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Synthesis and Characterization of Nickel–Poly(St-co-AA)Composite Nanospheres by Ultraviolet Irradiation†

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Nickel nanoparticles on poly(St-co-AA) spheres have been synthesised by seeded emulsion polymerization followed by ultraviolet reduction.

Much attention has been paid to the synthesis and characterization of nanometer particle–organic polymer composites, owing to their intriguing optical, electrical, mechanical and catalytical properties.[1–4]

These composites are considered to be highly functional materials, with wide potential application in electro-magnetic inference shield films, non-linear optical materials and active catalysts.

Ultrafine metal particles can be used as active catalysts. For practical use, ultrafine metal particles are supported on other materials. Fine polymer particles having high surface area and fluidity are also useful as ideal supporting materials.

Only a few methods have been used to prepare metal–polymer nanocomposites.[5,6] In general, two steps were needed: first, monomer was polymerized in the solution, with metal ions introduced before or after the polymerization. Secondly, metal ions in the polymer matrix were reduced by a reducing agent or by calcination.

In this study, we report a novel method for preparing metal–polymer nanospheres using UV-irradiation at room temperature. It was found that products formed by this method contained not only pure metal particles but also monodispersed metal–copolymer nanospheres.

$Ni(CH_3CO_2)_2 \cdot 4H_2O$, NH_4CO_2Me, isopropyl alcohol, potassium persulfate ($K_2S_2O_8$), sodium dodecyl sulfate (SDS), sodium dodecyl benzenesulfonate (SDBS), TritonX-200, Tween-80, OP, SPAN-40, poly(vinyl alcohol) (PVA), polyacrylamide (PAA) and cetyltrimethylammonium bromide (CTAB) were analytical grade. Styrene and acrylic acid were purified by vacuum-distillation under an N_2 atmosphere before use. Water was doubly distilled before use.

Potassium persulfate was added into solution of SDS. This mixture was stirred for 30 min, then styrene and acrylic acid were added into stirred mixture. The resulting emulsion was transferred into a 250 mL round-bottomed four-necked flask. The reaction emulsion was stirred at 400 rpm, while the temperature was kept at 80 °C for 7–8 h and N_2 gas continuously passed through the flask to give emulsion A.

Emulsion A can be regarded as a seeding solution; adding emulsifier, initiator and monomers, led to emulsion B after reaction again under the same experimental conditions. Then, emulsion B was decomposed, washed with water several times and desiccated at 80 °C and copolymer nanoparticles were successfully obtained.

An aqueous solution containing 0.05 mol L^{-1} $Ni(MeCO_2)_2 \cdot 4H_2O$ was prepared in advance. The prepared copolymer nanoparticles were dispersed into this solution and the color of the resulting solution was green. Surfactant was added to this solution which was transferred to a quartz tube. After bubbling with N_2, the green solution was irradiated with UV light for 50 h. After irradiation, some black precipitate was formed in the flask which was placed onto a permanent magnet to accelerate settling. The clear solution was decanted and the precipitate washed with water several times and desiccated *in vacuo*.

Photo-assisted deposition of noble metals (Pt, Pd, Ag, Rh, Au and Ir) has been studied in detail by Hermann *et al.*[7] In this study, the effects of various parameters governing the kinetics of photodeposition (light flux, solution, concentration, temperature, nature of ions) of noble metals on photosensitive supports were studied. The reaction principle is based upon stepwise reduction by hydrated electrons. The redox potential of nickel is at −0.246 V, *cf.* −2.77 V for hydrated electrons and hence nickel ions can be reduced by hydrated electrons. Reaction of Ni^{2+} ions with hydrated electrons produced during UV-irradiation in solution leads to the formation of metallic nickel nanoparticles. This process can be written in terms of eqns. (1) and (2).

$$Ni^{2+} + 2e^-_{aq} \rightarrow Ni^0 \text{ (reduction)} \qquad (1)$$

$$nNi^0 \rightarrow Ni_n \text{ (aggregation)} \qquad (2)$$

Because of the presence of carboxyl groups on the surface of poly(St-co-AA) nanospheres, Ni^{2+} ions are readily absorbed on the surface of copolymer nanospheres. Then such nickel ions are reduced by hydrated electrons, and the resulting nickel metal nanoparticles are immobilized on the surface of the copolymer nanospheres.

