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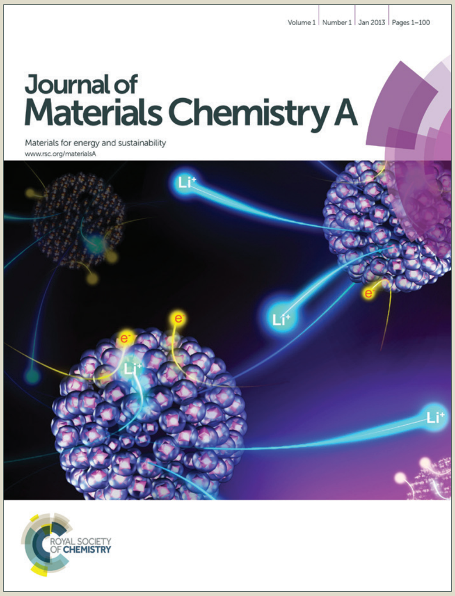

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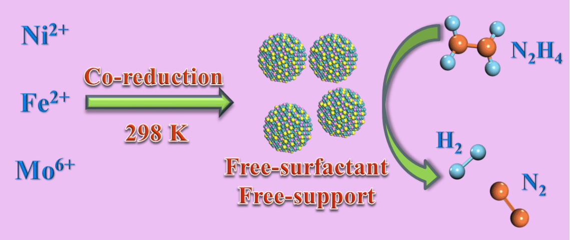

Noble-metal-free NiFeMo has been applied as the efficient catalyst for rapid and complete decomposition of hydrous hydrazine for hydrogen generation.

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COMMUNICATION

Noble-metal-free NiFeMo nanocatalyst for hydrogen generation from decomposition of hydrous hydrazine solution†

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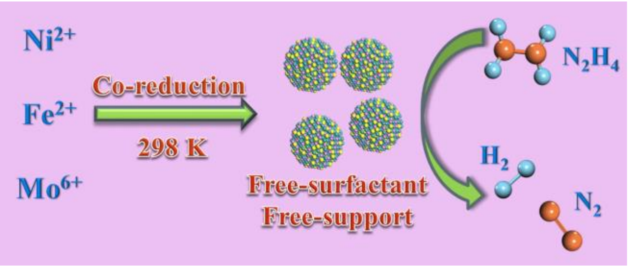
The noble-metal-free NiFeMo nanoparticles without any surfactant or support has been facilely synthesized and successfully applied as the highly efficient catalyst for rapid and complete decomposition of hydrous hydrazine (a promising hydrogen storage/generation material) for hydrogen generation at mild temperature. The surfactant/support free nanoparticles possess the well dispersion and small particle size. Moreover, upon the incorporation of Mo and Fe, the catalytic activity and hydrogen selectivity of the present trimetallic catalyst are remarkably improved compared with its mono-/bi-metallic counterparts.

Storing and generating hydrogen (H_2) safely and efficiently remain as the great challenge toward the fuel cell based H_2 economy.[1-7] Recently, hydrous hydrazine ($N_2H_4{\cdot}H_2O$) has been considered as a promising candidate as a H_2 storage/generation material due to its high H_2 content (8.0 wt%), relatively low cost and easy recharging as a liquid (the existing liquid-based fuel distribution infrastructure can be used).[8-9] Importantly, the decomposition of $N_2H_4{\cdot}H_2O$ does not generate any solid by-product, the only by-product of complete decomposition of $N_2H_4{\cdot}H_2O$ is nitrogen (N_2): $H_2NNH_2 \rightarrow N_2(g) + 2H_2(g)$,[10–34] which is environmentally friendly. For H_2 generation, the incomplete and undesirable side reaction ($3H_2NNH_2 \rightarrow 4NH_3(g) + N_2(g)$) must be avoided.[35-40] Therefore, it is of importance to develop effective catalysts for selective decomposition of $N_2H_4{\cdot}H_2O$ to H_2.

