catalysts

MDPI

Supplementary Materials

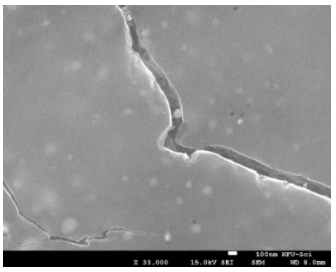
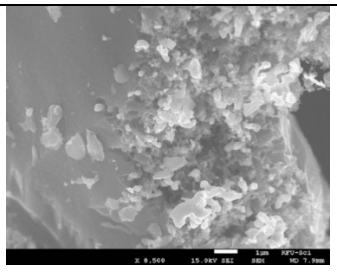
Hierarchical Graphitic Carbon Encapsulating Cobalt Nanoparticles for Catalytic Hydrogenation of 2,4-Dinitrophenol

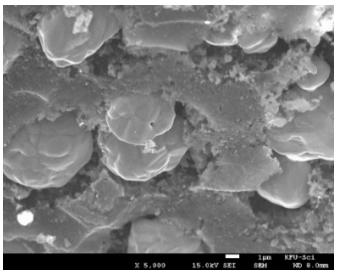
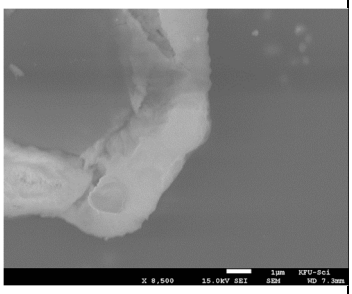
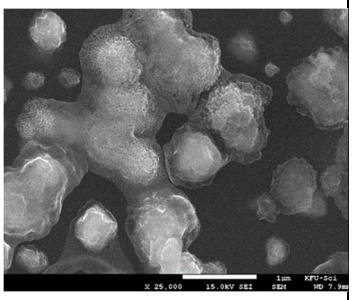
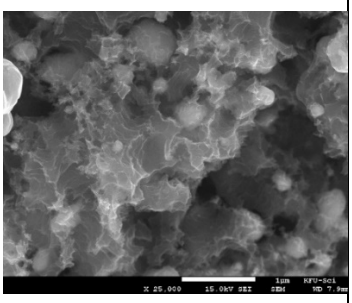
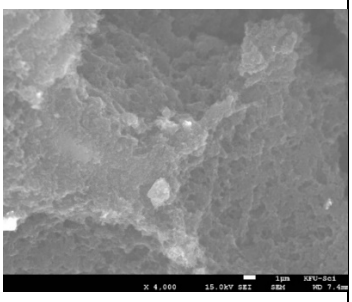
Hassan H. Hammud [1,*], Hassan Traboulsi [1,*], Ranjith Kumar Karnati [1], Syed Ghazanfar Hussain [2] and Esam Bakir [1,3]

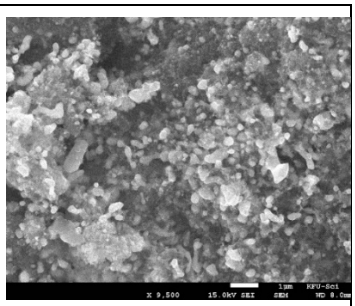
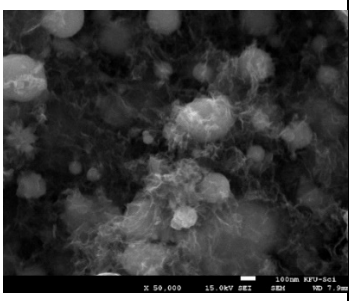
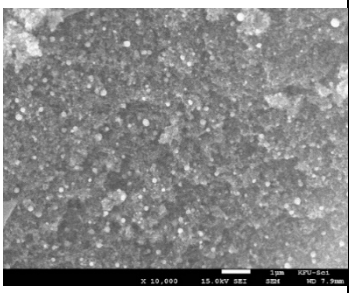
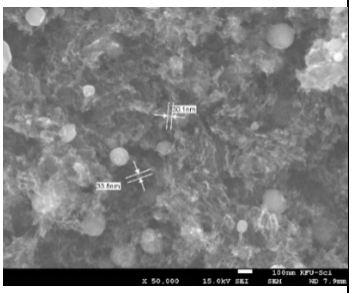
[1] Department of Chemistry, College of Science, King Faisal University, P.O. Box 400, Al-Ahsa 31982, Saudi Arabia; Rkarnati@kfu.edu.sa (R.K.K.); ebakir@kfu.edu.sa (E.B.)
[2] Department of Physics, College of Science, King Faisal University, P.O. Box 400, Al-Ahsa 31982, Saudi Arabia; sghazanfar@kfu.edu.sa
[3] Department of Chemistry, Faculty of Science, Ain shams University, Cairo 11566, Egypt
* Correspondence: hhammoud@kfu.edu.sa (H.H.H.); htraboulsi@kfu.edu.sa (H.T.)

