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Unprotected and Interconnected Ru⁰ Nano-chain Networks: Advantages of Unprotected Surfaces in Catalysis and Electrocatalysis

S. Anantharaj, M. Jayachandran and Subrata Kundu*

Electrochemical Materials Science (ECMS) Division, CSIR-Central Electrochemical Research Institute (CECRI), Karaikudi-630006, Tamilnadu, India.

* To whom correspondence should be addressed, *E-mail: skundu@cecri.res.in and subrata_kundu2004@yahoo.co.in*, Fax: +91 4565-227651; Tel: +91 4565-241487.

ABSTRACT

Seedless, surfactantless and support free unprotected, metallic, interconnected nano-chain networks of ruthenium (Ru) nanoparticles (NPs) had been successfully synthesized via the reduction of ruthenium(III) chloride (RuCl₃) with sodium borohydride (NaBH₄) at three different temperatures, viz. 30 °C, 45 °C and 60 °C. The molar ratio of RuCl₃ solution and borohydride was optimized to be 1:1.5 to get stable colloids with the optimum final solution pH of 9.7 \pm 0.2. Average diameter of the interconnected nano-chain networks prepared at 30 °C (Ru-30), 45 °C (Ru-45) and 60 °C (Ru-60) were 3.5 \pm 0.5 nm, 3.0 ± 0.2 nm and 2.6 ± 0.2 nm respectively. The morphology and composition dependent catalytic and electrocatalytic activities of these unprotected Ru nano-chain networks (Ru-30, Ru-45 and Ru-60) were studied in-detail. The catalysis study was done by taking the transfer hydrogenation of several substituted aromatic nitro compounds. It was observed that Ru-60 was relatively more active compared to Ru-30 and Ru-45 which was reflected in their rate constant values. The electrocatalytic activities of Ru-30, Ru-45 and Ru-60 were screened for anodic water splitting in alkaline medium (0.1 M NaOH) and found that all of them showed almost the same activity which required an over voltage of 308 ± 2 mV to get an anodic current density of 10 mA/cm². Meanwhile, the catalytic and elctrocatalytic performances of these unprotected Ru⁰ networks were compared with Ru⁰ nanomaterials prepared under similar conditions with three different surfactants viz., CTAB, SDS and

TX-100 which in turn revealed that unprotected Ru^0 networks are better catalysts than the ones stabilized with surfactants. The superior catalytic and electrocatalytic performance is due to the availability of unprotected Ru^0 surfaces. The present route may provide a new possibility of synthesizing other surfactant free, unprotected metal colloids for enhanced catalytic and electrocatalytic applications.

Introduction

Despite enjoying many advances in the field of nanostructured zero-valent metals for the past two decades, interesting results, findings, methodologies and applications have made them as one of the fascinating field of research in the scientific community around the globe. Stabilizing metals at the nanoscale and their subsequent applications in various fields such as electronics, optics, catalysis, energy conversion and in other emerging fields have become an unavoidable and essential requirement in the field of materials science. Among the various forms of metal based nanostructures, fabrication/synthesis of nanoparticles (NPs),¹ thin films (TFs).^{2,3} nano-chains,⁴ nanowires (NWs),⁵ nanorods (NRs),⁶ and nanofoams (NFs)⁷ were studied in depth by various physical and chemical routes. The chemistry of metal NPs such as Au,⁸ Ag,⁵ Pd⁹ and Pt¹⁰ with different morphologies have been focused more compared to relatively more reactive metals such as Ir,⁷ Rh,¹¹ Os,^{12,13} Cu,¹⁴ and Ru.¹⁵ Among the several transition metals with standard reduction potential (E^0) higher than that of hydrogen, Au, Ag, Pt and Pd are the most studied metals at nanoscale level compared to others. Beyond the successful reduction and stabilization of metal NPs at nano level, morphology, size and shape control are also significantly essential for many specialized applications. For the synthesis and control over morphological parameters, many physical and chemical methods such as hydrothermal,¹⁶ solgel,¹⁷ laser ablation,¹⁸ physical vapor deposition (PVD),¹⁹ chemical vapor deposition (CVD),²⁰ microwave assisted synthesis,²¹ sonochemical synthesis^{22,23} and wet chemical reductions^{7,24–26} are employed. Among them, wet chemical reduction at various reaction conditions is the most preferred. As wet chemical synthesis is a bottom-up approach, it offers a better control over size and shape of metal nanostructures. Besides, the morphology selectivity or control is usually achieved by adding external additives such as stabilizers, surfactants, templates, scaffolds,

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layered materials and other 3D matrices. The nature of these additives varies from a simple chemical to bio-macromolecules such as DNA²⁷ and cellulose²⁸ and even up to naturally occurring 3D matrices like alumina, clay and minerals like ferrite and silica.²⁹⁻³¹ All these materials basically offer selectivity over size, shape, morphology by acting as a structure determining platform for growth and as a host material. However, wet chemical routes to prepare metal nanomaterials with desired morphology without the addition of any such additives and external agents are highly limited and reported occasionally for the preparation of metal NPs such as Au,³²⁻³⁴ Pd,³⁵ Pt,³⁶ ternary metal nanocomposites like CuAgSe³⁷ and some metal oxides.^{38,39} Obviously, it is highly desired to prepare materials without any additives when it comes to practical applications to avoid many unwanted loss in efficiency due to these additives. Moreover, a nanomaterial synthesized without any support and surfactant will offer larger surface area compared to the ones with the additives.

Among the various transition metals, ruthenium is the one with a positive standard electrode potential of 0.68 V (Ru^{3+} to Ru^{0} in water) that makes it possible to reduce at the nanoscale and stabilize for further applications. In bulk, it is a hard metal with a color of silvery white. Moreover, it is one of the metals with melting point higher than 2300 °C with a density of 12.41 g/cm³. Applications of Ru as metal, metal oxide and as its complexes both in bulk and in nanoscale levels had been studied in catalysis and in electrocatalysis.^{40–46} There are many reports available for the synthesis of Ru metal nanomaterials with different morphology for specific applications. Chau et al. reported the β-cyclodextrin stabilized Ru NPs for hydrogenation reactions.⁴⁷ Salas et al. reported the preparation of Ru NPs in ionic liquids.^{48,49} Stabilization of Ru NPs was achieved by heavily fluorinated compounds as reported by Tristany and coworkers.⁵⁰ Ru NPs was prepared by a facile polyol reduction by Viau et al.⁵¹ In addition to these studies, reports on supported Ru metal NPs for catalytic applications are also available where β-Zeolite,⁵² Fe₃O₄,^{29,53–55} Graphene/reduced graphene oxide,^{15,56} silica,⁵⁷ rutile,⁵⁸ montmorillonite clay,³¹ nanostructured carbon⁵⁹ and polystyrene⁶⁰ are the common solid supports. Ru metal based nanoalloys and composites have been also prepared and used for many specific applications.^{61–67} Besides, spherical Ru NPs, Ru and Pt-Ru metal nanowires^{62,63} and nano-chains⁶⁸ were also reported earlier where surfactants were employed to stabilize them. However, there is no report for the synthesis and stabilization of Ru metal nano-chain networks without any external stabilizer such as surfactant, solid support, scaffolds, templates or structure warping agents. The

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only metal which is frequently reported at nanoscale without any external stabilizing agents is Au,^{32–34} for which phrases 'surfactant free synthesis' and the term 'unprotected' are often employed.

