

Electronic Supplementary Information (ESI)

a) Synthesis of cobalt colloid

In a typical preparation, 6 g AOT (Dioctyl sulfosuccinate, sodium salt, 98% Aldrich) is dissolved in 50 ml of 2,2,4-Trimethyl pentane or iso-octane (99.7+%, HPLC grade, Aldrich) deoxygenated by bubbling of Ar for several hours in a Schlenk tube under Ar. 26 ml of this mixture is placed in a separate Schlenk tube under Ar and 1.2 ml of a solution of 227 mg NaBH_4 (98%, Lancaster) in 10 ml of distilled water was added. The mixture was stirred and sonicated for 3-6 min. As a result, a transparent colorless solution of micelles of NaBH_4 (aq.) in iso-octane with AOT as surfactant was obtained. To the remaining solution of AOT in iso-octane in the first Schlenk tube were added 1.2 ml of a solution of 714 mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (98%, ACS reagent, Aldrich) in 10 ml of distilled water. The mixture was stirred and sonicated (as above), producing a transparent pink solution of CoCl_2 (aq.) micelles in iso-octane with AOT as surfactant. Both solutions were cooled in an ice-acetone bath with stirring. The above-mentioned solution of NaBH_4 was quickly added to the solution of CoCl_2 under a strong flow of Ar with vigorous stirring and while cooling with the ice-acetone bath. The reaction mixture showed first signs of colloid formation (i.e. the solution turning grayish) within 15 seconds after addition with a significant black color developing within 20-25 seconds. At the peak of the reduction step noticeable amounts of H_2 evolved producing vigorous bubbling. Effective stirring is therefore required during this stage. The mixture was left under the flow of Ar for 5 more minutes in the ice-acetone bath. The bath was then removed to allow a slow warming-up of the stirred reaction mixture to room temperature under the flow of Ar. This colloid solution contains significant amount of AOT surfactant, which has to be removed for a successful CNT growth.

b) Purification of cobalt colloid.

60 ml of methanol (dry, freshly distilled under N_2) was added to the deep black cobalt colloid solution obtained as described above. The mixture was stirred, manually shaken and allowed to settle for several hours (See Fig. S1). The almost transparent top and bottom layers were syringed out and discarded. Methanol (dry, freshly distilled under N_2)

was then added with stirring to the remaining viscous black flocculate (the volume of the added methanol determines the concentration of the purified colloid, typically 10-20 ml), to produce a deep black colloid solution. This “flocculation-purified” colloid can be used “as prepared” or can be filtered through a 0.2 µm PTFE syringe filter prior to deposition onto support. Both “as synthesised” and “purified” cobalt colloid solutions decompose within 1-2 days.

c) Synthesis of NiPd colloid.

Synthesis was performed according to method reported by P. Lu et al. The Ni:Pd ratio was 20:80. However, we have found that reflux of the reaction mixture can be substituted with heating to 80-120 °C. Moreover, reflux often forces sintering of the colloid, whereas milder heating is enough for the reaction to proceed without significant agglomeration.

d) Purification of NiPd colloid.

Addition of excess of dry acetone (HPLC grade Aldrich, usually 5-10 excess by volume) to the “as made” colloid results in precipitation of viscous black-brown residue within several hours. The liquid phase is then carefully decanted and the residue redissolved in freshly distilled methanol to produce deep black-brown homogenous solution of purified colloid. Such solution is stable and can be stored at room temperature. The volume of the methanol used to re-dissolve precipitated colloid determines final concentration of the purified colloid solution since synthesis and precipitation appear to be nearly quantitative.

e) Preparation of the silica-supported catalysts

Rather than employing as porous supports the popular (organic-template-derived) MCM-types (which have non-intersecting pores) and related silicas such as SBA-15, we have used a set of commercially available (from Grace Davison) desiccant silicas having narrow pore size distributions (designated Davison 634, having a pore diameter of 60 Å). These are made by reacting sodium silicate with a strong mineral acid (usually sulphuric acid); the pore size being controlled by gel time, final pH, temperature, concentration of reactants, etc. Compared to MCM-41 type silicas they are much lower in cost, more thermally and mechanically stable, less susceptible to structural collapse and available in

a range of granularities and pore diameters (38, 60, 150 and 250 Å). They also have some intersecting pores that facilitate the diffusion of the reactant species to the immobilized catalyst, and their respective surface areas are 700, 500, 415 and 300 m²g⁻¹.