Up to now, much effort has been done on synthesis and application of noble-metal containing nanocatalysts for H_2 generation from $N_2H_4{\cdot}H_2O$ under mild conditions (298-323 K).[10-25] However, most of these catalysts show moderate activities.[10-19] Additionally, the high costs and limited resources of noble metals restrict their large-scale applications.[27,38] To solve this problem, non-noble-metal nanomaterials are gained more and more research interests for seclective decomposition of $N_2H_4{\cdot}H_2O$.[26-34] Generally, minimization and high dispersion of the nanoparticles are the key factors to obtain more surface reactive sites to elevate the activities of the non-noble-metal nanomaterials. Thus, various surfactants or particle supports are applied during the syntheses of these nanocatalysts.[26-33] For example, it is found that, using hexadecyltrimethylammonium bromide (CTAB) as surfactant, NiFe alloy nanoparticles could catalyze the complete dehydrogenation of $N_2H_4{\cdot}H_2O$ at 343 K.[26] Meanwhile, supported non-noble-metal nanocatalysts such as Ni-Al_2O_3-HT,[27] NiFe-alloy/MgO,[29] Ni_3Fe/C[32] and FeB/MWCNTS[33] are active to the same reaction at room temperature. However, the usage of surfactants sometimes decrease the catalytic performance due to the more or less occupation of the active sites on the surface of nanocataylsts by surfactants.[26] For supported catalysts, the extra addition of supports brings the complicated preparation processes, such as multi-step synthesis, long reaction time and strict reaction conditions (high temperature, inert gas protection and post prcessing), leading to a great difficulty in both equipment and operation requirements.[27,29,32-33] More importantly, most of the catalytic activites of the reported non-noble-metal nanomaterials for dehydrogenation of $N_2H_4{\cdot}H_2O$ are still very low.[26-31] Based on the above reasons, exploring a facile strategy to obtain the well dispersed non-noble-metal nanocatalyst with excellent catalytic activity and 100% H_2 selectivity for H_2 generation from $N_2H_4{\cdot}H_2O$ at mild temperature is of good interest but still a big challenge.

Herein, the noble-metal-free $Ni_{0.6}Fe_{0.4}Mo$ nanoparticles (NPs) have been prepared through a facile one-step synthetic route at room temperature under ambient atmosphere within 10 minutes. The as-prepared NPs hold small particle size and high dispersion without the assistance of surfactant/support. As expected, the $Ni_{0.6}Fe_{0.4}Mo$ nanocatalyst exhibits the 100% H_2 selectivity and superior catalytic activity for the decomposition of $N_2H_4{\cdot}H_2O$ at 323 K.



Scheme 1. Schematic illustration for preparation and application of NiFeMo nanocatalyst for decomposition of $N_2H_4{\cdot}H_2O$ at mild conditions.

$Ni_{0.6}Fe_{0.4}Mo$ NPs was synthesized by a surfactant/support-free one-step coreduction method at 298K (Scheme 1), in which $NiCl_2{\cdot}6H_2O$, $Fe_2SO_4{\cdot}7H_2O$ and $Na_2MoO_4{\cdot}2H_2O$ were used as the metal precursors and $NaBH_4$ was added as the reducing agent. Fig. 1a shows the typical transmission electron microscopy (TEM) image of the as-prepared $Ni_{0.6}Fe_{0.4}Mo$ NPs. The NPs are well-dispersed with an average particle size of less than 5 nm. The corresponding energy dispersive X-ray (EDX) spectrum displays all the existences of Ni, Fe and Mo elements (Fig. 1b). The atomic ratio for Ni:Fe:Mo is detected to be 0.298:0.199:0.503 by EDX, and this is in good agreement with the theoretical value (0.6:0.4:1). The high-resolution TEM (HRTEM) image reveals the crystalline nature of the $Ni_{0.6}Fe_{0.4}Mo$ NPs, and the lattice spacing is measured to be 0.206 nm (Fig. 1c). The X-ray diffraction (XRD) pattern shows that the tri-metallic specimen has an crystalline peak centered at 43.95 (Fig. 1d, black trace), which is between the (111) plane of fcc Ni (JCPDS file: 04-0850), the (111) plane of fcc Fe structure (JCPDS file: 52-0513) and the (110) plane of body-centered cubic (bcc) Mo (JCPDS file: 65-7442).[26, 42, 43] Moreover, after heat treatment at 823 K for 3 h in argon (Ar), this sample is better crystallized into a fcc crystal structure (Fig. 1d, red trace). Compared with the pure fcc Ni, the diffraction peaks are slightly shifted to the lower angles, which may result from the addition of Fe and Mo atoms into the crystal lattice of Ni, and this is consistent with the HRTEM result. Based on the above analyses, the well dispersed $Ni_{0.6}Fe_{0.4}Mo$ NPs with alloy structure have been successfully synthesized through the present facile co-reduction method without support and surfactant at 298 K.