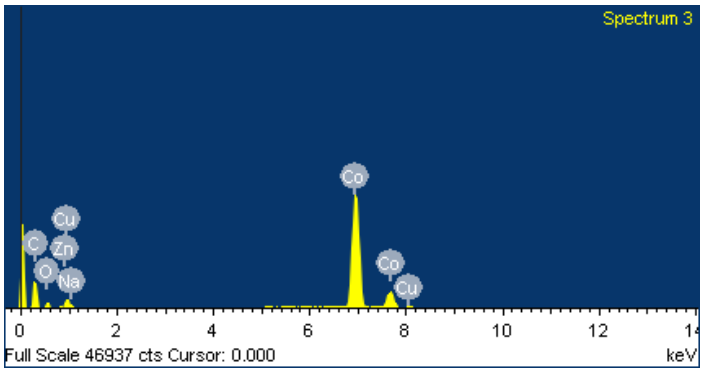
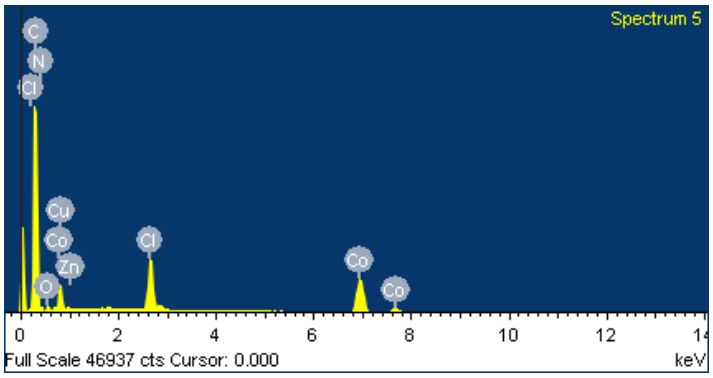
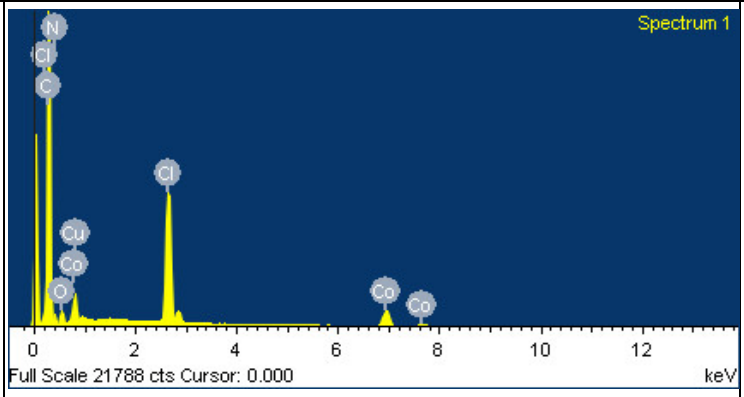
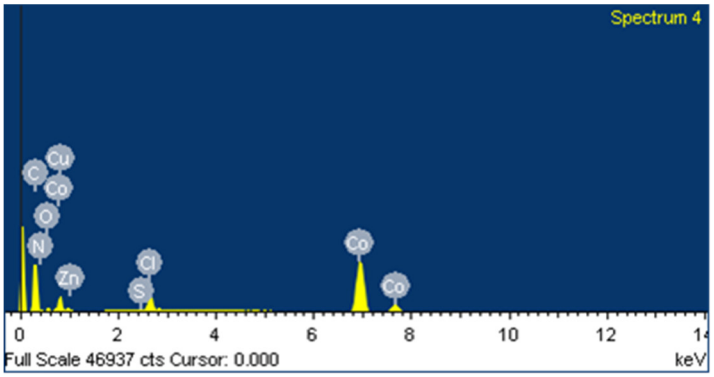
Supplementary Materials

Table S1. Effect of experimental conditions on the microscopic structure of the obtained cobalt carbon nanomaterials. In all the carbon source is anthracene, except pyrene was used in (B). All under nitrogen atmosphere except C under vacuum. Only the crucible in the case of (1) was not covered.

Sample number	Temperature	Time of Stage Heating	% yield	Results	SEM
A	500 ^{0}C	8h	65%	50-150 nm cobalt nanoparticles undeveloped beneath amorphous carbon layer Few nanoparticles are exposed	
B	600 ^{0}C	5 h	59%	Few nanoparticles of irregular size with 270 nm width Effect of type of carbon source	
C	600 ^{0}C	5 h	20%	Grey ash	-

D	600 ^{0}C	5 h Short	56%	-D1 Cobalt nanoparticles 100 nm in graphite sheets Other agglomerated into several micrometer spheroid particles	
E	600 ^{0}C	10 h long	38%	Cobalt agglomerated particles 5-10 micrometer on top of carbon amorphous layer, few cobalt nanoparticles embedded in carbon layer. Longer heating caused more agglomeration of cobalt nanoparticles into micro sized particles	
(1)	600 ^{0}C	8 h		100-2000 nm cobalt particles embedded in not fully developed graphite support	 
(1)-acid				(1)-acid When (1) was treated with 10% HCl the white cobalt particles were removed	

