Supplementary Information

Test confirming the formation of 4-chloro-1,2-phenylenediamine

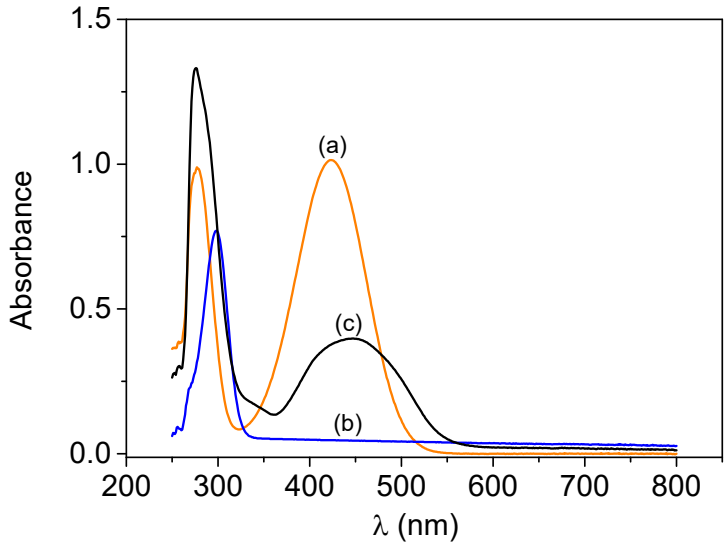
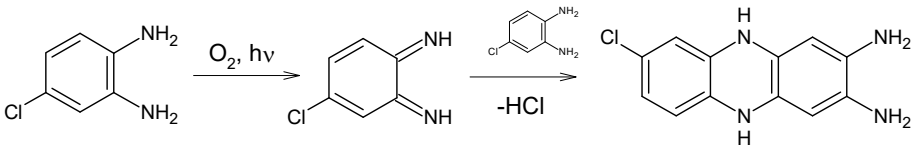


Fig. S01 Test confirming the formation of 4-chloro-1,2-phenylenediamine after the catalytic reduction of CNA. (a) CNA 0.25 mM, (b) mixture of CNA 0.25 mM + $NaBH_4$ 6 mM + K-Pd 8 mg L^{-1} after 12 min and (c) solution of (b) after centrifugation and 4 h exposition in sun light.

The solution of (b) purged with argon and exposed to sun light showed no evolution of the UV-Vis spectrum. The solution of (b) stored in the dark also showed no evolution of the UV-Vis spectrum. This clearly demonstrates the role of oxygen and light (visible light) for the conversion (photo-oxidation) of 4-chloro-1,2-phenylenediamine to 2,3-diamino-7-chlorophenazine with the formation of 4-chlorocyclohexa-3,5-diene-1,2-diimine as intermediate according to Equation S1 below.



Equation S1

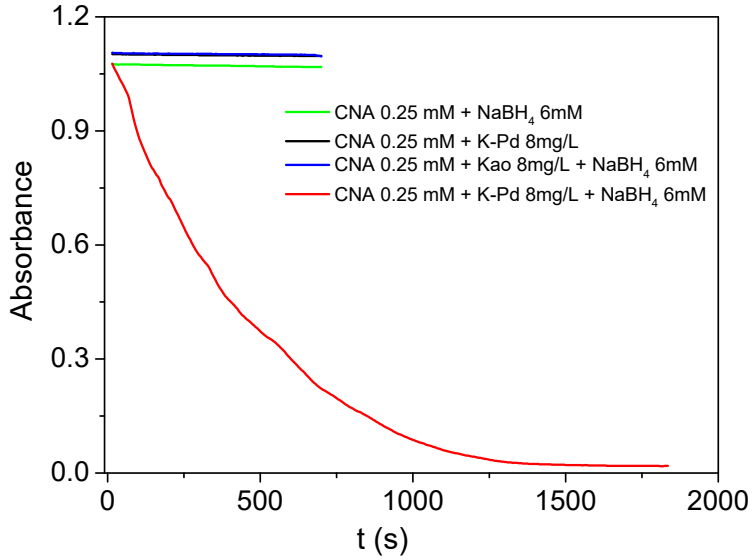


Fig. S02 Effect of various components on the variation of the absorbance at 423 nm as a function of time in a 0.25 mM CNA solution.

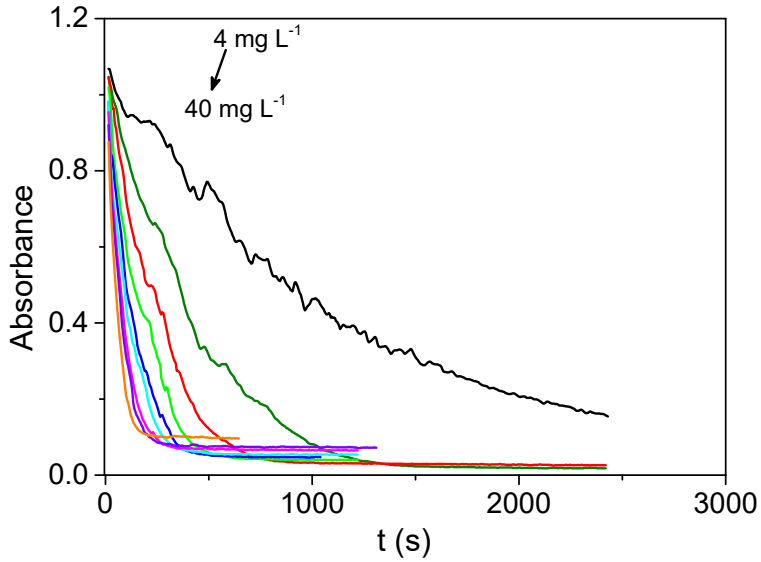


Fig. S03 Effect of K-Pd concentration on the variation of the absorbance at 423 nm of a 0.25 mM CNA solution in the presence of $NaBH_4$ (6 mM).

