Short communication

Robust nickel–polymer nanocomposite particles for hydrogen generation from sodium borohydride

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HIGHLIGHTS

- Electroless Ni plating on polymer nanospheres was performed by Pd-free Ni seeding.
- The particles proved efficient for H_2 production in hydrolysis of borohydride.
- The particles showed robust reusability for repeated process of H_2 production.
- Different distributions of Ni metals depend on the hydrophilicity of the particles.

ARTICLE INFO

ABSTRACT

Two types of polymer nanocomposite particles were developed through electroless plating of nickel onto polymer nanospheres for hydrogen production from sodium borohydride solution. Different distributions of Ni in the polymer particles can be obtained either in polymer core-metal shell morphology or homogeneously hybridized morphology, depending on the hydrophilicity of the polymers. The Ni–polymer particles exhibited high catalytic activities in hydrogen production reactions with excellent recyclability, which is important in portable clean energy generation technology.

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1. Introduction

Portable hydrogen energy devices demand new H_2 storage materials as efficient fuel sources with high energy density and low cost based upon pure H_2 suppliers [1–3]. Sodium borohydride is a nonflammable, non-toxic compound for such purposes [3–5]. In theory, 4 mol of H_2 can be produced from each mole of $NaBH_4$ by utilizing H atoms in water (see Eq. (1)):

$$NaBH_4 + 2H_2O \xrightarrow{\text{catalyst}} 4H_2 + NaBO_2 \qquad (1)$$

A suitable metal catalyst provides a high rate of H_2 generation via hydrolysis of $NaBH_4$ in a controllable reaction [3–10]. Magnetic Ni catalysts are potentially useful because of their economic and technical advantages in switching off the reaction by the use of a magnet [7–10]. However, Ni needs to be dispersed and stabilized in appropriate materials to achieve long-term durability without

formation of aggregates. Hydrophilic polymers are effective stabilizers for applications in H_2 production in water. The Ni-embedded polymers (Ni–polymer hybrids) have found great value in H_2 production from $NaBH_4$ and ammonia borane [7–11] due to flexible design of polymer structures and easy separation from reactants using a magnet. In our previous study, Ni/Pd alloy nanoclusters prepared by in situ reduction in aqueous solutions in bulk hydrogels showed good catalytic activity for H_2 production [9]. For faster response and higher metal loading, polymer nanoparticle stabilizers are preferred.

Ni–polymer hybrid particles are routinely prepared by an electroless plating approach in which palladium-activated polymer particles are used to coat with Ni prior to electroless plating [12–16]; however, the surface coating technique requires a high amount of expensive Pd metals. The use of strong acid-oxidant etchants or alkaline etchants to roughen polymer surfaces, followed by coating of a hydrophilic polymer layer before Ni salt adsorption onto polymers [17–19], may be destructive to polymer nanoparticles or lead to loss of vulnerable functional groups.

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Therefore, it is important to introduce a versatile, mild and economic method to prepare Ni-embedded polymer particles with long term durability to lower the cost of hydrogen production. In this paper, we report synthesis of Ni-activated polymer nanoparticles to act as surface seeding in lieu of Pd metal activators without strong acid or base etching. The approach represents a novel method of coating the polymer particles through electroless nickel plating. The Ni-embedded magnetic polymer particles (Ni–polymer particles) are applied to catalysis of H_2 generation from hydrolysis of $NaBH_4$. This approach differs from the Ni deposited hollow fibers for H_2 production [11] and expands the preparative method and applications of transition metals–polymer nanocomposite systems in portable hydrogen energy devices and borohydride fuel cell technology.

2. Methods

Two types of polymer particles, homopolymer particles of N-tert-butyl acrylamide (NtBAM) and its copolymer particles were prepared by precipitation polymerization in this study. The preparative method for Ni–polymer nanoparticles by a modified electroless plating procedure is illustrated in Scheme 1 of Supplementary Materials. Polymer particles were first impregnated with a $NiSO_4$ aqueous solution, before they were treated in a $NaBH_4$ solution to reduce the adsorbed Ni^{2+}. Subsequently, the reduced Ni in the polymer particles acted as seed particles for electroless plating in Ni^{2+} solutions. This effectively avoids the general need for the use of Pd activation and/or Sn sensitization. The experimental details for preparation of the nanocomposite particles and characterization of pure hydrogen production performance are described in Supplementary Materials.