(2)	300 ^{0}C 600 ^{0}C	3h 8 h Intermediate stage	37%	50-1000 nm cobalt nano particles embedded in graphite support	 
(3)	800 ^{0}C	5 h	38	Silver Metallics Nanoparticles 10-100 nm in graphene sheets	 
E	1000 ^{0}C	10h	18%	White grey ash	-

(1)H		Element (Aomic %) C 64.94 O 5.00 Cl 0.13 Co 28.55
(1)L		Element (Aomic %) C 82.54 N 9.91 O 3.32 Cl 1.46 Co 2.63
(1)acid		Element (Aomic %) C 81.12 N 10.13 O 3.45 Cl 3.38 Co 1.80
(2)		Element (Aomic %) C 76.30 N 7.30 O 3.83 Cl 1.26 Co 10.75

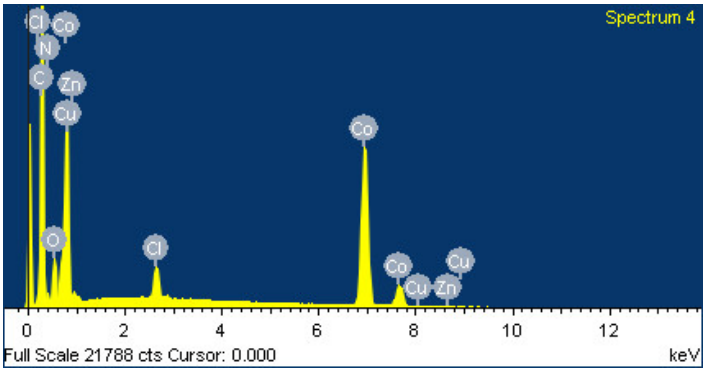
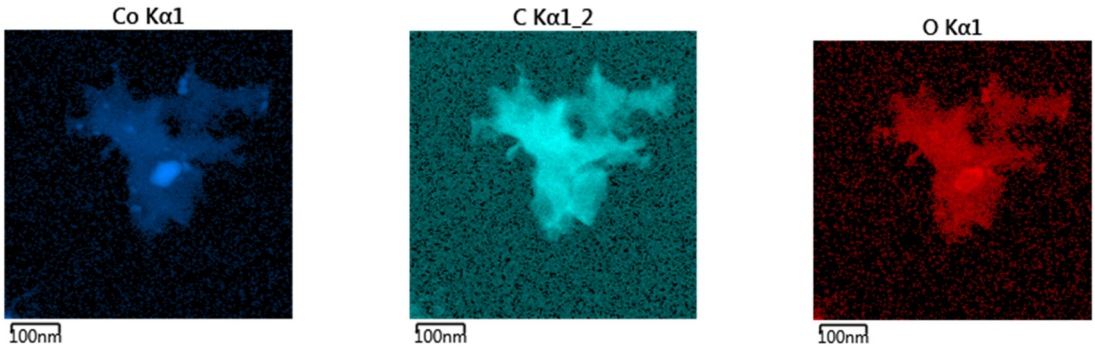
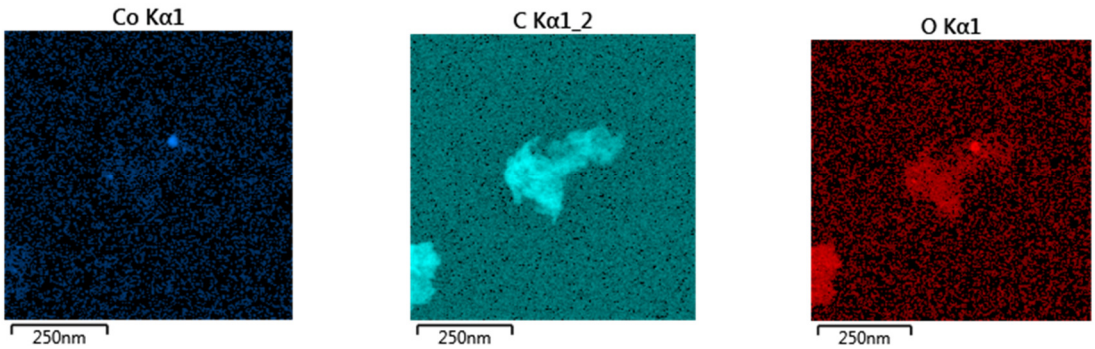
(3)		Element (Aomic %) C 72.69 N 5.11 O 5.90 Cl 0.76 Co 14.88

Figure S1. SEM-EDX spectrum of catalysts (**1**), (**2**) and (**3**). Where (1)H is for high %Co area and (**1**)L is for low %Co area. (**1**)-acid is (**1**) treated with 10% HCl.

