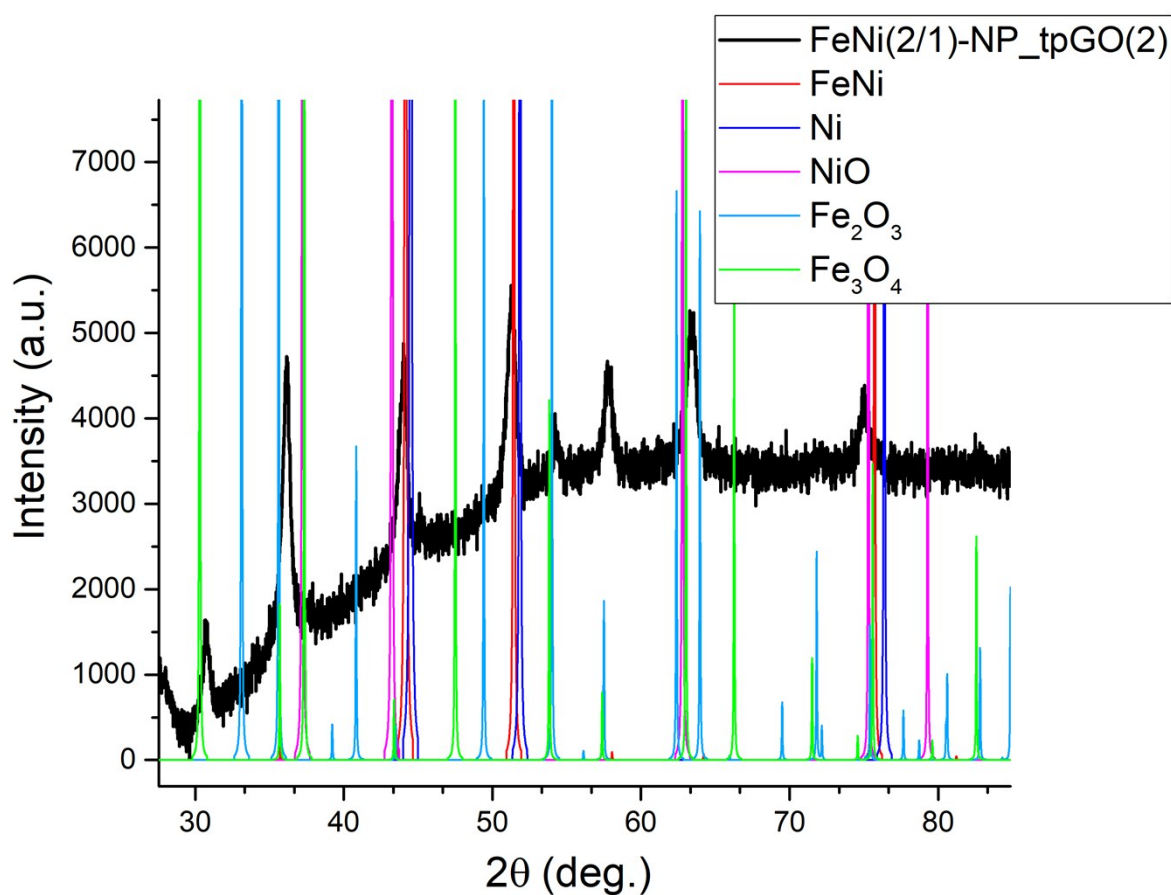
