Hydrogen generation of single alloy Pd/Pt quantum dots over Co₃O₄ nanoparticles via the hydrolysis of sodium borohydride at room temperature

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To satisfy global energy demands and decrease the level of atmospheric greenhouse gases, alternative clean energy sources are required. Hydrogen is one of the most promising clean energy sources due to its high chemical energy density and near-zero greenhouse gas emissions. A single alloyed phase of Pd/Pt nanoclusters as quantum dots (QDs) was prepared and loaded over Co₃O₄ nanoparticles with a low loading percentage (1 wt.%) for hydrogen generation from the hydrolysis of NaBH₄ at room temperature. L-glutathione (SG) was used as a capping ligand. It was found that the single alloy catalyst (Pd₀.₅–Pt₀.₅)ₙ(SG)ₘ/Co₃O₄ caused a significant enhancement in hydrogen generation in comparison to the monometallic clusters (Pdₙ(SG)ₘ and Ptₙ(SG)ₘ). Moreover, the Pd/Pt alloy showed a positive synergistic effect compared to the physical mixture of Pd and Pt clusters (1:1) over Co₃O₄. The QDs alloy and monometallic Pd and Pt clusters exhibited well-dispersed particle size in ~1 nm. The (Pd₀.₅–Pt₀.₅)ₙ(SG)ₘ/Co₃O₄ catalyst offers a high hydrogen generation rate (HGR) of 8333 mL min⁻¹ g⁻¹ at room temperature. The synergistic effect of Pd and Pt atoms in the nanoclusters alloy is the key point beyond this high activity, plus the prepared clusters’ unique atomic packing structure and electronic properties. The effect of the NaBH₄ concentration, catalyst amount, and reaction temperature (25–60 °C) were investigated, where HGR reaches 50 L min⁻¹ g⁻¹ at 60 °C under the same reaction conditions. The prepared catalysts were analyzed by UV–Vis, TGA, HR-TEM, XRD, and N₂ adsorption/desorption techniques. The charge state of the Pd and Pt in monometallic and alloy nanoclusters is zero, as confirmed by X-ray photoelectron spectroscopy analysis. The catalysts showed high recyclability efficiency for at least five cycles due to the high leaching resistance of the alloy nanoclusters within the Co₃O₄ host. The prepared catalysts are highly efficient for energy-based applications.

Bimetallic systems as heterogeneous catalysts have received tremendous scientific and industrial attention due to their excellent catalytic performance compared to monometallic systems¹–³. The synergistic effect and cooperative interactions between the two metals are the main reason beyond their activity, where the electrons transfer or exchange between the two metals in the bimetallic lattice enhances the catalytic activity of the bimetallic systems¹,²,⁴.

Recently, hydrogen as clean energy has been considered a key factor in the increasing depletion of fossil fuels and exacerbating the environmental pollution crisis⁵,⁶. Hydrogen is universally accepted as a clean energy source due to its relatively high energy density (142 MJ kg⁻¹) in comparison to diesel and gasoline (46 MJ kg⁻¹) and can reduce the amount of greenhouse gas and acid rain when used as fuel⁷. Hydrolysis of sodium borohydride (NaBH₄) has been reported to be a promising way to generate hydrogen due to its high hydrogen content (10.65 wt.%), low price, and nontoxicity (NaBH₄ + 2H₂O → NaBO₂ + 4H₂, ΔH = -300 kJ mol⁻¹)⁸–₁². Metal alloys such as NiB and CoB showed good activity in the hydrolysis of NaBH₄⁹,¹⁰,¹¹, where 5 wt. % CoB/CeO₂ showed

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hydrogen generation rate (HGR) of 533 mL g⁻¹ min⁻¹. Patel et al.⁴ reported the effect of electron transfer between metallic Co and B.

Noble metals such as Au, Pd, Ru, and Pt-based catalysts were reported as ideal candidates for hydrogen generation due to their excellent catalytic activity and high stability. Vol. 12(2022), 17040. Patil et al.⁴ reported the effect of electron transfer between metallic Co and B. 20 wt.% of Ru (19.9 nm), Pd (12.2 nm), and Pt (3.2 nm) over Co₃O₄ showed high catalytic activity in hydrolysis of NaBH₄, with a hydrogen generation rate (HGR) of 8333 mL g⁻¹ min⁻¹. Patil et al.⁴ reported the effect of electron transfer between metallic Co and B. 20 wt.% of Ru (19.9 nm), Pd (12.2 nm), and Pt (3.2 nm) over Co₃O₄ showed high catalytic activity in hydrolysis of NaBH₄, with a hydrogen generation rate (HGR) of 8333 mL g⁻¹ min⁻¹. Patil et al.⁴ reported the effect of electron transfer between metallic Co and B.