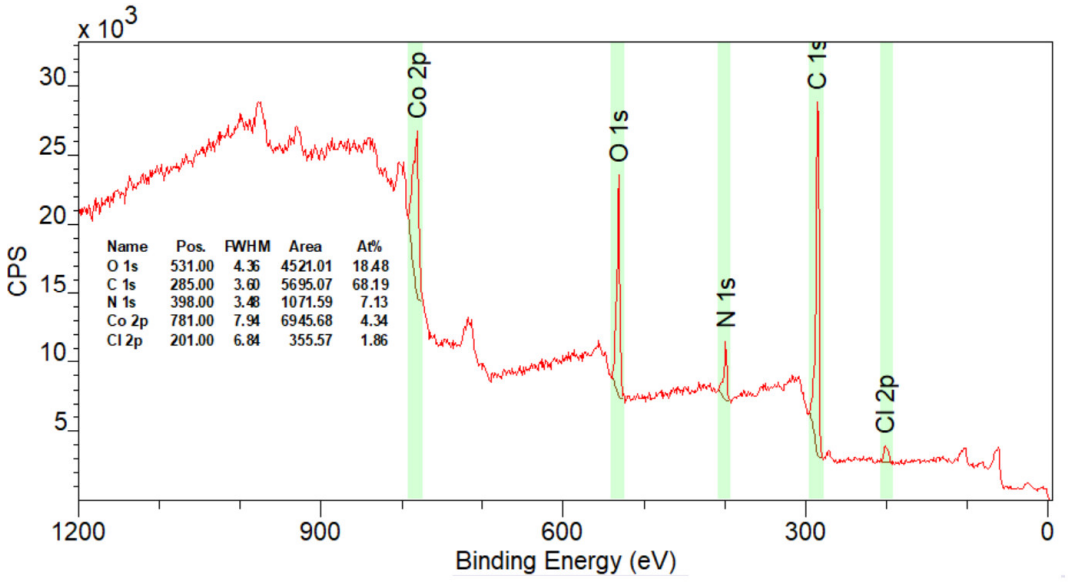


EDX of (**1**)

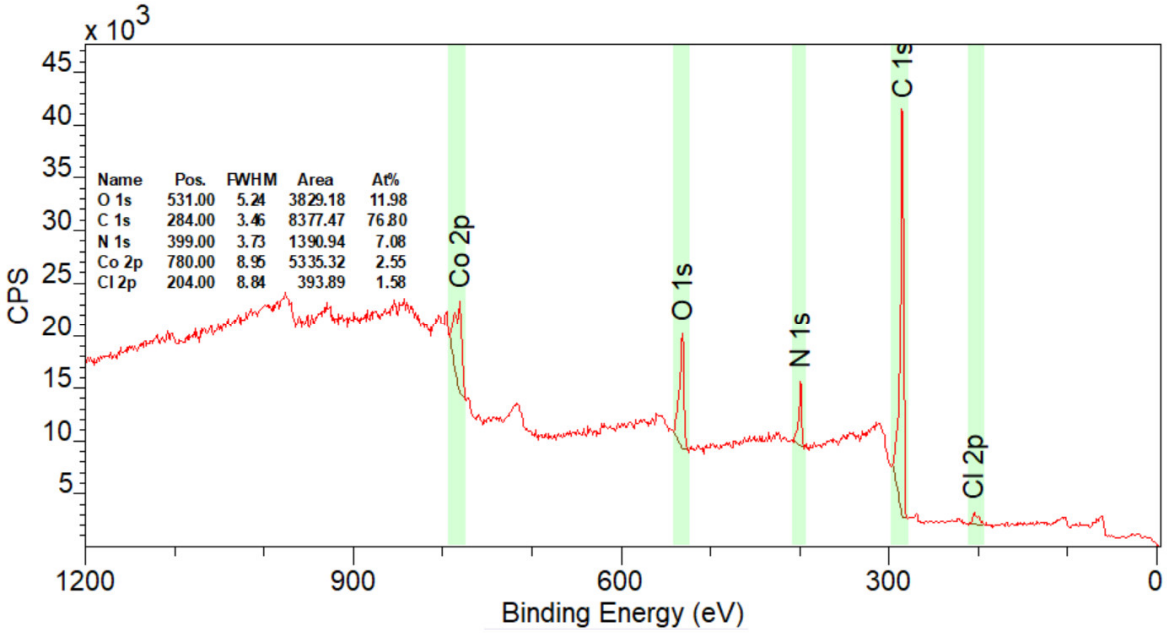


EDX of (**3**)

