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# Free-standing Pt–Ni nanowires catalyst for H<sub>2</sub> generation from hydrous hydrazine<sup>+</sup>

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Free-standing Pt–Ni nanowires were fabricated by a one-pot solvothermal method. Nanowires with an optimal Pt/Ni ratio of 1.86 exhibited a high activity and a 100% H<sub>2</sub> selectivity for hydrous hydrazine decomposition at mild temperatures, which are comparable to the levels of supported catalysts. Our study reveals for the first time that basic support is not a prerequisite for achieving favorable catalytic performance and provides a renewed perspective for the design of advanced catalysts for on-demand H<sub>2</sub> generation from hydrous hydrazine.

Safe and efficient approaches of hydrogen storage and delivery remain a central challenge for the widespread penetration of hydrogen energy technologies. Reversible hydrogen storage materials have long been sought as hydrogen vectors for the on-board applications; however, none has proven to be completely satisfactory.<sup>1,2</sup> Recently, on-demand hydrogen release from irreversible hydrides in conjunction with spent fuel regeneration received an ever-increasing attention as a promising alternative to the pressurized tanks for onboard and niche applications.<sup>3-6</sup> Among available chemical hydrides of interest,  $N_2H_4$ ·H<sub>2</sub>O is a leading candidate due to its high hydrogen content, low cost, satisfactory stability at ambient conditions and in particular generation of no solid by-products.<sup>7</sup>

Searching for active catalysts to selectively promote  $H_2$  generation from  $N_2H_4$ · $H_2O$  while suppression of the formation of  $NH_3$  is a central task in the development of  $N_2H_4$ · $H_2O$ -based hydrogen source system. In the past few years, a variety of group VIII transition metals and their alloys have been investigated as potential catalysts toward  $N_2H_4$ · $H_2O$  decomposition.<sup>8–35</sup> The alloys composed of noble and non-noble metals typically showed significantly improved activity and  $H_2$  selectivity over the end members.<sup>12–22,30–33,35</sup> Alloying was thus established as an effective strategy for boosting the catalytic performance. Immobilization of

catalyst nanoparticles onto basic supports is another extensively used strategy to enhance the catalytic performance.<sup>10-25,27,28,30-35</sup> Importantly, recent studies have suggested the additional roles of supports beyond their primary function of dispersion and stabilization of metal catalysts.<sup>10,11,19,23,25,35</sup> It was proposed that the basic sites of support might contribute toward the enhancement of H<sub>2</sub> selectivity. Moreover, supports may exert their effect on catalytic performance through metal-support interactions.<sup>10,23,25,35</sup> In practice, the joint application of alloying and basic support immobilization strategies has given rise to state-of-the-art catalysts, such as NiPt/CeO2 and CoPt/La(OH)3,15,31 which can catalyze the decomposition of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O to completion and rapidly generate H<sub>2</sub> at ambient temperatures. In general, encouraging progresses have been made in the development of supported alloy catalysts for N2H4·H2O decomposition reaction. However, nowadays, catalyst screening is primarily conducted through experimental trial and error and therefore from a mechanistic perspective, the state-of-theart catalysts are poorly understood. A major reason for this failure is that major factors (active component, support and metal-support interaction) influencing the catalytic performance are entangled in a complicated manner. Given this situation, improved understanding of the function of individual component phase, the nature of metalsupport interaction and its effects on catalytic performance is of clear significance for the development of high-performance N2H4·H2O decomposition catalysts. In our recent studies of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O-based H<sub>2</sub> generation system, we focused on the synthesis and property evaluation of support-free nanowire catalysts. The choice of one-dimensional (1D) nanostructure was based on its combination of high specific surface area, good mass-transfer performance as well as well-established synthesis methods.<sup>36-40</sup>

We herein report a facile fabrication of Pt–Ni nanowire and its appealing catalytic property for  $N_2H_4$ · $H_2O$  decomposition reaction. Surprisingly, the free-standing Pt–Ni nanowires with an optimal composition exhibited an impressively high activity and a 100%  $H_2$  selectivity for  $N_2H_4$ · $H_2O$  decomposition. This finding clearly indicated that a basic support is not a prerequisite for achieving favorable catalytic performance for  $N_2H_4$ · $H_2O$ decomposition, as opposed to the general belief.

