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Hydrolysis of sodium borohydride using Ru–Co-PEDOT nanocomposites as catalyst

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HIGHLIGHTS

- Ru–Co nanocluster synthesis.
- Incorporation of Ru–Co in PEDOT/PSS.
- Ru–Co-PEDOT uses as catalyst in hydrolysis of $NaBH_4$ to get rapid hydrogen.
- PEDOT goes to solution phase and Ru–Co act as free heterogeneous nanocatalyst.
- Reuses several times with high TC% effectively.

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ABSTRACT

It is well established that sodium borohydride, ($NaBH_4$) is one of the most safe and attractive hydrogen-storage materials for H_2 production. In this work, we have reported a zero valent Ruthenium–Cobalt (Ru–Co) based nanocluster incorporated conducting PEDOT/PSS nanocomposite as the catalyst for rapid hydrogen production from $NaBH_4$. Initially, Ru–Co nanocluster was synthesized by reduction of a mixture of Ruthenium(III) chloride and Cobalt(II) chloride using sodium borohydride solution. Although the Ru–Co itself showed good synergistic catalytic effect as compared to bare Ru and Co nanoparticles, but their performance was found to be exceptionally good when incorporated into the conducting polymer (PEDOT/PSS). The obtained catalyst was characterized by TEM, EDX, XRD, four-probe conductivity measurements, etc. The hydrolysis kinetics showed that the 85 wt% $NaBH_4$ + 15 wt% Ru–Co PEDOT/PSS nanocomposite sample in 1 M NaOH yielded best result among all other combinations. A hydrogen generation rate of 40.1 L min^{-1} g^{-1} at 25 °C was achieved, which makes it a noteworthy result as compared to other catalysts reported earlier.

1. Introduction

One of the critical challenges of today's world is generation of enormous amount of energy without contributing too much to the increasing global pollution. Unfortunately, the major source of energy till now is fossil fuels, which, in turn, creates a range of environmental problems. Because of this, including global warming caused by the combustion of fossil fuels, there has been a growing interest for the "hydrogen-economy" as a long-term solution toward a sustainable energy future. The development of hydrogen generation as well as hydrogen storage with the use of sustainable energy sources promises to improve numerous current problems such as air pollution, greenhouse gas production, and global security [1–7]. For real applications of H_2 energy, high gravimetric and volumetric density of hydrogen storage is required. Among various hydrogen storage systems, chemical hydrides are candidates with the greatest potential for success in terms of the low operation pressure, less cost and less energy losses [7–11]. These hydrides can evolve H_2 within few minutes in a controlled manner which is a less hazardous method, eliminating the most problematic step of carrying flammable H_2 gas. Among these chemical hydrides, hydrolysis of $NaBH_4$ produces hydrogen gas and water-soluble sodium metaborate, $NaBO_2$, in the presence of suitable catalyst [9,12–15]. By this way hydrogen can be generated safely for the fuel cell application.

$$NaBH_4 + 2H_2O \xrightarrow{(\text{Catalyst})} NaBO_2 + 4H_2 + \text{heat} \qquad (1)$$

Since the hydrolysis occurs only in the presence of a suitable catalyst, many transition metals or their derivative compounds have been tested as catalyst for this industrially important reaction

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presented in Eq. (1) [8,16–18]. The theoretical gravimetric hydrogen storage capacity of $NaBH_4$ is about 10.8 wt% but the effectiveness is generally reported to be below 7 wt% due to low solubility of $NaBO_2$ and the nature of the catalyst. In the presence of appropriate catalysts, the hydrolysis reaction of $NaBH_4$ can be easily initiated, controlled and even the rate of hydrogen generation can also be accelerated. Among various catalytic reagents, Ru has been widely tested as catalyst for hydrogen generation. Recently, non-toxic and non-noble metals like Ni, Co have been chosen as low cost catalyst instead of expensive Ru [19–23], although they have not yielded satisfactory results. Compared to these metal powdered catalysts, the supported catalysts are highly appreciated in the practical applications as they can prevent the aggregation of catalyst particles into larger agglomeration leading to decrease in catalytic activity and lifetime [24].

In this work, we have described the synthesis of a highly efficient heterogeneous catalyst for H_2 generation at very high rate. The catalyst was synthesized by the reduction of Ru(III) and Co(II) salts to form metallic nanoparticles followed by their incorporation into a conducting polymer blend PEDOT/PSS (poly-3,4-ethylenedioxythiophene/poly-styrenesulfonate) via in situ polymerization. Though the Ru–Co nanoparticles itself showed good synergetic effect with respect to bare Ru and Co nanoparticles, it expressed exceptionally good catalytic behavior when incorporated into the PEDOT/PSS. The conducting blend polymer of PEDOT/PSS is well known for its conducting nature, stability in long pH range and most importantly, solubility in water [25,26]. The catalytic activity of Ru and Co along with their different derivatives is well studied and reported. But, the concoction of these two metal nanoparticles showed superior performance from their expected additive values. In spite of that, the nanoparticles were mixed with the PEDOT/PSS to study the catalytic properties. In the hydrolysis process, the blend polymer easily gets solvated into the reaction medium, releasing the Ru–Co nanoparticles in free state to provide maximum surface to volume ratio for catalysis. Hydrolysis of $NaBH_4$ using this synthesized catalyst, not only accelerate the rate of hydrogen release, but also reduces the operation cost by recycling the used catalyst in further processes. After successful completion of 1st catalytic cycle, the remaining metal in their zero valance state can be used to regenerate the catalyst by further incorporation into the PEDOT/PSS polymer. We investigate the appropriate weight percentage of the catalyst components, molarity of the NaOH as well as the $NaBH_4$ loading. The effect of catalyst on the hydrogen release rate is also investigated along with its reproducibility, in order to develop a promising catalyst for hydrogen generation in real life.

