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# Nickel–Ceria Nanowires Embedded in Microporous Silica: Controllable Synthesis, Formation Mechanism, and Catalytic **Applications**

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strategy. The average diameter of Ni-CeO<sub>2</sub> NWs is just 2.9 nm, and the length is up to 102.7 nm. The resulting Ni-CeO<sub>2</sub>@SiO<sub>2</sub> exhibits high performance and 100% hydrogen selectivity for H<sub>2</sub> production from N<sub>2</sub>H<sub>4</sub> and N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> in aqueous solution. Unexpectedly, Ni-CeO<sub>2</sub>@SiO<sub>2</sub> also has good catalytic performance



and thermal stability for CO<sub>2</sub> methanation. The high catalytic performance of Ni-CeO<sub>2</sub>@SiO<sub>2</sub> can be attributed to the synergistic electronic effect and strong interaction between Ni NPs and CeO2 NWs with plenty of oxygen vacancies, as well as the unique structure effect. As an effective strategy, the present work provides an opportunity to embed ultrafine metal NPs-CeO<sub>2</sub> NWs into a microporous silica shell, which has broad application prospects in various catalytic fields.

# 1. INTRODUCTION

In view of the growing fuel demand with very limited fossil fuel resources and environmental imbalance due to the overemission of greenhouse gases  $(CO_2)$ , the development of alternative clean energy is one of the most accepted solutions to the energy crisis. Hydrogen has been considered as a promising energy carrier in a future energy society, which could satisfy the increasing demand for the sustainable and clean energy supply.<sup>1-5</sup> Hydrous hydrazine (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, 8.0 wt % H) and hydrazine borane ( $N_2H_4BH_3$ , 15.4 wt % H), as safe and efficient hydrogen storage media, have received tremendous attention due to their high hydrogen contents, CO-free hydrogen production, and simple byproducts.<sup>6-14</sup> Hydrocarbon fuels are another type of energy carrier, and the production of hydrocarbon fuels using CO<sub>2</sub> as a raw material has attracted great research interest in recent years. Hydrocarbon fuels derived from CO<sub>2</sub> through the methanation process are considered a general catalytic pathway.<sup>15–19</sup>

Non-noble-metal Ni nanocatalysts have been widely investigated for various interdisciplinary chemical processes, such as catalytic reforming, catalytic dehydrogenation and hydrogenation, fuel cell electrocatalysis, and so on, because they are known to have a certain catalytic property and are more abundant and cheaper than precious metal nanocatalysts.<sup>20-29</sup> However, the activity and stability of these catalysts are far from ideal, which will restrict their practical applications. Therefore, the search for novel nickel-based heterogeneous catalysts with improved catalytic property and stability for various catalytic fields is of current research interest.

Recent studies have shown that the performance of nickelbased catalysts can be markedly improved via introducing a certain amount of  $CeO_2$ .<sup>30–36</sup> For instance, compared to pure Ni nanoparticles (NPs), the activity of Ni NPs modified with a small amount of CeO2 increased 3-fold, and the selectivity of  $H_2$  increased from 67 to 99% for  $H_2$  production from  $N_2H_4$ . Ni NPs supported on  $CeO_2$  with different morphologies have also been studied intensively.<sup>30,31,37</sup> To maximize the active interface, Ni/CeO<sub>2</sub> nanowires (NWs) are of great interest owing to the distinct advantages of CeO2 NWs, which are derived from their low dimensionality and high specific surface area.<sup>38</sup> However, most of them show unsatisfactory stability, because the NWs themselves have high surface energy prone to distort, sinter, and agglomerate into larger NPs. As a result, the original superior performance is lost. Therefore, it is crucial to develop a protection strategy to stabilize the NWs against aggregation. To our knowledge, core-shell structures,

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especially those with a meso-/microporous size distribution, have been widely used in catalysis, as a porous structure can provide channels for the reaction species to reach the surface of the active sites. Among these core—shell structures, metal NPs coated with SiO<sub>2</sub> are becoming more important in various fields because of the chemical inertness, controlled porosity, and thermal stability of SiO<sub>2</sub>.<sup>39–44</sup>

In this work, for the first time, we report the synthesis of the wormlike core—shell-structured Ni-CeO<sub>2</sub>@SiO<sub>2</sub> with ultrafine Ni-CeO<sub>2</sub> NWs of 2.9 nm in diameter by a reversed-micelle method. Self-assembly of the Ni NPs with CeO<sub>2</sub> NWs and stabilization of them with a microporous SiO<sub>2</sub> shell are simultaneously performed via a simple one-pot synthesis route. The Ni-CeO<sub>2</sub>@SiO<sub>2</sub> catalyst shows good catalytic performance and durability for H<sub>2</sub> production from N<sub>2</sub>H<sub>4</sub> and N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> in the aqueous solution as well as the CO<sub>2</sub> methanation reaction in the gas phase.