To prepare size-selected metal nanoclusters (quantum dots, QDs), a great deal of work should be done; for example, deposition of Pt clusters over single-crystal supports such as MoO₃ and TiO₂ under ultrahigh vacuum (UHV) conditions 10⁻⁹ mbar. This model of catalysis is very complicated and largely deviated from the real world of catalytic conditions. Monolayer-protected nanoclusters of noble metals have recently gained much attention in the catalysis field due to their unique atomic packing structure and electronic properties. In our previous work, platinum nanoclusters protected with l-cysteine and N-acetyl-l-cysteine over TiO₂ showed high catalytic activity in the oxidation of styrene and solar degradation of methylene blue, respectively. Pd nanoclusters protected with N-acetyl-l-cysteine exhibited superior catalytic activity in hydrogenation of α, β-unaturated aldehydes such as cinnamaldehyde. Moreover, size-selected gold clusters (Au₂₅(SCH₂CH₂Ph)₁₈, Au₃₈(SCH₂CH₂Ph)₂₄, and Au₁₄₄(SCH₂CH₂Ph)₆₀) over ceria showed high catalytic activity in the oxidation of carbon monoxide at a low temperature.

To the best of our knowledge, this is the first time to prepare a single alloyed Pd/Pt quantum dots (QDs) in regime of 1 nm by simple way in a large yield. A very low loading percentage (1 wt.%) from the prepared alloy over Co₃O₄ achieved a high hydrogen yield with a hydrogen generation rate (HGR) of 8333 mL g⁻¹ min⁻¹. Additionally, a comparison between the activity of the single alloy and the physical mixing of Pd and Pt nanoclusters was studied, where the alloy exhibited a positive synergistic effect and the physical mixing showed a negative synergistic effect. Where, the physical mixture of palladium and platinum nanoclusters (1:1) was loaded over the Co₃O₄ nanoparticles for comparison. 1 wt.% (Pdₐ₋₅–Ptₐ₋₅)(SG)ₙ/Co₃O₄ catalyst showed the best catalytic activity in the hydrolysis of NaBH₄, more than the monometallic Ru or Pt catalysts. The Ru-Co alloys over γ-Al₂O₃ showed higher HGR in NaBH₄ hydrolysis than single monometallic samples. Ni–Pt/Co₃O₄ over granular activated carbon catalyst achieved complete and rapid decomposition of hydrazine hydrate to generate H₂ with a 100% selectivity at moderate temperature in the presence of 1 M NaOH. Moreover, the salisylaldimine-Ni complex has shown 90% increment in NaBH₄ hydrolysis than pure Ni catalyst with a maximum hydrogen production rate of 2240 mL min⁻¹ g⁻¹.

Experimental

Chemicals. Potassium hexachloropalladate (IV) (K₂PdCl₆, 98%, Sigma–Aldrich), chloroplatinic acid (H₂PtCl₆.6H₂O, ≥ 37.5% Pt basis, Sigma–Aldrich), sodium borohydride (NaBH₄, ≥ 96%, Aldrich), l-glutathione (99%, Sigma–Aldrich) and ethanol were used for preparing the protected Pd and Pt nanoclusters and the Pd–Pt alloy nanoclusters. Cobalt (II, III) oxide (Co₃O₄) nanopowder, < 50 nm particle size (99%, Sigma–Aldrich), and ethanol were used for preparing the protected Pd and Pt nanoclusters and the Pd–Pt alloy nanoclusters. Co₃O₄ nanoparticles for comparison. 1 wt.% (Pdₐ₋₅–Ptₐ₋₅)(SG)ₙ/Co₃O₄ catalyst showed the best catalytic activity in the hydrolysis of NaBH₄, more than the monometallic Ru or Pt catalysts. The Ru-Co alloys over γ-Al₂O₃ showed higher HGR in NaBH₄ hydrolysis than single monometallic samples. Ni–Pt/Co₃O₄ over granular activated carbon catalyst achieved complete and rapid decomposition of hydrazine hydrate to generate H₂ with a 100% selectivity at moderate temperature in the presence of 1 M NaOH. Moreover, the salisylaldimine-Ni complex has shown 90% increment in NaBH₄ hydrolysis than pure Ni catalyst with a maximum hydrogen production rate of 2240 mL min⁻¹ g⁻¹.