In the case of the cobalt colloid, *ca.* 50 ml of the “as prepared” colloid was flocculated with methanol as described above and the precipitate was re-dispersed in 20 ml methanol. 5 ml of this solution was filtered through 0.2 µm PTFE 25 mm syringe filter, diluted with 40 ml of methanol, and added to 10.470 g of the Davison Silica, having a pore diameter of *ca.* 60 Å, in a schlenk tube, under argon, with vigorous stirring and the solvent was removed in *vacuo*.

In the case of the NiPd colloid, 30 ml of the “as prepared” colloid was flocculated with 60 ml of acetone in a schlenk tube under argon. The liquid phase was discarded and the precipitate was re-dissolved in 20 ml of methanol. 8 ml of this homogeneous deep black-brown colloidal solution was diluted with 30 ml of methanol and the mixture was added with vigorous stirring under argon to 10.486 g of the Davison Silica, having a pore diameter of *ca.* 60 Å. The solvent was removed in *vacuo* and the resulting solid was calcined in *vacuo* (*ca.* 130 °C).

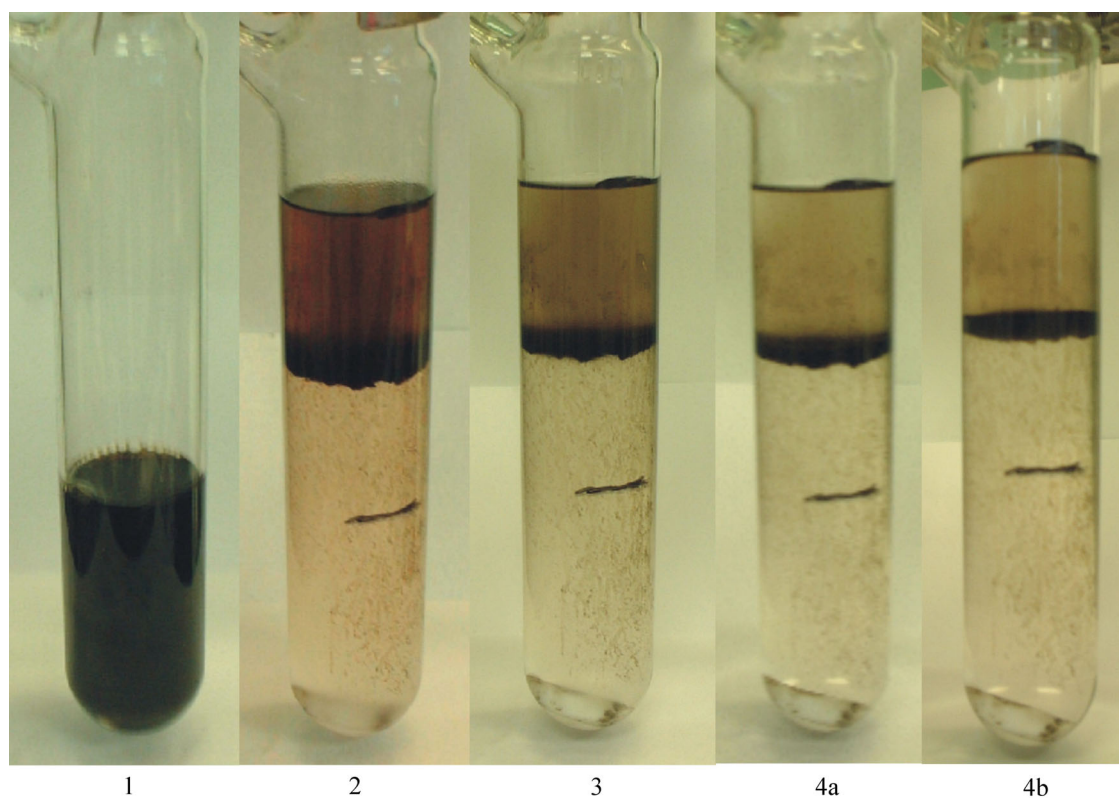


Fig. S1. Flocculation of Co colloid on addition of methanol with time (1-“as made”; 2 - 20 min; 4 – 3 hr.).