

Nanocomposite hydrogel as a template for synthesis of mono and bimetallic nanoparticles

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Abstract. Nanocomposite hydrogels (NC gels) with polymer–clay network assemblies are useful in a number of applications because of their unique properties and characteristics. Herein, we describe a distinctive strategy for the preparation of discrete monometallic (Ag, Au, and Pd) and bimetallic (Pt-Pd, Au-Pd) nanoparticles that uses a nanocomposite hydrogel composed of a polymer–clay network. Thermoresponsive NC gels were synthesized by the *in-situ* free-radical polymerization of *N*-isopropylacrylamide in the presence of clay (synthetic hectorite) nanosheets (CNSs). Since CNSs have strong affinities for metals ions that facilitate the concentration of metal precursors around them, the reduction of metal ions by ascorbic acid in NC gels provides well-dispersed, non-aggregated spherical monometallic and bimetallic nanoparticles (NPs) that are strongly immobilized within the polymer-clay network. The resulting hybrid NP-NC gels, which contain monometallic or bimetallic NPs, exhibit high catalytic activities for the hydrogenation of nitrophenol to aminophenol. The combination of well-defined metal NPs and mechanically tough NC gels opens up new possibilities for the design of environmentally friendly and sustainable functional NP-NC-gel materials.

Keywords: nanomaterials, nanocomposites, bimetallic nanoparticles, polymer gels, polymer-clay network

1. Introduction

Nanocomposite hydrogels (NC gels) with unique organic–inorganic (polymer–clay) network assemblies have drawn great interest as excellent hydrogels that can overcome the severe drawbacks associated with conventional chemically cross-linked hydrogels [1–5]. Specifically, NC gels composed of poly(*N*-isopropylacrylamide) (PNIPAM) and exfoliated inorganic clay, such as synthetic hectorite, have displayed extraordinary optical, mechanical, and swelling/deswelling properties [3]. In addition, NC gels can be prepared effortlessly at ambient temperature in an aqueous system [3, 6], to provide a variety of shapes, sizes, and surface morphologies, along with novel surface characteristics such as unique sliding friction,

ultrahigh hydrophobicities, cell harvesting, self-healing, and contractive-force-generating capabilities [3, 7, 8], which makes them useful in many new applications. NC gels have also contributed to a wide range of developments as new stimuli-responsive soft and wet materials [9–12]. These observations provide encouragement for the further extension of NC-gel templates to bulk materials that encompass nano-sized metal configurations distributed within their structures; these metal-imbedded gels are prospective materials for use in catalysts and sensors, among other applications [12].

Progress in the development of novel methods for the synthesis of metal nanoparticles (NPs) continues to be motivated by prospective applications that are

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facilitated by their unique properties [13, 14]. Numerous studies have been conducted into strategies for the preparation of noble-metal-based NPs, including NP-hydrogel fusions that are formed by exploiting the benefits of the interspatial regions enclosed by crosslinking points as nanoreactors or nanocarriers [15–20]. An NC gel consisting of a polymer-clay matrix is appropriate for concentrating metal ions because the exfoliated clay contains effective chelation sites. Recently, we reported the exploitation of NC gels as templates for the *in-situ* preparation of Pt NPs, which we attributed to the mild reducing ability of clay [12]. Consequently, NC gels that encompass metal ions are encouraging as ‘reactors’ for the well-regulated production of metal NPs, where strong interactions between the clay and metals essentially play imperative roles that govern the evolution of inorganic NPs [21]. It is worth noting that low-cost inorganic clay is deliberately used in a number of materials applications [22–24]. In the present study, we focused on the syntheses of mono-metallic (Ag, Au, and Pd) and bimetallic (Pt-Pd and Au-Pd) NPs within NC gels by carrying out the reduction of NC-gel-absorbed metal ions within a hydrogel matrix. This resulted in the creation of small, uniform, and stable NPs within the NC gel. The ensuing NP-hybrid-NC-gel materials, consisting of NPs effectively immobilized in polymer–clay networks, were then used to catalytically reduce nitrophenol.