Preparation of Pdₐ(SG)ₙ nanoclusters. 79.466 mg potassium hexachloropalladate (IV) (K₂PdCl₆, 0.2 mmol) was dissolved in 10 mL double-distilled water, 43.02 mg l-glutathione (0.14 mmol) was dissolved in 3 mL double-distilled water, and added to the palladium solution, under vigorously stirring (~ 1100 rpm) at room temperature. During the addition of the l-glutathione solution, the orange color of the palladium salt became light orange, and then the color changed to red. After 30 min. of stirring, a freshly prepared aqueous solution of NaBH₄ (75.66 mg, 2 mmol, dissolved in 3 mL double-distilled water) was added dropwise over the resulting solution while stirring vigorously (~ 1100 rpm). The red solution converted quickly to black, indicating the reduction of the palladium salt and the formation of palladium nanoclusters. The reaction was allowed to proceed under constant stirring for 1 h. The mixture was evaporated under a vacuum to near dryness, and then the particles were precipitated by adding ethanol. The black-brown precipitate was re-dissolved in double-distilled water and re-precipitated by ethanol. This step should be repeated three times to remove excess NaBH₄. The resulting precipitate was then collected through centrifugal precipitation and washed with ethanol to remove the unreacted material. The black-brown solid consisting of Pdₐ(SG)ₙ nanoclusters was finally dried overnight at 100°C.

Preparation of Ptₐ(SG)ₙ nanoclusters. 81.96 mg chloroplatinic acid (H₂PtCl₆.6H₂O, 0.2 mmol) was dissolved in 10 mL double-distilled water, and 43.02 mg l-glutathione (0.14 mmol) was dissolved in 3 mL double-distilled water and added to the platinum solution, under vigorously stirring (~ 1100 rpm) at room temperature. During the addition of the l-glutathione solution, the yellow solution of platinum salt showed some turbidity...
after adding the ligand, then the color changed to orange and finally to canary yellow. After 30 min stirring, a freshly prepared aqueous solution of NaBH₄ (75.66 mg, 2 mmol, dissolved in 3 mL double-distilled water) was added dropwise over the resulting solution while stirring vigorously (~1100 rpm). The canaries yellow color solution converted gradually to black, indicating the reduction of the platinum salt and formation of platinum nanoclusters. The reaction was allowed to proceed under constant stirring for 1 h. Then, the Pt₄(SG)₉ nanoclusters were separated, purified, and dried as described in the case of Pd₄(SG)₉ nanoclusters.

Preparation of (Pd₀.₅–Pt₀.₅)n(SG)₉ nanoclusters. 40.98 mg chloroplatinic acid (H₂PtCl₆·H₂O, 0.1 mmol) was dissolved in 5 mL double-distilled water (solution A). 32.73 mg potassium tetrachloropalladate (II) (K₂PdCl₄, 0.1 mmol) was dissolved in 5 mL double-distilled water (solution B). Solution A was mixed with solution B for 30 min., and then 43.02 mg L-glutathione (0.14 mmol) was dissolved in 3 mL double-distilled water and added to the solution vigorously stirring (~1100 rpm) at room temperature. The L-glutathione solution reacted with the mixed solutions of the two salts simultaneously. After adding the ligand, the yellow solution showed some turbidity; then the color changed to orange and finally to canary yellow. After 30 min. stirring, a freshly prepared aqueous solution of NaBH₄ (75.66 mg, 2 mmol, dissolved in 3 mL double-distilled water) was added dropwise over the resulting solution while stirring vigorously (~1100 rpm). The canaries yellow color solution converted gradually to black, indicating the platinum and palladium salts reduced simultaneously to form Pd–Pt single alloy nanoclusters. The reaction was allowed to proceed under constant stirring for 1 h. Then, the (Pd₀.₅–Pt₀.₅)n(SG)₉ alloy was separated, purified, and dried as described in the case of Pd₄(SG)₉ nanoclusters.

Loading of the prepared nanoclusters over Co₃O₄. The 1 wt.% of catalysts (Pd₄(SG)₉/Co₃O₄, P₄(SG)₉/Co₃O₄, Pd₄(SG)₉ + Pt₄(SG)₉/Co₃O₄, and (Pd₀.₅–Pt₀.₅)n(SG)₉/Co₃O₄) were prepared by a well-known impregnation method. 0.5 g of Co₃O₄ nanoparticles were suspended in 50 mL double-distilled water in an ultrasonic bath for 30 min., 5 mg of the clusters were dissolved in 10 mL double-distilled water, and then added to the Co₃O₄ slurry. The slurry was stirred 24 h at room temperature, and then the loaded catalyst was collected by centrifuge at 6000 rpm, for 10 min. The brown color of the clusters solution becomes colorless, confirming the transfer of all clusters amount to the Co₃O₄ surface. The loaded catalysts were dried in an oven at 100 °C overnight.

