A NEW SYNTHESIS OF CHEMICALLY INTERESTING AND HIGH TEMPERATURE STABLE NANO ALLOY PARTICLES USING CYANOGEL CHEMISTRY

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Alloys based on precious metals are of special importance for their catalytic and magnetic properties. Minimizing its dimension to nano scale while keeping it stable is expected to drastically improve the performance in catalysis and high-density magnetic recording (1). Here we report the first case of synthesizing near-homogeneous nanometer sized Pd-Co alloy particles and thin films that are highly stable toward high temperature through sol-gel processing of a cyanogel system. The reported methodology is synthetically attractive and can be applied to a variety of alloy systems since cyanogels containing just about any transition metal can be synthesized.

Cyanogels are coordinate polymers characterized by bridging cyano groups that link metal centers (2). Bi-metal alloys can be prepared by sintering cyanogels under inert atmosphere (3) (Fig. 1). In the present study, Pd-Co cyanogels were prepared by mixing aqueous solutions of Na_2PdCl_4 and $K_3Co(CN)_6$ under various conditions. The mixture was spin cast to form a cyanogel thin film, which was then sintered under inert atmosphere to form nanosized Pd-Co alloy particles. The as prepared cyanogel thin films were characterized by FTIR, which indicated the quantitative conversion of terminal cyanides in the reactant to bridging cyano groups. (Fig. 2). Both the as prepared thin film and the sintered product were characterized by TEM. The cyanogel thin film was found to be composed of gel particles with uniform size of 2~3nm. These gel particles formed both agglomerations and 2-dimension super lattice structures, presumably due to electronic repulsive interactions (Fig. 2). Sintered films were determined to be metallic and have a homogenous composition that reflected the metal stoichiometry of the starting cyanogel polymer. The films were composed of particles in the nanometer size range. The size and homogeneity of the alloy products could be tuned by manipulating reaction conditions in cyanogel preparation and gel processing temperatures. Fairly monodispersed populations could be formed ranging in average size from ~3nm to ~30nm as shown in Figure 3.

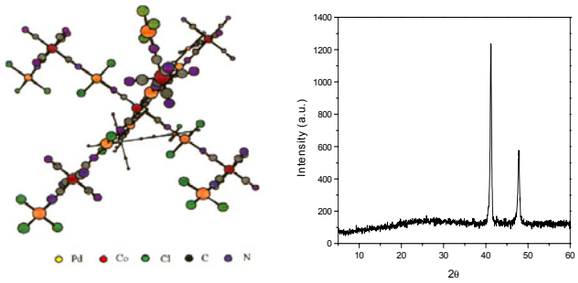

Figure 1 Left: Proposed molecular structure of Pd/Co cyanogels. Right: x-ray powder diffraction analysis of a Pd/Co alloy prepared by sintering Pd/Co cyanogel at 650°c under Ar.

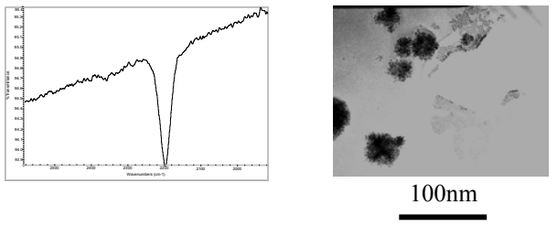

Figure. 2: FTIR spectrum and TEM image of an as prepared Pd/Co cyanogel thin film

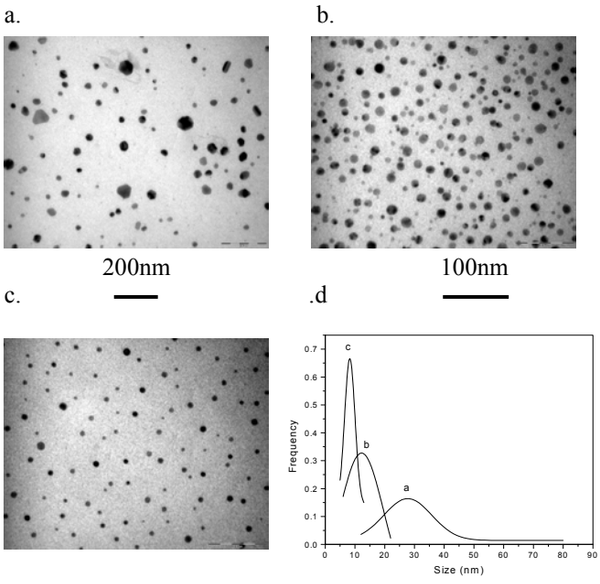

Figure. 3 Sintered Pd/Co cyanogel thin films prepared under the following conditions:

a. Room temperature, 60mM reactants, 3000 RPM spin coating rate.
b. 0°C, 60mM reactants, 3000 RPM spin coating rate.
c. 0°C, 1mM reactants, 4000RPM spin coating rate.
d. Particles size and distribution in samples a, b and c.

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