2. Experimental section

2.1. Materials

As an inorganic clay, synthetic hectorite ‘Laponite XLG’ (Rockwood, Ltd., UK; $[\text{Mg}_{5.34}\text{Li}_{0.66}\text{Si}_8\text{O}_{20}(\text{OH})_4]\text{Na}_{0.66}$; layer size = 30 nm diameter \times 1 nm thick; cation-exchange capacity = 104 m equiv./100 g) [2] was used after washing with ethanol/water (90/10 w/w) and freeze-drying. *N*-Isopropylacrylamide (NIPAM) (Kohjin Co., Japan) was purified by recrystallization from 2:1 (w/w) toluene:*n*-hexane, followed by drying under vacuum at 40 °C. Potassium persulfate (KPS) and *N,N,N',N'*-tetramethylethylenediamine (TEMED) (Tokyo Chemical Industry Co. Ltd., Japan) were used as initiator and accelerator, respectively, during the synthesis of the NC gels. Analytical grade ascorbic acid, silver nitrate (AgNO_3), sodium tetrachloroaurate(III) $[\text{Na}(\text{AuCl}_4) \cdot 2\text{H}_2\text{O}]$, potassium tetrachloroplatinate(II) (K_2PtCl_4), 4-nitrophenol, and sodium borohydride (NaBH_4) were purchased from Wako Pure Chemical

Industries, Ltd., Japan, and potassium tetrachloropalladate(II) (K_2PdCl_4) was obtained from Alfa Aesar. All reagents were used without further purification, unless otherwise stated. Ultrapure water, supplied by a PURIC-MX system (Organo Co., Japan), was used for all experiments.

2.2. NC gel synthesis

A nanocomposite hydrogel with a PNIPAM-clay network is referred to as an ‘NC n gel’, where n refers to the clay content ($C_{\text{clay}} = n$ mol% in the reaction solution), by analogy with terminology used in previous papers [3]. The procedure for the syntheses of the NC gels in this study is the same as that reported previously. Briefly, the NC5 gel was synthesized from a transparent aqueous solution of inorganic clay (Laponite XLG, 0.76 g), monomer (NIPAM, 2.26 g: 1 M), and water (19 mL). An accelerator (TEMED, 16 μL) and an aqueous solution of the initiator (KPS, 0.02 g, 1 mL) were added while stirring at 1 °C. Free radical polymerization was conducted in a water bath (20 °C) for 24 h. The NC gel was synthesized in glass tube with inner diameters of 5.5 mm. Oxygen was excluded from the water and the system throughout these syntheses. The resulting transparent NC5 gel was rinsed several times with Milli-Q water.

2.3. Synthesis of mono and bimetallic nanoparticles within the NC gel

Samples of the as-prepared NC5 gel ($\phi 5.5$ mm \times 12 mm), after washing with water, were immersed in individual aqueous solutions (10 mL, 10 mM) of various metal precursors (AgNO_3 , NaAuCl_4 , K_2PdCl_4 , $\text{K}_2\text{PtCl}_4 + \text{K}_2\text{PdCl}_4$, and $\text{NaAuCl}_4 + \text{K}_2\text{PdCl}_4$) and incubated at 25 °C for 24 h. The resulting swollen NC gels were quickly rinsed with Milli-Q water within several seconds and placed separately into freshly prepared solutions of ascorbic acid (10 mL, 100 mM) at 25 °C for 24 h, which reduced the metal ions within the NC-gel matrix.

2.4. Catalytic reduction of *p*-nitrophenol

A 0.1 g sample of an NP-containing NC5 gel (NP-NC5 gel) was added directly to 1 mL of a 0.2 mM aqueous solution of *p*-nitrophenol and 1 mM NaBH_4 in a 1 mm quartz cuvette. Time-resolved UV-vis absorption spectra of the solution above the hydrogel were acquired at room temperature using a Hitachi U-4100 UV-vis double-beam spectrometer.

2.5. Materials characterization

Transmission-electron microscopy (TEM) images were obtained for ultrathin films (60 nm) of the dried NP-NC5 gels using a high-resolution field-emission transmission-electron microscope (JEM-2200TFE, JEOL) operating at 200 kV. Energy-dispersive X-ray spectroscopy (EDS) was performed using a scanning transmission-electron-microscopy (STEM) detector fitted to the JEM-2200TFE system. XRD patterns were obtained using a Rigaku SmartLab X-ray diffractometer with monochromated Cu-K α radiation (40 kV, 100 mA).