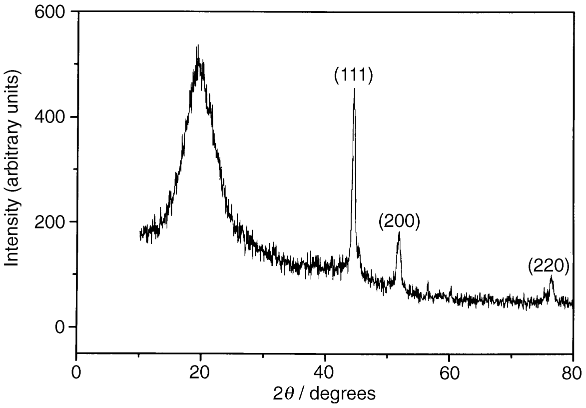

Fig. 1 X-Ray diffraction pattern of metal nickel particles immobilized on poly(St-co-AA) nanospheres

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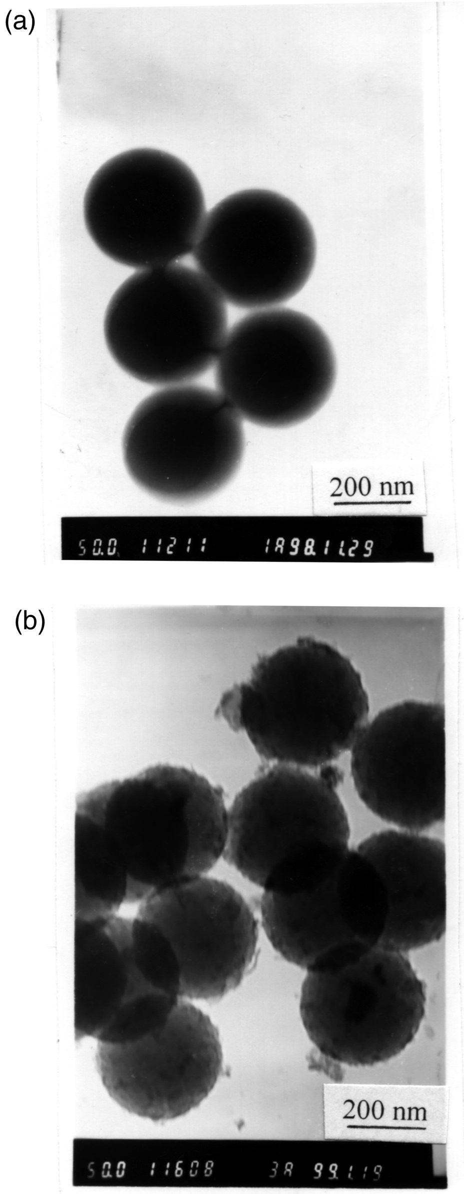

Fig. 2 (a) TEM image of poly(St-co-AA) nanospheres and (b) TEM image of metal nickel particles immobilized on poly(St-co-AA) nanospheres.

UV-irradiation was performed using a cylindrical low pressure mercury lamp ($\lambda = 253.7\,\text{nm}$) or a high pressure mercury lamp ($\lambda_1 = 365\,\text{nm}$, $\lambda_2 = 313\,\text{nm}$). The size and morphology of poly(St-co-AA) and nickel–poly(St-co-AA) composite nanospheres were investigated by transmission electron microscopy (TEM). TEM images were obtained using a Hitachi Model H-800 transmission electron microscope and X-ray diffraction patterns (XRD) were recorded using a $\mathrm{D_{max}}\ \gamma_\mathrm{A}$ X-ray diffractometer with graphite monochromated Cu-K_α radiation ($\lambda = 0.154178\,\text{nm}$).

Fig. 1 shows the XRD pattern of typical nickel–poly(St-co-AA) composite nanospheres. The broad peak at $2\theta = 19.3^\circ$ is attributed to the diffraction of non-crystalline co-polymer. The other three peaks with 2θ values of 44.5, 51.8 and 76.4° correspond to the 111, 200 and 220 crystal planes, respectively, of metallic crystalline nickel. The average size of nickel particles estimated by Scherr's equation is 10 nm in good agreement with the TEM result.

Fig. 2(a) shows a TEM image of poly(St-co-AA) particles. The particles are spherical and of 300 nm diameter. Fig. 2(b) shows a TEM image of nickel immobilized on poly(St-co-AA) particles. The particle size of nickel–poly(St-co-AA) composite nanospheres is 320 nm.

In summary, UV-irradiation has been used for the first time to prepare nickel–poly(St-co-AA) composite nanospheres at room temperature. By appropriate control of the experimental parameters, we can predict that UV-irradiation may be extended to the preparation of a variety of transition metal–copolymer composite nanospheres. Moreover, other polymer systems in which an anionic copolymer latex can serve as core particles can also be applied as supporting materials.

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