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# Novel synthesis of highly catalytic active Cu@Ni/RGO nanocomposite for efficient hydrogenation of 4-nitrophenol organic pollutant

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## ABSTRACT

A novel method for the synthesis of non-noble metal based catalyst, copper–nickel-reduced graphene oxide (Cu@Ni/RGO) is established using two step methodology. First, the Ni/RGO nanocomposite was synthesized by the simultaneous reduction of Ni<sup>2+</sup> ions and graphene oxide (GO) under reducing conditions, and after that Cu nanoparticles (Cu NPs) were encapsulated on them. We discuss the role of in-situ generated hydrogen radical (H<sup>•</sup>) through spillover of H<sub>2</sub> on Ni/RGO which led the formation of crystalline Cu NPs, easily. The structure, composition and morphology of Cu@Ni/RGO nanocomposite were characterized by several related techniques. Further, we explored the practical application of non-noble metal based catalyst Cu@Ni/RGO for catalysis reaction due to its high catalytic performance towards reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). It showed a remarkable high activity 90 s at room temperature (RT) with excellent stability up to 5 cycles.

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## Introduction

Recently, bimetallic metal NPs gained lots of interest due to their fine structure, specific electronic structures, extra defect sites/voids, additional degree of freedom, special geometrical structure and composition [1,2]. They have been utilized for a number of applications as sensors/biosensors,

energy storage devices and various kinds of catalysis reactions [3]. For instance, Liu et al. synthesized the rhenium-modified Rh–Ir alloy catalyst for one-pot conversion of furfural into 1,5-pentanediol [4]. Very recently, Cui et al. has been demonstrated the Pt/Au alloy nanowire array use for early detection of phosphate [5]. Similarly, Lang et al. reported the Pd–Ag alloy dendritic nanowires for hydrogen

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sensor application [6]. More interestingly, Pozun et al. systematically investigated the catalytic activity of the bimetallic NPs catalyst for hydrogenation reaction and emphasized the role of electronic density of states (DOS) of surface species [7]. They have developed the idea based on Brønsted–Evans–Polanyi (BEP) relation for surface reactions/adsorption energies; emphasized the role of electronic structure in metals, specifically the d-band center which was first modeled by Newns. Moreover, for heterogeneous catalysis reactions, integration of metal NPs with various kind of supports is also fast growing area of research due to enhance kinetics and selectivity [8].

Recently, it has been speculated that newly discovered carbon allotrope ‘graphene’ gained a great deal of attention due to its low density, high thermal and electrical conductivity and theoretically large specific surface area 2630 m<sup>2</sup>/g along with its chemical inertness and robustness [9]. Due its large surface area it can accommodate several kinds of NPs with good support and finds various applications [10,11]. Very recently, Chen et al. demonstrated the Suzuki–Miyaura and Sonogashira carbon coupling (SCC) reactions using Ag–Pd/RGO nanocatalyst [12]. Similarly, Kim et al. reported the excellent use of the RGO support material in bimetallic alloy condition for catalytic electrooxidation of formic acid using Au–Pt/RGO nanocomposite [13]. However, for many catalytic reactions the use of noble metal elements is not suitable due to their high cost and less abundance.

4-NP is a common organic pollutant and effluent in many drugs and dyes industries and for their reduction it has been reported that catalyst is indeed needful for the accomplishment of reaction [14]. For reduction of 4-NP it has been reported that catalyst with hydrogen spillover capability is more pronounced [15]. For instance, very recently Krishna et al. reported the successful reduction of 4-NP using Ag@Co/RGO nanocomposite in a very short time (90 s) [16]. Sun et al. demonstrated the reduction of 4-NP using Pd/RGO nanocomposite within 120 s [17]. Similarly, Barman et al. presented the high catalytic activity of Pd/RGO and Pt/RGO nanocomposites towards reduction of 4-NP [18]. However, rate of reduction of 4-NP with non-noble metals catalyst was slow. For instance, Chen et al. demonstrated the reduction of 4-NP with Ni/RGO in 180 min [19]. The slow reduction process on Ni/RGO can be anticipated on the basis of surface oxidation of metallic species during the reaction and further lowering the electronic conductivity.