3. Results and discussion

The objective of the proposed synthesis procedure was the creation of uniform and well-dispersed mono-metallic (Ag, Au, and Pd) and bimetallic (Pt-Pd and Au-Pd) NPs within the NC gel matrix that are exceedingly functional and have high thermal and dispersion stabilities. The NC5 gel, which is composed of PNIPAM and synthetic hectorite ($C_{\text{clay}} = 5 \text{ mol}\%$), was initially prepared according to the procedure reported previously (Figure 1a) [3]. The NC5 gel was obtained as a uniform, transparent, and mechanically tough hydrogel, and exhibited notable tensile mechanical properties (tensile strength = 120 kPa, elongation at break = 1010%), a considerable degree of swelling in water ($W_{\text{gel}}/W_{\text{dry}} = 50$ at 20 °C), and a well-defined thermo-responsive transition at 34 °C (lower critical solution temperature: LCST) derived from the coil-to-globule transition of the constituent PNIPAM.

NC5-gel samples were separately immersed in aqueous solutions of Ag, Au, and Pd-metal precursors (10 mM), after which they were maintained in the

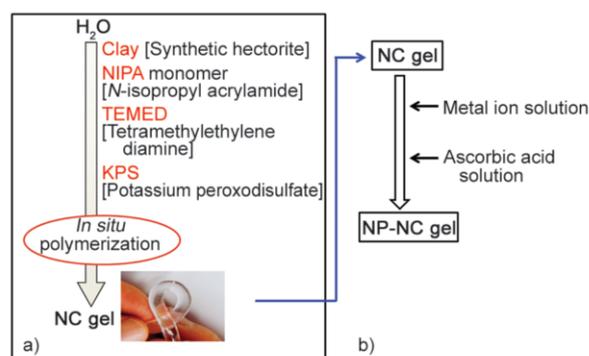


Figure 1. (a) Protocol for the synthesis of an NC gel under ambient conditions. (b) Incorporation of metal NPs into the NC gel by immersion in an aqueous metal-precursor solution followed by reduction by immersion in aqueous ascorbic acid.

dark at 25 °C for 24 h, during which time they swelled (Figures 1b and 2a).

The resulting swollen NC gels were quickly rinsed with Milli-Q water for a few seconds and immersed in freshly prepared aqueous solutions of ascorbic acid (100 mM); reductions of the corresponding metal ions were conducted within the NC-gel matrices while standing for 24 h at 25 °C (Figure 2b).

Data on the sizes and shapes of the NPs were obtained by transmission-electron microscopy (TEM). Figure 3a shows a high-angle annular dark-field scanning TEM (HAADF-STEM) image of an ultrathin section of the dried Ag/NP-NC gel, which reveals that small and well-defined Ag/NPs, with diameters of 40–50 nm, are distributed throughout the NC-gel sample. The EDS image shown in Figure 3b confirms the formation of Ag/NPs in the NC gel. The formation of uniform and well-dispersed Ag/NPs in the NC gel is attributed to the exfoliated clay nanosheets (CNSs)