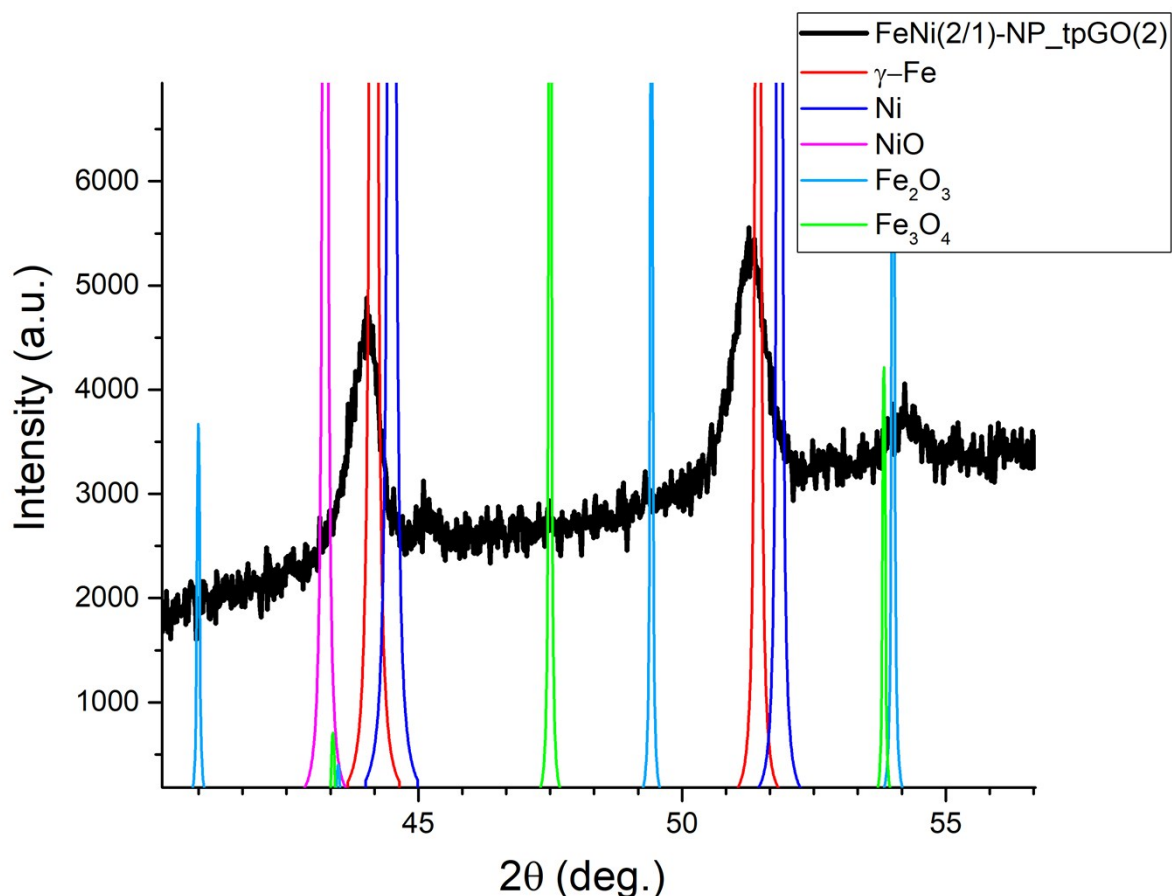