On considering its unique catalysis application, Ru is one among the most used transition metals for catalysis along with Pt, Pd, Ni, Ir, Au and Ag. Ruthenium, as Ru⁰, RuO₂, mononuclear complexes, multinuclear complexes, bimetallic NPs such Pt-Ru, Ru-Ir and as composites with some other metal oxides were used extensively in many catalytic studies.^{62,65–67,69–71} Among them, the important chemical transformations are hydrogenations of alkenes,⁴⁹ arenes,⁴⁷ carbonyl compounds⁷² and nitroarenes,^{40,59,73} N-alkylation of sulfonamides, sulfinamides and amines,²⁹ conversion of syngas to isoparaffins,⁵² conversion of nitriles⁵⁴ and Heck and Suzuki type coupling reactions.⁷⁴ On the other hand, Ru, RuO₂ and its bimetallic and oxide composites have extensively been studied as electrocatalysts for various reactions such as oxygen evolution reaction (OER), hydrogen evolution reaction (HER), HCl oxidation and in methanol oxidation reaction.^{61–64,66,67,75} Water splitting by anodic oxidation with Ru electrocatalyst is the well documented electrocatalytic application in which it competes with the state-of-the-art catalyst Ir.⁷⁶ Nowadays, non-noble metal catalysts are also used as anodes in water electrolyzer but in our case the main reason for choosing Ru for OER is to emphaize the advantages of the unprotected Ru⁰ surfaces over the protected ones. While considering the versatile applicability of Ru and its compounds, surfactant and any kind of supports free Ru nanomaterial is highly desired and required as the surface area offered by surfactant free nanomaterials is obviously higher than the other nanomaterials surrounded by scaffolds, surfactants, templates and supports. To the best of our knowledge, this is the first ever report on the synthesis of unprotected Ru metal nano-chain networks, which is surfactant free and synthesized without any solid support and external stabilizers and the examination of their catalytic and electrocatalytic performances.

In this article, for the first time, we present the facile and fast synthesis of surfactant and support free unprotected metallic Ru interconnected nano-chain networks of three different average chain diameter by a simple wet chemical reduction of known RuCl₃.xH₂O solution with sodium borohydride at three different temperatures viz., 30 °C, 45 °C and 60 °C. The molar ratio of RuCl₃.xH₂O solution and sodium borohydride solution were optimized accordingly to get a stable colloidal solution of Ru⁰ nano-chain networks and the optimum final solution pH in all the

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three was found to be 9.7 ± 0.2 . The eventual average chain diameter of Ru-30, Ru-45 and Ru-60 networks were 3.5 ± 0.5 nm, 3.0 ± 0.2 nm and 2.6 ± 0.2 nm respectively. The synthesized materials were characterized using all essential spectroscopic and microscopic techniques to elucidate the morphology and chemical nature of the sample and a detailed discussion is elaborated in the results and discussions section. The catalytic performance of Ru-30, Ru-45 and Ru-60 were inspected by taking several, different nitro compounds viz., nitrobenzene, 4-nitrophenol (4-NP), 4-nitroaniline (4-NP), 4-nitrostyrene (4-NS), 2-nitrophenol (2-NP), 2-nitroaniline (2-NA) and 2-bromo-6-nitrotoluene (2-B-6-NT). Moreover, the electrocatalytic activity of Ru-30, Ru-45 and Ru-60 nanomaterials for anodic water splitting for OER in alkaline medium were tested and discussed in subsequent sections.

Experimental Section

Synthesis of Interconnected Ru⁰ Nano-chain Networks.

A stock solution of ruthenium(III) chloride hydrate (RuCl₃,xH₂O) of concentration 0.01 M was prepared using Milli Q water. A solution of 0.1 M sodium borohydride was prepared freshly in ice-cold condition and used for each trial. In a typical synthesis, desired amount of Ru³⁺ stock solution was taken into 250 mL beaker and stirred on a hot plate magnetic stirrer. Then the freshly prepared borohydride solution was added into the Ru³⁺ solution at the rate of 10 mL per 30 s. From the color change and the primary absorption spectral results the successful formation of Ru⁰ NPs was confirmed. To find out the optimum molar ratio between RuCl₃.xH₂O and the borohydride to get a stable colloidal solution of interconnected Ru⁰ nano-chain networks, the ratio was systematically changed and the results are as tabulated in Table 1 along with the final pH of each solutions. Depending on the reaction scheme, the rate of addition of borohydride was also varied wherever required. From Table 1, we can infer that at 30 °C, 45 °C and 60 °C, except the molar ratio of 1:1.5 others were found unable to produce a stable colloidal solution of interconnected Ru⁰ nano-chain networks. Depending on the molar ratio and the temperature, the aggregation and precipitation time of Ru⁰ particles varied from 1 min to 55 min. The stable darkbrown colloidal solution of interconnected Ru⁰ nano-chain networks obtained at 30 °C, 45 °C and 60 °C when the ratio of metal precursor and borohydride was 1:1.5 and the final pH was about 9.7 \pm 0.2. Other than 30 °C, 45 °C and 60 °C, we also tried our synthesis at 75 °C and 90 °C but as borohydride is a vigorously reacting reductant, we experienced drastic spillage and

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bumping of the reaction mixture at 75 °C and 90 °C. To ensure the complete reduction of Ru^{3+} to Ru^0 , reaction mixtures were continuously stirred for 3 h further. Moreover, to find out the stability of the colloidal solution obtained, a part from all the three solutions were kept in light under ambient conditions and another part was kept in dark and at 5°C. The later ones were found stable for more than a month and the one kept in light and in ambient conditions got precipitated in 12-15 days. However, when the settled solutions were sonicated for 10 min, we obtained the stable dark-brown colloidal solution with the stability that almost equals to that of the freshly prepared solutions. This implies that though the colloidal solutions are not stable for a long period of time, it can be made stable at any time by a simple sonication assisted redispersion. The catalytic performance was evaluated for the as-synthesized solutions of interconnected Ru^0 nano-chain networks obtained at 30° C, 45 °C and 60° C. The electrocatalytic water splitting was carried out using the interconnected Ru^0 nano-chain networks obtained at 30° C, 45 °C and 60° C. The electrocatalytic sequence is depicted as Scheme 1.

Catalytic Hydrogenation of Nitroarenes to Aminoarenes.

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Hydrogenation of nitroarenes to aminoarenes is solely catalyzed metals and metal NPs and has been studied intensively with various catalysts and various nitro compounds. The catalytic performance of interconnected Ru⁰ nano-chain networks viz., Ru-30, Ru-45 and Ru-60 were examined for the hydrogenation of seven different nitroarenes. In all these catalysis reactions, the volume catalyst solutions were kept about 20 μ L. Similarly, the volume and concentration of the borohydride solution were also kept constant which were about 100 μ L and 0.1 M respectively. To find out the actual concentration of nitro compound at each point, calibration curve for all the nitro compounds has been prepared using standard solutions of known concentration. The details of concentrations of each nitro compound are tabulated in Table S1 (online SI section). The details on volume and concentration of the nitro compounds taken are listed in Table S2 in online supporting information (SI) section. For a typical hydrogenation reaction of 4-Nitrostyrene (4-NS) with these three catalysts, 0.5 mL of 10⁻⁶ M stock solution of 4-NS was taken into a glass vial of 15 mL volume into which 20 μ L of Ru-30, Ru-45 and Ru-60 were added and shaken well for homogeneity. Then the volume of the reaction mixtures was made 4 mL with water. Soon after adding a freshly prepared ice-cold solution of

100 μ L of 0.1 M sodium borohydride, the mixture was shaken for a moment and then about 3.5 mL of the solution was taken out into quartz cuvette of path length 1 cm² and analyzed through a double beam UV-Visible spectrophotometer. Time-dependent UV-Vis analyses at a regular time interval of 60 sec were done after the addition of borohydride. The resultant UV-Vis spectra of other nitroarenes hydrogenation reactions were plotted together and discussed in results and discussion section (under main text) and in online SI section. The same procedure was followed for other nitroarenes with required change in their concentration depending on their molar absorptivity.