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Fig. 1 (a) TEM image; (b) SAED pattern; (c) HRTEM image of the framed region in (a); (d) HAADF-STEM image and EDS line-profiles along the arrows shown in (d); (e–f) EDS elemental mapping results of  $Pt_3Ni_2$  nanowires.

Pt-Ni nanowires with tuneable compositions were fabricated by a one-pot solvothermal method.<sup>41</sup> Control experiments help identify that the Pt-Ni nanowires with a nominal Pt-Ni molar ratio of 3:2 exhibited an optimal catalytic performance for the  $H_2$  generation from  $N_2H_4$ · $H_2O$  and were thus chosen for a more comprehensive study. Transmission electron microscopy (TEM) image of the solvothermal sample clearly showed the successful synthesis of 1D nanowires without the usage of any template or external field (Fig. 1a). These nanowires, with a diameter of 10-20 nm, and a length of up to hundreds of nanometers, were interconnected and interlocked together to form a network-like structure. Such an open structure could offer abundant active sites and numerous channels for rapid mass transfer of reactants and products. A close examination by high-resolution TEM (Fig. 1c and Fig. S1, ESI<sup>+</sup>) revealed that these nanowires actually comprised aligned ultrathin wires of 2-3 nm in diameter and the nanowire surface was decorated by randomly dispersed nanoparticles of 1-3 nm in size (highlighted by red circles Fig. 1c). It was observed that these nanowires and nano-pyramids possess similar crystalline structure and the interplanar spacings of 0.221-0.225 nm were found to be intermediate between those for the (111) planes of fcc Pt (0.227 nm) and fcc Ni (0.203 nm). These results clearly indicated the formation of single-phase Pt-Ni solid solution alloy with a nanocrystalline nature. In good accordance with this observation, the selected area electron diffraction (SAED) pattern displayed concentric rings, characteristic for nanocrystalline materials (Fig. 1b). The X-ray diffraction (XRD) patterns (Fig. 2a) showed weak and wide diffraction peaks at positions intermediate between those of monometallic Pt and Ni samples, and the peaks were observed to shift towards higher angles with increasing Ni/Pt precursor ratio. The formation of Pt-Ni alloy was further confirmed by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging in combination with energy-dispersive X-ray spectroscopy (EDS) analysis. The EDS line-profiles (Fig. 1d) acquired from randomly



Fig. 2 (a) XRD patterns of Pt–Ni nanowires with different Pt/Ni ratios and monometallic Ni, Pt samples; (b and c) XPS spectra of Pt<sub>3</sub>Ni<sub>2</sub> and relevant monometallic samples in the Pt 4f and Ni 2p regions.

selected regions showed synchronous changes in Pt and Ni signals. The elemental mapping results (Fig. 1e-g) indicated a uniform dispersion of Pt and Ni elements throughout nanowires without an appreciable segregation. Another strong evidence supporting the Pt-Ni alloying was obtained from highresolution X-ray photoelectron spectroscopy (XPS) analysis. As seen in Fig. 2b and c, the Pt 4f and Ni 2p core level spectra of the Pt-Ni sample could be fitted to the characteristic peaks of a major metallic species and a minor bivalent species. A close examination of XPS spectra revealed that Pt<sup>0</sup> in the Pt–Ni sample showed a positive binding energy (BE) shift by 0.21 eV with regards to the pristine Pt. Moreover, metallic Ni<sup>0</sup> exhibited a negative BE shift by 0.37 eV relative to the monometallic Ni reference. These results indicated an electron transfer from Pt to Ni as a response to Pt-Ni alloying and as demonstrated below, this modification in the electronic structure rendered the Pt-Ni alloy with favorable catalytic properties for N2H4·H2O decomposition to generate H<sub>2</sub>.