The catalytic reaction for the hydrolysis of NaBH₄. The hydrolysis of NaBH₄ has been performed at room temperature (25 °C), over 5 mg of the prepared catalysts (Pd₄(SG)₉/Co₃O₄, Pt₄(SG)₉/Co₃O₄, Pd₄(SG)₉ + Pt₄(SG)₉/Co₃O₄, and (Pd₀.₅–Pt₀.₅)n(SG)₉/Co₃O₄). 1 g of NaBH₄ was added to 100 mL of water (corresponding to 1 wt.%), and the catalyst was added. The reaction solution was stirred at 1000 rpm. The hydrogen-generated volume was measured using the water displacement method. (Pd₀.₅–Pt₀.₅)n(SG)₉/Co₃O₄ was used as a model catalyst to study the effect of catalyst weight (5, 15, 30, and 50 mg) in the hydrolysis of 1 wt.% NaBH₄ solution at 25 °C.

5 mg of the (Pd₀.₅–Pt₀.₅)n(SG)₉/Co₃O₄ catalyst was chosen to employ different NaBH₄ solutions such as 0.189, 0.5, 1, and 2 wt.%. The same amount of the catalyst was used to follow up the reaction at different temperatures 25, 45, and 60 °C, of the 1 wt.% NaBH₄ solution.

In the recyclability study, 5 mg of (Pd₀.₅–Pt₀.₅)n(SG)₉/Co₃O₄ catalyst was repeatedly used five times to generate H₂ using 1 wt.% NaBH₄ solution at 25 °C. Once the hydrolysis reaction of NaBH₄ was completed, a new NaBH₄ solution was added for a second cycle, and so on.

Results and discussion

Optical properties and chemical composition of the prepared nanoclusters. Metal nanoclusters exhibit some absorption in a visible region, and these absorptions come from the excitation of plasmon resonance electrons or interband transitions. These absorption peaks’ positions and width depend on the metal type, particle size, protecting ligand, and chemical charge. Pt nanoparticles in regime 4–10 nm show an absorption peak at 215 nm. The intensity of this peak decreases by decreasing particle size and is essentially undetectable for smaller clusters less than 2 nm. S-containing Pd(II) complexes exhibited surface plasmon peak at 350–500 nm, corresponding to the charge transfer between the metal and ligand. The prepared Pd and Pt nanoclusters and Pd/Pt alloy nanoclusters in water show featureless absorption curves in the UV–vis region, where their color is dark brown (Fig. 1–1). These absorption curves agree with the theoretical calculations by Creighton and Eadon. As shown in Fig. 1–1, there are no peaks or noise in the 350–500 nm region, indicating the prepared nanoclusters are pure from the intermediated complex (Pd(II)-SG), and all the palladium ions are reduced to Pd(0). Moreover, the prepared nanoclusters are pure from the unreacted l-glutathione ligand, which shows one absorption peak at 224 nm.

Thermogravimetric analysis (TGA) is used to obtain the ratio between the organic and metallic parts in the protected nanoclusters. Therefore, the metal-to-ligand ratio (M/L) and the average chemical formula of the MPCs can be estimated. Figure 1–II shows the TGA curves of the prepared nanoclusters and the pure ligand. According to the TGA curves, the protecting ligand in Pd₄(SG)₉, Pt₄(SG)₉, and (Pd₀.₅–Pt₀.₅)n(SG)₉ nanoclusters decompose in two decomposition steps. The ligand decomposition is completed at 900 °C; the residual is the metallic part. The weight percentage of the metallic part of the prepared nanoclusters Pd₄(SG)₉, Pt₄(SG)₉, and (Pd₀.₅–Pt₀.₅)n(SG)₉ are 50.18, 62.1, and 56 wt. % (Table 1). The average metal/ligand ratio (M/L) and the average molecular formula of the prepared nanoclusters are calculated and summarized in Table 1.
The particles size and charge of the prepared nanoclusters. High resolution-transmission electron microscopy (HR-TEM) was used to measure the particle size of the prepared nanoclusters. Figure 2 (I, II, and III) shows the HR-TEM images of the prepared clusters (Pd\textsubscript{n}(SG)\textsubscript{m}, Pt\textsubscript{n}(SG)\textsubscript{m}, and (Pd\textsubscript{0.5–Pt\textsubscript{0.5}})\textsubscript{n}(SG)\textsubscript{m}, respectively. The particle size of the prepared clusters is ~ 1 nm, which appears as QDs. The single alloy QDs (Pd\textsubscript{0.5–Pt\textsubscript{0.5}})\textsubscript{n}(SG)\textsubscript{m}) shows a particle size that is uniformly distributed similar to the monometallic nanoclusters (Pd\textsubscript{n}(SG)\textsubscript{m} and Pt\textsubscript{n}(SG)\textsubscript{m}). This indicates that the method can be used for bimetallic and monometallic QDs preparation.