## Supplementary Information for Growth of the invar nanoparticles on the graphene oxide support

### 1. The sample prepared with the original Fe<sup>3+</sup>/Ni<sup>2+</sup> ratio 2/1

In a control experiment we took Fe<sup>3+</sup> and Ni<sup>2+</sup> in the ratio 2/1, i.e. theoretically relevant for invar. The product, obtained after the two-step preparation process (impregnation and annealing) was characterized by XRD, Mossbauer spectroscopy, and SEM. The XRD pattern (Fig. S1) shows the signals at 43.4°, 50.6°, and 74.5°, that can be ascribed to the (111), (200), and (220) crystal planes of the FeNi alloy, or to fcc Fe. The XRD pattern contains also signals of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and NiO. In this respect, this sample is similar to that, described in the main text (Fig. 3).



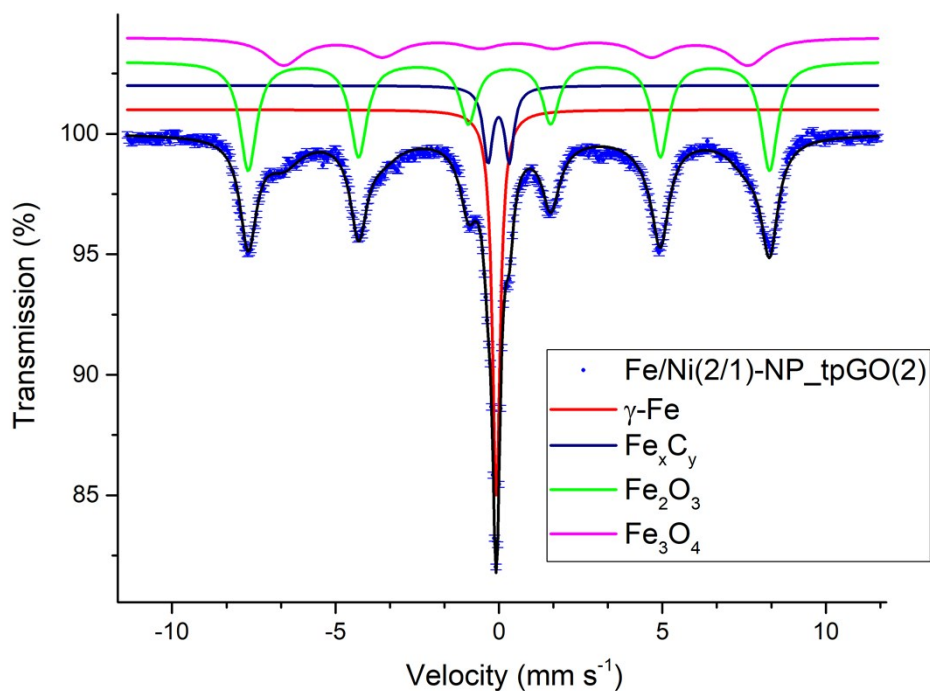


**Figure S1.** The XRD data for the Fe/Ni-NP\_tpGO sample obtained at the original Fe<sup>3+</sup>/Ni<sup>2+</sup> ratio 2/1. Top: full two theta angle range; bottom: extension of the 40° - 55° region.

However, the Mossbauer data for this sample is very different (Fig. S2, Table S1). The main product is not the FeNi alloy, but Fe<sub>2</sub>O<sub>3</sub>. The composite contains also iron carbide, Fe<sub>3</sub>O<sub>4</sub>, and gamma-iron [1]. Thus, the signals at 43.4°, 50.6°, and 74.5° on the XRD spectrum (Fig. S1), are associated with gamma-iron, but not with the FeNi alloy.

The XPS data shows presence of iron in the quantity of 3.5% (Fig. S3). However, nickel was not even detected in this sample. The detection level of the instrument toward nickel is ~0.4 %. Thus, we can state that the Fe/Ni ratio in the sample is >9/1.