#### 2. EXPERIMENTAL SECTION

2.1. Chemicals. All chemicals were from commercial sources and used as received. Methanol (CH<sub>3</sub>OH, Tianjin Fuchen Chemical Reagent, 99.5%), hydrazine hemisulfate salt (N<sub>2</sub>H<sub>4</sub>·1/2H<sub>2</sub>SO<sub>4</sub>, Sigma-Aldrich, 99.5%), acetone ((CH<sub>3</sub>)<sub>2</sub>CO, Nanchang Chemical Works, 99.5%), hydrous hydrazine (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, Aladdin, 98%), n-pentane (C<sub>5</sub>H<sub>12</sub>, Sigma-Aldrich, 99.5%), polyethylene glycolmono-4-nonylphenyl ether ( $n \approx 5$ ; NP-5, TCI), sodium hydroxide (NaOH, Tianjin Fuchen Chemical Reagent, >96%), 1,4-dioxane (C4H8O2, J&K Chemical, 99.8%), cerium nitrate hexahydrate  $(Ce(NO_3)_3)$ . 6H<sub>2</sub>O, Aladdin, 99.95%), cyclohexane (C<sub>6</sub>H<sub>12</sub>, Tianjin Fuchen Chemical Reagent, 99.5%), sodium borohydride (NaBH<sub>4</sub>, Xiya Reagent, 99.5%), ammonia solution (NH<sub>3</sub>·H<sub>2</sub>O, Tianjin DaMao Chemical Reagent Factory, 28%), nickel nitrate hexahydrate (Ni-(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Aladdin, 98%), and tetraethoxysilane (TEOS, Aldrich, 98%) were used as received. Hydrazine borane (N2H4BH3) was prepared according to the procedure reported in literature.<sup>4</sup> Ultrapure H<sub>2</sub>O was obtained by reversed osmosis followed by ion exchange and filtration.

2.2. Preparation of Catalysts. 2.2.1. Preparation of Ni-CeO2@ SiO<sub>2</sub>. The Ni-CeO<sub>2</sub>@SiO<sub>2</sub> core-shell nanocatalyst was synthesized by a simple one-pot synthesis route in the microemulsion system on the basis of literature reports.<sup>52-55</sup> Typically, 2.16 mL of aqueous solution containing 0.250 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.116 g of Ce(NO<sub>3</sub>)<sub>3</sub>. 6H<sub>2</sub>O was injected into 480 mL of cyclohexane solution in the presence of NP-5 (20.160 g). After stirring at 298 K for 15 h, 2.16 mL of NH3·H2O (28 wt %) was then added. After 2 h, 2.49 mL of tetraethoxysilane was injected into the microemulsion system and further stirred for 48 h. CH<sub>3</sub>OH (120 mL) was added as a demulsifier to change the interfacial adhesion between the organic and aqueous phases, Van der Waal's forces, surface tension, and interfacial free energy, and the emulsion system will be broken. 56-58 The sample was collected by centrifugation and washed with acetone and cyclohexane. After drying in a vacuum oven at room temperature, the sample was calcined at 873 K for 2 h and then heated to 1073 K for another 2 h in air. Finally, the obtained product was reduced with 25%  $H_2/N_2$  at 873 K for 4 h to obtain the 6.7 wt %Ni-5 wt %CeO2@SiO2 core-shell nanocatalyst. The synthesis of other xNi-5 wt %CeO2@SiO2 coreshell nanocatalysts with different nickel loadings  $(x_i m_{Ni}/m_{Ce+Ni+SiO_2} =$ 2.8, 4.7, 8.6, and 10 wt %) were also prepared using the homologous method via changing the initial amount of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and maintaining cerium loading at 5 wt %. Similarly, to synthesize other 6.7 wt %Ni-yCeO2@SiO2 core-shell nanocatalysts with different cerium loadings (y,  $m_{Ce}/m_{Ce+Ni+SiO_2} = 1, 3, 9$  wt %), stoichiometric amounts of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were added, while the nickel loading was kept at 6.7 wt %.

2.2.2. Preparation of Ni@SiO<sub>2</sub> and CeO<sub>2</sub>@SiO<sub>2</sub>. The synthetic solution was homologous to that of Ni-CeO<sub>2</sub>@SiO<sub>2</sub>. The aqueous

solution contained only  $Ni(NO_3)_2 \cdot 6H_2O$  or  $Ce(NO_3)_3 \cdot 6H_2O$  in this process. The final catalyst is labeled as  $Ni@SiO_2$  or  $CeO_2@SiO_2$ .

2.2.3. Preparation of Free Ni-CeO<sub>2</sub> Catalyst without Silica. The free Ni-CeO<sub>2</sub> catalyst without silica synthesized via a reverse micelle system which was similar to that of Ni-CeO<sub>2</sub>@SiO<sub>2</sub> (no addition of TEOS).

2.2.4. Preparation of Ni-CeO<sub>2</sub>/SiO<sub>2</sub>. For a comparison study, Ni-CeO<sub>2</sub>/SiO<sub>2</sub> was prepared by a traditional wet impregnation method. A certain amount of silica spheres (SiO<sub>2</sub>) prepared via a reverse micelle system similar as that of Ni-CeO<sub>2</sub>@SiO<sub>2</sub> (no addition of Ni and Ce precursors) was used as the support. The silica spheres were impregnated with a certain amount of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O aqueous solution under continuous stirring at 298 K for approximately 12 h. After drying in a vacuum oven at room temperature, the sample was calcined at 873 K for 2 h and then heated to 1073 K for another 2 h in air. Finally, the obtained product was reduced with 25% H<sub>2</sub>/N<sub>2</sub> at 873 K for 4 h to obtain the catalyst.