Electrocatalytic Study on the Interconnected Ru⁰ Nano-chain Networks by Taking Oxygen Evolution as a Test Reaction.

As the catalytic study on the hydrogenation of nitroarenes, electrocatalytic water splitting ability of interconnected Ru^0 nano-chain networks viz., Ru-30, Ru-45 and Ru-60 were also examined. GC electrode of 0.0732 cm² area was taken as bare working electrode. For better adhesion of our catalyst, binder nafion (5%) solution was mixed with our catalysts solution in the ratio of 1:9 by sonication. About 3 mg of each Ru-30, Ru-45 and Ru-60 were homogenized with 1 mL of water and 5% nafion (9:1) solution by sonication separately. About 5 μ L of the resultant ink was casted carefully on the calibrated GC surface ensuring a catalyst loading of 0.015 mg in each GC surface and dried in ambient conditions for 10 h. In each modification, the catalyst loading was kept constant about 0.205 mg/cm². The modified GC electrodes were then used as working electrode. About 20 mL of 0.1 M NaOH is taken with a Pt-foil counter electrode and an Hg/HgO reference electrode. The electrocatalytic activity was studied by running cyclic voltammetry (CV) at a scan rate of 10 mV/s. Stability and the kinetics were analyzed by chronoamperometry, steady state polarization techniques and electro impedance spectroscopy and other required electrochemical characterizations. The detailed discussion is given in the results and discussions section.

Results and Discussions

UV-Visible Spectroscopic Study.

The UV-Visible absorption spectroscopic studies were done to follow the chemical changes that occurred during and after the syntheses of colloidal Ru⁰ nanomaterials at different

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temperatures viz., 30 °C, 45 °C and 60 °C. The absorption spectrum for the metal ion precursor (Ru^{3+}) and the synthesized colloidal Ru^{0} nanomaterials at different time intervals after the addition of borohydride was recorded and given as Figure 1. Curve a in Figure 1 is the absorption spectrum of the Ru³⁺ solution in which two humps at 487 nm and 304 nm are observed which is as expected for Ru³⁺ solution and also in good agreement with earlier reports.⁷⁷ Curves b, c and d, e are the absorption spectra of the reaction mixture of Ru³⁺ solution and borohydride at 30 °C and 45 °C after 5 and 30 min from the addition of borohydride respectively. Curve b and d have a sharp and intense peak at 257 nm which is due to the formation of Ru²⁺ ions intermediate by the reduction of Ru³⁺ ions at the initial stage.⁷⁷ Curves c and e are the absorption spectra of the same reaction mixture after 30 min where we can see the clear and sharp drop almost about 99% in the intensity of Ru²⁺ peak observed at 257 nm. This clearly indicates that when the synthesis was done at 30 °C and 45 °C, initial reduction product was Ru^{2+} rather than Ru^{0} and on continued stirring further reduction of Ru^{2+} took place to form metallic Ru⁰ particles. However, there in curve c and e still a small hump is seen indicating the unreacted Ru²⁺ ions. Curves f and g are the absorption spectra of the reaction mixture performed at 60 °C. Curve d was recorded at 5 min from the addition of borohydride and curve e was recorded when it was 30 min. Unlike the curves observed at 30 °C, the absorption spectra of reaction mixture performed at 60 °C showed a gradual steep increase in the absorption while approaching the lower wavelength regions. This is attributed to the interference caused by the rapid evolution of H₂ gas from the reaction mixture as the temperature was high.^{42,51,77} This rapid evolution assisted the rapid reduction of Ru^{3+} to Ru^{0} within 5 min unlike the one performed at 30 $^{\circ}$ C where it took more than 30 min. Even though the reduction was rapid and formed Ru⁰ in 5 min, a very small hump in curve f at 256 nm indicates the existence of some unreacted Ru²⁺ ion at this stage. When the stirring was further continued and temperature kept constant about 60 °C for 30 min, the resultant absorption spectra (curve g) almost had no peak in the region characteristic to Ru²⁺ ions. Moreover, the total reduction in the absorption from higher to lower wavelength side is noted which is due to the reduced evolution of H₂ gas from the reaction mixture. One more absorption spectrum of Ru-60 was taken after 3 h from the synthesis and given as curve h which is of comparable intensity to that of Ru-30 and Ru-45. This in turn strongly supports our attribution to the increased intensity in the reaction mixture performed at 60 °C. The overall UV-Visible studies showed the successful formation of metallic Ru⁰ particles

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by the reduction of Ru^{3+} solution by borohydride. These results are in good resonance with the earlier report of Li et al.⁷⁷

Transmission Electron Microscopic (TEM) Studies.

Transmission electron microscopic (TEM) and high resolution transmission electron microscopic (HR-TEM) studies were carried out to find the morphology, size, nature of the material and their fine structures. Figures 2, A-I are the TEM, HR-TEM and SAED pattern images of Ru-30, Ru-45 and Ru-75 respectively where Figures 2, A-C are of Ru-30, Figures 2, D-F are of Ru-45 and Figures 2, G-I are of Ru-60. Figure 2A, 2D and 2G reveal overall morphologies of Ru-30, Ru-45 and Ru-60 at low magnification respectively. It is clear from these images that all of them have almost the similar morphology of dense, interconnected networks of Ru⁰ nano-chains. However, it can also be observed that the nature of the interconnected chains gradually becomes less dense while going from Ru-30 to Ru-60. This is because of the rapid evolution of H_2 gases and short reaction time taken at high temperatures that restricted the adjacent chain fusion by not providing sufficient time for the Ru⁰ particles formed initially. On the other hand, inset histograms of 2A, 2D and 2G reveal a linear variation in the average chain diameter of interconnected chains and the average diameters are 3.5 ± 0.5 nm, 3.0 \pm 0.2 nm and 2.6 \pm 0.2 nm for Ru-30, Ru-45 and Ru-60 respectively. Figures 2B, 2E and 2H are the HR-TEM images that project the lattice fringes and fine structures of Ru-30, Ru-45 and Ru-60 respectively. From the measured d-spacing values various planes are assigned accordingly. Figures 2C, 2F and 2I are selected area electron diffraction (SAED) of Ru-30, Ru-45 and Ru-60 respectively. The observed ring patterns are calibrated according to the diffraction planes from which they originate and found that both SAED and XRD analysis (given in online SI section as Figure S2) are in good agreement and with the ICDD card data of number 88-1734.⁷⁸ The overall TEM, HR-TEM and SAED analyses had revealed that the morphologies of Ru-30, Ru-45 and Ru-60 are interconnected nano-chain networks with the difference in the density of the network structures and the average chain diameter of the individual chains that are fused together with the adjacent chains.

X-ray Photoelectron Spectroscopic (XPS) Analysis.