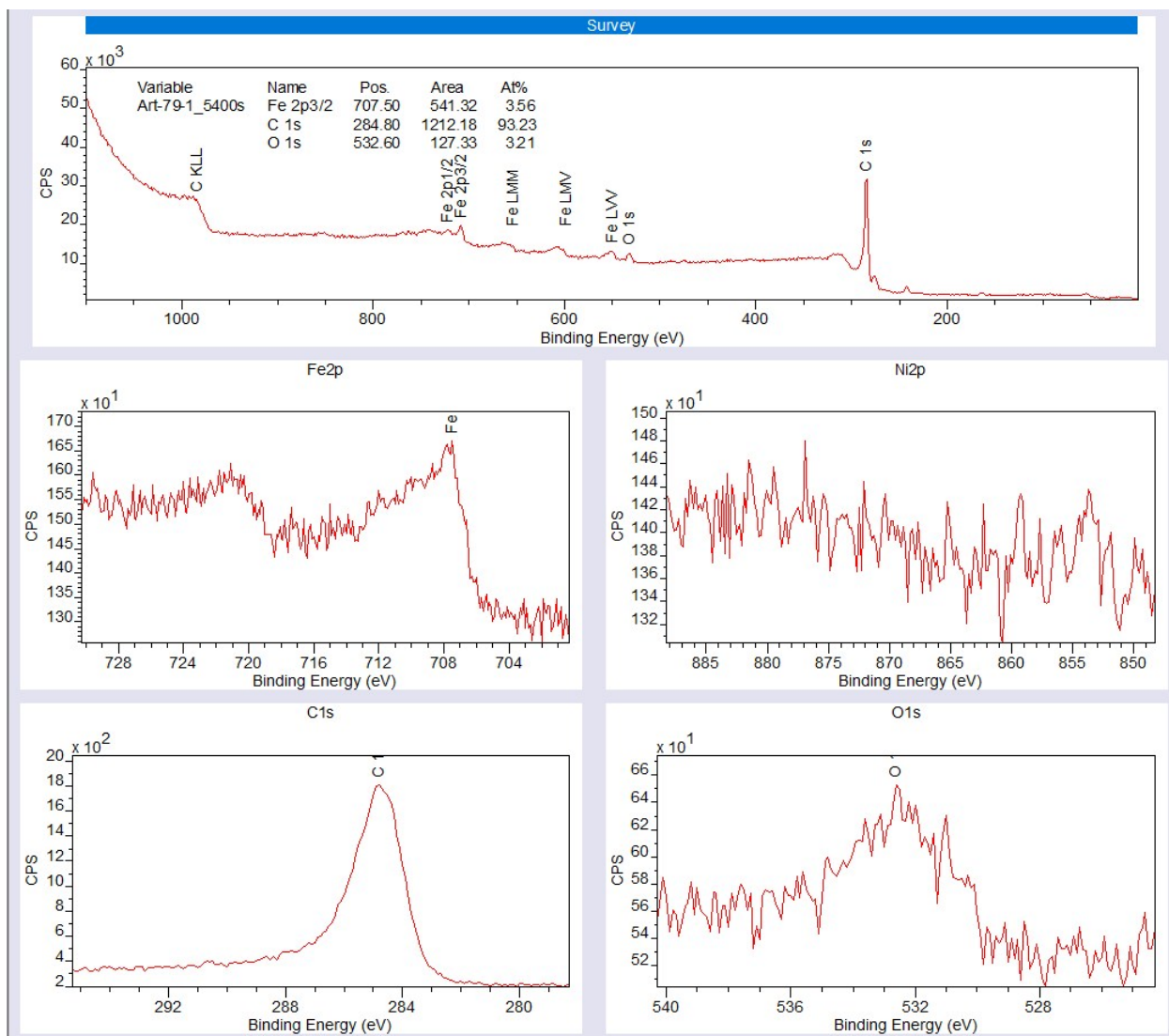
The shape of the as-grown nanocrystals (Fig. S4) is also different from the crystals of FeNi (Fig. 5 of the main text). Thus, the use of the theoretical Fe<sup>3+</sup>/Ni<sup>2+</sup> ratio 2/1 on the impregnation step does not lead to formation of the invar alloy nanoparticles. Most likely, this is related to the difference in the affinity of the two ions toward GO, as will be shown below.