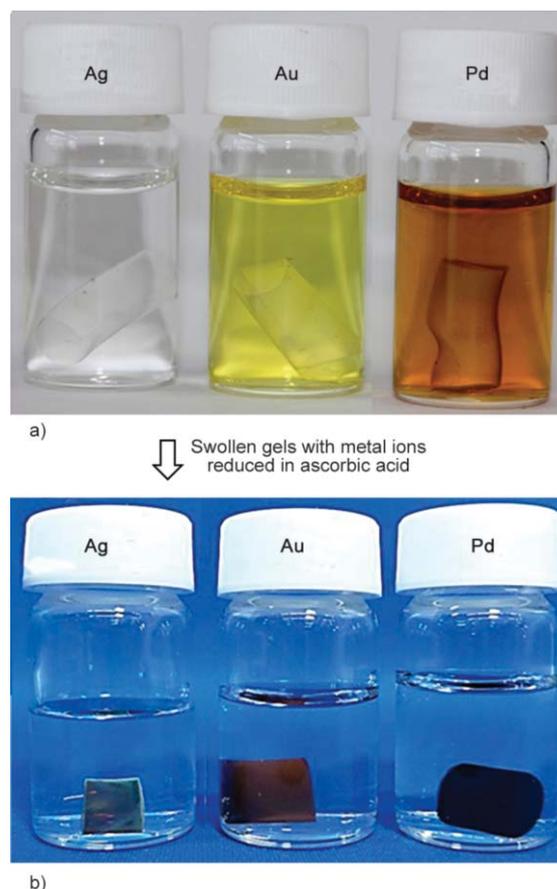


Figure 2. Optical images depicting the preparation of NP-NC gels (where NP = Ag, Au, and Pd NPs). (a) Absorption of Ag, Au, or Pd metal ions into the NC gel through the swelling process (24 h, 25 °C). (b) Each swollen NC gel was immersed in ascorbic acid solution (100 mM), which resulted in the reduction of the metal ions within the NC gel.

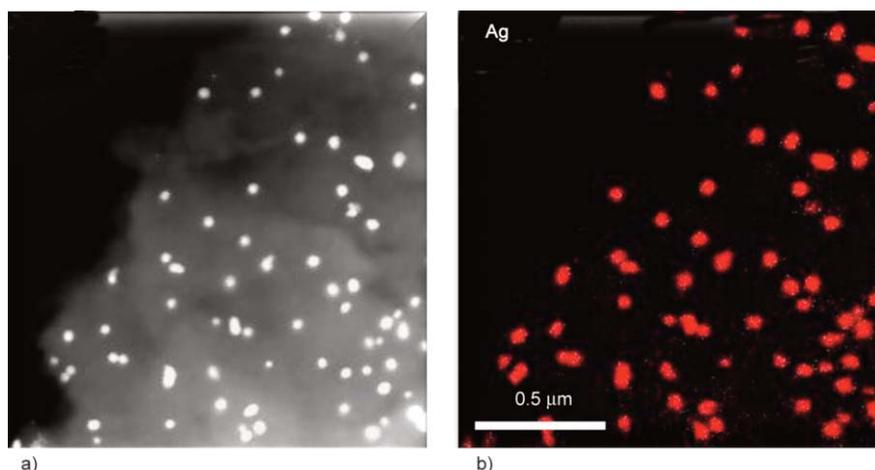


Figure 3. (a) HAADF-STEM image of Ag/NPs in the NC gel matrix. (b) EDS image showing well-defined Ag NPs.

that are uniformly dispersed in the NC gel and form a three-dimensional polymer-clay network; reduction occurs effectively near the clay nanosheet (CNS) surface, resulting in a new nanostructured, polymer-clay-NP hybrid material.

Similarly, Figure 4a shows a HAADF-STEM image of an ultrathin section of the dried Au/NP-NC gel. Well-defined Au NPs, with an average diameter of 85 nm, are observed to be well dispersed over the NC gel sample, as confirmed by the EDS image displayed in Figure 4b. A Pd/NP-NC gel was also prepared in the same manner (figure not shown).

Figure 5 shows wide-angle X-ray diffraction (XRD) patterns of the Ag, Au, and Pd NPs prepared within the NC-gel matrices. In all cases, multiple diffraction peaks that are indexed to the *fcc* lattices of the corresponding Ag, Au, and Pd crystals were observed.

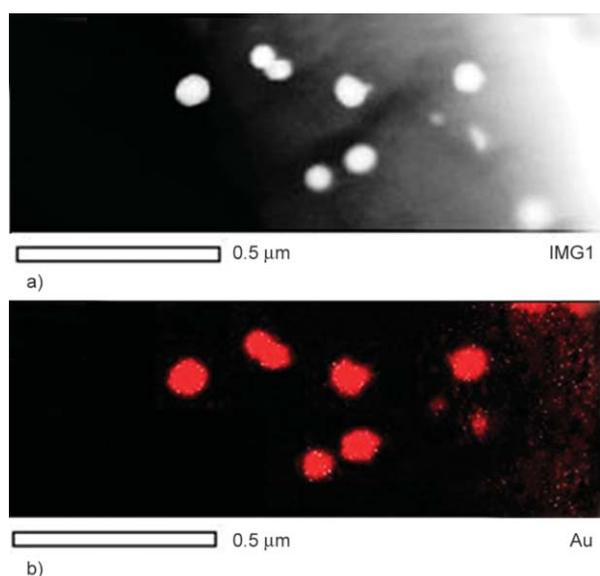


Figure 4. (a) HAADF-STEM image of Au NPs in the NC gel matrix. (b) EDS image showing well-defined Au NPs.