The particle charge of the prepared nanoclusters is characterized by X-ray photoelectron spectroscopy (XPS). The Pd 3d XPS spectrum of the Pd\textsubscript{n}(SG)\textsubscript{m} clusters is shown in Fig. 3-I. The binding energies of the Pd 3d\textsuperscript{5/2} and 3d\textsuperscript{3/2} electrons are at 335.42 and 340.66 eV\textsuperscript{16} respectively, corresponding to Pd(0). These findings are in agreement with those obtained for Pd nanoparticles loaded on Co\textsubscript{3}O\textsubscript{4} nanoparticles\textsuperscript{43,44}. Figure 3-II shows the XPS spectrum of platinum atoms in Pt\textsubscript{n}(SG)\textsubscript{m} clusters, the binding energies of the Pt 4F\textsuperscript{5/2} and 4F\textsuperscript{7/2} electrons are 74.58 and 71.19 eV, respectively, that are corresponding to Pt(0)\textsuperscript{45}. The charge of Pd and Pt atoms in the single alloy nanoclusters (Pd\textsubscript{0.5–Pt\textsubscript{0.5}})\textsubscript{n}(SG)\textsubscript{m} are also zero, as confirmed by XPS analysis (Fig. 3-III,IV), where the binding energies of the Pd 3d\textsuperscript{5/2} and 3d\textsuperscript{3/2} electrons are 335.44 and 340.70 eV, and for Pt 4F\textsuperscript{5/2} and 4F\textsuperscript{7/2} electrons are 74.36 and 71.02 eV, respectively. The absence of the two peaks of Pd\textsuperscript{4+} at 339.2 and 342.9 eV indicates the presence of Pd in metallic form (neither as PdO\textsubscript{2} nor Pd(OH)\textsubscript{4})\textsuperscript{43}.

Table 1. The thermogravimetric analysis data for the prepared nanoclusters.

| Catalysts                  | Weight (%) at 900 °C | M/S ratio | Molecular formula |
|----------------------------|----------------------|-----------|-------------------|
| (Pd\textsubscript{0.5–Pt\textsubscript{0.5}})\textsubscript{n}(SG)\textsubscript{m} | 56.00                | 1:0.38    | (Pd–Pt)\textsubscript{3}nLn     |
| Pd\textsubscript{n}(SG)\textsubscript{m} | 50.18                | 1:0.34    | Pd\textsubscript{3}nLn          |
| Pt\textsubscript{n}(SG)\textsubscript{m} | 62.10                | 1:0.30    | Pt\textsubscript{n}Ln           |

Figure 2. High resolution-transmission electron microscopy (HR-TEM) images of the prepared clusters Pd\textsubscript{n}(SG)\textsubscript{m} (I), Pt\textsubscript{n}(SG)\textsubscript{m} (II), and (Pd\textsubscript{0.5–Pt\textsubscript{0.5}})\textsubscript{n}(SG)\textsubscript{m} (III). The three clusters show a monodisperse particle size of around 1 nm.
Texture properties and crystallinity of the prepared catalysts. Liquid nitrogen at −196 °C is used to determine the surface texture properties of the pure support (Co3O4) and the doped Co3O4 with the prepared nanoclusters (Pdn(SG)m/Co3O4, Ptn(SG)m/Co3O4, Pdn(SG)m + Ptn(SG)m/Co3O4 and (Pd0.5–Pt0.5)n(SG)m/Co3O4) by measuring the adsorption/desorption isotherms (Fig. 4). According to the IUPAC classification of hysteresis loops, the sorption isotherms of the prepared catalysts and the pure support are type H3 hysteresis loops46–48. The surface areas of the prepared catalysts and support are summarized in Table 2. The values of surface area that are measured by BET equation (SBET) and T-method (St) for all the investigated catalysts are close to each other, which confirms the correct choice of standard t-curves for pore analysis and indicates the absence of ultra-micropores in these catalysts26,33.