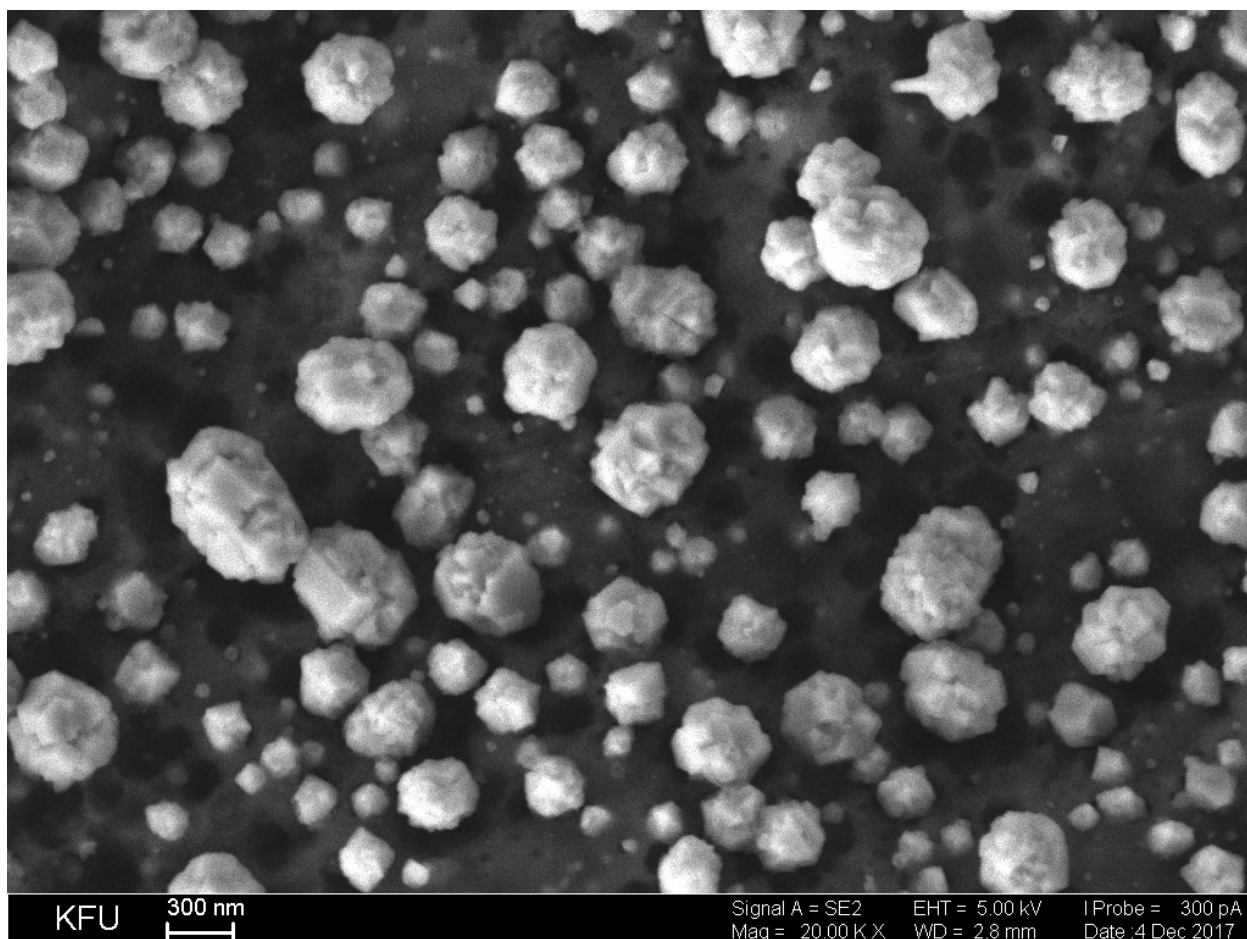
**Figure S2.** The Mossbauer data for the Fe/Ni-NP\_tpGO sample obtained at the original Fe<sup>3+</sup>/Ni<sup>2+</sup> ratio 2/1. Measured at 300 K.

**Table S1.** The content of the different iron phases in the Fe/Ni-NP\_tpGO sample obtained at the original Fe<sup>3+</sup>/Ni<sup>2+</sup> ratio 2/1, based on the Mossbauer spectroscopy data. Measured at 300 K.

Component	Phase	$\delta$ (mm/s), $\pm 0.01$ mm/sec	$H$ (kOe), $\pm 1$ kOe	Contribution (%), $\pm 0.5\%$
Singlet	$\gamma$ -Fe	-0.08		17.8
Doublet	Fe <sub>x</sub> C <sub>y</sub>	-0.004		8
Sextet 1	Fe <sub>2</sub> O <sub>3</sub>	0.31	493.8	51.2
Sextet 2	Fe <sub>3</sub> O <sub>4</sub>	0.53	439.8	23