3. Results and discussion

Nanospheres of NtBAM homopolymers containing hydrophobic cores and hydrophilic amide groups exposed to the surface of the particles in aqueous solutions were prepared in this study (see experimental details in Supplementary Materials). In such particles, hydrophobic tert-butyl groups are oriented toward the interior of the particles when the particles are formed during polymerization. Meanwhile, copolymers of NtBAM with a hydrophilic comonomer, 2-acrylamide-2-methyl propanesulfonic acid (AMPS), and a third comonomer, N-isopropyl acrylamide (NIPAM), i.e., P(NIPAM-co-AMPS-co-NtBAM) nanospheres, were also prepared by a precipitation polymerization process without a stabilizer or emulsifier. Fig. 1a and b displays a SEM image of the PNtBAM homopolymer particles and that of the P(NIPAM-co-AMPS-co-NtBAM) nanospheres, respectively, after Ni was deposited by the seeding and electroless plating process. The SEM images show nearly spherical beads of the homopolymer

and copolymer samples. In the PNtBAM particles, the hydrophobic cores of the PNtBAM spheres bring about little absorptivity of water molecules in the interior. The average diameters of such particles measured in SEM (Fig. 1a) and TEM images (Fig. 2a) in vacuum turn out to be nearly the same as the hydrodynamic diameters measured by dynamic light scattering in water (180 nm). The Ni cations for seeding and electroless plating are less likely to have access to the interior cores of the PNtBAM particles during the preparation. Consequently, in the TEM image (Fig. 2a), most of the nickel metals are located on the surface of PNtBAM spheres and the Ni–PNtBAM particles have a metal-shell and a PNtBAM core.

In the case of the hydrophilic copolymer particles, the TEM image in Fig. 2b shows that nickel is highly dispersed in the copolymer gel particles. The average size of the copolymer gels before electroless plating is 210 nm, while that after plating is about 225 nm. Introduction of nickel expands the size of the copolymer particles slightly. The nickel metal is continuously spread throughout the gel particles because of enough pores existing in the hydrophilic particles. Dynamic light scattering characterization of the Ni embedded copolymer particles in water shows their hydrodynamic diameters of 411.9 nm, which are larger than the diameters shown in the TEM image because the gel particles swell in water during the characterization by dynamic light scattering.

For characterization of the Ni metals in the polymer particles, their lattice images were observed by using high-resolution TEM. Fig. 2(c and d) shows that lattice spacings of the Ni in the PNtBAM particles and copolymer particles are 0.240 nm and 0.239 nm, respectively, which correspond quite well to those of nickel oxide (NiO) (0.2410 nm, 1 1 0 plane, referring to XRD card 03-065-6920). The lattice spacings are only slightly contracted by 0.4% and 0.8%, respectively, which can be explained in terms of a lattice stress [20].

XPS analysis confirmed the oxidation state of the Ni. Ni $2p_{3/2}$ and $2p_{1/2}$ peaks at 855.6 and 873.1 eV, respectively, (in Fig. 1S in Supplementary Materials) correspond to the binding energies of bulk NiO or NiO nanoparticles [21]. Shake-up (satellite) peaks at 861.1 and 879.4 eV also corroborate the presence of paramagnetic NiO, since Ni(0) and square-planar complex of Ni(II) do not produce satellite peaks [22]. Weak peaks appear at 852.2 and 869.4 eV (in Fig. 1S(b) in Supplementary Materials), due to $2p_{3/2}$ and $2p_{1/2}$ binding energies of Ni(0), respectively. Hence, the nickel in the polymers is mainly in the form of NiO, with a minor amount of Ni(0).

In order to verify Ni contents in the polymers before and after electroless plating, ICP-AES analysis was undertaken according to the following steps. A certain amount of the particles was mixed with concentrated HCl (37%, 30 mL) for 30 min at 60 °C, followed by centrifugation and measuring the Ni contents in the solution by ICP-AES analysis. The results (Table 1) show that the PNtBAM homopolymer has lower loading capability than the copolymer gel. Although Ni-loading from the seeding is low, it is important
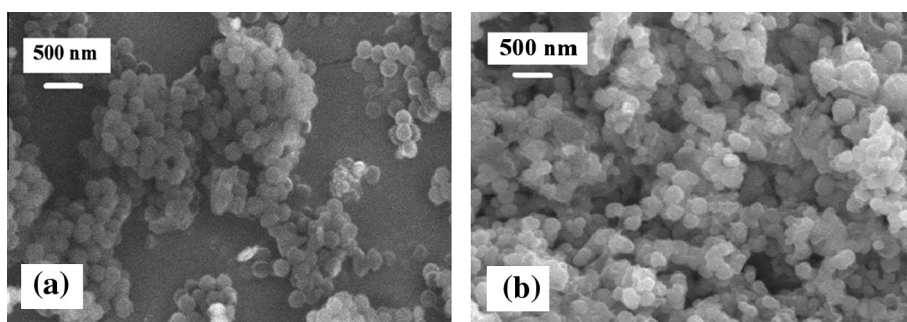

Fig. 1. SEM image of (a) Ni–P(N-tert-butyl-acrylamide) and (b) Ni–P(NIPAM-co-NtBAM-co-AMPS). Scale bar = 500 nm.