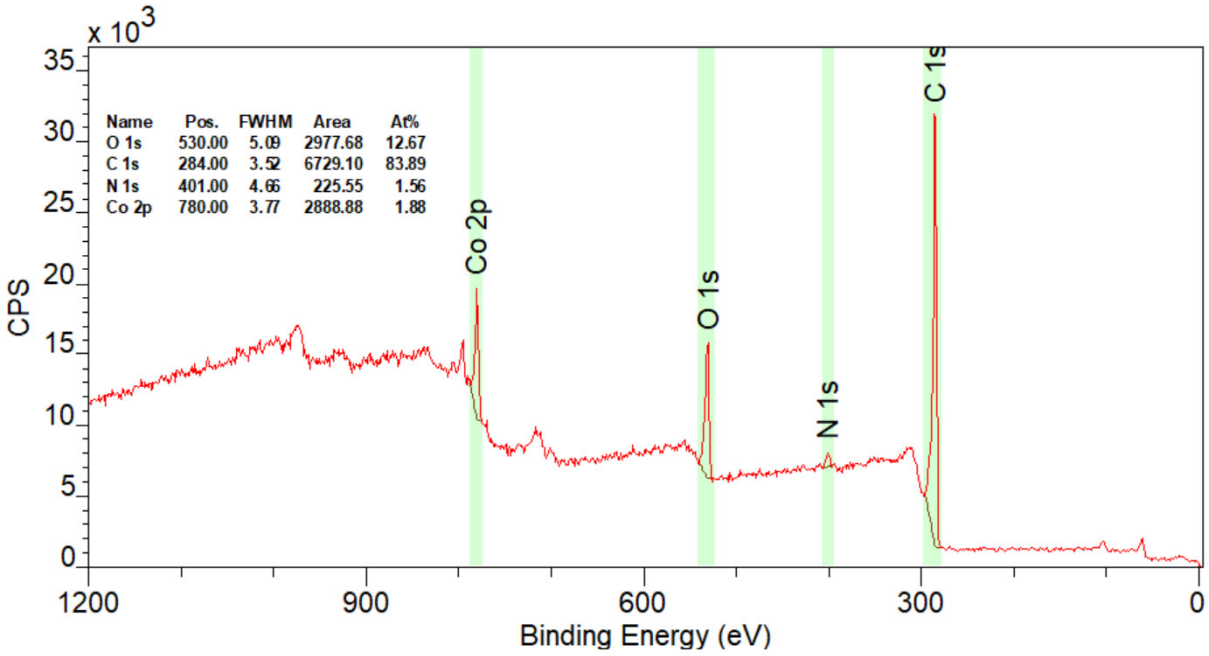
Figure S2. TEM-EDX of nano-catalysts (**1**) and (**3**).



(a) XPS survey spectrum of (**1**).



(b) XPS survey spectrum of (**2**).



(c) XPS survey spectrum of (**3**).

Figure S3. a) b) and c) XPS survey spectrum of nano-catalyst of (**1**), (**2**) and (**3**) respectively.

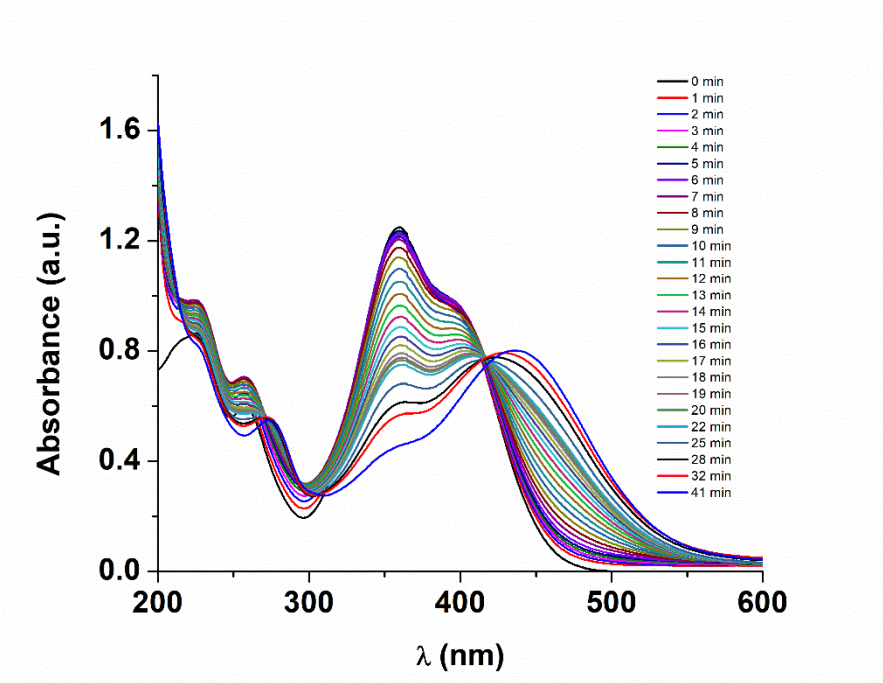


Figure S4. Time-dependent UV-visible absorption spectrum for the reduction of DNP with $NaBH_4$ in the presence of nano-catalyst (**1**). Solvent: Water, [DNP] = 8.5 ×10^{-5} M; [$NaBH_4$] = 0.003 M; ℓ = 1 cm; T = 25°C; 0.18 mg/ml of catalyst was used.