X-ray photoelectron spectroscopic (XPS) studies were done for Ru-30, Ru-45 and Ru-60. Figure 3A is the survey spectra of Ru-30, Ru-45 and Ru-60 where various peaks for Ru 3d, Ru

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 $3p_{3/2}$ and Ru $3p_{1/2}$, Ru 2s, Na 1s and O 1s are observed at the binding energy values of 280.2 eV, 461.9 eV, 484.8 eV, 740.7 eV, 1071 eV and 529.9 eV respectively. All these peaks and their corresponding binding energy values are in agreement with the previous studies of zero-valent Ru atoms.⁷⁹⁻⁸¹ A peak with considerable intensity for O 1s is also observed due to the spontaneous formation of passive RuO_x film on the unprotected Ru surface when it is drawn out of the colloidal solution and dried for making XPS samples. The characteristic peak of OKLL is also observed at 980.7 eV. The peak at 1071 eV is of Na 1s come from the reductant sodium borohydride used. High resolution spectra of Ru 3d and Ru 3p for all three catalysts were taken and given as Figures 3, B-G. Figures 3B, 3C and 3D are the high resolution scan of Ru 3d in Ru-30, Ru-45 and Ru-60 respectively in which the corresponding binding energy values of Ru $3d_{5/2}$ and Ru $3d_{3/2}$ are observed at 280.50 eV and 284.9 eV for Ru-30, 280.52 eV and 284.83 eV for Ru-45 and 280.49 eV and 284.78 eV for Ru-60 respectively. It is also found that all these Ru 3d peaks have two comparatively poor intense peaks at the binding energy values of 282.1 ± 0.02 eV for Ru $3d_{5/2}$ and of 286.06 \pm 0.03 eV for Ru $3d_{3/2}$ which arise mainly from the passive oxide film formed on the metallic Ru surface as observed earlier because of its reactive nature in open atmosphere.⁷⁹⁻⁸¹ Figures 3E, 3F and 3G are the respective high resolution scans of Ru 3p state of Ru-30, Ru-45 and Ru-60 where a doublet due to spin orbit coupling that resulted two states as Ru $3p_{3/2}$ and Ru $3p_{1/2}$ with a peak to peak separation of ~22.9 eV was observed. The positions of the doublets were 461.90 eV and 484.81 eV for Ru-30, 461.88 eV and 484.85 eV for Ru-45 and 461.87 eV and 484.77 eV for Ru-60. Like Ru 3d, each Ru-3p states also have two less intense peaks due to the passive oxide film were observed at 464.07 \pm 0.03 eV, and at 486.64 \pm 0.05eV. All the observed binding energy values are nicely matching with the earlier reports of metallic Ru in many forms.^{79–81} From the XPS results, it is concluded that the formation of metallic Ru⁰ nanomaterials was successful under the stated conditions. Survey scans are in agreement with the EDS analyses (given in online SI section as Figures S3, (A-C) and proved that synthesized unprotected Ru⁰ nano-chains are free from foreign stabilizers.

Mechanism for the Formation of Interconnected Ru Nano-chain Networks.

The probable formation mechanism of these interconnected Ru nano-chain networks is proposed from the spectroscopic and microscopic studies carried out. The reaction happens here is given below.

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Thus the reduction of Ru³⁺ was effected in aqueous medium. The last step given inside the parenthesis is the formation of boric acid and the equilibrium between the boric acid and borate oxyanion which is one of the conjugate base of boric acid. Depending on the pH of the medium, the concentration of the boric acid and the borate oxyanion will vary. UV-Vis spectra (Figure 1) of precursors and the reaction mixture at different stages revealed that the reduction of Ru^{3+} to Ru^{0} was so fast when it is done in high temperature (60 °C) compared to 30 °C and 45 °C. Moreover, the HR-TEM analyses revealed the interconnected nano-chain networks morphology for Ru-30, Ru-45 and Ru-60. But the actual difference among them was in the density (density in the sense how much closer the individual chains are in the network structures) and in the average diameter of the interconnected chains. When the synthesis was carried out at 30 °C, the rate of evolution of hydrogen was relatively slower which allowed the nucleation and growth to proceed for a longer time thereby resulting in larger individual particles $(3.5 \pm 0.5 \text{ nm})$ and the formed particles had grown along their own preferred direction and got fused with the adjacent particles that ultimately resulted in chains. These chains had further undergone cross fusion with other chains in the vicinity and hence created denser network like structures. Curve c of Figure 1 shows that for complete reduction of the intermediate Ru²⁺ ions took a longer time of 30 min by borohydride. The same was witnessed by visual observation also. The initial pale brown color of the Ru²⁺ ions in solutions changed to dark brown after 30 min. This was the main factor for forming larger particles and more interconnections within the network structure. Besides, when the reaction was carried out at a 45 °C, the initial reduction product (Ru²⁺) took

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nearly 17 min for the complete reduction to Ru⁰ (curve e, Figure 1). The average chain diameter of the networks formed at 45 °C is 3.0 ± 0.2 nm which is relatively less than that of Ru-30. This indicates that relatively faster reduction at 45 °C decreases growth of the particles by not providing sufficient time. However, the density of the network structure looks almost similar. This tells us that though the average diameter of the ultimate chain structures is less than Ru-30, the time of 17 min is still more than sufficient for cross fusion that resulted in interconnected nano-chain networks as denser as Ru-30. On the other hand, when the same reaction was carried out at the temperature of 60 °C, the reduction Ru^{3+} to Ru^{0} was completed within a short time (5 min). The corresponding absorption curves are shown in curve f and g in Figure 1. Curve f in Figure 1 is the absorption spectrum of the reaction mixture (carried at 60 °C) obtained immediately after the addition of borohydride where there was no / a weak peak characteristic to the intermediate Ru^{2+} ions was observed. This indicated the immediate reduction of Ru^{3+} to Ru^{0-} at higher temperature. Curve g is the absorption spectrum of the same reaction mixture 5 min after the reduction borohydride which in turn clearly supports fact of immediate reduction of Ru^{3+} and the non-existence of Ru^{2+} for a long period of time unlike the ones observed in the previous cases. These observations leads to the fact for the formation of interconnected nanochain networks of unprotected Ru^0 particles with the smaller average diameter (2.6 ± 0.2 nm) and lesser interconnections across individual chains of the network structure requires high temperature to initiate and complete the reaction in a shorter time. Further, reason for the smaller average chain diameter and less number of interconnections among the chains might be due to the rapid reduction caused by the rapid evolution of hydrogen gas. As the reduction was so fast and there was no chance for the existence of intermediate Ru²⁺ ions for a significant period of time in the reaction mixture to assist the further growth of the individual particles, the reaction terminates with the smaller particles and had less number of interconnections than Ru-30 and Ru-45. These observations clearly tell us that temperature is the main factor that took control over average diameter and nature of the network structure.

To confirm that the observed morphology is the actual morphology in its native state too, laser diffraction particle sizing (LDPS) technique was used. This is the technique which measures the average size of the particles in its native state. In our case, it is not just the particle but it is interconnected nano-chain network. The measured average particle diameter for Ru-30, Ru-45 and Ru-60 are 721 nm, 708 nm and 632 nm respectively (Figure S4, A-C). This clearly

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indicates that in solution, Ru is not present just like a particle whereas it has the same morphology what had been observed through TEM analysis. Moreover, it reveals that the observed morphology is not just due to the evaporation phenomena on TEM grid. If it is present as large particles with the sizes measured through LDPS, the same size of particle could be detected in TEM. However, it is not the case. Apart from this, we also believe that a larger particle might not be transformed into an interconnected chain-like structure upon drying with an average chain diameter of 2.5 to 3.5 nm. Hence, it is clear that the synthesized colloids have the same morphology in its native states too.

Stability of Unprotected Ru⁰ Nano-chain Networks and Its Dependence on pH.

Stability of material prepared without any external stabilizing agents mainly depends on other coexisting byproducts and residual ions along with it in solution. In reaction mechanism section above, we proposed that boric acid and its conjugate base will be in equilibrium which depends on pH of the solution. Besides, Na⁺ and Cl⁻ ions are also there. Hence we strongly believe that these are the actual stabilizer that stabilizes them by electrostatic interactions. Similar stabilization of Au NPs by these ions in solution was observed by Deraedt et al.³² where they find an exceptional stabilizing activity of excess borohydride on Au NPs by forming the hydridic bonds on the surface. As in our synthesis of Ru colloids, no external agent was added. Hence, obviously the only thing that is stabilizing should be the excess borohydride. However, borohydride is reactive and it won't be in the solution after some time. Hence, in later time electrostatic interactions between the Cl⁻ ions and B(OH₄)⁻ ions adsorbed on the surface of Ru NPs and the Na⁺ ions in the solution would stabilize the unprotected Ru nano-chains. The same mechanism was proposed for the stabilization of Au NPs was proposed by Deraedt et al.³² The proposed formation and stabilization mechanism are depicted as Scheme 2. Moreover, we also believe that the formation of the interconnected chains can also be a significant factor in the stabilizing action.