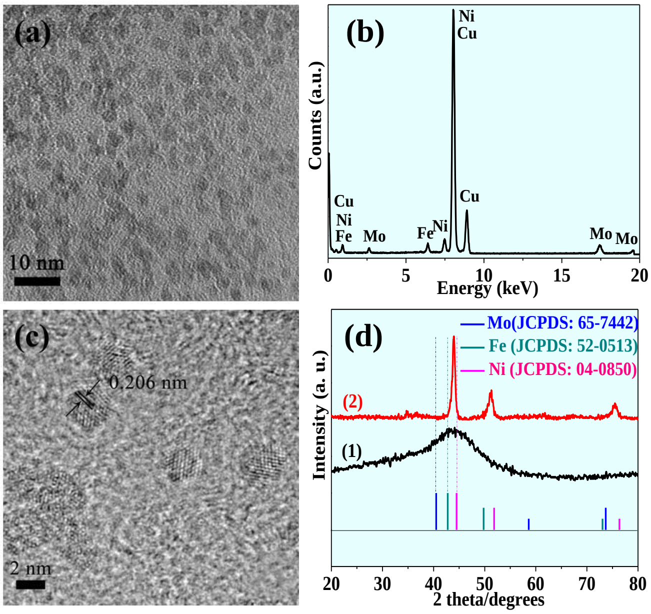


Fig. 1 TEM image (a), the corresponding EDX spectrum (b) and HRTEM image (c) for the $Ni_{0.6}Fe_{0.4}Mo$ NPs; (d) X-ray diffraction patterns for the $Ni_{0.6}Fe_{0.4}Mo$ NPs before (1) and after (2) heat treatment at 823 K for 3 h in argon atmosphere.

To investigate the effect of Mo on the chemical state of $Ni_{0.6}Fe_{0.4}Mo$, the X-ray photoelectron spectroscopy (XPS) analyses after Ar sputtering have been applied on $Ni_{0.6}Fe_{0.4}Mo$ and $Ni_{0.6}Fe_{0.4}$ for comparison. It can be seen from Fig. 2 that the incorporation of Mo into bi-metallic $Ni_{0.6}Fe_{0.4}$ NPs can result in the change of the binding energy (BE) of the component elements. After Mo addition, BE of Ni $2p_{3/2}$ is negatively shifted from 852.6 to 852.1 eV (Fig. 2a). Meanwhile, BE of Fe $2p_{3/2}$ is also negatively shifted from 708.0 to 707.4 eV (Fig. 2b). Whereas, BE of Mo $3d_{5/2}$ (228.6 eV, Fig. 2c) is shifted to the higher value relative to that of metallic Mo^0 (228.0 eV).[44] Base on the XPS analyses, it can be seen that, in alloy of $Ni_{0.6}Fe_{0.4}Mo$, Mo acts as an electron donor for atoms of Ni and Fe. Such electron transfer in $Ni_{0.6}Fe_{0.4}Mo$ has the potential to endow itself with the high catalytic activity to H_2 generation from $N_2H_4{\cdot}H_2O$ decomposition. Moreover, since crystal growth can be limited by co-deposition of multi-element,[26] the addition of Mo results in the smaller particle sizes of $Ni_{0.6}Fe_{0.4}Mo$ relative to $Ni_{0.6}Fe_{0.4}$ (Fig. S1†), which may provide more active sites for H_2 generation from the decomposition of $N_2H_4{\cdot}H_2O$. In addition, no element of B has been detected in specimen of $Ni_{0.6}Fe_{0.4}Mo$ by XPS (Fig. S2†).