The growth process of Pt-Ni nanowires during the solvothermal process was followed by TEM (Fig. S2, ESI<sup>+</sup>). It was observed that most of the tiny nanoparticles self-assembled to form 1D architecture after 10 min of the reaction. As the solvothermal reaction proceeded, coalescence of adjacent nanoparticles exclusively occurred in an aligned direction, resulting in the formation of nanorods and eventually nanowires. After the reaction for 4 h, the nanowire assemblies were formed and further prolongation of the reaction time exerted no significant influence on the nanowire morphology. Based on the observed structural evolution, Pt-Ni nanowire was grown through the oriented attachment of nanoparticle building blocks that were formed at the very beginning of solvothermal process.42,43 According to Lou and coworkers,41 amine is formed via the reaction of DMF and KOH in the solvothermal process, which serves an important dual function in the formation of nanowire assemblies. First, the adsorbed amine acts as a structure-directing agent to guide the growth of 1D nanowires. Second, it serves as a stabilizer to avoid the coalescence



Fig. 3 (a) XPS N1s spectrum and (b) TG-MS profiles of the as-prepared  $Pt_3Ni_2$  nanowires; (c) kinetic curves of  $N_2H_4$ · $H_2O$  decomposition over the as-prepared and annealed  $Pt_3Ni_2$  samples.

of laterally overgrown nanowires. In the present study, the presence of amine groups on the sample surface was unambiguously confirmed by combining XPS and thermogravimetric-mass spectrometry (TG-MS) analyses. XPS survey scans of the sample showed N 1s peak at 397.2 eV, which corresponds to the amine groups (Fig. 3a).<sup>44</sup> In the synchronous TG-MS analysis (Fig. 3b), the signal at m/z = 15, corresponding to a fragment of amine group was observed at a temperature range of 200-330 °C.45 However, the interference from the desorbed water (m/z = 18 and 17) made it impossible to quantify the amount of adsorbed amine group on sample surface. To evaluate the effect of surface amine groups on the catalytic decomposition of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, we annealed the Pt<sub>3</sub>Ni<sub>2</sub> sample at 300 °C under Ar atmosphere for 1 h and compared its catalytic performance with the as-prepared catalyst. As seen in Fig. 3c, the annealed sample exhibited only a slight activity degradation compared to the as-prepared sample, which might be ascribed to the sintering and agglomeration of nanowires at an elevated temperature. This preliminary study suggested that surface amine group does not possess a profound effect on the catalytic decomposition of N2H4·H2O over the Pt-Ni alloy.

Property tests of a series of Pt-Ni nanowires catalysts revealed a strong composition-dependence of catalytic performance for  $N_2H_4$ · $H_2O$  decomposition. As shown in Fig. 4a, the activity and H<sub>2</sub> selectivity increased with the increment in Pt/Ni ratio and reached an optimal level in the sample with a nominal Pt/Ni molar ratio of 3:2. As determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Table S1, ESI<sup>†</sup>), the actual Pt/Ni atomic ratio (1.86) of this sample was higher than the precursor ratio. This is indicative of an incomplete reduction of Ni<sup>2+</sup> in the solvothermal process due to its much lower reduction potential (-0.257 V vs. SHE) relative to those of Pt(IV) complexes (+0.68 V vs. SHE for  $[PtCl_6]^{2-}/[PtCl_4]^{2-}$  and +0.755 V vs. SHE for  $[PtCl_4]^{2-}/Pt$ ). The Pt<sub>3</sub>Ni<sub>2</sub> nanowires enabled a complete decomposition of  $N_2H_4$ · $H_2O$  at mild temperatures with the presence of 2 M NaOH. The turnover frequency of the reaction reached up to 726  $h^{-1}$  at 50 °C and 1800  $h^{-1}$  at 70 °C. Furthermore, it showed a 100% H<sub>2</sub> selectivity in a temperature range of 30-70 °C (Fig. 4b), and such temperature-independence of a reaction in terms of selectivity is highly desirable for practical applications. Based on the temperature-dependent reaction rate, the apparent activation energy of N2H4·H2O decomposition over the Pt3Ni2 nanowires was determined to be approximately  $60.5 \text{ kJ mol}^{-1}$ . To our knowledge, this is the first report of a support-free catalyst that possesses comparable catalytic properties for N2H4·H2O decomposition reaction to that of the supported