**Figure S3.** for the Fe/Ni-NP\_tpGO sample obtained at the original Fe<sup>3+</sup>/Ni<sup>2+</sup> ratio 2/1.

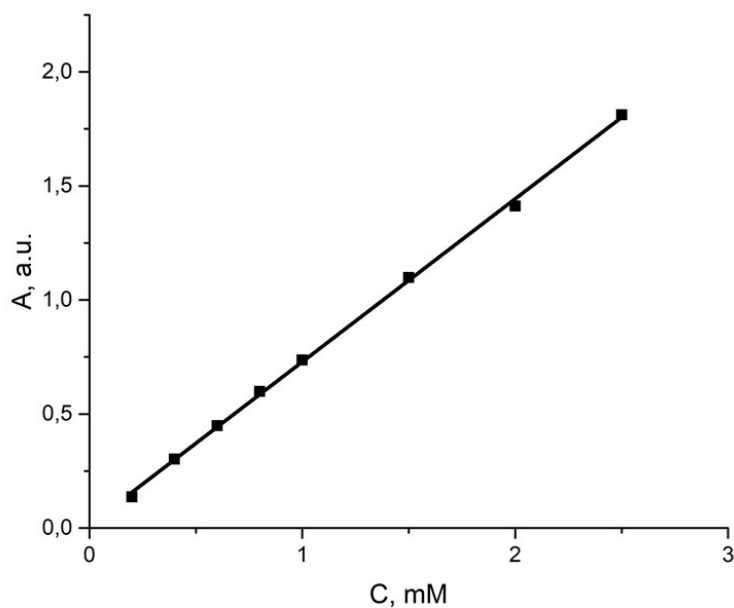


**Figure S4.** The SEM image of the Fe/Ni-NP\_tpGO sample obtained at the original Fe<sup>3+</sup>/Ni<sup>2+</sup> ratio 2/1.

## 2. The affinity of the Fe<sup>3+</sup> and Ni<sup>2+</sup> ions toward GO

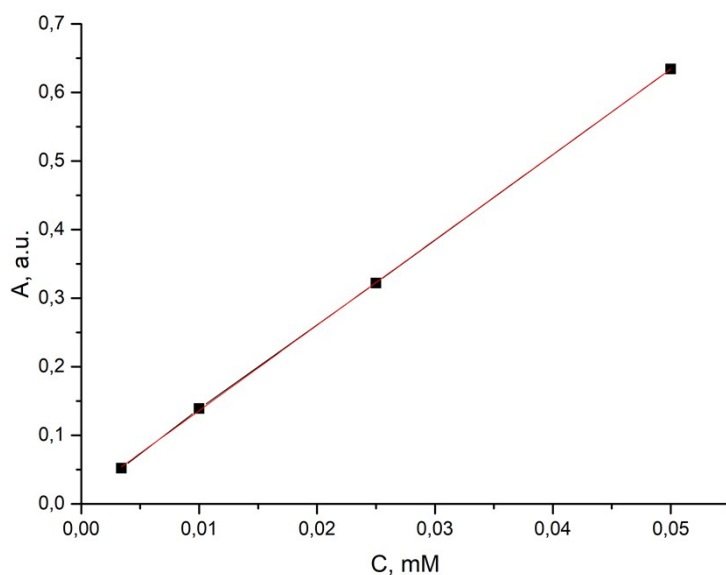
To attain the theoretical Fe/Ni ratio 2/1 of the ions, adsorbed on the GO surface, one needs to determine the respective affinities of Fe<sup>3+</sup> and Ni<sup>2+</sup> toward GO, which are not equal.

To determine the sorption capacity of GO toward Fe, the analytical method based on the sulfosalicylic acid (SSA) indicator was used. First, the calibration curve was built as the following. Six solutions of Fe(NO<sub>3</sub>)<sub>3</sub> with concentrations of 0.2 mM, 0.4 mM, 0.6 mM, 0.8 mM, 1mM, and 2.5 mM in 10 mL fixanal solution were prepared. Then 0,1 mL of 20% (w/v) sulfosalicylic acid solution was added to each solution and mixed. All solutions became crimson color. Then the absorbance at 507 nm relative to the reference solution (0.1 mL of SSA in fixanal solution) was measured for each solution with the use of the Hitachi U-2900 UV-Vis Double Beam Spectrophotometer. Then absorption vs concentration graph for these points was plotted (Fig. S4).