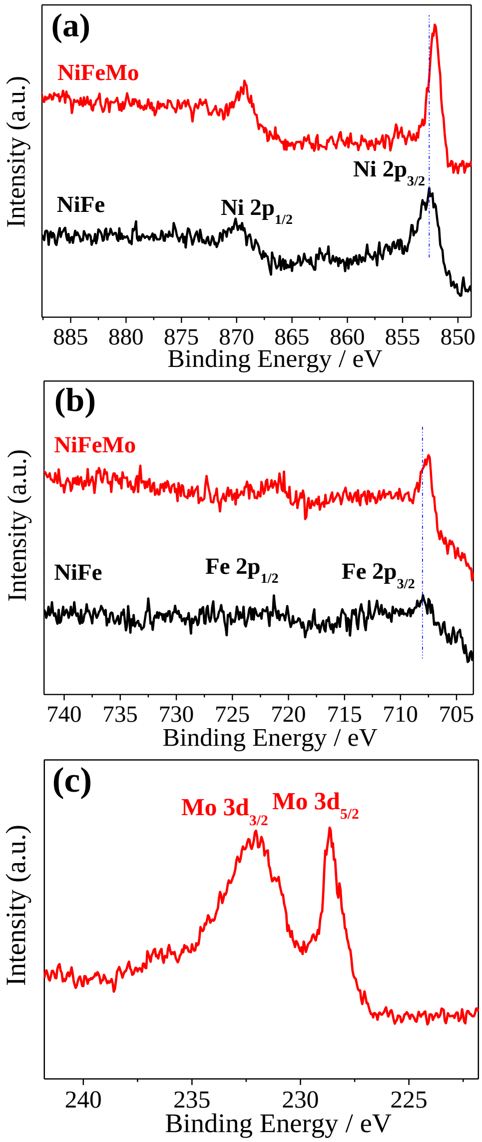


Fig. 2 XPS spectra of (a) Ni 2p and (b) Fe 2p for the $Ni_{0.6}Fe_{0.4}$ and $Ni_{0.6}Fe_{0.4}Mo$ nanocatalyst; (c) Mo 3d for the $Ni_{0.6}Fe_{0.4}Mo$ nanocatalyst.

The catalytic performances of $Ni_{0.6}Fe_{0.4}Mo$ together with its bi-/mono-metallic counterparts for H_2 generation from $N_2H_4·H_2O$ in the presence of NaOH at 323 K by magnetic stirring are presented in Fig. 3. It can be seen that Ni is the key active element for all the prepared catalysts. Without Ni addition, monometallic Fe and Mo and bimetallic FeMo NPs almost shows no activity (Fig. 3b-d). This is consistent with the previous reports that Ni is the representative non-noble metal towards the decomposition of $N_2H_4·H_2O$.[11-32] With Ni addition, the activities of Ni, $Ni_{0.6}Fe_{0.4}$, NiMo and $Ni_{0.6}Fe_{0.4}Mo$ have been enhanced obviously (Fig. 3a, e-g), in which only the trimetallic $Ni_{0.6}Fe_{0.4}Mo$ can lead to the complete decomposition of $N_2H_4·H_2O$ within a short time (15 min) at 323 K [$n(N_2+H_2)/nN_2H_4 = 3.0$, Fig. 3a]. Noteworthy, change the molar ratio of Ni:Fe:Mo to some other values results in the serious decrease in its activity or selectivity (Fig. S3†, S4†). Namely, the optimum molar ratio of Ni:Fe:Mo is determined to be 0.6:0.4:1.0. After the catalytic reaction over $Ni_{0.6}Fe_{0.4}Mo$, the ultraviolet visible (UV-Vis) spectrum indicates no existence of hydrazine in the solution (Fig. S5†). Moreover, the generated gas is identified by mass spectrometry (MS) to be H_2 and N_2 with an H_2/N_2 ratio of 2.0 (Fig. S6†). Therefore, the UV-Vis and MS results reveal the 100% conversion and selectivity for highly efficient NH_3-free H_2 generation from $N_2H_4·H_2O$ over the as-prepared $Ni_{0.6}Fe_{0.4}Mo$ catalyst. NH_3-free H_2 is crucial for fuel cell application, since the formation of NH_3 may seriously poison the Nafion membrane and the fuel-cell catalysts.[45] The initial TOF over $Ni_{0.6}Fe_{0.4}Mo$ is measured to be 28.8 h^{-1} [Eq. (S1)] at 323 K. To the best of our knowledge, this initial TOF value is much higher than the most widely reported noble-metal-free heterogeneous catalysts for $N_2H_4·H_2O$ decomposition,[26-31] and is even superior to most of those noble-metal-containing catalysts (Table S1†).[10-19] This superior activity of $Ni_{0.6}Fe_{0.4}Mo$ may be attributed to the electrical modification of Ni in the alloy structure of $Ni_{0.6}Fe_{0.4}Mo$, and also the small particle size and good dispersion of $Ni_{0.6}Fe_{0.4}Mo$ resulted from the present easy synthetic method. It should be noted that magnetic stirring has no negative effect on the catalytic performance of the magnetic-element-containing $Ni_{0.6}Fe_{0.4}Mo$ towards N_2H_4 decomposition (Fig. S7†).