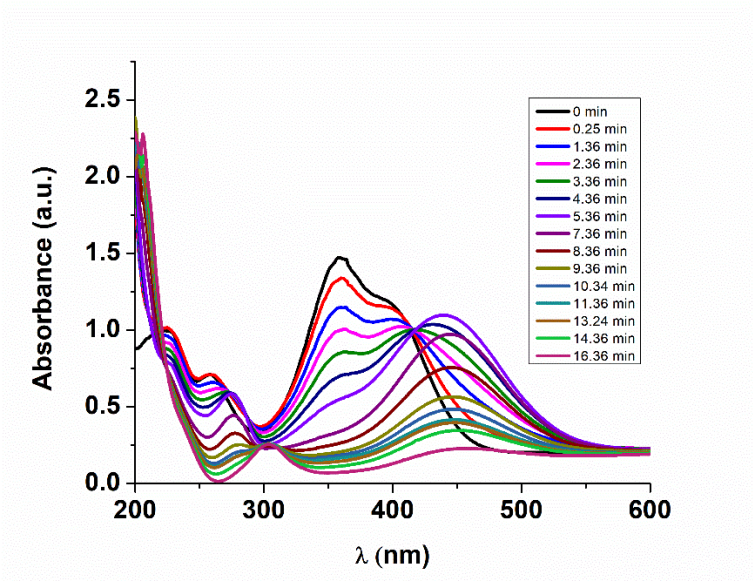


Figure S5. Time-dependent UV-visible absorption spectrum for the reduction of DNP with $NaBH_4$ in the presence of nano-catalyst (**3**). Solvent: Water, [DNP] = 8.5 ×10^{-5} M; [$NaBH_4$] = 0.003 M; ℓ = 1 cm; T = 25°C; 0.18 mg/ml of catalyst was used. .

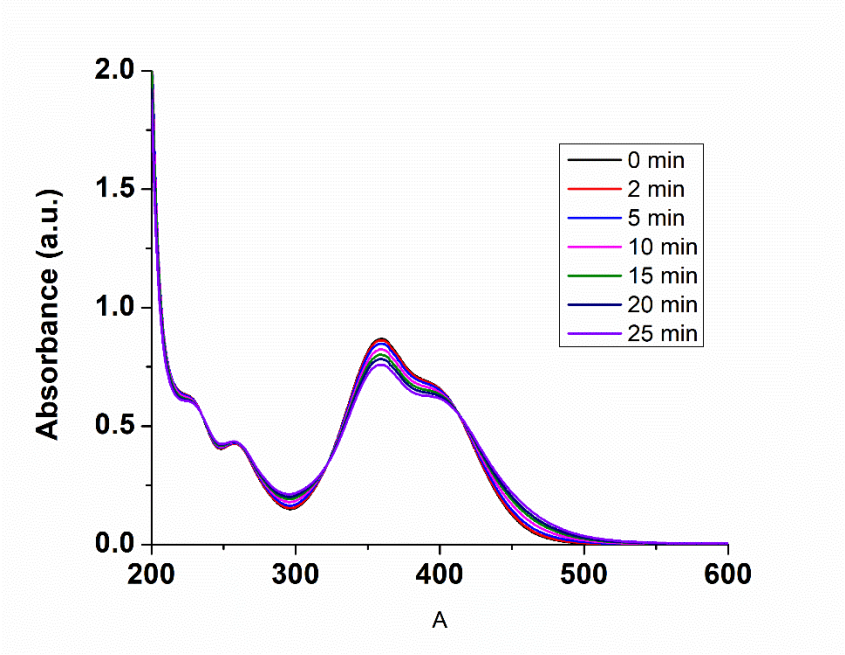


Figure S6. Time-dependent UV-visible absorption spectrum for the reduction of DNP with $NaBH_4$ in absence of catalyst. Solvent: Water, [DNP] = 8.5 ×10^{-5} M; [$NaBH_4$] = 0.003 M; ℓ = 1 cm; T = 25°C.