**2.3. Catalytic Dehydrogenation of N<sub>2</sub>H<sub>4</sub> and N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub>.** The reaction equipment for measuring the H<sub>2</sub> production from the dehydrogenation of N<sub>2</sub>H<sub>4</sub> or N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> is as follows. Typically, a three-necked flask reactor containing the NaOH (2.0 M) and prepared catalyst (containing 0.1 mmol of Ni) was fixed in a water bath at 343 K under ambient atmosphere. In order to prevent the influence of any released NH<sub>3</sub>, a trap filled with hydrochloric acid (0.1 M) was placed between the water-filled gas buret and the reaction flask. The gas production started when 1 mmol N<sub>2</sub>H<sub>4</sub>:H<sub>2</sub>O or N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> was injected into the reaction flask. The volume of the evolved gas was monitored via the gas buret and recorded at consequent times. The selectivity ( $\alpha$ ) toward H<sub>2</sub> generation from N<sub>2</sub>H<sub>4</sub> could be calculated according to eq 1:

$$N_2H_4 \rightarrow 2\alpha H_2 + (2\alpha + 1)/3N_2 + 4(1 - \alpha)/3NH_3$$
 (1)

which could be deduced from eqs 2 and 3:

$$N_2H_4 \rightarrow N_2 + 2H_2 \tag{2}$$

$$3N_2H_4 \rightarrow N_2 + 4NH_3 \tag{3}$$

The selectivity  $(\beta)$  toward H<sub>2</sub> generation from N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> could be calculated according to eq 4:

$$N_{2}H_{4}BH_{3} + 3H_{2}O \rightarrow B(OH)_{3} + (3 + 2\beta)H_{2} + (2\beta + 1)/3N_{2} + 4(1 - \beta)/3NH_{3}$$
(4)

which could be deduced from eqs 2, 3, and eq 5:

$$N_2H_4BH_3 + 3H_2O \rightarrow N_2H_4 + B(OH)_3 + 3H_2$$
 (5)

As NH<sub>3</sub> is highly solution in hydrochloric acid and water, the gas volume measured by the gas buret contained only hydrogen and nitrogen, from which the molar ratio  $\lambda = n_{(\text{H}_2+\text{N}_2)}/n_{(\text{N}_2\text{H}_4)}$  and  $\gamma = n_{(\text{H}_2+\text{N}_2)}/n_{(\text{N}_2\text{H}_4\text{BH}_3)}$  could be calculated.<sup>59–61</sup> Therefore, the hydrogen selectivity  $\alpha$  and  $\beta$  could be obtained according to eqs 6 and 7, respectively.

$$\alpha = \frac{3\lambda - 1}{8} \quad \left(\lambda = \frac{n(H_2 + N_2)}{n(N_2H_4)}; \frac{1}{3} \le \lambda \le 3\right)$$
(6)

$$\beta = \frac{3\gamma - 10}{8} \quad \left( \gamma = \frac{n(H_2 + N_2)}{n(N_2 H_4 B H_3)}; \frac{10}{3} \le \gamma \le 6 \right) \tag{7}$$

The turnover frequency (TOF) reported in this work is based on the apparent TOF value of the number of metal Ni atoms in the catalysts, and its calculation formula is as follows eq 8:

$$\Gamma OF = \frac{V P_{\text{atm}}}{R T n_{\text{Ni}} t}$$
(8)

 $P_{\rm atm}$  is the atmospheric pressure, V is the volume of the released hydrogen when the conversion reached 50% for N<sub>2</sub>H<sub>4</sub> or 100% for N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub>, R is the general gas constant, T is the room temperature

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Figure 1. (a) SEM image, (b, c) TEM images, (d) HAADF-STEM image, and (e-j) EDX mapping of Ni-CeO<sub>2</sub>@SiO<sub>2</sub> catalyst.



Figure 2. (a) SEM image and (b) TEM image of Ni@SiO<sub>2</sub>. (c) SEM image and (d) TEM image of CeO<sub>2</sub>@SiO<sub>2</sub> catalysts.

(298 K),  $n_{\rm Ni}$  is the overall molar amount of Ni atoms in the sample, and *t* is the half-completion reaction time for dehydrogenation of N<sub>2</sub>H<sub>4</sub> or completed reaction time for dehydrogenation of N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub>.

**2.4. Characterization.** Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT-2200 X-ray diffractometer

instrument operating at 40 kV and 40 mA, with Cu target K $\alpha$ -ray radiation ( $\lambda = 1.5418$  Å). The detailed morphology and microstructures of the as-synthesized catalysts were recorded via using scanning electron microscopy (SEM, SU8020) and transmission electron microscopy (TEM, JEM-2100) with an energy-dispersive

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Figure 3. XPS spectra of (a) Ni 2p and (b) Ce 3d for the as-synthesized catalysts after 300 s of argon etching.

spectroscopy (EDX) detector. Scanning transmission electron microscopy (STEM, Talos F200X, FEI, USA) was combined with energy dispersive X-ray (EDX) mapping. X-ray photoelectron spectroscopy (XPS) test was carried out with a ESCALABMKLL X-ray photoelectron spectrometer with Al K $\alpha$  as the excitation source. The Ar sputtering tests were carried out on background vacuum of 3.2  $\times$  10<sup>-6</sup> Pa and a sputtering acceleration voltage of 1 kV. The N<sub>2</sub> adsorption–desorption isotherm was used to evaluate the specific surface areas of the catalysts at 77 K on BELSORP-mini II apparatus. The specific surface areas of the catalysts were evaluated via Brunauer–Emmett–Teller (BET) equation.