**Figure S5.** Calibration curve for iron ion analysis by UV-Visible spectrophotometric technique

To determine the sorption capacity of GO toward Ni, the analytical method with the use of the dimethylglyoxime (DMG) method was employed. To build the calibration curve, the four solutions with exact concentration of nickel ions of 0.0034 mM, 0.01 mM, 0.025 mM, and 0.05 mM in 50 mL of solution, consisting of 10 mL 14M  $\text{NH}_4\text{OH}$ , 0.2 mL of 1% iodine and 1 mL of 1% dimethylglyoxime in ammonia solution, were prepared. After the dimethylglyoxime addition, all solutions became orange color. Then the absorbance at 460 nm relative to water was measured for each solution. Then absorption vs. concentration graph for these points was plotted (Fig. S2).



**Figure S6.** Calibration curve for nickel ion analysis by UV-Visible spectrophotometric technique

The sorption capacity of GO toward the two metals.

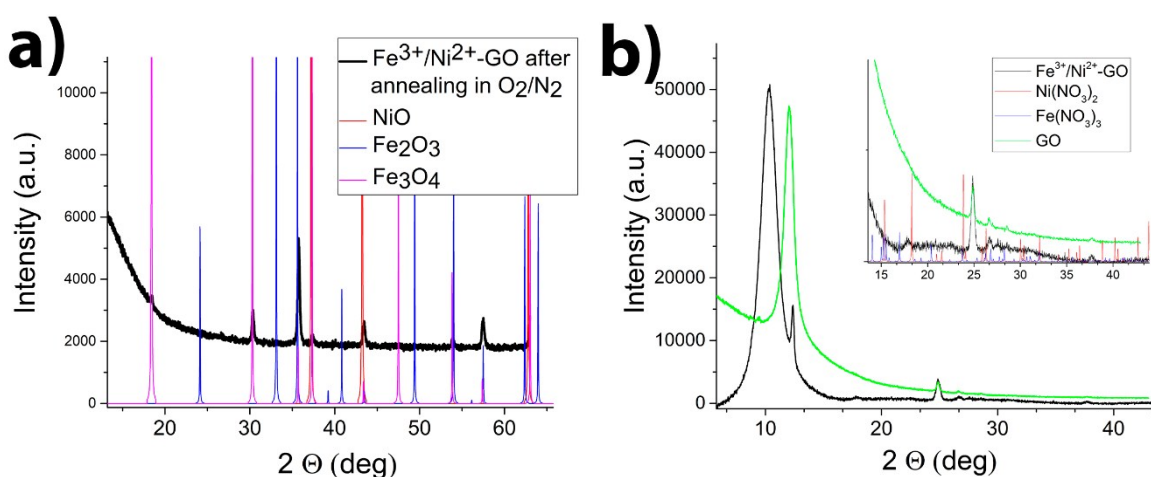
$\text{Fe}(\text{NO}_3)_3$  solution (15 mL, 0.08%) was added to GO solution (15.0 mL, 0.4%) with stirring. Thus, the solution with concentration of 1 mM with respect to the iron ions and 0.2% with respect to GO was prepared. The solution was further stirred on a magnetic stirrer for 15 minutes. The resulted solution was centrifuged  $\sim 20$  min at 6000 rpm until complete separation of GO, and the supernatant was decanted. 2 mL of the supernatant was diluted with fixanal to 10 mL. Then 0,1 mL of 20% (w/v) sulfosalicylic acid solution was added and mixed. Then the absorbance at 507 nm was measured. Taking into account dilution factor, the concentration of iron ions in the supernatant was determined as **0.04 mM**.