To discover the full potential of this approach, we also synthesized bimetallic NPs, such as Pt-Pd and Au-Pd NPs, in a similar fashion, except that two metal precursors were used. In the case of the Pt-Pd NPs (Figure 6), the as-prepared NC gel was immersed in a mixed solution of the metal precursors ($K_2PtCl_4 + K_2PdCl_4$; 5 mM each) at 25 °C for 24 h. The swollen NC gel was then quickly washed with Milli-Q water and immersed in a fresh aqueous solution of ascorbic acid (100 mM) at 25 °C for 24 h in order to reduce the metal ions within the NC-gel matrix to bimetallic Pt-Pd NPs. The morphologies of bimetallic NPs are difficult to control by conventional methods; consequently precisely formulating these NPs can be challenging.

Figure 6a displays a representative TEM image of an ultrathin section of the dried Pt-Pd/NP-NC gel, which reveals the successful formation of well-defined Pt-Pd NPs, with diameters of 50–55 nm that well distributed over the NC gel sample. The high-resolution (HR) TEM image (Figure 6b) displays clearly visible lattice fringes that provide evidence

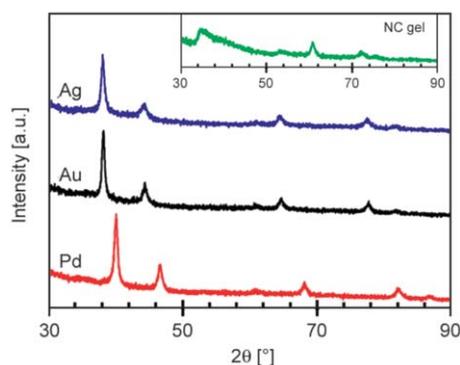


Figure 5. Wide-angle XRD patterns of dried Ag, Au, and Pd/NP-NC5-gel powders. An inset figure shows the XRD pattern for pure dried NC5 gel.

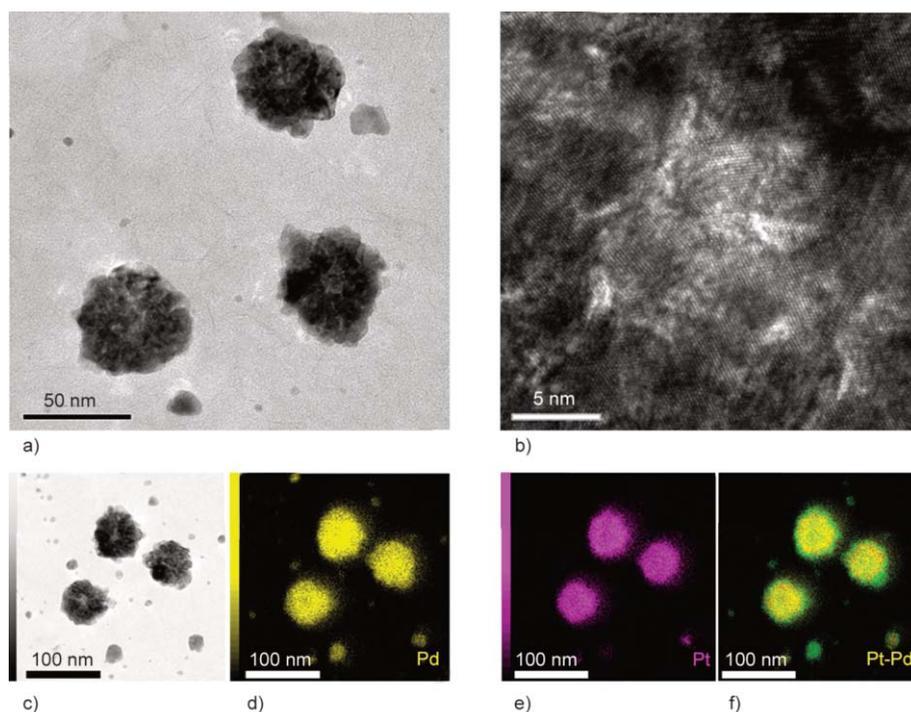


Figure 6. Bimetallic Pt–Pd NPs prepared in the NC5 gel matrix. (a) Low-magnification TEM image. (b) HRTEM image. (c) HAABF-STEM image. (d) Pd EDS map. (e) Pt EDS map. (f) Overlay of (d) and (e) that reveals the presence of finely distributed Pt and Pd.