#### 3. RESULTS AND DISCUSSION

3.1. Characterization of Ni-CeO<sub>2</sub>@SiO<sub>2</sub> and Related Catalysts. SEM and TEM were used to analyze the structure of the prepared Ni-CeO<sub>2</sub>@SiO<sub>2</sub> sample. The SEM images (Figures 1a and S1a,b) display the Ni-CeO<sub>2</sub>@SiO<sub>2</sub> catalyst with a tortuous wormlike morphology of about 20 nm in diameter. TEM was used to further characterize the detailed morphology and size of the synthesized catalyst. As shown in Figure 1b,c, the elongated nickel-ceria NWs are totally encapsulated in the microporous SiO<sub>2</sub> shell to form the unusual wormlike structure. The length and diameter of these Ni-CeO<sub>2</sub> NWs are in the range of 64.7-180.6 nm and 2.2-3.7 nm, and the mean length and diameter are about 102.7 and 2.9 nm, respectively (Figure S2a,b). The ultrafine Ni NPs with mean size of 2.2 nm were observed embedded in CeO<sub>2</sub> NWs (Figure S3). High-resolution TEM (HRTEM) was conducted to analyze the crystal structure (Figure S4a). The Ni-CeO<sub>2</sub>@SiO<sub>2</sub> catalyst displays the *d*-spacing of 0.310 and 0.203 nm corresponding to the (111) lattice planes of CeO2 and Ni, respectively. Moreover, the selected-area electron diffraction (SAED) image shows that the Ni-CeO<sub>2</sub>@SiO<sub>2</sub> catalyst has a crystalline nature (Figure S4b). The EDX spectrum verifies the presence of Ni, Ce, Si, and O elements in the Ni-CeO<sub>2</sub>@SiO<sub>2</sub> sample (Figure S5). The spatial distribution of the Ni-CeO<sub>2</sub>@ SiO<sub>2</sub> catalyst was provided via high-angle annular dark-field scanning TEM (HAADF-STEM) and elemental mapping patterns. As shown in the images presented in Figure 1d-j, the Si and O elements are spread throughout the entire sample, while the Ce element was only found at the core position. The Ni and Ce elements appeared at similar positions, indicating that all of the Ni-CeO<sub>2</sub> NWs are totally encapsulated in SiO<sub>2</sub> shells and that Ni NPs deposit on the CeO<sub>2</sub> NWs.

For comparison, we conducted two controlled experiments to synthesize Ni@SiO<sub>2</sub> without addition of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and CeO<sub>2</sub>@SiO<sub>2</sub> without addition of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O during the synthetic process. In sharp contrast to the wormlike structure of Ni-CeO<sub>2</sub>@SiO<sub>2</sub>, the uniform spherical nanostructure Ni@SiO<sub>2</sub> were observed in Figure 2a,b, in which the monodisperse and ultrafine Ni NPs with a size of 2.3 nm (Figure S6) were embedded into the SiO<sub>2</sub> nanospheres of about 25 nm in diameter with high uniformity in size and shell thickness. As shown in Figure 2c,d, similar to the shape of Ni-CeO<sub>2</sub>@SiO<sub>2</sub>, wormlike CeO<sub>2</sub>@SiO<sub>2</sub> core-shell structures were also obtained, indicating that CeO<sub>2</sub> NWs were the key for the formation of wormlike structure. Recognizing the significant importance of CeO2 NWs structures, we monitored the cerium-content-dependent morphological evolution of the Ni-CeO<sub>2</sub>@SiO<sub>2</sub> catalyst by TEM imaging (Figure S7a-d). Interestingly, the lengths of Ni-CeO<sub>2</sub> NWs increase inside the wormlike SiO<sub>2</sub> shell as the increase of cerium contents. When cerium content is 1 wt % (Figure S7a), there are a lot of axiolitic core-shell structures of Ni-CeO<sub>2</sub>@SiO<sub>2</sub> besides some short wormlike structures. However, when the cerium contents increase from 1 to 9 wt % (Figure S7a-d), the lengths of Ni-CeO<sub>2</sub> NWs increase gradually inside the wormlike SiO<sub>2</sub> shell.

The phase composition and crystalline structures of the assynthesized Ni-CeO2, Ni-CeO2@SiO2, Ni-CeO2/SiO2, and Ni@SiO<sub>2</sub> samples were further characterized via powder XRD. As exhibited in Figure S8, a wide peak with  $2\theta$  scope of 15–  $35^{\circ}$  is observed in all SiO<sub>2</sub>-containing samples, which can be classified as amorphous silica. As for the as-prepared Ni-CeO2@SiO2 catalyst, three crystalline peaks are centered at 44.5, 51.8, and 76.4°, which are attributed to the (111), (200), and (220) planes of Ni (Powder Diffraction File (PDF) No. 04-0850, Joint Committee on Powder Diffraction Standards (JCPDS, 2004)). Three Ni peaks are also observed in other three samples. However, compared to the spectrum of free Ni-CeO<sub>2</sub> or Ni-CeO<sub>2</sub>/SiO<sub>2</sub> sample, a small and broad peak of CeO<sub>2</sub> (PDF No. 43-1002, JCPDS, 2004) is observed at around  $2\theta = 28.5^{\circ}$  in Ni-CeO<sub>2</sub>@SiO<sub>2</sub> catalyst, owing to the smaller size of CeO<sub>2</sub> NWs and/or the stronger core (Ni- $CeO_2$ )-shell (SiO<sub>2</sub>) interaction as well as the shielding effect of the porous silica shell.