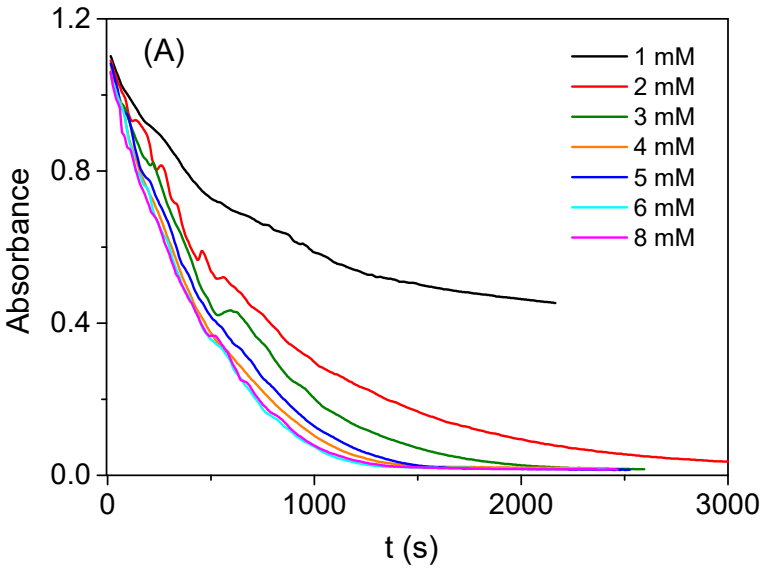


Fig. S04 Effect of $NaBH_4$ concentration on the variation of the absorbance at 423 nm of a 0.25 mM CNA solution in the presence of K-Pd (8 mg L^{-1}).

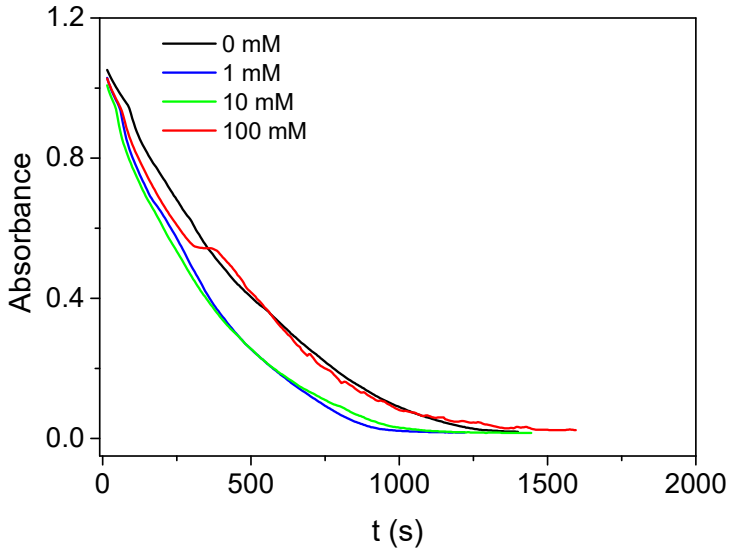


Fig. S05 Effect of KCl concentration on the variation of the absorbance at 423 nm of a 0.25 mM CNA solution in the presence of K-Pd (8 mg L^{-1}) and $NaBH_4$ (6 mM).

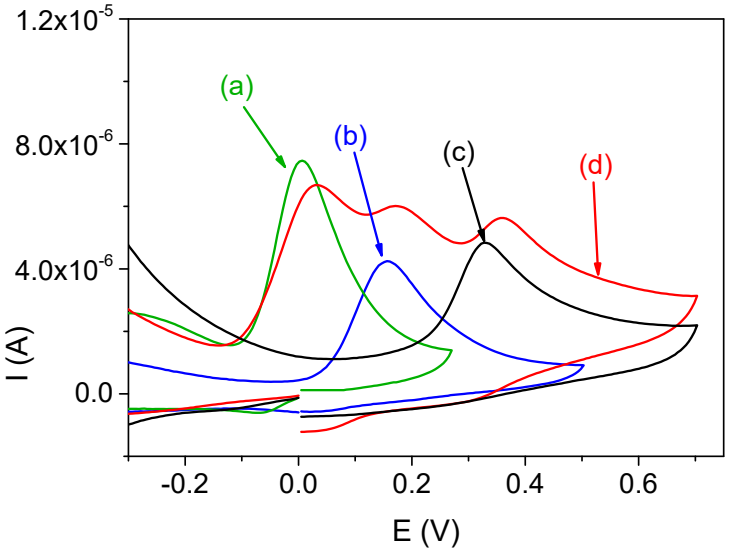


Fig. S06 Cyclic voltammograms recorded at Au/K-Pd immersed in a phosphate buffer solution 0.1 M, pH 6.6 in presence of (a) 4-nitrocatechol 0.1 mM, (b) p-nitrophenol 0.1 mM, (c) CNA 0.1 mM and (d) the mixture CNA 0.1 mM, p-nitrophenol 0.1 mM and 4-nitrocatechol 0.1 mM.