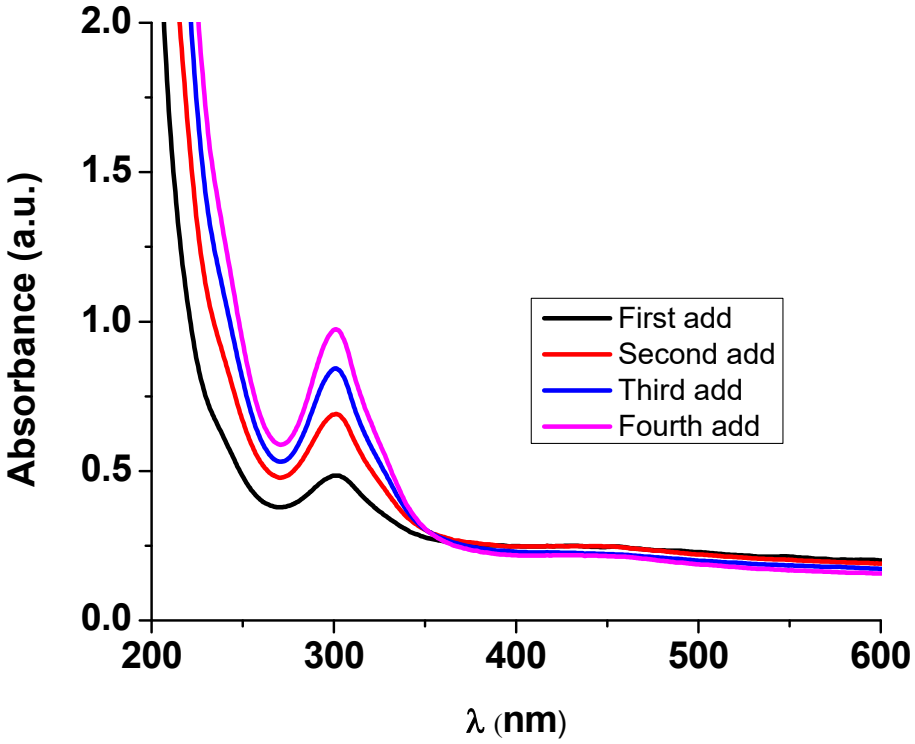


Figure S7. After regeneration of (**2**): complete reduction for new four successive cycles of addition of 50 mL of 2,4-dinitrophenol (4.4×10^{-3} M). Catalyst: 0.2 mg/ml. Solvent: Water 3mL; [$NaBH_4$] = 0.017 M; T = 25°C.

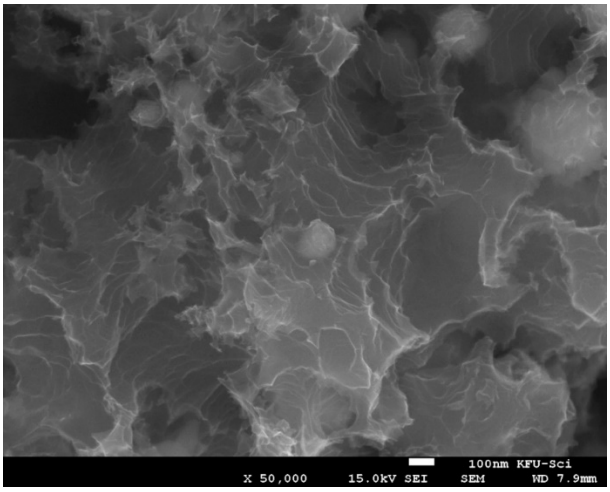
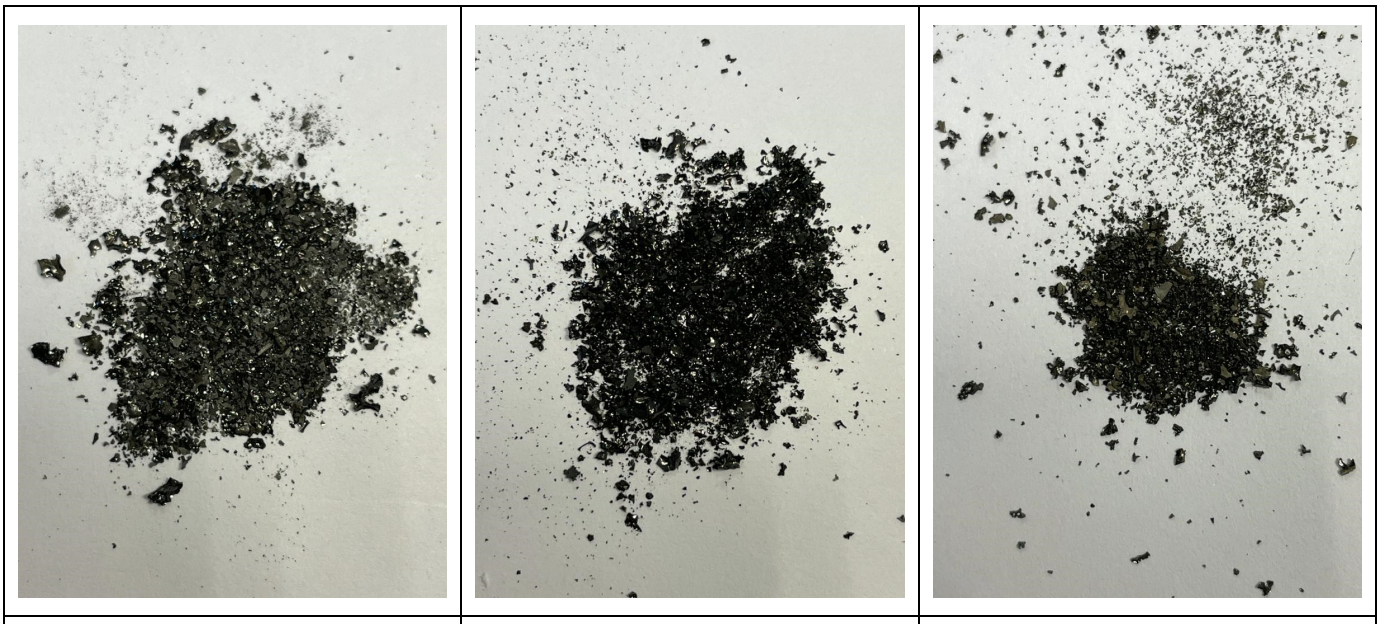


Figure S8. SEM of the used catalyst (1).



