Water as a Solvent: Kinetics and Products of the Reaction of Graphene Nanoplatelets with Noble Metal Ions

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Introduction

- Graphene nanocomposites with single atoms or small clusters are of interest for various catalytic processes, e.g. batteries, fuel cells, water electrolysis, and chemical synthesis
- Typically, graphene oxide is reduced in the presence of metal salts to produce metal-graphene nanocomposites
- But graphene itself exhibits reductive properties and can react with metal ions in higher oxidation states when suspended in water as a solvent
- While direct reactions (dip and coat or wet coating) of graphene with metal salts have been described several times, less is known about the kinetics

Results

- Graphene nanoplatelets (GNP) react with palladium (II), iridium (IV), platinum (IV), and gold (III) when dispersed in oxygen-containing water
- The kinetics of the metalates were measured and evaluated as pseudo 1. or pseudo 2. order kinetics (Table 1)
- The products were metal-supported GNP. The metals on the GNP were found to be single atoms or clusters by HR-TEM (see Figure 1)
- The maximum metal loading increased from 3.3% by mass for palladium to 44% by mass for gold
- The metals were found to be in primary oxidation states (Table 2)
- A linear correlation was found between metal content and oxidation-reduction potential

Experimental

A flask was equipped with sensors for T, pH, and EC. A 5 µm ceramic filter frit was inserted, and the filtrate was continuously pumped through a cuvette placed in the photometer and back into the flask with a cassette pump. The UV-Vis spectrometer was set to the wavelengths (Au(III): 290 nm, Pt(IV): 260 nm, Ir(IV): 489 nm, and Pd(II): 425 nm in 10 mM HCl), and the background was recorded. Then the UV/VIS was started for a running time of 10 to 60 minutes.

Stock solutions of potassium tetrachloroplatinate(IV) (5 mM), ammonium tetrachloroiridate(IV) (10 mM), and auric acid (10 mM) were prepared in deionized water. The respective stock solution was added to water to obtain a defined noble metal concentration. Solid $(NH_4)_2[PdCl_4]$ was weighed and added directly to 10 mM HCl.

A certain mass of GNP was added, and the time-dependent decrease in metalate UV-Vis absorption was measured (see **Picture 1**).

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Picture 1. Experimental setup for measuring the kinetics of GNP with metalates.

Table 1. Best fit of kinetic data.

Process	Kinetic type	Evaluation time (min)	k_1 (min^{-1})	R^2 adj
0.04 mM $HAuCl_4$ in 250 ml AW, 100 mg GNP	1st	1.67 - 3.33	2.19 ± 0.05	0.9901
0.2 mM $(NH_4)_2IrCl_6$ in 250 ml AW, 100 mg GNP, 1. Dosage	1st	8.20 - 9.90	3.1 ± 0.1	0.9834
0.2 mM $(NH_4)_2IrCl_6$ in 250 ml AW, 100 mg GNP, 2. Dosage	1st	16.6 - 19.5	0.287 ± 0.001	0.9996
			k_2 (mM^{-1} min^{-1})	
0.04 mM K_2PtCl_6 in 250 ml DI, 100 mg GNP, 1. Dosage	2nd	2.50 - 7.33	27.0 ± 0.1	0.9978
0.04 mM K_2PtCl_6 in 250 ml DI, 100 mg GNP, 2. Dosage	2nd	20.5 - 27.5	5.14 ± 0.05	0.9946
0.04 mM K_2PtCl_6 in 250 ml DI, 100 mg GNP, 3. Dosage	2nd	36.0 - 58.0	1.84 ± 0.01	0.9924
0.4 mM $(NH_4)_2PdCl_4$ in 10 mM HCl, 500 mg GNP	2nd	3.82 - 4.20	8.1 ± 0.1	0.9822
0.4 mM $(NH_4)_2PdCl_4$ in 10 mM HCl, 500 mg GNP reg	2nd	3.72 - 3.97	2.97 ± 0.05	0.9860

Table 2. Metal content and oxidation state (XPS-Results).

Metal	Metal (Atom-%)	Metal (Mass-%)	Oxidation states (%)
Gold	0.9	12	Au(0): 94
	5	44	Au(0): 95
Iridium	0.9	13	Ir(IV): 100
Platinum	0.3	4.5	Pt(II): 87, Pt(IV):10
Palladium	0.2	3.3	Pd(II): ~55, Pd(0): ~40

There was a strong tendency toward a primary oxidation state.