Considering the high cost of noble metals and slow reduction process of Ni/RGO, it is crucial to develop new materials for this catalysis reaction with retention of catalytic activity and lower price. In this aspect, it is highly desirable for this reaction synthesis of conductive material along with spillover capability. Cu is easily abundant, low price and highly conductive transition metal which can a good alternative to noble metals [20]. Several methods have been developed for the synthesis of Cu NPs such as photochemical irradiation, electrochemical reduction and thermal decomposition [21,22]. Apart of them, wet chemical synthesis of Cu NPs is more fascinating due to the easy reduction of salt solution [23]. Here, we report the step-wise novel synthesis of Cu@Ni/RGO nanocomposite and its application for the efficient hydrogenation of 4-nitrophenol organic pollutant.

## Experimental

### Materials

Graphite powder, NaNO<sub>3</sub>, potassium permanganate (KMnO<sub>4</sub>), nickel chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O), copper sulphate (CuSO<sub>4</sub>·5H<sub>2</sub>O), conc. H<sub>2</sub>SO<sub>4</sub> (96%), HCl (36.5%), H<sub>2</sub>O<sub>2</sub> (30% v/v), sodium hydroxide (NaOH), sodium borohydride (NaBH<sub>4</sub>), 4-NP, and hydrazine hydrate (65%) were purchased from Sigma Aldrich Co. All other chemicals were of analytical grade and all aqueous solutions were prepared in double distilled (DD) water (>18.2 MΩ cm) from a Milli-Q Plus system (Millipore).

### Synthesis

#### Synthesis of GO

Graphene oxide (GO) was synthesized by the modified Hummers method as previous reported [16]. Briefly, natural flake graphite (1.5 g) was dispersed in ice cooled conc. H<sub>2</sub>SO<sub>4</sub> (70 mL) by stirring 30 min. Afterward, NaNO<sub>3</sub> (0.75 g) and KMnO<sub>4</sub> (9 g) were slowly mixed in acidic solution by maintaining the temperature less than 35 °C under continuous stirring for 4 h. The temperature was then increased to 35 °C and excess DD water (540 mL) was added into the solution and the suspension was heated up to 98 °C for 30 min. Finally, 15 mL H<sub>2</sub>O<sub>2</sub> (30% v/v) was slowly poured into the solution for quench the reaction. After completion of reaction, resultant suspension was centrifuged (3000 rpm) in order to remove the residual unexfoliated graphite and subsequently filtered and washed with DD water and dilute HCl (until the pH of the filtrate was neutral) for removing remaining impurities and oxidizing agents. The resulting filter cake was re-dispersed in DD water to make the 1 mg/mL dispersion.

#### Synthesis of Ni/RGO nanocomposite

To synthesize the Ni/RGO nanocomposite, 100 mL of aqueous GO dispersion (1 mg/mL) was placed in 4-neck round bottom (RB) flask and mechanically stirred. Then, 600 mg of NiCl<sub>2</sub>·6H<sub>2</sub>O was mixed and the temperature of reaction was gradually increased up to 85 °C. Further, under an inert atmosphere of high purity Ar gas, 18 mL of hydrazine hydrate was slowly poured inside the reaction mixture and was continuously stirred for 25 min. Then, 450 mg of NaBH<sub>4</sub> was very slowly added while maintaining of stirring and inert atmosphere. Finally, 15 mL aqueous solution of NaOH (1 M) was slowly added and stirred for further 150 min. After completion of reaction the product was filtered and washed with ethanol and DD water to remove the impurities. Finally, vacuum dried at 100 °C for 3 h and referred as Ni/RGO.

#### Synthesis of Cu@Ni/RGO nanocomposite

The Cu@Ni/RGO nanocomposite was prepared as follows: first, Ni/RGO dispersion was prepared in DD water (50 mL, 2 mg/mL) by ultrasonication (15 min) then, 600 mg of CuSO<sub>4</sub>·5H<sub>2</sub>O was added in aqueous dispersion and mixed for 20 min with stirring. Afterward, 1 M NaOH (10 mL, aq.) solution was added in Ni/RGO dispersion to increase the pH of mixture and stirred for 10 min at RT. After stirring the precipitate was filtered and re-dispersed in 25 mL DD water by

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