Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for: Adjusting the thermoelectric properties in copper(I) oxide - graphite - polymer pastes and the applications of such flexible composites

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1 Experimental procedures

1.1 Measurement sequence

During the measurement, the temperature setting and data acquisition are made automatically, to improve the reproducibility of the results. The temperature of the Deben Peltier heating stage is adjusted according to a temperature program and read every 10 s, using instructions sent over a USB-to-RS232 adapter cable by the software CoolTerm 1.4.4. The steps of this temperature program are graphically illustrated in Fig. S1 and explained in detail below. The voltage or electrical resistance between the two copper contacts is also measured every 10 s using the software FlukeView Forms 3.4.

As it can be seen in Fig. S1, a small period of tempering at 393 K takes place before the measurements. Since the electrical contact is made between inhomogeneous particles, this tempering is required to decrease the electrical resistance of the samples and to permit the determination of the thermoelectric properties. A short time of cooling at 283 K is also beneficial, ensuring that all measuring points (between 283 K and 373 K) are obtained in the same conditions.

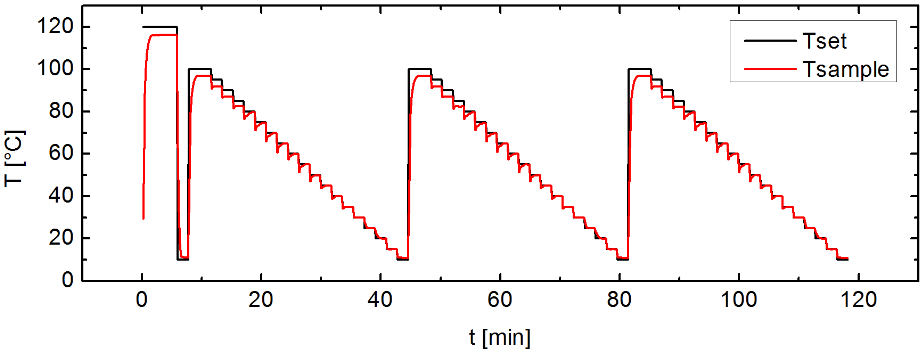


Figure S1: The step-wise changes of the temperature during a measurement. The black line represents the desired temperature, while the red line represents the temperature achieved by the heating plate without a sample (in air), registered by its internal thermometer.

The instructions for the heating plate are generated using a programming code, written in C++ (see Fig. S2). The code reads several parameters from an input file ("parameters.txt"), which are used to model the temperature program, and then writes the sequence in the output file ("code.txt"). The description of the parameters read in the input and printed in the instructions file is given below, in Table S1.

Table S1: Input variables and written commands for the control of the Deben Peltier heating stage. The values corresponding to the temperature program in Fig. S1 are also presented.

Parameter	Value	Description
dT [K]	5	temperature difference between 2 consecutive points
dmin [min]	2	time between 2 consecutive temperatures
dmess [s]	10	time between two read points (limited to 10 s by CoolTerm)
Tmin [°C]	10	lowest temperature for measurements
Tmax [°C]	100	highest temperature for measurements
cycl [-]	3	number of measurement cycles
t120 [min]	6	time for tempering at 120 °C
t10 [min]	2	time for cooling at 10 °C
t100 [min]	4	time for tempering at Tmax
"3120\n"	3120	set T > 120 °C > send
"?\n"	?	ask T > send
"A\n"	A	heat plate off > send

```
#include<iostream.h>
#include<stdio.h>
#include<conio.h>
#include<math.h>

 int main()
 {int dT,Tmin,dmin,dmess,Tmax,T,cycl,m,n,i,j,k;
 int t120,t10,t100,t120i,t10i,t100i;

 freopen("parameters.txt","r",stdin);
 freopen("code.txt","w",stdout);
 scanf("%d%d%d%d%d%d",&dT,&dmin,&dmess,&Tmin,&Tmax,&cycl);
 scanf("%d%d%d%d%d%d",&t120,&t10,&t100);

m=(Tmax-Tmin)/dT;
n=dmin*60/dmess;

 printf("3120\n");
 t120i=t120*60/dmess;
 for(i=1;i<t120i;i++)
    printf("?\n");

 printf("310\n");
 t10i=t10*60/dmess;
 for(j=1;j<t10i;j++)
     printf("?\n");

 for(i=1;i<=cycl;i++)
          {printf("3%d\n",Tmax);
           t100i=t100*60/dmess;
           for(j=1;j<t100i;j++)
              printf("?\n");

           for(j=1;j<=m;j++)
                    {T=Tmax-j*dT;
                     printf("3%d\n",T);
                     for(k=1;k<n;k++)
                               printf("?\n");
                    };
          };
 printf("A\n");
 }
```

Figure S2: C++ programming code employed to write the instructions, which are used by CoolTerm 1.4.4 to control the Deben Peltier heating stage. Variables and output are further explained in Table S1.

2 Statistic data interpretation

The average value ($\bar{S}$) and the uncertainty (σ_S) of the Seebeck coefficient are determined from the linear regression through the measured data points. These two results are taken from Origin, without further handling.