for the formation of crystalline NPs. Figure 6c shows a high-angle annular bright-field STEM (HAABF-STEM) image, while the corresponding EDS maps (Figures 6d–6f) reveal the presence of uniformly composed Pt and Pd bimetallic NPs. These results indicate that the formation of bimetallic Pt–Pd NPs is the result of nucleation control and the prevention of mutual metal cluster–cluster aggregation in the presence of the network CNSs. The exfoliated CNSs within the NC gel play very important roles in controlling the concentrations of the Pt and Pd ions. The subsequent adsorption of ascorbic acid induces the controlled reduction of metal ions near the CNS surfaces, where the NC gel matrix helps to spontaneously separate the deposited Pd and Pt, resulting in the formation of bimetallic Pt–Pd NPs and the prevention of their random growth. In the absence of the clay, i.e., in case of a conventional chemically cross-linked PNIPAM gel, the reduced Pt and Pd metals ions form large inhomogeneous particles devoid of well-defined structures. Hence, we infer that the presence of the CNS is pivotal for the fabrication of bimetallic NPs; achieving this outcome within a polymer network is otherwise very challenging.

Bimetallic Au–Pd NPs were also synthesized by the methodology described above. The TEM image of an ultrathin section of the dried Au–Pd/NP-NC gel

(Figure 7a) reveal well-defined Au–Pd NPs, and the HR-TEM image (Figure 7b) exhibits visible lattice fringes that are evidence of the formation of crystalline bimetallic NPs. Figure 7c shows a HAABF-STEM image and the corresponding EDS overlay map is shown in Figure 7d, which reveals a uniform Au and Pd elemental composition.

The as-prepared monometallic and bimetallic NPs were highly stable within the NC gel matrix. Representative optical images of the Pd/NP-NC and Pt–Pd/NP-NC gels immersed in water for 72 h reveal no signs of leaching; as the surrounding water remains clear (Figure 8). Similar observations were made even at a high temperature (50 °C), above the LCST, where both NP-NC gels underwent shrinkage due to the coil-to-globule transition of the PNIPAM in each gel. This indicates that, once formed, the metal NPs remain intact within the NC gel; this property is extremely important for NP-NC gel applications.

To evaluate their catalytic activities, we tested the abilities of the Pd/NP-NC and Pt–Pd/NP-NC gels to catalyze the reduction of aqueous 4-nitrophenol with NaBH_4 , as a model system (Figure 9a). The light-yellow color of the 4-nitrophenol solution immediately changed to an intense yellow upon addition of NaBH_4 , due to the formation of the 4-nitrophenolate ion. NaBH_4 solution itself is not capable of reducing