(1)	(2)	(3)

Figure S9. Image of cobalt hierarchical carbon nanomaterials Co@HGC catalyst (**1**), (**2**) and (**3**).

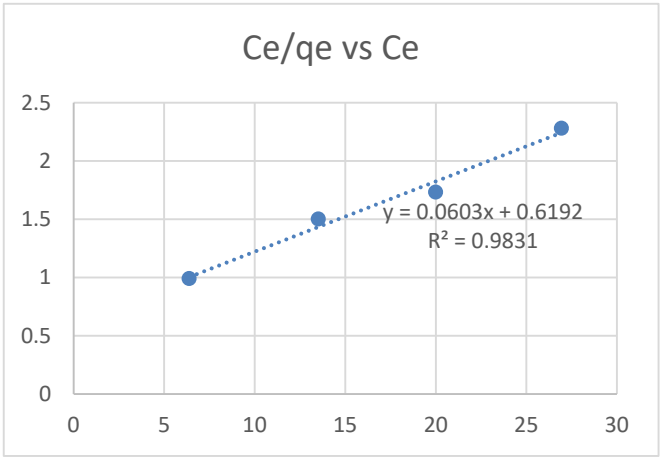
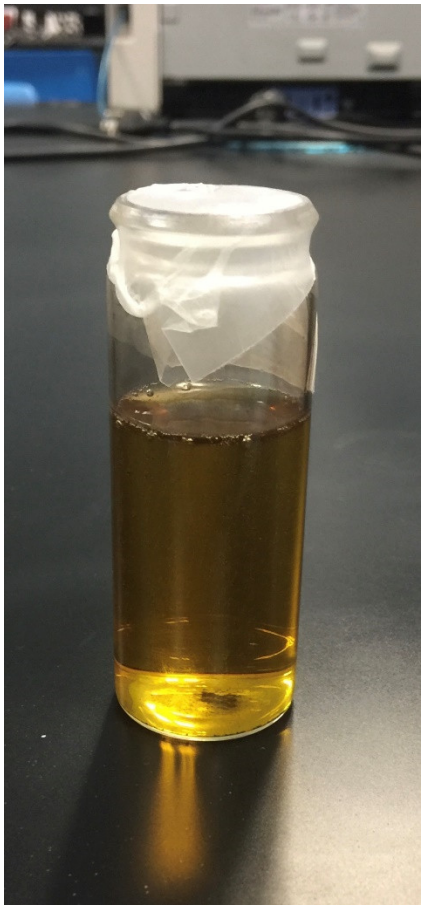
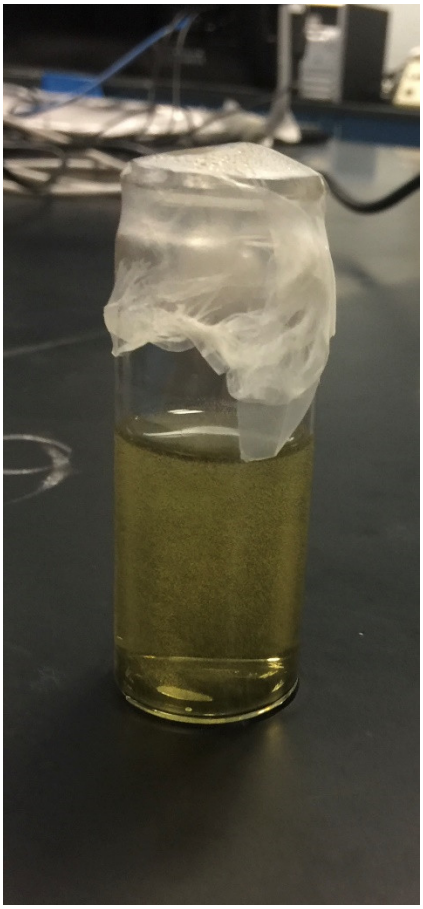


Figure S10. Langmuir adsorption isotherm for 2,4-DNP by catalyst (**3**). Where Ce (mg/L) is the remaining concentration of 2,4-DNP and qe (mg/g) is the experimental capacity.



Begining of reaction of 2,4-DNP with catalyst (3)

After 5 minutes of reaction



Close to end of reaction after 10 minutes

Figure S11. Tracked observation of hydrogen gas generation during reduction experiment of 2,4-DNP by catalyst (3) in presence of sodium borohydride.