of the metal surface can reduce overall catalytic efficiency [15]. Nowadays, the design of much more efficient catalysts is an active area of research. The effectiveness of a heterogeneous catalyst is evaluated as a function of its catalytic performance. Of the noble metal catalysts, Ru as a 4d transition metal has shown an unusual and interesting catalytic behavior [16–18]. Ru-based nanocatalysts are proved to be of great significance in several heterogeneous and electro-catalytic reactions [19–22].

The activity and selectivity of Ru-based nanocatalysts for the structure-sensitive reactions were strongly dependent on the
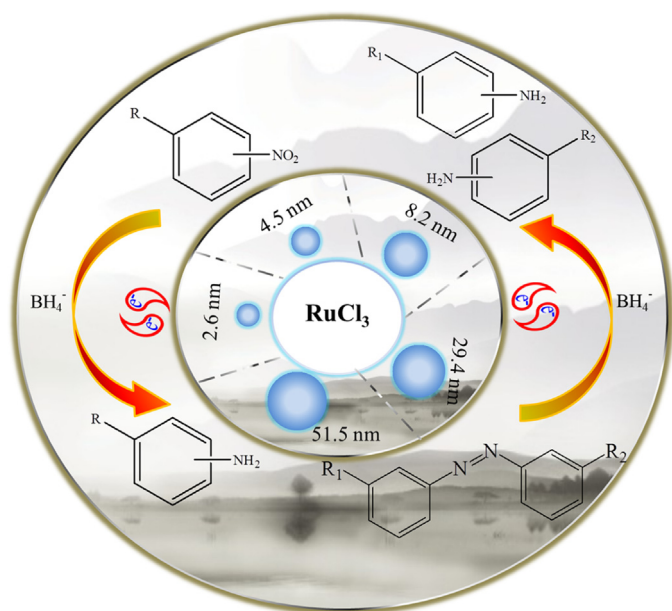
Scheme 1. Schematic illustration of the size-controllable synthesis of Ru NPs for the catalytic reduction of NACs and azo dyes.

morphology and surface structures of Ru nanocrystals [23–25]. Therefore, the size-controllable synthesis of Ru NPs would build a solid foundation for tuning and optimizing their catalytic performances in these important reactions, and is beneficial for the collection of nanocatalysts for the next circulation [23,26]. This is of fundamental interest but remains a significant challenge. Currently, research efforts on Ru NPs have been mostly limited to: a) the demands of high temperatures for the synthesis of small Ru NPs with several nanometers in diameters; [17,26–28], b) the limited catalytic performances and the difficult separation of small NPs, due to their high surface energy and the inherent tendency to agglomerate; [29–31], c) the complicated and harsh reaction conditions for the preparation of large Ru NPs; [13,32,33], d) the lack of sufficient active centers and the optimal microstructure for Ru NP nanocatalysts with high efficiencies; [34] and e) shape-dependent surface-enhanced Raman scattering property of Ru NPs [23]. There is lack of an efficient strategy for the controllable preparation of Ru NPs, especially the building of highly active catalytic system at ambient temperatures. It is imperative and challenging to develop a facile and step-economic synthetic methodology for the controllable preparation of Ru NPs ranging from several nanometers to tens of nanometers. Size controllable preparation of Ru NPs provides a possible for the easy separation of nanocatalysts for the next catalytic applications. The size effect of Ru NPs on the catalytic performances is not fully understood, and the potential catalytic application of Ru NPs in the important reactions is still a major concern.

In this manuscript, uniform Ru NPs with the size ranging from 2.6 to 51.5 nm were facilely prepared by simply adjusting the pH and temperatures of the reaction. Ru NPs exhibited remarkable size dependent catalytic activity with the activity being higher in the ranging of 2.6–8.2 nm and lower from 8.2 to 51.5 nm. Size-controllable synthesis of Ru NP nanocatalysts endowed them with fascinating tailor catalytic activity and selectivity of catalytic systems for the substantially catalytic reduction/degradation of NACs and azo dyes within a few minutes (Scheme 1). Ru NPs show size dependent superior catalytic performance, which is about 64-fold, 46-fold, 32-fold, 22-fold, 15-fold and 12-fold higher than that of Ir NPs, Au NPs, Au@Au NPs, Ag NPs, Au@Ag NPs and Pt NPs. Size-dependent Ru NPs could be easily separated from the reaction

mixture and reusable without obvious loss of catalytic activity or selectivity. Controlled and facial synthesis of metal nanocrystals gives us opportunities to tailor their properties and explore their potential catalytic applications.