Apart from this, we have carried out a detailed study on the relation between the stability and the final solution pH. From Table 1, it can be seen that the final solution pH varied depending on the molar ratio of the reactants ($Ru^{3+}:BH_4^{-}$). The formed Ru colloidal solution is stable only when the pH is 9.7 ± 0.2 which is of 1:1.5 ratio. With the molar ratio of 1:1 and 1.5:1,

the resultant solution is neutral (7.0 ± 0.1) and slightly acidic (6.7 ± 0.07) respectively. Here the stability is of considerable time and order of stability is Ru-60>Ru-45>Ru-30. With all other molar ratio, the resultant solution is not as stable as the ones discussed above. The pH of those solutions was either acidic or highly alkaline (see Table 1 for details). In these conditions, temperature played a little role over the stability. In acidic and highly basic conditions, at low temperature, precipitation was not effected quickly. This may be due to the slow reduction of Ru^{3+} and the existence of Ru^{2+} in solution for a considerable time. When those Ru^{2+} gets reduced to Ru⁰, precipitation occurred immediately. To check the role of pH, we had taken 3 mL of Ru-30, Ru-45 and Ru-60 prepared using the ratio of 1:1.5 separately and increased the pH gradually by adding 1 M NaOH drop by drop and observed that when the pH reached 10.50, precipitation began and on continued addition of NaOH, precipitation occurred with enhanced rate. Similarly, we had reduced the pH of these stable colloids by adding $0.5 \text{ M H}_2\text{SO}_4$ drop by drop and found that when the pH reached 6.60 precipitation occurred and the rate was enhanced upon continued addition. Hence, we concluded that the stability was mainly due to the byproducts and other coexisting ions that provided appropriate electrostatic environment depending on the overall solution pH and in our present case, the optimum pH is 9.7 ± 0.2 .

Catalytic Nitroarenes Hydrogenation.

The detailed procedure of the catalytic reduction reactions of all the nitro compounds (4-NP, 4-NA, 4-NS, 2-NP, 2-NA, 2-B-6-NT and NB) are already explained in the experimental part. Nitroarenes hydrogenation is the conventional and most studied catalytic reaction using zero valent metal NPs that includes both noble and non-noble metals.^{40,53,59} Despite being a well-studied and well documented reaction, nitroarenes hydrogenation by metal NPs continues to draw greater attention when it is about enhancement in the catalytic activity. Hence, any attempt to increase the catalytic rate and reducing the reaction time will be a fruitful outcome. In our case we have comparatively examined the catalytic activity of our unprotected Ru⁰catalysts (Ru-30, Ru-45 and Ru-60). Though we tried all the above nitro compounds for their hydrogenation, only the following five compounds viz., 4-NP, 4-NS, 4-NA, 2-NP and 2-NA are completely reduced by Ru-30, Ru-45 and Ru-60. Interestingly, Ru-60 was able to hydrogenate 2-B-6-NT whereas Ru-30 and Ru-45 were inactive. This is may be due to larger average diameter and denser interconnected chains in Ru-30 and Ru-45 networks that restrict the coordination of 2-B-6-NT in

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a preferred direction to effect the hydrogenation whereas with Ru-60 this hindrance was overcome by the smaller size and lesser interconnections. Besides the size and dense nature, we also believe that the retention of considerable amount of Ru²⁺ ions on Ru-30 and Ru-45 surfaces may also be the key factor showing a significant reluctance in this reaction. Moreover, the same may be the reason for having lower rate constant values in all the reaction relative to Ru-60. However, the hydrogenation of 2-B-6-NT by Ru-60 was also not a complete one. Apart from this, none of them catalyzed the reduction of NB hydrogenation. Here, the catalytic reduction reaction of 4-NS is discussed in details and others are included in the SI section. For the hydrogenation of 4-NS, the time dependent UV-Vis spectra and respective ln(conc) vs time plots for Ru-30, Ru-45 and Ru-60 are given as Figures 4, A-F. It can be seen from the figures that, the rate constant value is the highest for Ru-60 and also the time taken by Ru-60 is relatively less. All the reactions followed first order kinetics with respect to the nitro arenes and the corresponding rate constant values for Ru-30, Ru-45 and Ru-60 are 4.00×10^{-1} min⁻¹, 4.10×10^{-1} min^{-1} and $4.8 \times 10^{-1} min^{-1}$ respectively. This indicates that Ru-60 is more active than the other two. Similarly, the time dependent UV-Vis spectra for other nitro compounds hydrogenations by Ru-30, Ru-45 and Ru-60 are given in online SI section as Figures S5, A-M which is in the order of 4-NP, 4-NA, 2-NP, 2-NA and 2-B-6-NT (only for Ru-60) respectively. The corresponding first order plots for Ru-30, Ru-45 and Ru-60 are also provided in the same order in the online SI section as Figures S5, N-Z. Moreover, for a comparative interpretation, the catalytic activity of Ru-30, Ru-45 and Ru-60, C_t/C_0 vs. Time (T) were plotted for each catalytic hydrogenation reaction and given as Figure 5. From Figure 5, it is clear that the rate of disappearance of reactant in all the catalytic hydrogenation reaction was faster for Ru-60 than Ru-30, Ru-45. Similarly, the rate of disappearance of reactants with Ru-45 is almost parallel with Ru-30. Beyond the time of the reaction, order and rate of the reaction, other quantitative parameters like conversion, selectivity, yield, turnover number and turnover frequency for each reaction were also calculated according to the literature reports^{40,56,59,72-73} and the detailed calculations are provided in online SI section. The results are provided as Table 2.

To find the superiority of our unprotected catalyst, we have prepared Ru^0 nanomaterials with three different surfactants such as cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and Trixon-100 (TX-100) which are cationic, anionic and neutral surfactants respectively. Formation of Ru^0 nanomaterials with these surfactants were primarily

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confirmed from their absorption spectra, TEM micrographs and their electron diffraction patterns which are given as Figures S5, A-G in online SI section. We have chosen only the hydrogenation of 4-NS and studied their catalytic activities under the same conditions. The resultant timedependent UV-Vis spectra and their corresponding kinetic plots are given as Figures S7, A-F in online SI section. From this, it can easily be evidenced that unprotected Ru⁰catalysts are better than the ones capped by surfactants. Results of this comparative study are given in Table 2. We have also compared our results with other reports where the same metallic Ru NPs in other forms were used to hydrogenate nitroarenes are also compared and tabulated as Table S3 in online SI section. The chosen works are the closely related to the catalytic studies of this report where we found that our catalysts are comparatively better than others in terms of time and yield. However, it was observed that the dendrimer encapsulated Ru NPs⁷³ of less average individual particle size than our catalysts showed slightly higher rate constant value than ours. The much higher k values observed for Ru/rGO⁵⁶ and Ru/CNF⁵⁹ catalysts are due to different reaction conditions they employed such as high pressure and temperature unlike us where we carried out our reaction at room temperature. The catalytic performance of our catalysts with noble metal catalysts and other non-ruthenium catalysts for 4-NP reduction was also compared and given as Table S4 in online SI section. From these, we found that very few reports were reported with slightly higher rate constant values than our catalysts. Hence, we strongly believe that the unprotected surfaces of the Ru particles are the reason for the enhanced catalytic activity. The overall catalytic study revealed that Ru-60 is relatively a more active catalyst than Ru-30 and Ru-45 and all of them were are significantly more active than Ru-TX-100, Ru-CTAB and Ru-SDS prepared under similar conditions. Interestingly, when compared with other Ru catalyst for the same and similar reactions, our catalysts were almost superior with few exceptional cases.^{59,73} The overall catalytic activity of Ru-30, Ru-45 and Ru-60 are depicted in Scheme 3.