XPS measurements were adopted to characterize the valence state and surface composition of Ni-CeO<sub>2</sub>@SiO<sub>2</sub> and the control samples Ni@SiO<sub>2</sub> and free Ni-CeO<sub>2</sub>. As shown in Figure S9, the survey XPS spectrum of the Ni-CeO<sub>2</sub>@SiO<sub>2</sub> sample reveals the existence of Ni, Ce, Si, and O elements. In the high-resolution XPS spectra (Figure 3a), the Ni  $2p_{3/2}$  and Ni  $2p_{1/2}$  peaks at 852.5 and 869.8 eV for Ni-CeO<sub>2</sub>@SiO<sub>2</sub> are observed, corresponding to Ni<sup>0</sup>. Besides, there are NiO with the binding energies of 853.7 and 871.4 eV, which were due to the oxidation of ultrafine Ni NPs after exposure to air during the sampling process for XPS.<sup>33,62,63</sup> The reason for the assynthesized Ni-CeO<sub>2</sub>@SiO<sub>2</sub> sample without NiO before

exposure to air can be understood as the intermediate NiO NPs being easily reduced to Ni<sup>0</sup> NPs by 25% H<sub>2</sub>/N<sub>2</sub> at 873 K.<sup>64,65</sup> For the Ce 3d spectra (Figure 3b), it can be observed that the Ce  $3d_{5/2}$  and Ce  $3d_{3/2}$  peaks at ( $U_{0-5}$ : 886.3, 887.8 eV and 900.6, 904.0, 907.2, 919.6 eV) are assignable to Ce<sup>4+</sup>, whereas the Ce  $3d_{5/2}$  and Ce  $3d_{3/2}$  peaks at ( $V_{0-3}$ : 882.3, 884.5 eV and 902.1, 905.5 eV) can be assigned to Ce<sup>3+</sup> species. It is worth mentioning that the ratio of integrated peak areas of  $Ce^{3+}/(Ce^{3+} + Ce^{4+})$  was calculated to evaluate the  $Ce^{3+}$ concentrations in the catalysts. The Ce<sup>3+</sup> concentration of Ni-CeO<sub>2</sub>@SiO<sub>2</sub> (41.5%) is relatively larger than that for free Ni-CeO<sub>2</sub> (35.0%), which indicated a stronger interaction between Ni NPs and  $CeO_2$  with richer oxygen vacancies in the Ni-CeO<sub>2</sub>@SiO<sub>2</sub> sample.<sup>31,33</sup> Besides, the XPS spectra of Ni 2p displayed that the Ni peaks of the Ni-CeO2@SiO2 catalyst move negatively relative to the Ni peaks of the Ni@SiO2 catalyst (Figure 3a). This phenomenon demonstrates that electrons are transferred from CeO<sub>2</sub> to Ni in the Ni-CeO<sub>2</sub>@ SiO<sub>2</sub> catalyst. Such electron transfer and strong interaction between Ni NPs and CeO<sub>2</sub> with plenty of oxygen vacancies in Ni-CeO2@SiO2 catalyst are assumed to contribute to improved catalyst performance.

 $N_2$  adsorption-desorption isotherms of Ni-CeO<sub>2</sub>@SiO<sub>2</sub>, Ni-CeO<sub>2</sub>, and Ni@SiO<sub>2</sub> catalysts have been determined at 77 K. The results can be observed in Figure 4 and Table S1. Ni-



Figure 4.  $N_2$  adsorption-desorption isotherms of the freshly reduced Ni-CeO<sub>2</sub>@SiO<sub>2</sub>, Ni-CeO<sub>2</sub>, and Ni@SiO<sub>2</sub> catalysts.

CeO<sub>2</sub>@SiO<sub>2</sub> and Ni@SiO<sub>2</sub> samples display increasing N<sub>2</sub> adsorption at  $P/P_0 = 0.8-1.0$ , indicating that the exist of a mesopore structure due to the stack of these NPs.<sup>52–54</sup> Interestingly, they possess a steep absorption stage when  $P/P_0 < 0.05$ , demonstrating that the two core–shell structured samples have micropores, further proved via the pore diameter distribution plot in Figure S10. The micropores were formed after removal of the structure-directing agent (NP-5) by calcination in air.<sup>43,66</sup> The micropores in the SiO<sub>2</sub> shell allow reactants and product molecules to access and leave the active center, which is of critical importance for core–shell structure catalysts.

**3.2. Formation Mechanism of Ni-CeO<sub>2</sub>@SiO<sub>2</sub>.** In order to understand the formation mechanism of Ni-CeO<sub>2</sub>@SiO<sub>2</sub> with the wormlike core-shell structure (Scheme 1, Route 1), we have synthesized Ni@SiO<sub>2</sub> (Scheme 1, Route 2) and CeO<sub>2</sub>@SiO<sub>2</sub> (Scheme 1, Route 3) by similar methods. First, to investigate the formation mechanism of the CeO<sub>2</sub> and Ni-CeO<sub>2</sub> NWs, a little of the reverse micelle solution was extracted before injecting the tetraethoxysilane (TEOS) for the