Fig. 4 (a) Kinetic curves of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O decomposition over different catalysts at 50 °C. The inset shows the reaction rate and H<sub>2</sub> selectivity as a function of Pt content of the catalyst; (b) kinetic curves of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O decomposition over Pt<sub>3</sub>Ni<sub>2</sub> nanowires as a function of reaction temperature. The inset shows the determination of apparent activation energy from the Arrhenius plot; (c–e) cyclic kinetic curves of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O decomposition over Pt<sub>3</sub>Ni<sub>2</sub> nanowires at (c) 30 °C; (d) 50 °C; (e) 70 °C. The kinetic curve of the post-treated catalyst at 70 °C for 1 h is included in (d).

catalysts (Table S2 and Fig. S3, ESI<sup>†</sup>).<sup>12,18,21,32,35,46–48</sup> This result challenges the conventional notion that basic support is indispensable for achieving favorable catalytic performance. Evidently, for support-free Pt–Ni catalysts, it is the Pt–Ni alloying that is responsible for dramatic improvements in activity and H<sub>2</sub> selectivity. Improved understanding of the mechanism by which Pt–Ni alloy selectively facilitates H<sub>2</sub> generation from N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O and the composition-sensitive catalytic performance may shed light on the design and construction of active sites with higher intrinsic activity. Nevertheless, theoretical elucidation of catalytic decomposition of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O over Pt–Ni alloy is quite tedious owing to the multiple kinetic steps and conformational changes of complex molecules, as well as the diversity of surface sites.

Finally, we tested the stability of the Pt<sub>3</sub>Ni<sub>2</sub> nanowire catalyst. As well documented in literature, supported N2H4·H2O decomposition catalysts generally suffer from poor stability under alkaline condition. In this study, we observed the same problem during the cyclic usage of Pt<sub>3</sub>Ni<sub>2</sub> nanowires. As shown in Fig. 4c, the catalyst showed over 70% activity loss after five cycles at 30 °C while maintaining a 100% H<sub>2</sub> selectivity. These results suggested that the decomposition pathway of N2H4 over Pt<sub>3</sub>Ni<sub>2</sub> was essentially remained unchanged but activity rapidly decreased with the available active sites. XRD analysis of the post-used catalyst did not show any appreciable change in the phase structure (Fig. S4a, ESI<sup>+</sup>); however, HRTEM observation revealed the formation of ultrathin Ni(OH)<sub>2</sub> nanosheets on the catalyst surface (Fig. S4c and d, ESI<sup>†</sup>). Consistently, the XPS analysis of the post-used sample clearly identified the characteristic signals observed from Ni(OH)<sub>2</sub> (Fig. S4b, ESI<sup>+</sup>). In addition to this phase transformation, our study further

suggested another possibility accounting for the activity decay. It was found that the activity decay was supressed at higher reaction temperatures, as opposed to the expectation that a faster transformation kinetics will be observed at higher temperature. It was observed that the activity loss of the Pt<sub>3</sub>Ni<sub>2</sub> catalyst after 5 cycles decreased from over 70% at 30  $^{\circ}$ C to 65% at 50  $^{\circ}$ C and further to 53% at 70  $^{\circ}$ C (Fig. 4c–e). A reasonable explanation for this phenomenon is the poisoning of active sites by the intermediates/products of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O decomposition, which could be alleviated at higher reaction temperatures. This speculation was supported by the observation that the activity of the post-used catalyst was partially restored after treating at 70 °C for 1 h from 254 to 370  $h^{-1}$  (Fig. 4d). Based on the above results, the activity decay of Pt<sub>3</sub>Ni<sub>2</sub> and many other N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O decomposition catalysts is a complicated phenomenon that may involve surface composition and phase changes and poisoning effects. In this regard, in-depth studies are required to shed light on the nature and solution of this common and critical problem.

In summary, the free-standing Pt–Ni nanowires with an actual Pt/Ni ratio of 1.86 exhibited a comparable catalytic performance for H<sub>2</sub> generation from N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O to those of the supported catalysts. This finding challenges the conventional notion that basic support is inevitable for achieving desirable catalytic properties for N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O decomposition and provide a renewed perspective for the design of high-performance catalysts to promote the practical application of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O.

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### Conflicts of interest

There are no conflicts to declare.

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