Electrocatalytic Water Splitting.

Interesting results obtained in the catalytic hydrogenation of nitroarenes triggered us to study the electrocatalytic performances of Ru-30, Ru-45 and Ru-60. Ru is one of the most studied transition metal along with Ir for anodic water splitting. As the need for renewable energy got much attention over the globe, the inevitability of producing H_2 at cheaper cost has becomes one of the essential things in energy sector. Ru and RuO₂ are studied in many forms.

Among them following are some important reports where Ru is used as a metal,⁸² as its oxide (RuO_2) ,⁸³ as its mononuclear/polynuclear complexes,^{69,70} as bimetallic materials^{71,84} and as metal oxide composite materials.⁶⁷ Hence, it is essential to study the electrocatalytic activity of unprotected Ru-30, Ru-45 and Ru-60 catalysts for OER. As described in the experimental section, the electrocatalytic studies were carried out initially for Ru-30, Ru-45 and Ru-60 by running a cyclic voltammogram at a sweep rate of 10 mV/s in 0.1 M NaOH. The resultant CV is given as Figure S8 in online SI section. The drop due to uncompensated resistance (R_u) was corrected by carrying out electro impedance spectroscopic analysis the corresponding Nyquist and Bode plots are given as Figures 6, A-B. From these Nyquist and Bode plots, the R_u value found was about 22.36 Ohm/cm². From these figures, we can see that Ru-30, Ru-45 and Ru-60 required an overvoltage of 308 ± 2 mV to produce 10 mA/cm² of OER current density. Unlike catalysis results, almost similar electrocatalytic activity was observed for all the three catalysts. It can be explained as follows, the catalytic property of any metallic catalyst is mainly dependent on the atoms on the surface. In our case, Ru-30 and Ru-45 were found to be having considerable Ru²⁺ ions on their surfaces as evidenced by respective UV-Vis and XPS analyses whereas with Ru-60, it is not the case. However, when it comes to electrocatalysis, especially when it is anodic water splitting, the metal taken will undergo vigorous oxidation known as anodization. These oxides are the actual catalysts that cause the water splitting. In our case all the Ru atoms was oxidized to RuO₂ that catalyzed the water splitting. This might be the reason for the similar electrocatalytic activity. Hence, we chose Ru-60 and done further electrochemical analysis. Figure 7A is the cyclic voltammogram (CV) of Ru-60 modified GC electrode with uncompensated resistance (curve a) and iR free CV (curve b) ran at 10 mV/s in 0.1 M NaOH. It can be seen that the benchmarking OER current density of 10 mA/cm² is achieved at 1.538 V (vs. RHE). Hence, the overvoltage is 308 mV which is significantly lower. Figure 7B is the chronoamperometric curve of Ru-60 modified GC under the same experimental condition at 1.55 V and it is observed that the modified catalyst is stable for more than 10 h.

Like catalysis study, we also conducted similar comparative electrocatalytic study with the Ru-CTAB, Ru-SDS and Ru-TX-100 adapting the same procedure. Figure 7C is the CV of Ru-60, Ru-CTAB, Ru-SDS and Ru-TX-100 ran at 10 mV/s in 0.1 M NaOH where curve a is the CV of Ru-60, curve b is of Ru-CTAB, curve c is of Ru-SDS and curve d is of Ru-TX-100. The required over voltages for getting an anodic current density of 10 mA/cm² by these surfactant

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stabilized Ru⁰ nanomaterials are 361 mV, 385 mV and 441 mV for Ru-CTAB, Ru-SDS and Ru-TX-100. From this, unprotected Ru⁰ catalysts were found more reactive than the ones covered with surfactants which in turn emphasize the significance of unprotected surfaces in electrocatalysis. In all the cases backward sweep is taken for the calculation of overvoltage to avoid any non-faradaic contribution to the total current and the same was extended for Tafel analyses also. The corresponding steady state polarization curves for Ru-60, Ru-CTAB, Ru-SDS and Ru-TX-100 are given together as Figure 7D from which the order of the Tafel slopes were found to be 95 mV/dec for Ru-60, 215 mV/dec for Ru-CTAB, 202 mV/dec for SDS and 163 mV/dec for Ru-TX-100. This again implies that the kinetics is sluggish when the catalysts were stabilized with surfactants. The comparative electrocatalytic OER results are tabulated as Table 3. Though the chronoamperometric analysis showed the robustness of our catalyst, we carried out post cyclic CV under the same condition again after a vigorous electrolysis for 10 h which is given as Figure S8 in the online SI section. From Figure S9, a loss which was not beyond 0.05 V in terms of overpotential was observed. It may be due to leaching of catalyst in alkaline solutions which was observed earlier by others for Ru catalysts in OER where the leaching product was the volatile RuO₄.^{85,86} Moreover, the stability of the Ru-60 modified GC was examined by a potential sweeping between the same potential window at a scan rate of 10 mV/s. The reultant voltammograms are given together as Figure 8 from which a stedy decrease in the oveerall activity as well as a stedy increae in the overpotential can be observed and the increase in the overpotential is not more than 0.05 V. Both constant potential electrolysis and potential sweeping caused the similar change in the electrocatalytic activity of the Ru-60 modified GC and imply its robutness under these harsh conditionns.

Besides, determination of real surface area or the electrochemical surface area (ECSA) of the working electrode is an important parameter in an electrocatalytic reaction which will provide quantitative information about the electrocatalytic processes. In our case, we have determined the ECSA from the double layer capacitance (C_{DL}) of the Ru-60 modified GC electrode as done by others.^{87,88} The double layer charging currents (i_c) were measured in the non-faradaic region from the CV curves ran at different scan rates such as 1 mV/sec, 5 mV/sec, 10 mV/sec, 30 mV/sec, 50 mV/sec, 70 mV/sec, 100 mV/sec, 150 mV/sec, 200 mV/sec, 240 mV/sec, 300 mV/sec, 500 mV/sec and 800 mV/sec in the same potential window. The resultant CVs are given together as Figure 9. The double layer charging current was increased as expected

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due to the gradual increase in the scan rates. The relationship between double layer charging current (i_c) and the scan rate (v) is given in equation (3).

$$i_c = \nu C_{DL} \tag{3}$$

Hence, the plot of double layer charging currents (i_c) against the scan rates yielded straight lines the slope of which is a direct measure of the double layer capacitance of the electrode as seen in Figure 10. The relationship between the ECSA and the double layer capacitance (C_{DL}) is given in equation (4).