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preparation of wormlike CeO2@SiO2 core-shell structure (Scheme 1, Route 3), and this sample was centrifuged to obtain a sample for the TEM characterization. The TEM image (Figure S11a) clearly displays the existence of typical Ce-containing NW shape in the absence of SiO<sub>2</sub> shell, which is considered to be  $Ce(OH)_{x}$  NWs (coexistence of  $Ce(OH)_{3}$  and  $Ce(OH)_4$ , 3 < x < 4). This can be explained by  $Ce(NO_3)_3$ being extremely unsteady in aqueous ammonia solution and prone to hydrolysis to produce  $Ce(OH)_3$  (eq S1).<sup>67</sup> The  $Ce(OH)_3$  species can be oxidized to  $Ce(OH)_4$  in the existence of  $O_2$  (eq S2). However, in those closed reverse micelle systems, this oxidation process is very slow, and the lateral growth is limited by the hydroxyl groups, thus the resulting  $Ce(OH)_r$  tends to deposit on the tips of the other  $Ce(OH)_r$ species, which promotes the  $Ce(OH)_x$  species self-assembled into  $Ce(OH)_r$  NWs<sup>38</sup> meanwhile accompanied by Ni(OH)<sub>2</sub> (eq S3) species deposit on  $Ce(OH)_r$  NWs to form Ni(OH)<sub>2</sub>- $Ce(OH)_r$  NWs in the self-assembly process, as evidenced by TEM in Figure S11b. The dark dots on the Ni(OH)<sub>2</sub>- $Ce(OH)_x$  NWs indicate the existence of Ni(OH)<sub>2</sub> species. Meanwhile, we also found that the  $Ni(OH)_2$ -Ce(OH)<sub>x</sub> NWs are unstable without SiO<sub>2</sub> shell protection. After washing and drying in vacuum oven at 313 K, the shape of the prepared  $Ni(OH)_2$ -Ce(OH)<sub>r</sub> NWs did not exist (Figure S11c). After further calcination and reduction of Ni(OH)<sub>2</sub>-Ce(OH)<sub>2</sub>, NWs, the free Ni-CeO<sub>2</sub> NPs were obtained. The TEM image shows that the Ni-CeO<sub>2</sub> NPs are severely agglomerated with irregular morphologies (Figure S11d). Furthermore, after the Ni-CeO<sub>2</sub> NPs are supported on surface of the SiO<sub>2</sub> nanosphere, the Ni-CeO<sub>2</sub>/SiO<sub>2</sub> catalyst is still heavily aggregated (Figure S11e). These results indicate that the stability of  $Ni(OH)_2$ -Ce(OH)<sub>r</sub> NWs is closely related to the protection of the microporous  $SiO_2$  shell. As shown in the Scheme 1 (Route 1), the resulting  $Ni(OH)_2$ -Ce $(OH)_x$  NWs with the SiO<sub>2</sub> shell can be dehydrated directly during the calcination process in the presence of air to form NiO-CeO2@SiO2. Subsequently, the NiO-CeO2@SiO2 sample was reduced in H2 atmosphere to obtain the final wormlike Ni-CeO<sub>2</sub>@SiO<sub>2</sub> core-shell catalyst.

The possible formation mechanism of Ni-CeO2@SiO2 by the one-pot synthesis route in the inverse microemulsion system has been described in Scheme 1 (Route 1). The aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was injected into cyclohexane solution in the presence of NP-5 to form the water-in-oil microemulsion. Ni(OH)<sub>2</sub> NPs and  $Ce(OH)_r$  NWs will undergo nucleation, growth, and selfassembly procedure after injecting NH<sub>3</sub>·H<sub>2</sub>O (28 wt %) into the above solution, leading to Ni(OH)<sub>2</sub>-Ce(OH)<sub>2</sub>. NWs in the inverse microemulsion system. TEOS was further injected into the microemulsion containing H<sub>2</sub>O and NH<sub>3</sub>·H<sub>2</sub>O. Then, the OH<sup>-</sup> will directly launch a nucleophilic attack on the silicon atomic nucleus, causing the Si-O bonds to be weakened and eventually broken. The TEOS could be hydrolyzed to generate  $SiO_2$  on the basis of chemical reactions (eqs S4 and S5), and the hydrolysis reactions were proceeding on the interface between water and oil, resulting in the formation of a SiO<sub>2</sub> shell on Ni(OH)<sub>2</sub>-Ce(OH)<sub>x</sub> NWs. The thickness of the SiO<sub>2</sub> shell was gradually increased with prolonging the hydrolysis and condensation time of TEOS (Figures S12a-d and S13ad). The final Ni-CeO<sub>2</sub>@SiO<sub>2</sub> catalyst was obtained by calcining and reducing the Ni(OH)<sub>2</sub>-Ce(OH)<sub>x</sub>@SiO<sub>2</sub> in air and hydrogen atmosphere.

**3.3. Catalytic Activity.** First, the obtained Ni-CeO<sub>2</sub>@SiO<sub>2</sub> together with Ni@SiO<sub>2</sub>, free Ni-CeO<sub>2</sub>, Ni-CeO<sub>2</sub>/SiO<sub>2</sub> were

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Scheme 1. Synthetic Scheme for the Preparation of (Route 1) Ni-CeO<sub>2</sub>@SiO<sub>2</sub>, (Route 2) Ni@SiO<sub>2</sub>, and (Route 3) CeO<sub>2</sub>@SiO<sub>2</sub> Catalysts





Figure 5. (a) Time course plots for gas generation from hydrous hydrazine (200 mM, 5 mL) and (b) the corresponding hydrogen selectivity and TOF value over different catalysts ( $n_{Ni}/n_{HH} = 0.1$ ) at 343 K.

used as catalysts for H<sub>2</sub> production from N<sub>2</sub>H<sub>4</sub> in aqueous solution. As presented in Figure 5a,b, remarkably, among the prepared catalysts, Ni-CeO<sub>2</sub>@SiO<sub>2</sub> shows the highest catalytic performance, with which 3.0 equiv of  $(H_2+N_2)$  can be generated within 7.1 min at 343 K. The TOF value of Ni- $CeO_2(aSiO_2)$  catalyst is calculated to be 219.5 h<sup>-1</sup>, which is equivalent to the most advanced nonprecious metal catalysts (Table S2).<sup>1-4,6,7,10,20-23,31-33</sup> It should be noted that for  $N_2H_4$  decomposition changing the nickel (Figure S14a,b) or cerium loading (Figure S14c,d) to some other values results in the decrease of the catalytic property; thus, the optimum nickel and cerium loading are determined to be 6.7 and 5 wt %, respectively. Therefore, except as otherwise noted, the Ni-CeO2@SiO2 catalyst discussed in this work is 6.7 wt % Ni-5 wt % CeO<sub>2</sub>@SiO<sub>2</sub>. In contrast, the Ni@SiO<sub>2</sub> catalyst takes 8.7 min to release 1.8 equiv.  $(H_2+N_2)$ . In addition, 2.8 and 1.9 equiv of  $(H_2+N_2)$  were evolved in 29.1 and 18.3 min, respectively, in the presence of free Ni-CeO<sub>2</sub> and Ni-CeO<sub>2</sub>/ SiO<sub>2</sub> catalysts (Figure 5a,b). This superior activity of the wormlike Ni-CeO<sub>2</sub>@SiO<sub>2</sub> core-shell structure catalyst can be attributed to the synergistic electronic effect and strong interaction between Ni NPs and CeO<sub>2</sub> with plenty of oxygen vacancies, as well as the unique structure effect.