X-ray diffraction is used to measure the crystallinity of the prepared catalysts. Figure 5 illustrates the XRD diffractograms of the prepared catalysts and Co3O4. The characteristic diffraction planes of the Co3O4 are (111), (220), (311), (222), (511) and (440) appear at 2θ equal to 19.0°, 31.2°, 36.7°, 38.5°, 44.8°, 55.5°, 59.3° and 65.4°, respectively (Fig. 5a)49,50. The prepared catalysts show the same XRD pattern as pure Co3O4, and no new peaks related to the presence of Pd or Pt clusters are detected, where the doping percentage is very low (1 wt.%) (Fig. 5b–e). This means the crystallinity of pure Co3O4 does not affect loading with the prepared clusters. Also, there is no significant difference in either diffraction angle or peak width between the Co3O4 and prepared catalysts, indicating that the crystal structure of Co3O4 is not affected by doping. The crystalline size \( d_{Co3O4} \) of bare Co3O4 is calculated using Debye–Scherrer Equations51 as 20 nm for the broadening of (311) peak reflection (Fig. 5). The \( d_{Co3O4} \) value for 1 wt.% (Pd0.5–Pt0.5)n(SG)m/Co3O4 catalyst is less than bare Co3O4 18.6 nm (Fig. 5)26,33.

The catalytic activity of the prepared catalysts. The hydrolysis reaction of NaBH4 for hydrogen generation is chosen as a model reaction to estimate the catalytic activities of Pdn, Ptn, physical mixture (Pdn + Ptn) clusters and the single alloy clusters (Pd0.5–Pt0.5)n/Co3O4 nanoparticles as support. Figure 6 shows the volume of generated hydrogen at room temperature (25 °C) against reaction time over the prepared catalysts. 5 mg of 1 wt.% Pdn(SG)m/Co3O4 catalyst produces the maximum hydrogen volume i.e. 500 mL from the hydrolysis of NaBH4 solution (1 g NaBH4 in 100 mL H2O) within 26 min. stirring. Ptn(SG)m nanoclusters over Co3O4 show more activity than Pd clusters in the hydrolysis of NaBH4 solution, where the Pt(SG)m/Co3O4 catalyst produces
the maximum hydrogen volume within 18 min. stirring at room temperature (Fig. 6). However, the physical mixing of Pd and Pt clusters over Co₃O₄ with the same doping percentage (~1 wt.%) shows lower catalytic activity than 1 wt. % Ptn(SG)m/Co₃O₄ catalyst. Surprisingly, the single alloy of Pd and Pt QDs (Pd₀.₅–Pt₀.₅)n(SG)m/Co₃O₄) shows amazing catalytic activity, where it reaches the maximum hydrogen volume i.e. 500 mL, within

| Catalysts                  | S_{BET} (m² g⁻¹) | S_{t} (m² g⁻¹) |
|----------------------------|------------------|----------------|
| (Pd₀.₅–Pt₀.₅)n(SG)m/Co₃O₄ | 56.3             | 56.3           |
| Pdn(SG)m + Ptn(SG)m/Co₃O₄| 54.7             | 54.7           |
| Pdn(SG)m/Co₃O₄            | 56.8             | 56.8           |
| Ptn(SG)m/Co₃O₄            | 55.2             | 55.2           |
| Co₃O₄                     | 60.3             | 60.3           |

Table 2. Specific surface area data for the prepared catalysts and pure support.

Figure 4. N₂ adsorption/desorption isotherms of the prepared catalysts and pure support show sorption isotherms type H3 according to the IUPAC classification.

Figure 5. X-ray diffractograms of the pure Co₃O₄ support (a), and prepared catalysts: Pdn(SG)m/Co₃O₄ (b), Ptn(SG)m/Co₃O₄ (c), Pdn(SG)m + Ptn(SG)m/Co₃O₄ (d), and Pd₀.₅–Pt₀.₅)n(SG)m/Co₃O₄ (e).
only 12 min. stirring (Fig. 6) with HGR of 8333 mL min⁻¹ g⁻¹. The HGRs for the NaBH₄ hydrolysis reaction over the prepared catalysts are summarized in Table 3.

The excellent synergetic interaction between Pd and Pt atoms in the single alloy (Pd₀.₅–Pt₀.₅)n(SG)m QDs plays a crucial role in the observed high catalytic activity. This positive synergistic effect does not appear in the physical mixing of nanoclusters over the support (Pd₃(SG)m + Pt₃(SG)m/Co₃O₄) by the same doping percentage. Since there are two types of synergetic effect (positive and negative)52, if the qualitative effect of electronic interaction between the components of the bimetallic system and the geometric effects due to changes in lattice constants are in the same direction as the bimetallic system will enhance the reaction effectively in comparison to the monometallic systems. However, if the electronic and geometric effect direction is opposite, the lower activity will be received52.