$$ECSA = C_{DL}/C_s \tag{4}$$

Where, C_s is the specific capacitance of RuO₂. The detailed study on the specific capacitance of RuO₂ was carried out by many under identical experimental conditions both in alkaline and acidic media. Typically in alkaline medium RuO₂ is reported to have the specific capacitance that vary from 0.013 mF/cm² to 0.019 mF/cm².⁸⁹⁻⁹⁵ In our calculation we have used the specific capacitance (C_s) value of 0.015 mF/cm². Detailed calculation is provided in the online SI section. The real or the electrochemical chemical surface area (ECSA) determined through this method for Ru-60 modified GC electrode was 99.2 cm². Based on the ECSA, the specific activity of our material is found to be 0.1008 mAcm⁻²_{ECSA} (see SI section for detailed calculation). The observed value is is higher than the report of Lee et al.⁸² and comparable to the report of McCrory et al.⁹⁶ where they have taken the measured current density at 1.59 V vs RHE, whereas, we have taken at 1.54 V vs RHE. The turnover frequency (TOF) of our catalyst was calculated by assuming Ru monolayer formation upon modifying GC with Ru-60, as we and others reported earlier for other similar noble metal electrocatalysis.⁹⁷⁻⁹⁸ The number of Ru atoms on Ru monolayer was taken from the report of Brongersma et al. (pp-217-218).⁹⁹ Detailed TOF calculation is given in online SI section. The calculated TOF value is 4.72 s⁻¹. The overall electrocatalytic study revealed that Ru-30, Ru-45 and Ru-60 had similar electrocatalytic activity in alkaline water splitting (OER) which required an overvoltage of 308 ± 2 mV to generate 10 mA/cm² of OER current density with an ECSA value of 99.2 cm². However, the electrocatalytic study had also revealed the advantage of having unprotected Ru catalyst form its lower overvoltage (308 \pm 2 mV) required to generate a current density of 10 mA/cm² and with a significant TOF value of 4.72 s⁻¹. While comparing our results with the other reports^{67,69-71,82-84} where Ru was used in many forms, it can be concluded here that the unprotected Ru surfaces

showed good activity in terms of lower oxygen overpotential (10 mA/cm² OER current density at 308 ± 2 mV), loading (0.205 mg/cm²) and the TOF value (4.72 s⁻¹). Although our catalysts have shown better electrocatalytic activity, there are reports with comparable activity in terms of overpotential and specific activities.^{82,84,96} Moreover, it should not be forgotten that though the synthesized material remains as Ru⁰ in solution when it is exposed to atmosphere the surface gets oxidized to some of its oxides RuO_x and upon anodizing which are the actual catalysts that do water splitting. However, in case of surfactants protected Ru⁰ nanomaterials such kind of oxidation likely to be harder at lower over potential regions which may render down their electrocatalytic activity.

Conclusion.

In summary, three different interconnected, unprotected Ru NPs as nano-chain networks were prepared by a simple wet chemical reduction route using borohydride without any external stabilizer at three different temperatures viz., 30 °C, 45 °C and 60 °C. The optimum molar ratio between Ru^{3+} and BH_4^{-} and the pH for getting stable colloids are 1:1.5 and 9.7 \pm 0.2. Temperature was increased systematically to vary the average chain diameter as 3.5 ± 0.5 nm, 3.0 ± 0.2 nm and 2.6 ± 0.2 nm for Ru-30, Ru-45 and Ru-60 respectively. Comparative and systematic studies on catalytic nitroarenes hydrogenation and electrocatalytic water splitting in alkaline solution were done and found that unprotected Ru⁰ catalysts are better catalysts than the ones stabilized by surfactants in both catalysis and electrocatalysis. Among Ru-30, Ru-45 and Ru-60, significant difference in the catalytic behavior was noticed which was attributed mainly due to the presence of Ru²⁺ ions on the surface of Ru-30 and Ru-45.In all the reactions, Ru-60 was found to be more active. Interestingly, all of them were found to show supreme catalytic activity over other Ru catalysts in many forms with solid supports for the same and similar reactions with few exceptions. The highest first order rate constants for Ru-30, Ru-45 and Ru-60 were found to be 4.0×10^{-1} min⁻¹, 4.1×10^{-1} min⁻¹ and 4.8×10^{-1} min⁻¹ respectively. The unprotected Ru⁰ nano-chain networks were found to be superior with noble metal catalysts in terms of catalytic activity. Electrocatalytic anodic water splitting was catalyzed by all of them with almost similar efficiency. The required overvoltage for generating the OER current density of 10 mA/cm² was just 308 ± 2 mV which is better than many other reported values for Ru catalysts. The ECSA was determined to be 99.2 cm² and the TOF was 4.72 s⁻¹. The specific

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activity is as good as very few earlier reports which is $0.1008 \text{ mAcm}^{-2}_{\text{ECSA}}$. As a consequence of unprotected Ru⁰ nano-chain networks, superior catalytic activity and good performance in electrocatalytic water splitting were achieved. In future, the same protocol can be extended to prepare many other metal nanomaterials with unprotected surfaces for better catalytic and electrocatalytic performances without contaminating the system by the use of any foreign stabilizing agents such as stabilizers, surfactants, supports, scaffolds and templates.

Online Supporting Inormation (SI) Available.

Information on reagents, instrumentation and analytical techniques employed are elaborated. Detailed calculation of conversion, selectivity, yield, TON, TOF and the rate constants for catalytic nitroarenes hydrogenation is given. TOF calculation for the electrocatalytic water splitting is explained. Calibration curves for finding the real concentrations of the nitro compounds as Figures S1, A-F and the corresponding concentration are provided as Table S1. Details on the construction of calibration curves are given. XRD and EDS spectra are given as Figures S2 and S3, A-C. The detailed concentration of nitroarenes taken for catalytic study and other reaction parameters are tabulated as Table S2. The comparative interpretation for the catalytic activity of unprotected Ru⁰ nano-chain networks with the Ru catalysts in other forms and noble metal catalysts are provided as Table S3 and Table S4. The LDPS particle size distribution is provided as Figure S4, A-C. The time dependent UV-Vis spectra and the corresponding first order kinetic plots for all other nitroarenes except 4-NS are provided as Figures S5, A-M and Figures S5, N-Z. UV-Vis spectra, TEM micrographs and electron diffraction patterns of Ru-CTAB, Ru-SDS and Ru-TX-100 are provided as Figures S6, A-I. The time-dependent UV-Vis spectra for the hydrogenation of 4-NS by Ru-CTAB, Ru-SDS and Ru-TX-100 and their corresponding ln(conc.) vs time plots are given as Figures S7, A-F. CV of Ru-30, Ru-45 and Ru-60 are given together as Figure S8. Post cycle CV for Ru-60 after 10 h of chronoamperometric analysis is given as Figure S9. CV of Ru-60 modified GC with the -1 to 1 V of potential window for identifying non-faradaic region is given as Figure S10. This material is available free of charge via the Internet at http://pubs.rsc.org.

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Figure Captions:

Figure 1: UV-Visible (UV-Vis) absorption spectra of Ru^{3+} solution and the reaction mixtures for the formation Interconnected unprotected Ru^{0} nano-chain networks.

Figure 2: (A-I) TEM, HR-TEM micrographs and SAED patterns of the interconnected unprotected Ru⁰ nano-chain networks. Figure 2, A-C are of Ru-30, D-F are of Ru-45 and G-I are of Ru-60 respectively.

Figure 3: X-ray photoelectron spectroscopic (XPS) analysis of interconnected, unprotected Ru nano-chain networks:(A) is the survey spectra of Ru-30, Ru-45 and Ru-60; (B-D) are the high resolution 3d scans of Ru-30, Ru-45 and Ru-60 respectively; (E-G) are the high resolution Ru 3p scans of Ru-30, Ru-45 and Ru-60 respectively.

Figure 4: (A) is the time dependent UV-Vis absorption spectra of the catalytic hydrogenation of 4-NS by Ru-30; (C) is the time dependent UV-Vis absorption spectra of the catalytic hydrogenation of 4-NS by Ru-45; (E) is the time dependent UV-Vis absorption spectra of the catalytic hydrogenation of 4-NS by Ru-60; (B), (D) and (F) are the corresponding first order plots.

Figure 5: C_t/C_0 vs. Time plot of all the catalytic hydrogenation reactions studie by Ru-30, Ru-45 and Ru-60. Note: In all the cases the rate of disappearance of reactant when catalysed by Ru-60 is comparatively higher than Ru-30, Ru-45.

Figure 6: (A)and (B) are the Nyquist Bode impedance plots for the electrochemical system under study for finding R_u .