To investigate the effect of the thickness of the SiO<sub>2</sub> shell on the dehydrogenation of N<sub>2</sub>H<sub>4</sub>, the catalytic performance of Ni-CeO<sub>2</sub>@SiO<sub>2</sub> with different thickness of the SiO<sub>2</sub> shell was tested. As shown in Figure S15a,b, the catalytic activity of the Ni-CeO<sub>2</sub>@SiO<sub>2</sub> catalysts increases when the thickness of the SiO<sub>2</sub> shell increases from 5.8 to 8.2 nm, but it decreases with further increases of the thickness of the SiO<sub>2</sub> shell to 9.1 nm. The decrease in activity of Ni-CeO<sub>2</sub>@SiO<sub>2</sub> with a thick shell was due to the restricted diffusion of reactant molecules.

To get the activation energy  $(E_a)$  of the hydrazine dehydrogenation catalyzed by Ni-CeO<sub>2</sub>@SiO<sub>2</sub>, the reactions were conducted at different temperatures ranging from 338 to 353 K (Figure 6a). The dehydrogenation reactions were completed within 10.2, 7.1, 5.5, and 4.3 min at 338, 343, 348, and 353 K, respectively, corresponding to TOF values of 126.8, 219.5, 279.1, and 339.6 h<sup>-1</sup> (inset of Figure 6b). There are different rate constants k at different temperatures, which are determined from the slope of the linear part of each plot when the conversion reaches 50%. The  $E_a$  is evaluated to be 59.26 kJ mol<sup>-1</sup> according to the Arrhenius plot (ln k vs 1/T) (Figure 6b), which is comparable to reported noble-metal-containing catalyts.<sup>1,10,22,23,32</sup> The durability of catalyst is crucial for practical use. The cycle experiments were evaluated via pubs.acs.org/IC



**Figure 6.** (a) Time course plot for gas generation from hydrous hydrazine (200 mM, 5 mL). (b) Corresponding Arrhenius plot and the inset shows the corresponding TOF values of dehydrogenation of  $N_2H_4$ . (c) Time course plot for gas generation from hydrazine borane aqueous solution (200 mM, 5 mL), and (d) plot of ln *k* versus 1/T for hydrogen generation from hydrolysis of the BH<sub>3</sub> group (Part 1) and decomposition of the  $N_2H_4$  moiety of  $N_2H_4BH_3$  (Part 2) over Ni-CeO<sub>2</sub>@SiO<sub>2</sub> catalyst with ( $n_{Ni}/n_{HH} = 0.1$ ) at different temperatures.

consecutive injecting the same amount of  $N_2H_4$ · $H_2O$  (1 mmol) into the three-necked round-bottomed flask when the previous reaction was finished. As displayed in Figure S16a,b, it can be observed that the selectivity of H<sub>2</sub> remains at 100%, and the catalytic activity decreases slightly during 10 continuous reaction cycles over the Ni-CeO2@SiO2 catalyst. In contrast, Ni-CeO<sub>2</sub> showed an obvious activity lose after 5 runs as compared with the initial catalytic activity (Figure S17a,b), indicating that the Ni-CeO2@SiO2 sample possesses excellent durability in the catalytic dehydrogenation of N<sub>2</sub>H<sub>4</sub>. For the dehydrogenation of N<sub>2</sub>H<sub>4</sub>, the dissociative adsorption of the N<sub>2</sub>H<sub>4</sub> molecule on the Ni-CeO<sub>2</sub> NWs surface produces adatoms of H first. The H atoms have good mobility and can combine with another absorbed H atom to generate H<sub>2</sub>. With the stepwise dissociative of H atoms in  $N_2H_4$ ,  $N_2$  is finally released (Scheme S1).<sup>5</sup>

Hydrazine borane  $(N_2H_4BH_3)$  has recently been developed as a ideal solid material for chemical H<sub>2</sub> storage, from which hydrogen can be released through hydrolysis of the BH<sub>3</sub> moiety and decomposition of the  $N_2H_4$  group.<sup>45-51,68,69</sup> In this work, the catalytic performence of the Ni-CeO2@SiO2 catalyst for the H<sub>2</sub> production from N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> was also tested. As shown in Figure 6c, the complete dehydrogenation of N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> over Ni-CeO<sub>2</sub>@SiO<sub>2</sub> catalyst at 343 K finished in 6.8 min corresponding to a high TOF value of 442.5  $h^{-1}$ , which is a relatively high value as compared with the reported value for nonprecious metal catalysts (Table S3).<sup>8,9,24,46-50,70</sup> The values of rate constant k at different temperatures were determined from the slope of hydrolysis of the BH<sub>3</sub> moiety (Part 1) and decomposition of N<sub>2</sub>H<sub>4</sub> group (Part 2) in each plot of Figure 6c, respectively. According to the Arrhenius plot of ln k versus 1/T, the obtained  $E_{a1}$  value of hydrolyzing the BH<sub>3</sub> moiety (Part 1) and the  $E_{a2}$  value of decomposing the N<sub>2</sub>H<sub>4</sub> group (Part 2) are calculated to be 22.65 and 58.03 kJ