Figure 7 shows the effect of catalyst weight on the hydrolysis of NaBH₄. (Pd₀.₅–Pt₀.₅)n(SG)m/Co₃O₄ catalyst was chosen to study this factor. 5, 15, 30, and 50 mg of the catalyst were added to the NaBH₄ solution (1 g NaBH₄ in 100 mL H₂O) at room temperature (25 °C). As shown in Fig. 7, the time to reach the maximum hydrogen volume (500 mL) decreases with the increase in the weight of the catalyst. Where the time to reach the maximum hydrogen volume decreases from 12.0 to 1.5 min. over 5 and 50 mg of (Pd₀.₅–Pt₀.₅)n(SG)m/Co₃O₄, respectively (Fig. 7).

Different concentrations of NaBH₄ solution (0.189, 0.5, 1 and 2 wt.%) were tested over 5 mg of (Pd₀.₅–Pt₀.₅)n(SG)m/Co₃O₄ catalyst at 25 °C (Fig. 8-I). The reaction time decreases with the increase of the NaBH₄ concentration. The maximum hydrogen volume was reached within 19, 15, 12, and 9 min. of the 0.189, 0.5, 1, and 2 wt. % NaBH₄ solution over (Pd₀.₅–Pt₀.₅)n(SG)m/Co₃O₄ catalyst, respectively (Fig. 8-I). The effect of reaction temperature was also tested for hydrogen generation from the 1 wt.% NaBH₄ solution over 5 mg of (Pd₀.₅–Pt₀.₅)n(SG)m/Co₃O₄ catalyst at different temperatures at 25, 45, and 60 °C; the reaction time decreased with the temperature increasing (Fig. 8-II). The maximum hydrogen volume was reached within only 2 min stirring over 5 mg of (Pd₀.₅–Pt₀.₅)n(SG)m/Co₃O₄ catalyst at 60 °C with HGR 50,000 mL min⁻¹ g⁻¹ (Fig. 8-II).

The best property of heterogeneous catalysis is easily separating the catalyst from the reaction mixture and reusing it until its activity decreases26–28,32,33,38. Thus, the ability of the (Pd₀.₅–Pt₀.₅)n(SG)m/Co₃O₄ catalyst to recycle is tested for the hydrolysis of 1 wt.% NaBH₄ solution at room temperature using 5 mg from the catalyst. After each run, the catalyst was collected and reused without any treatment. The HGRs values were nearly identical for the 5 cycles (Fig. 9). These results reveal that the (Pd₀.₅–Pt₀.₅)n(SG)m/Co₃O₄ catalyst can be reused, and their catalytic activity is quite consistent without significant change.

![Figure 6. Hydrogen generation from NaBH₄ hydrolysis over the prepared catalysts. Reaction conditions: 1 g of NaBH₄ in 100 H₂O; catalyst, 5 mg; at 25 °C.](https://doi.org/10.1038/s41598-022-21064-z)

![Table 3. Hydrogen generation rate (HGR) for NaBH₄ hydrolysis reaction over different catalysts. Catalytic test: 1 g of NaBH₄ in 100 H₂O; Catalyst, 5 mg; at 25 °C.](https://doi.org/10.1038/s41598-022-21064-z)
The NaBH₄ hydrolysis reaction mechanism can be further illustrated in view of Langmuir–Hinshelwood model. Where, Kojima et al.⁵³ reported the hydrolysis mechanism of NaBH₄ over Pt/LiCoO₂ catalyst, according to the Langmuir–Hinshelwood model. It was found that BH₄⁻ ions are adsorbed on Pt, while H₂O molecules are adsorbed on the oxide support to give H₂ and B(OH)₄⁻⁵³. These findings were confirmed by Liu et al.⁵⁴ using X-ray absorption. Co₃O₄ played the same role as LiCoO₂ for Pt/Co₃O₄ catalyst as claimed by Hung et al.⁵⁵. The suggested mechanism of NaBH₄ hydrolysis over the (Pd₀.₅–Pt₀.₅)ₙ(SG)ₘ/Co₃O₄ catalyst is demonstrated in Fig. 10, according to the Langmuir–Hinshelwood model. The catalytic process involves two different adsorption sites. The first site is suggested to be electron-rich Pt₀ and Pd₀ nanoclusters, whereas the second site is electron-deficient (Coδ⁺). The hydrolysis of the four hydrides of BH₄⁻ occurs one after the other by reaction with one adsorbed H₂O for each hydride (Fig. 10)⁵⁶.