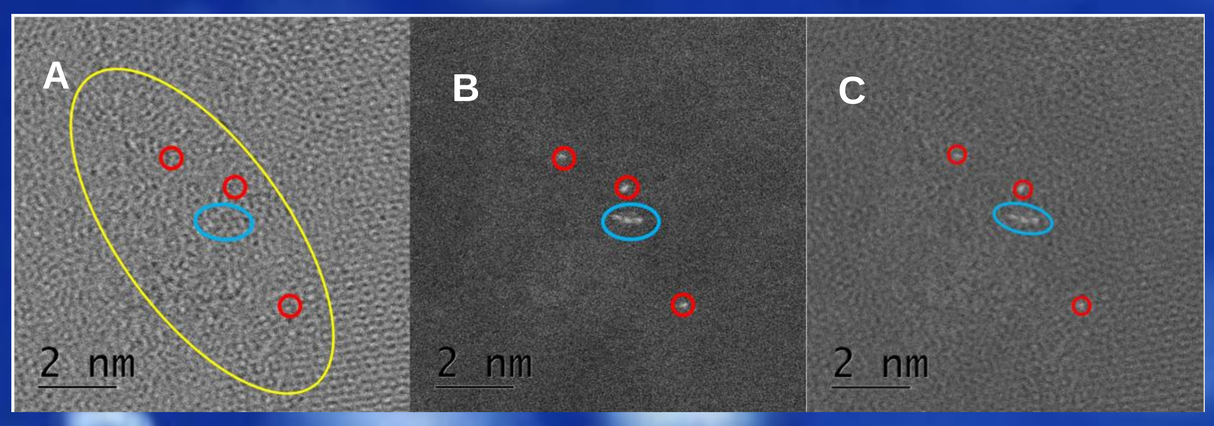
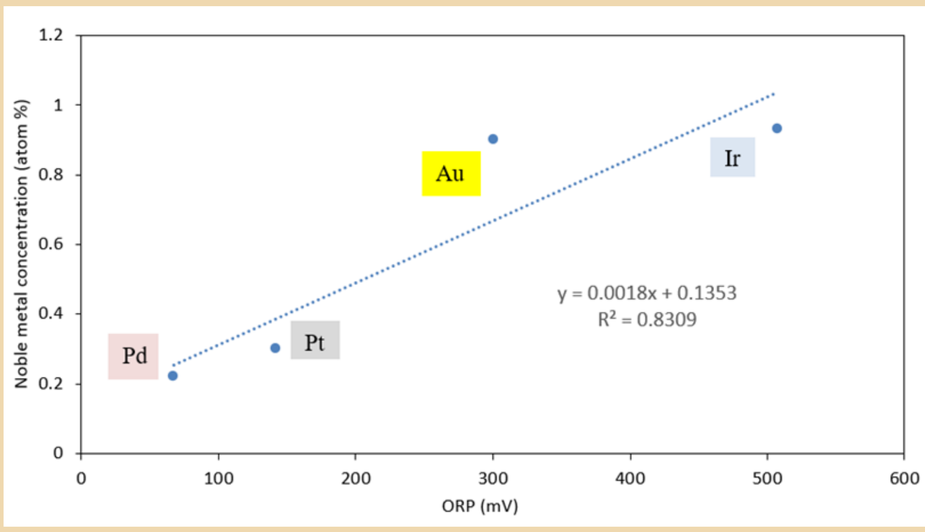


Figure 1. HR-STEM of gold atoms (red) and a small cluster (blue) on GNP; (A) STEM-BF, (B) HAADF; (C) Bright and dark field pictures superimposed; Disordered GNP zone (yellow).

Figure 2. Metals on GNP versus ORP.



The measured oxidation-reduction potential (ORP) correlates with the metal content.

Wasser 2026

Literature
Konradt, N. et al. Kinetics and Products of the Reaction of Graphene Nanoplatelets with Noble Metal Ions to Nanocomposites with Single Atoms and Clusters. *Materials Plus* **2024**, 121–153. https://doi.org/10.37256/mp.3220244863.