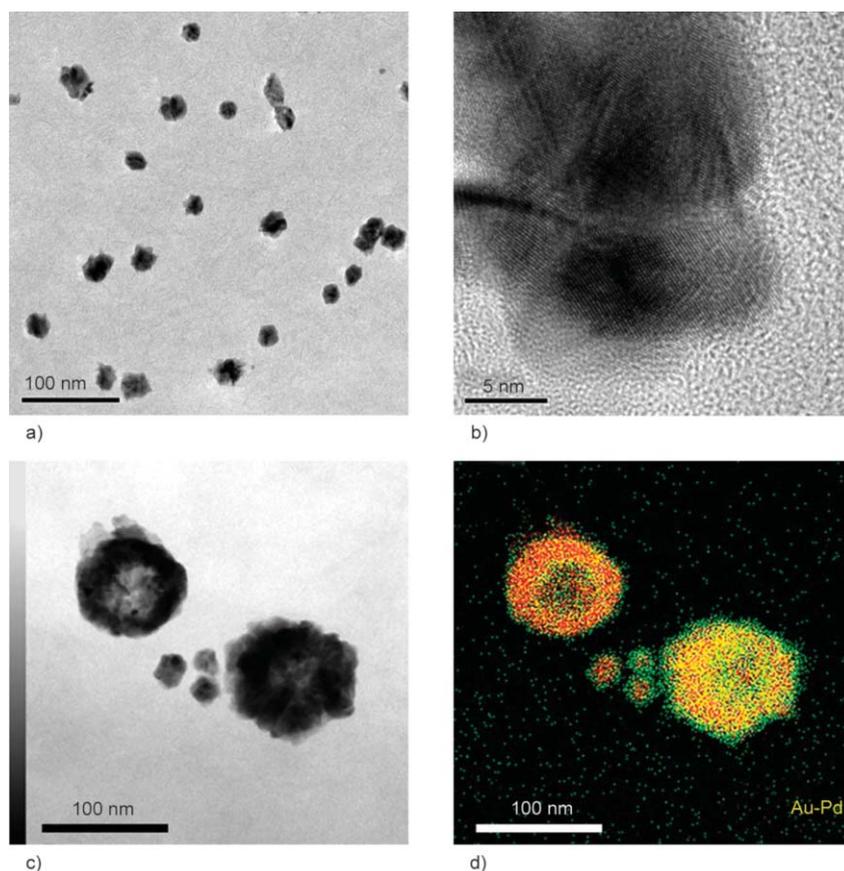


Figure 7. Bimetallic Au–Pd NPs prepared in the NC5 gel matrix. (a) Low-magnification TEM image. (b) HRTEM image. (c) HAADF-STEM image. (d) EDS Au-Pd overlay map that reveals the presence of finely distributed Au and Pd.

4-nitrophenol in the absence of a catalyst, and its absorption band at around 400 nm remained unchanged even after 90 min (Figure 9b).



Figure 8. Optical images demonstrating a lack of nanoparticle leaching from the Pd/NP-NC and Pt-Pd/NP-NC gels following immersion in pure water for 72 h under ambient conditions.

However, the presence of the Pd/NP-NC gel or Pt-Pd/NP-NC gel (0.1 g) catalyzed the reduction of 4-nitrophenol, and the strong ultraviolet (UV) absorption peak at 400 nm diminished over 25 and 15 min, respectively, as displayed in Figures 9c and 9d, indicating high catalytic activity. While the reduction of 4-nitrophenol was very slow in the presence of NaBH_4 alone, rapid reduction was observed in the presence of each NP-NC gel. It is highly likely that other useful reactions are also accelerated by the action of these NP-NC gels; we believe that these materials will be applicable to a wide range of catalysis processes.

The proposed mechanism that underpins the formation of the mono and bimetallic NPs in the NC-gel matrix is shown in Figure 10. As depicted, when the NC gel is immersed in the aqueous metal-precursor solution, the metal ions penetrate the NC gel and interact with the silanol groups (Si-OH) on the CNS surfaces to form complexes, which results in the concentration of metal ions around the CNS surfaces of the polymer-clay network. The resulting swollen NC gel imbedded with metal ions is then immersed