A comparison with different catalysts used for hydrogen generation via NaBH₄ hydrolysis is listed in Table 4. As shown in Table 4, the prepared catalysts in this work showed superior catalytic activity in hydrogen generation from the hydrolysis of NaBH₄ using a relatively low noble metal loading (1 wt.%). Where (Pd₀.₅–Pt₀.₅)ₙ(SG)ₘ/Co₃O₄ catalyst showed the highest hydrogen yield in the Table 4 with HGR equal to 8333 mL g⁻¹ min⁻¹. Moreover, 1 wt.% loading percentage of monometallic Pt and Pd clusters over Co₃O₄ exhibited HGR 5555 and 3846 mL g⁻¹ min⁻¹, however, the 20 wt.% Pt and Pd nanoparticles over the same support exhibited only 4713 and 2109 mL g⁻¹ min⁻¹. This high catalytic activity is due to the unique atomic packing structure and electronic properties of the nanoclusters.
Conclusions

In conclusion, a single alloy of Pd/Pt quantum dots over Co₃O₄ (Pd₀.5–Pt₀.5)(SG)ₘ/Co₃O₄ exhibited promising catalytic activity in hydrogen generation from the hydrolysis of NaBH₄. The maximum hydrogen volume i.e. 500 mL was reached within only 12 min. of stirring at room temperature with HGR 8333 mL min⁻¹ g⁻¹. However, the physical mixing of the prepared two clusters (Pdₙ(SG)ₘ and Ptₙ(SG)ₘ) over Co₃O₄ exhibited a lower hydrogen yield in comparison to the single alloy clusters. The time to reach the maximum hydrogen volume decreases with the increase of the (Pd₀.5–Pt₀.5)(SG)ₘ/Co₃O₄ catalyst weight (5, 15, 30, and 50 mg). Moreover, the effect of NaBH₄ concentration (0.189, 0.5, 1 and 2 wt.%) over 5 mg of (Pd₀.5–Pt₀.5)(SG)ₘ/Co₃O₄ catalyst at 25 °C was studied. The hydrolysis of the NaBH₄ reaction was measured at different temperatures of 25, 45, and 60 °C, where 5 mg of (Pd₀.5–Pt₀.5)(SG)ₘ/Co₃O₄ catalyst produced the maximum hydrogen volume within only

Figure 9. Recyclability of 1 wt.% (Pd₀.5–Pt₀.5)(SG)ₘ/Co₃O₄ catalyst for hydrogen generation from the hydrolysis of NaBH₄. Reaction conditions: 1 g of NaBH₄ in 100 H₂O; catalyst, 5 mg; at 25 °C.

Figure 10. Suggested mechanism of NaBH₄ hydrolysis over (Pd₀.5–Pt₀.5)(SG)ₘ/Co₃O₄ catalyst, according to the Langmuir–Hinshelwood model.
2 min stirring at 60 °C, with HGR 50,000 mL min⁻¹ g⁻¹. The extremely catalytic activity of this catalyst attributes to the ultra-small particle size and the synergistic effect between Pd and Pt atoms in the alloy quantum dots.

Data availability
All data generated or analyzed during this study are included in this published article (and its Supplementary Information files).

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### Table 4. Comparison among catalysts used for the hydrolysis of NaBH₄ for hydrogen generation.

| Catalysts | Catalyst mass (mg) | NaBH₄ (wt.%) | HGR (mL min⁻¹ g⁻¹) | Ref |
|-----------|--------------------|-------------|--------------------|-----|
| 5.4 wt.% Ru/Al₂O₃ | 500 | 10 | 65.5 | 17 |
| Pt/Pd/CNT | - | 0.1 | 126 | 18 |
| 10 wt.% PtRu/LiCoO₂ | 125 | 5 | 30 | 19 |
| 2 wt.% Ru/MMT | 32 | 1 | 541 | 19 |
| 5 wt.%CoB/CoO₂ | 200 | 1 | 533 | 19 |
| 3 wt.% Ru/graphite | 300 | 10 | 666.6 | 19 |
| 20 wt.% Pt/CoO₂ | 50 | 10 | 2109 | 11 |
| Pt/LiCoO₂ | 50 | 20 | 3100 | 11 |
| 20 wt.% Pt/CoO₂ | 50 | 10 | 4713 | 11 |
| 1 wt.% (Pd₅–Pt₅)n(SG)m/CoO₂ | 5 | 1 | 8333 | This Work |
| 1 wt.% Pt(SG)m/Co₃O₄ | - | - | 5555 | 11 |
| 1 wt.% Pd(SG)m/Co₃O₄ | - | - | 3846 | 11 |

Table 4. Comparison among catalysts used for the hydrolysis of NaBH₄ for hydrogen generation.
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**Author contributions**

M.F. wrote the main manuscript text and prepared Figs. 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10. All authors reviewed the manuscript.

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**Competing interests**

The authors declare no competing interests.

**Additional information**

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