## **Invited**

## Synthesis and functions of platinumpolymer-clay nanocomposite gels fabricated via exfoliated claymediated in situ reduction

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Since the first synthesis of nanocomposite hydrogels (NC gels) with a unique organic (polymer)/inorganic (clay) network structure was reported,[1] NC gels have received a great deal of attention as super hydrogels that can overcome many of the serious disadvantages associated with conventional chemically crosslinked hydrogels (OR gels).[2] In particular, NC gels consisting of poly(Nalkylacrylamide)s such isopropylacrylamide) (PNIPA) or poly(N,N-dimethyl acrylamide) (PDMAA), and exfoliated inorganic clay such as hectorite or montmorillonite, have been shown to have extraordinary optical, mechanical, swelling/de-swelling properties.[3,4] Furthermore, NC gels can be prepared easily at ambient temperature in an aqueous system, providing a variety of shapes, sizes, and surface morphologies, along with novel characteristics such as unique sliding friction, ultrahigh hydrophobicity, support for stem cell proliferation, self-healing ability, and non-toxicity, which allows for their use in many new applications.[4-8]

Pt nanoparticles (Pt NPs) are currently used in many areas of nanoscience and technology. To date, numerous studies have been reported on the design of noble metal-based nanomaterials including NP-hydrogel composites that fabricated by exploiting the interspatial area between crosslinking points as a nanoreactor or nanocarrier. However, there have been very limited studies on Pt NP-hydrogel composites because it is difficult to prepare a material with fine and well-dispersed Pt NPs immobilized within a hydrogel. Furthermore, since the inherent properties of Pt NPs strongly depend on their size, dispersion, and the supporting material, new nanostructured Pt

materials with tailored morphologies and performances are still greatly desired.

Here, we report the synthesis, structure, and hydrogel-based properties of novel nanostructured Pt material, Pt-NC gel, consisting of ultrafine Pt NPs strongly immobilized within a unique polymer-clay network. [9] Pt-NC gels were synthesized through exfoliated clay-mediated in situ reduction of Pt ions in the NC gel at ambient temperature. [9,10] Pt NPs were trapped on the clay surface, at the edges of the clay nanoplatelets. Ultrafine Pt NPs were also obtained as a stable suspension from the NC gel, without any stabilizing agents. The combination of ultrafine Pt NPs and mechanically tough NC gel may open up new possibilities for designing functional Pt-gel materials

## References

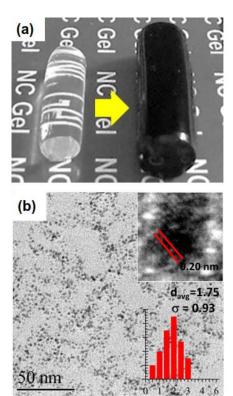
- [1] K. Haraguchi, T. Takehisa Adv. Mater., 14 (2002) 1120-1124.
- [2] K. Haraguchi, Curr. Opin. Solid State Mat. Sci., 11 (2007) 47-54.
- [3] K. Haraguchi, H-J. Li, Angew. Chem. Int. Ed., 44 (2005) 6500-6504.
- [4] K. Haraguchi, Polym. J., 43 (2011) 223-241.
- [5] K. Haraguchi, Macromol. Rapid Commun., 32 (2011) 1253-1258.
- [6] K. Haraguchi, Macromolecules, 45 (2012) 385-391.
- [7] N. Kotobuki, K. Haraguchi, J. Biomed. Mater. Res. A, 101 (2013) 537-546.
- [8] N. Jing, G. Li, K. Haraguchi, Macromolecules, 46 (2013) 5317-5328.

- [9] K. Haraguchi, D. Varde, Polymer, 55 (2014) 2496-2500.
- [10] D. Varade, K. Haraguchi, Langmuir, 29 (2013) 1977-1984.

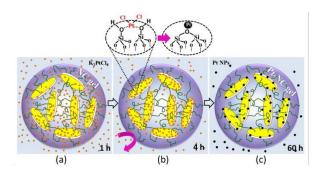




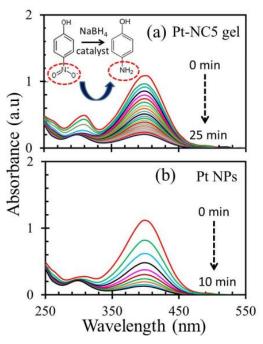
**Figure 1.** NC gels with various sphaes, e.g., rod, bulk, film, sheet, and deformations such as knotted and stretched NC gel, compression of NC gels with different clay contnet, and strong resistance against bar-pushing by a thin film of NC gel.



**Figure 2.** (a) Color changes of the N-NC5 gel kept in an aqueous solution of  $K_2PtCl_4$  in the dark at 25  $^{\circ}C$  for 60 h. (b) show the TEM images of the dried Pt-NC5 gel. The histogram shows the Pt NP size distribution in the Pt-NC5 gel. The inset shows the HR-TEM image, revealing the lattice fringes of crystalline Pt NPs.



**Figure 3.** Schematic representation of the formation of the Pt-NC gel: (a) Pt ions penetrate the N-NC gel, (b) Pt ions (PtCl<sub>2</sub>) interact with the silanol groups on the clay surface and are reduced to Pt<sup>0</sup>, (c) Pt NPs are formed by the migration of Pt, and are subsequently trapped on the clay surface.



**Figure 4.** Catalytic reduction of 4-nitrophenol by NaBH4 in the presence of (a) dried Pt-NC5 gel powder (3.5 mg), and (b) dried Pt NPs (1 mg) obtained in the surrounding solution. The strong UV absorption peak at 400 nm corresponds to the nitrophenolate ions.