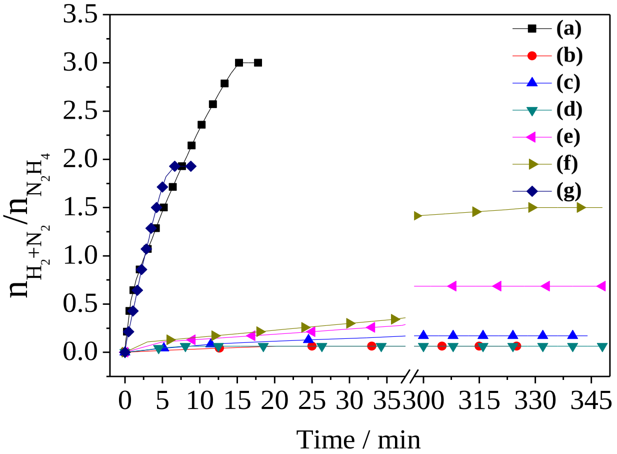


Fig. 3 Time-course plots for the decomposition of hydrazine aqueous solution (0.5 M, 4 mL) to H_2 catalyzed by a) $Ni_{0.6}Fe_{0.4}Mo$, b) Fe, c) Mo, d) FeMo, e) Ni, f) $Ni_{0.6}Fe_{0.4}$ and g) NiMo NPs with NaOH (1.8 M, 4 mL) at 323 K.

To determine the effect of NaOH, the catalyst promoter in dehydrogenation of $N_2H_4·H_2O$,[13, 26] different amounts of NaOH are employed for the same catalytic reaction (Fig. S8†). It is found that the selectivity and activity of $Ni_{0.6}Fe_{0.4}Mo$ are improved with the increase of NaOH amount from 0 to 7.2 mmol, while further increase the NaOH amount has no obvious impact on the performance of $Ni_{0.6}Fe_{0.4}Mo$.

In order to obtain the activation energy (E_a) of the $N_2H_4·H_2O$ decomposition catalyzed by $Ni_{0.6}Fe_{0.4}Mo$ NPs, the reactions at different temperature (298-323 K) are carried out and the results are shown in Fig. S8†. As expected, the catalytic system shows the improved decomposition kinetics with the increasing temperature, and exhibits nearly 100% H_2 selectivity at the examined temperature range (Fig. S9a†). The Arrhenius plot of ln TOF vs. 1/T for this catalyst is plotted in Fig. S8b†, from which E_a calculated is 50.7 kJ/mol [Eq. (S2)], which is very similar to the previously reported values for the catalytic decomposition of $N_2H_4·H_2O$.[27-28]

The recycling stability of the $Ni_{0.6}Fe_{0.4}Mo$ is tested at 323 K under ambient atmosphere. It can be clearly seen that, the H_2 selectivity and activity almost has no decline after the 3rd run (Fig. S10†, Table S2), indicating the good stability of the present tri-metallic $Ni_{0.6}Fe_{0.4}Mo$ NPs for H_2 generation from $N_2H_4·H_2O$ at the mild temperature.

In summary, a facile methodology for synthesis of noble-metal-free $Ni_{0.6}Fe_{0.4}Mo$ NPs has been proposed through a coreduction route at room temperature under ambient atmosphere. The resultant $Ni_{0.6}Fe_{0.4}Mo$ catalyst without support and surfactant exhibits the excellent catalytic performance for the decomposition of hydrazine aqueous solution at mild temperature. The obtained catalyst which owns the priorities of the high performance and low-cost may further encourage the practical application of hydrazine as a promising H_2 generation/storage material.

Acknowledgments

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Notes and References

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† Electronic Supplementary Information (ESI) available: Experimental details, results of TEM, EDS, XRD, XPS, UV-vis and MS, and TOF list for different nanocatalysts tested in hydrogen generation from the decomposition of hydrazine are supplied. See DOI:10.1039/b000000x/

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