2. Experimental

2.1. Materials

Sodium borohydride ($NaBH_4$), Cobalt chloride hexahydrate ($CoCl_2$, $6H_2O$), and Sodium hydroxide (NaOH) were purchased from Merck-India. Ruthenium chloride ($RuCl_3$, xH_2O), 3,4-ethylenedioxythiophene (EDOT) monomer and poly-styrenesulfonate (PSS) were supplied from Sigma–Aldrich. Ammonium peroxydisulphate (APS) was purchased from Merck. Deionized water from a Millipore's Milli-Q ultra purification system having resistivity greater than 18.2 MW-cm was used in sample preparation. EDOT is distilled prior to use but except that all chemicals were of reagent grade and used as received without further purification.

2.2. Preparation of Ru–Co nanoparticles

Ru–Co nanoparticles were prepared by the reduction of their chloride salts with $NaBH_4$ [27]. 10 mL of 2 mM aqueous $RuCl_3$ solution was mixed with 10 mL of 2 mM $CoCl_2$ and 2 mL of 0.112 M of aqueous $NaBH_4$ solution was then added to this solution mixture dropwise under vigorous stirring condition. Molar ratio of $NaBH_4$ to (Ru + Co) must be greater than 5 times to ensure complete reduction of metal ions to its zero oxidation state. Complete reduction of the metal ions was indicated by ceasing of effervescence from the reaction mixture. The dark brown Ru–Co nanoparticles were precipitated, rinsed with acetone, filtered and dried under vacuum oven at 60 °C.

2.3. Preparation of Ru–Co-PEDOT/PSS nanocomposite

The Ru–Co nanoparticles were incorporated with the PEDOT/PSS through the oxidation of the EDOT monomer via in situ polymerization [28]. Aqueous dispersion was prepared by introducing 2 ml of PSS with 1.5 ml of distilled EDOT monomer in 1:1 mol ratio stirring in 100 ml of water. This solution was added to 100 ml colloidal dispersion containing specified quantities of Ru–Co nanoparticles and 2.28 g of APS (in 1:2.5 mol ratio w.r.t. monomer) as oxidant was added to this mixture. Polymerization reaction was allowed to continue for 20 h under vigorous stirring. Resulting dark blue colored nanocomposite samples remained in the dispersed phase. In order to isolate the samples in the solid-state, precipitation of the nanocomposites were carried out using ethanol as the non-solvent. The precipitates were washed and dried in a vacuum.

2.4. Characterization of catalyst

The morphology of prepared catalyst was identified using a JEOL-JEM, 2010, Transmission Electron Microscope (TEM) at 200 kV, whereas the elemental compositions on catalyst surface were analyzed with energy dispersive spectra (EDS). Phase identification and insertion of Ru–Co into the PEDOT was confirmed using powdered X-ray diffractometer (Philips PW 1710) with Cu Kα (λ = 1.5406 Å) radiation.

2.5. Catalyst performance test

The catalytic activity of the catalyst was measured by a self-assembled instrument where the amount of hydrogen generation was measured by using the classical water-displacement method. $NaBH_4$-catalyst mixture was prepared by the 'mortar' route as follows. $NaBH_4$ powder and catalyst (Ru–Co-PEDOT/PSS) were mechanically mixed together in a mortar for half an hour. In a typical measurement, 1 M NaOH solution was added in a sealed round bottom flask containing varied amount of catalyst (fitted with an outlet for collecting evolved H_2 gas) to initiate hydrolysis reaction as shown in Scheme 1. As the reaction proceeds, the water displaced by hydrogen gas in the graduated cylinder connected to the reaction flask was continually monitored. To get a clear idea about the experiment and instrumentation procedure, we have given a schematic diagram of our self assembled instrument and mechanism in Schemes 1 and 2.

In case of Ru–Co-PEDOT/PSS catalyst, once the H_2 liberation was completed, the flask was detached from the apparatus and the NaOH solution containing free Ru–Co nanoparticles was centrifuged and washed repeatedly. The residue was then dried and again used to produce the Ru–Co-PEDOT/PSS catalyst by incorporating into the PEDOT/PSS system in order to check the reproducibility of the catalyst.

3. Result and discussion

Our main objective is to improve the hydrogen generation rate through hydrolysis of $NaBH_4$ using the prepared catalyst in its