2. Experimental

2.1. Materials and reagents

$RuCl_3 \cdot nH_2O$ was purchased from Sigma-Aldrich. Polyvinylpyrrolidone (PVP), sodium borohydride ($NaBH_4$), n-propanol, p-nitrotoluene (p-NT), p-nitrochlorobenzene (p-NCB), p-nitrobenzoic acid (p-NBA), p-nitrophenol (p-NP) and p-nitroaniline (p-NA), orange i, asic orange ii, methyl orange, congo red, methyl red, sudan red i, sodium indigotindisulfonate and quinoline yellow were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All reagents were of analytical grade and were used without further purification. Millipore-Q water was used throughout this study.

2.2. Instrumentation and measurement

The morphology of NPs was characterized by JEOL JEM-2100 transmission electron microscope operated at 200 kV. UV–vis spectra were recorded using a double beam UV–vis spectrophotometer with 1 cm quartz cuvette (Model TU-1901). The extent of electronic changes of Ru NPs was measured by X-Ray photoelectron spectroscopy (PHI5000, Japan). The hydrodynamic sizes and zeta potential of Ru NPs were determined by Zeta potential/nanometer particle size analytical instrument (Brookhaven instruments Corporation). Phase identification of the Ru NPs was conducted with X-ray diffraction (XRD, D8, Bruker AXS Co., Ltd) using CuKα radiation source ($\lambda = 1.54051 \text{ Å}$) over the 2θ range of 3–90°.

2.3. Size controllable synthesis of Ru NPs

An appropriate amount of PVP was dissolved into 10 mL n-propanol with the final concentration of 50 mM. An aliquot of 500 μL 100 mM $RuCl_3 \cdot nH_2O$ was added into the above solution under stirring at 30 °C. The pH of the solution was measured to 3.5. The color of the solution gently changed from dark red to light yellow to dark brown. After 10 h, a transparent dark brown homogeneous colloidal Ru NPs was obtained. An amount of 3 mL acetone was added into 1 mL as-prepared Ru NP solutions. The mixtures were shaking for 2 min and centrifuged at 5400 g for 10 min. The precipitates were dissolved in 1 mL of Millipore-Q water. The average sizes of Ru NPs were 51.5 ± 3.2 nm. By increasing the temperature to 70 °C and 98 °C, the sizes of Ru NPs changed to 4.5 ± 0.9 and 2.6 ± 0.5 nm, respectively.

More different sized Ru NPs were attempted to synthesize by adjusting the pH of solution. When the pH was adjusted to 5.2 and 7.4 by adding 1 M NaOH aqueous solution, the sizes of Ru NPs changed to 29.4 ± 2.5 and 8.2 ± 1.2 nm, respectively.

2.4. Preparation of Au NPs, Ag NPs, Au@Au CS NPs, Au@Ag CS NPs, Pt NPs and Ir NPs

12.1 ± 1.5 nm Au NPs and 10.8 ± 1.2 nm Ag NPs were synthesized according to the previous reported methods [35,36]. Au@Au CS NPs were prepared by the reduction of $HAuCl_4$ on the surface of 10 nm Au NPs [36,37]. The detail procedures were given as follows: an amount of 100 μL 100 nM Au NPs was added into the mixtures of 500 μL 0.1 M PBS and 100 μL 1% PVP. After stirring for 5 min, 20 μL 5 mM of $HAuCl_4$ solution and 20 μL 10 mM of $NH_2OH–HCl$ solution were added into the above solution. The mixtures were shaking for