Figure 7: (A) Cyclic voltammogram (CV) of electrocatalytic water splitting by Ru-60 modified GC electrode where curve a is the CV of the same with uncompensated resistance (R_u), curve b is the CV of the same with iR drop correction. (B) is chronoamperometric i-t profile for the same Ru-60 modified GC electrode. (C) Cyclic voltammogram (CV) of electrocatalytic water splitting by Ru-60, Ru-CTAB, Ru-SDS and Ru-TX-100 modified GC electrodes respectively. (D) is the corresponding steady state polarization curves.

Figure 8: Potential sweeping test up to 200 cycles on Ru-60 modified GC at a scan rate of 10 mV/s.

Figure 9: CV response of Ru-60 modified GC electrode at different scan rates.

Figure 10: The plot of double layer charging current obtained at different scan rates against the scan rates for determining the double layer capacitance (C_{DL}) and ECSA.

Table 1: The detailed final concentrations and all other reaction parameters for the synthesis of Ru nano-chain networks.

Table 2: The detailed results of catalytic hydrogenation of all the nitro compounds by both Ru-30, Ru-45 and Ru-60.

Table 3: Results of the comparative OER studies on unprotected Ru nano-chain and Ru nanomaterials stabilized by TX-100, CTAB and SDS.

Scheme 1: The time dependent snapshots taken during the synthesis of Ru-30, Ru-45 and Ru-60.

Scheme 2: Schematic depiction of the proposed mechanism for the formation interconnected unprotected Ru⁰ nano-chain networks and its stabilization.

Scheme 3: Schematic depiction for the catalytic hydrogenation using Ru-30, Ru-45 and Ru-60 nanomaterials as catalyst. The catalyst and yields are mentioned in different color for clarity where black color indicates for Ru-30, blue color for Ru-45 and red color for Ru-60 respectively.





Figure 1





Figure 2, A-I







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Figure 3, E-G

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Figure 4, A-F

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Figure 5



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Figure 6, A-B





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Figure 8



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Figure 10

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Trial No.	Ru ³⁺ : BH ₄ ratio	Final pH of the reaction mixture	Final conc. of Ru ³⁺ (M)	Final conc. of BH4 (M)	Temp. (°C)	Observation
1	2:1	5.81	5.0×10 ⁻³	2.5×10 ⁻²	30	Precipitated in 15 min
	2:1	5.93	5.0×10 ⁻³	2.5×10 ⁻²	45	Precipitated in 7 min
	2:1	5.91	5.0×10 ⁻³	2.5×10 ⁻²	60	Precipitated in 1 min
2	1:1	6.98	1.0×10 ⁻³	5.0×10 ⁻²	30	Precipitated in 25 min
	1:1	7.02	1.0×10 ⁻³	5.0×10 ⁻²	45	Precipitated in 37 min
	1:1	7.16	1.0×10 ⁻³	5.0×10 ⁻²	60	Precipitated in 55 min
3	1:1.5	9.88	5.0×10 ⁻⁴	3.3×10 ⁻²	30	Stable colloid
	1:1.5	9.73	5.0×10 ⁻⁴	3.3×10 ⁻²	45	Stable colloid
	1:1.5	9.92	5.0×10 ⁻⁴	3.3×10 ⁻²	60	Stable colloid
4	1.5:1	6.54	6.6×10 ⁻³	5.0×10 ⁻³	30	Precipitated in 20 min
	1.5:1	6.66	6.6×10 ⁻³	5.0×10 ⁻³	45	Precipitated in 28 min
	1.5:1	6.51	6.6×10 ⁻³	5.0×10 ⁻³	60	Precipitated in 35 min
5	1:2	11.23	2.5×10 ⁻³	5.0×10 ⁻²	30	Precipitated in 12 min
	1:2	11.35	2.55×10 ⁻³	5.0×10 ⁻²	45	Precipitated in 9 min
	1:2	11.41	2.55×10 ⁻³	5.0×10 ⁻²	60	Precipitated in 3 min
6	1:4	13.01	6.12×10 ⁻⁴	7.5×10 ⁻²	30	Precipitated in 7 min
	1:4	13.12	6.12×10 ⁻⁴	7.5×10 ⁻²	45	Precipitated in 3 min
	1:4	13.06	6.12×10 ⁻⁴	7.5×10 ⁻²	60	Precipitated in 1 min

Reactant	Catalyst	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)	TON (10 ⁻¹)	TOF (M/h)	1 st order k (x 10 ⁻¹ min ⁻¹)
4-NP	Ru-30	16	99	100	99	1.948	3.896	2.670
	Ru-45	15	99	100	99	1.893	3.653	2.689
	Ru-60	14	100	100	100	2.397	4.794	2.800
Attribut	Ru-30	13	99	100	99	1.348	2.023	2.900
4-NA	Ru-45	12	100	100	100	1.456	2.123	3.191
ive Con	Ru-60	10	100	100	100	1.301	2.604	3.433
This article is the second sec	Ru-30	15	100	100	100	0.161	0.321	4.000
	Ru-45	14	100	100	100	0.169	0.33	4.121
	Ru-60	14	100	100	100	0.200	0.399	4.800
	Ru-TX-100	25	99	100	99	0.053	0.101	1.174
	Ru-CTAB	17	100	100	100	0.069	0.121	1.82
	Ru-SDS	16	100	100	100	0.055	0.136	1.838
à	Ru-30	13	99	100	99	2.474	3.711	2.213
8 2-NP	Ru-45	13	99	100	99	2.373	3.657	2.253
	Ru-60	10	100	100	100	3.094	4.642	2.400
2-NA	Ru-30	9	99	100	99	0.120	3.600	3.010
	Ru-45	8	99	100	99	0.136	3.687	3.290
	Ru-60	7	100	100	100	1.439	4.320	3.400
	30	-	0	0	0	-	-	-
2-B-6-NT	45	-	0	0	0	-	-	-
	60	3	91.94	100	91.94	0.799	2.340	8.20

Catalyst	<i>E</i> @ 10 mAcm ⁻² (mV)	η @ 10 mAcm ⁻² (mV)	Tafel (mV/dec)	Specific activity	TOF @ <i>ŋ</i> =308 mV (s ⁻¹)	Cript
TT 1				(mA/cm ⁻ _{ECSA})		S
Unprotected Ru ⁰ nano-chain networks	1538	308 ± 2	95	0.1008	4.72	Man
Ru ⁰ - TX-100	1673	443	163	-	-	oted
Ru ⁰ - CTAB	1591	361	215	-	-	ccet
Ru ⁰ - SDS	1615	385	202	-	_	e A

Table 3



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Scheme 1





3

Scheme 3

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Unprotected and Interconnected Ru⁰ Nanochain Networks: Advantages of Unprotected Surfaces in Catalysis and Electrocatalysis



ABSTRACT

Surfactant and support free, metallic, interconnected and unprotected nanochain networks of ruthenium (Ru) had been successfully synthesized at three different temperatures, viz. 30 °C, Ru-45 and 60 °C. Individual particle sizes of the interconnected nano-chain networks prepared at 30 °C (Ru-30), 45 °C (Ru-45) and 60 °C (Ru-60) were of 3.5 ± 0.5 nm, 3.0 ± 0.2 nm and 2.6 ± 0.2 nm respectively. All of them were screened for catalytic nitro arenes hydrogenation and OER studies. In catalysis, Ru-30, Ru-45 and Ru-60 are found to be highly active with the highest k_{1st} of 0.48 min⁻¹ and in electro catalysis, it required an overvoltage of 308 ± 2 mV to generate 10 mA/cm² of current density. This superior catalytic activities and electrocatalytic activities are due to the advantages of having unprotected Ru⁰ surfaces.