$\text{Ni}(\text{NO}_3)_2$  solution (50 mL, 0,6%) was added to GO solution (50.0 mL, 0.4%) with stirring. Thus, the solution with concentration of 1 mM with respect to the Ni ions and 0.2% with respect to GO was prepared. The dispersion was further stirred on a magnetic stirrer for 15 minutes. The resulted dispersion was centrifuged  $\sim 20$  min at 6000 rpm until complete separation of GO, and the supernatant was decanted. 2 mL of the supernatant was added to 10 mL of  $\text{NH}_4\text{OH}$  (14M), 0.2 mL of 1% iodine and 1 mL of 1% dimethylglyoxime solution, and was diluted with water to 50 mL. Then the absorbance at 460 nm relative to the reference solution was measured. Taking into account the dilution factor, the concentration of  $\text{Ni}^{2+}$  in the supernatant was determined as **0,6mM**.

Thus, the GO affinity toward  $\text{Fe}^{3+}$  is significantly higher than that toward  $\text{Ni}^{2+}$ . The obtained data was assessed by different approaches. Finally, the Fe/Ni ratio on the impregnation step was chosen as 1/7.

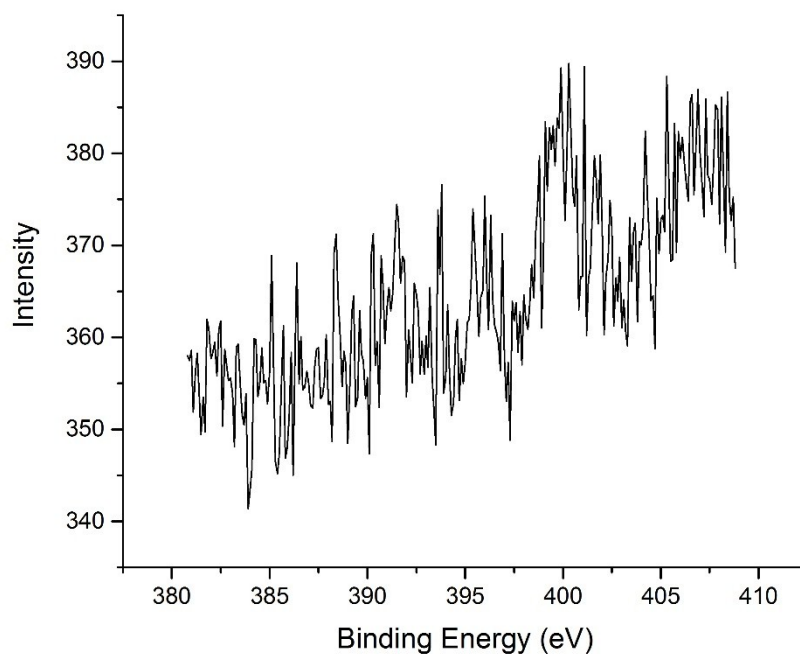
### 3. Additional data for the $\text{Fe}^{3+}/\text{Ni}^{2+}$ -GO composite, discussed in the main text

#### 3.1. Additional XRD data



**Figure S7.** a) The XRD pattern of  $\text{Fe}^{3+}/\text{Ni}^{2+}$ -GO after annealing in synthetic air ( $\text{O}_2/\text{N}_2$ ). b) The XRD pattern of  $\text{Fe}^{3+}/\text{Ni}^{2+}$ -GO. The modeled patterns for bulk forms of  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Ni}(\text{NO}_3)_2$ , and the experimental spectrum for parent GO are given as reference. The data shows that  $\text{Fe}^{3+}/\text{Ni}^{2+}$ -GO does not contain the two nitrates. We were not able to assign the two weak reflexes at 12.4 and 24.8  $2\theta$ , since they do not relate to the known salts and oxides of the two metals.

### 3.2. Additional XPS data



**Figure S8.** The N1s XPS spectrum of  $\text{Fe}^{3+}/\text{Ni}^{2+}$ -GO, obtained during the liquid phase impregnation step. The lack of definitive signals, especially at 405 eV, where nitrates should manifest, if present, confirms that the nitrate ions were efficiently removed during the purification procedures.