mol<sup>-1</sup>, respectively (Figure 6d). Ni-CeO<sub>2</sub>@SiO<sub>2</sub> catalyst also has a good durability in hydrogen generation from N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> (Figure S18a,b). Although the catalytic activity of Ni-CeO<sub>2</sub>@SiO<sub>2</sub> shows a slight decrease after six cycles. The slight decrease of the catalytic performance was nearly removed via washing the catalyst with water. This phenomenon can be ascribed to the deactivation influence of the increasing metaborate accumulated during the hydrolysis of the BH<sub>3</sub> moiety of N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub>.<sup>24</sup> The plausible catalytic mechanism of N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> dehydrogenation over Ni-CeO<sub>2</sub>@SiO<sub>2</sub> catalyst is clarified in Scheme S2. The interaction between the N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> molecule and Ni-CeO<sub>2</sub> NWs surface will generate the activated complex species, for which attack by a H<sub>2</sub>O molecule leads to dissociation the B-N bonding of the N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub>. When the BH<sub>3</sub> moiety of N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> is catalytically hydrolyzed by metal NPs, concurrently, the resulting  $N_2H_4$  group is decomposed to produce H<sub>2</sub> and N<sub>2</sub>.

The designed Ni-CeO2@SiO2 can be used as a universal catalyst owing to its synergistic electronic effect and strong interaction between Ni NPs and CeO<sub>2</sub> NWs with plenty of oxygen vacancies, as well as the unique structure effect. Therefore, the wormlike Ni-CeO2@SiO2 core-shell catalyst was also applied in a gas-phase reaction. To assess the catalytic functionality of the Ni-CeO<sub>2</sub>@SiO<sub>2</sub> for gas-phase reactions, we carried out the CO<sub>2</sub> methanation reaction from 200 to 450  $^{\circ}$ C. As a result, Ni-CeO<sub>2</sub>@SiO<sub>2</sub> exhibits superior catalytic activity for  $CO_2$  methanation than Ni@SiO<sub>2</sub> (Figure S19a-c). These results further confirm that the property of the catalyst can be enhanced by incorporation of the CeO<sub>2</sub> since the synergistic electronic effect and strong interaction between Ni NPs and CeO<sub>2</sub> NWs with plenty of oxygen vacancies. Long-term thermal stability tests of Ni-CeO2@SiO2 and Ni@SiO2 at 400 °C for 60 h were also carried out. As displayed in Figure S19d, the catalytic activity of Ni-CeO<sub>2</sub>@SiO<sub>2</sub> and Ni@SiO<sub>2</sub> barely declined. It reveals that the  $SiO_2$  shell confinement can curb the sintering of the active metal and improve the thermal stability of the catalysts in the high temperature reactions.

#### 4. CONCLUSIONS

In summary, a wormlike Ni-CeO2@SiO2 core-shell catalyst with a self-assembled Ni-CeO2 NWs as the core and microporous SiO<sub>2</sub> as the shell was successfully synthesized by a simple one-pot synthesis route in the reverse micelle system. The formation mechanism of novel nanostructure Ni- $CeO_2$  (@SiO\_2 is discussed in detail. The obtained Ni-CeO\_2 (@ SiO<sub>2</sub> catalyst showed superior catalytic performance and durability for H<sub>2</sub> generation from N<sub>2</sub>H<sub>4</sub> and N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> aqueous solution with TOF of 219.5 and 442.5  $h^{-1}$  at 343 K, respectively. Moreover, the Ni-CeO2@SiO2 also has good catalytic activity and thermal stability for CO<sub>2</sub> methanation. For comparison, we synthesized the core-shell structure Ni@ SiO<sub>2</sub> nanospheres and SiO<sub>2</sub>-free Ni-CeO<sub>2</sub> in a homologous way. The Ni@SiO<sub>2</sub> shows much lower activity, whereas the SiO<sub>2</sub>-free Ni-CeO<sub>2</sub> catalyst exhibits poor stability. The excellent catalytic property of the Ni-CeO2@SiO2 catalyst is related to the synergistic electronic effect and strong interaction between Ni NPs and CeO<sub>2</sub> NWs with plenty of oxygen vacancies, as well as the unique structure effect. As an effective strategy, this work also opens a new route to synthesize highly efficient nanocatalysts for applications in various catalytic fields.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00600.

SEM images; length and diameter distributions; HRTEM image and SAED pattern; EDX spectrum; TEM images; XRD patterns of different catalysts; survey XPS spectrum; pore size distributions curve of different catalysts; SiO<sub>2</sub> shell thickness distribution; catalytic activities influenced by Ni or Ce loading or by the thickness of SiO<sub>2</sub> shell; durability of N<sub>2</sub>H<sub>4</sub> decomposition catalyzed by Ni-CeO<sub>2</sub>@SiO<sub>2</sub> or by Ni-CeO<sub>2</sub>@ SiO<sub>2</sub> catalyst; durability and mechanism of N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> dehydrogenation catalyzed by Ni-CeO<sub>2</sub>@SiO<sub>2</sub> catalysts; structure parameters of catalysts measured by N<sub>2</sub> sorption isotherms (PDF)

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## **Author Contributions**

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#### Notes

The authors declare no competing financial interest.

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