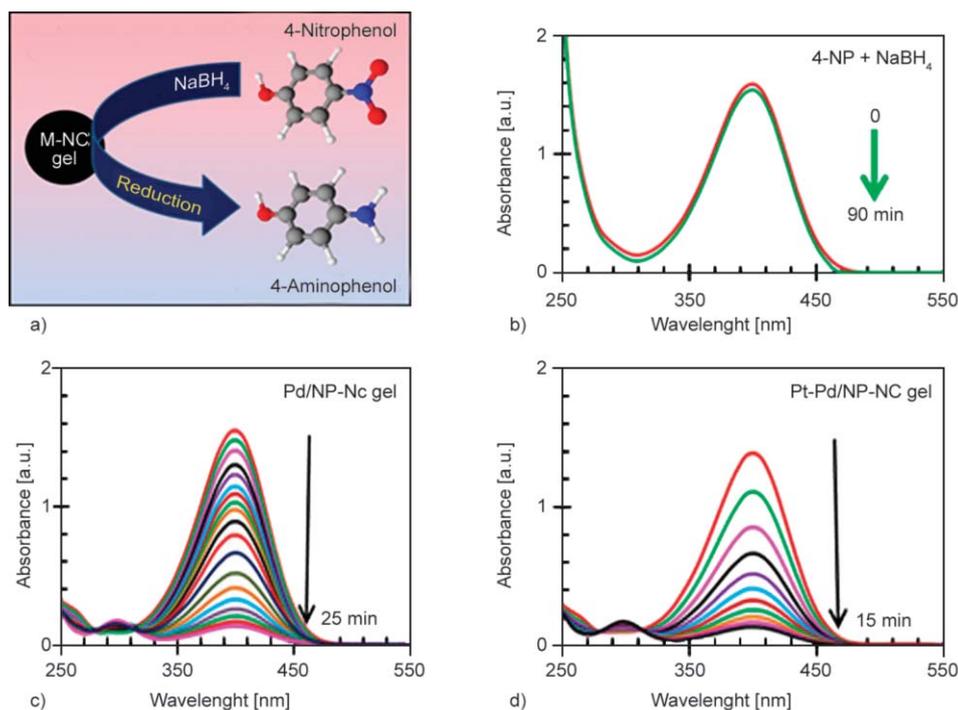


Figure 9. (a) Model reaction depicting the catalytic conversion of 4-nitrophenol into 4-aminophenol by an NP-NC gel. (b) The strong UV absorption peak at 400 nm corresponds to the nitrophenolate ion. However no change in the reaction occurs in the absence of a catalyst. Catalytic reduction of 4-nitrophenol by NaBH₄ occurred in the presence of (c) the Pd/NP-NC gel (0.1 g), where the reaction was complete in 25 min, and (d) the Pt-Pd/NP-NC gel (0.1 g), where the reaction was complete in 15 min.

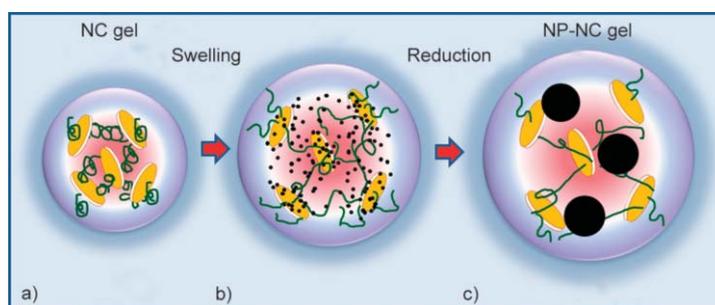


Figure 10. Depicting the formation of the hybrid NP-NC gel: (a) metal ions penetrate into the NC gel, (b) metal ions interact with the silanol groups on the clay surface, and (c) metal NPs are formed by the ascorbic-acid reduction of ions, which are subsequently trapped near the clay surface.

in the freshly prepared ascorbic acid solution, which results in the subsequent reduction of metal ions near the CNS surface and the creation of well-defined metal NPs that remain intact in the polymer-clay network matrix of the NP-NC gel. Thus, the CNSs play important roles in controlling the dispersion and the stabilization of metal NPs. Polymer gels without clay are not only very weak and brittle but also difficult to synthesize well dispersed size controlled metal NPs. Also, we have used ascorbic acid here for the slow and controlled synthesis of metal NPs as it is mild reducing agent compared to NaBH₄. Moreover, we had tried to reduce the metal ions in NC gel using NaBH₄ but we found lots of bubbling around

NC gel as soon as we dip the metal-ion swollen NC gel in NaBH₄ solution. Also the mechanical strength of NC gel goes down. This clearly indicates that NaBH₄ disturbs the structure of NC gel and also it does not allow controlled reduction of metal NPs within NC gel.

4. Conclusions

We succeeded in preparing nanostructured NP-NC gels at ambient temperature; these gels are composed of well-defined mono and bimetallic NPs that are strongly immobilized within the polymer-clay network. The metal ions initially interact with the silanol groups of the CNSs during the swelling of the NC

gel and are then slowly reduced to the corresponding metal NPs near to the CNSs. This trapping process means that the NPs do not move out of the NC gel matrix, even upon repeated swelling and deswelling in water. Furthermore, the present work revealed the new possibility of preparing stable hybrid NP-NC-gel materials that exhibit excellent catalytic properties, thereby further expanding the scope of their applications in many advanced research fields. This novel combination of nanoparticles and mechanically tough NC gels opens up many new functional-nanomaterial design possibilities for their widespread use in a variety of reactions and applications.

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