The average value ($\bar{R}$) and the uncertainty (σ_R) of the electrical resistance is calculated with the help of Eq. 1 and Eq. 2, with $n = 3$.

$$\bar{R} = \frac{\sum\limits_{i=1}^{n} R_i}{n} \tag{1}$$

$$\sigma_R = \sqrt{\frac{\sum\limits_{i=1}^{n} (R_i - \bar{R})^2}{n-1}} \tag{2}$$

Using Eq. 3, we determine the average values of the electrical conductivities ($\bar{\sigma}$). The length ($l = 4.6\ mm$), and area ($A = \pi r^2 = 78.5\ mm$) of the samples are constrained by the measurement cell. For the calculation of the uncertainties of σ and of the power factor ($PF = \sigma S^2$), Eq. 4 and Eq. 5 are employed.

$$\bar{\sigma} = \frac{l}{\bar{R} \cdot A} \tag{3}$$

$$\%\sigma_\sigma = \%\sigma_R \tag{4}$$

$$\%\sigma_{PF} = \sqrt{\%\sigma_\sigma^2 + \%\sigma_S^2 + \%\sigma_S^2} \tag{5}$$

3 Further comments and supplementary figures

3.1 Calculation of the Seebeck coefficient

The voltage of our investigated samples is linearly dependent on the temperature applied at the lower end, in the range of 283 K to 373 K. Therefore, a linear fit can be found for the mentioned interval (see Fig. 1(c) from the main article). According to the integral method of determining the Seebeck coefficient, the differential of the fit ($dU_{ab}(T_1, T_2)$) with respect to the temperature at the hot side (T_2) represents the Seebeck coefficient at that point (see Eq. 6 taken from Ref. S1). Since a linear fit is appropriate for the mentioned interval, its differentiation with respect to T_2 gives a constant, the slope. As a result, we can assume, that the Seebeck coefficient is constant in the given range.

$$S_{ab}(T_2) = S_b(T_2) - S_a(T_2) = \frac{dU_{ab}(T_1, T_2)}{dT_2} \tag{6}$$

To investigate the difference between the results, we have also calculated the Seebeck coefficient by the differential method for the temperature of 298 K. In this case, we have determined the Seebeck coefficient as the slope of the linear fit over a smaller temperature interval, between 278 K and 308 K. The results can be seen in Fig. 1(b) from the main paper. The Seebeck coefficient has a value of $611 \pm 51\,\mu\mathrm{V\,K^{-1}}$, in comparison to $649 \pm 6\,\mu\mathrm{V\,K^{-1}}$ for the integral method. The results are similar, with deviations caused by the uncertainty, which is larger for a smaller amount of measured points. At the same time, the temperature difference becomes more difficult to control, when $\mathrm{T_2}$ approaches room temperature ($\mathrm{T_1}$). This can be especially observed for the data point at 298 K.

The average Seebeck coefficients obtained for the interval of 283-373 K are plotted in Fig. S3, as a function of the molar ratio of graphite. The uncertainties of the points appear smaller than those in the main article, as explained above. The data points are again fitted as logistic sigmoid functions (see Eq. 7, as given in Origin; its inflection point (x_{flex}, y_{flex}) is presented in Eq. 8), and the coefficients are compared with those obtained from the differential method, in Table S2. The similarity of the curves presented here with those from the main article further supports the legitimacy of both methods, integral and differential, in our case.

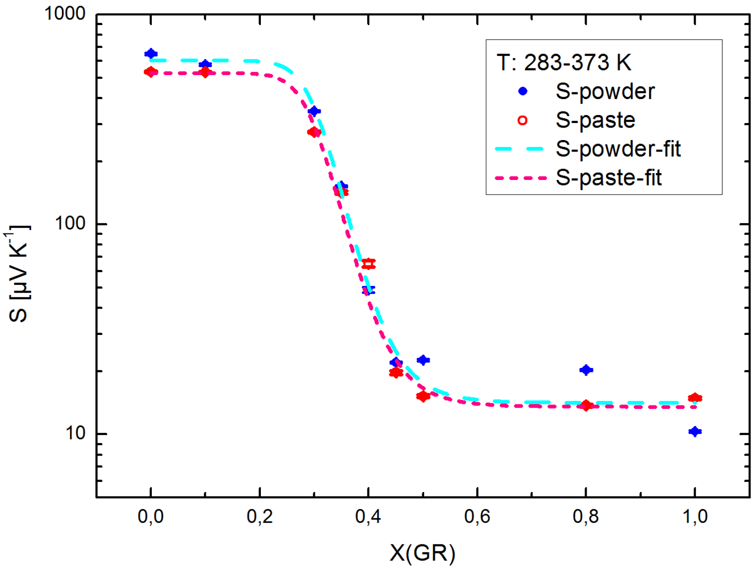


Figure S3: Logarithmic plot of the Seebeck coefficients of graphite-Cu_2O mixtures, as a function of graphite molar fraction, X(GR). The sigmoid fits of the data points are also depicted.

$$y = \frac{A1 - A2}{1 + (x/x0)^p} + A2 \tag{7}$$

$$(x_{flex}, y_{flex}) = \left(x0 \sqrt[p]{\frac{p-1}{p+1}}, \frac{(p+1)A1 + (p-1)A2}{2p} \right) \tag{8}$$

Table S2: Parameters from the logistic sigmoid fits of the determined Seebeck coefficients, as a function of graphite molar fraction (see Eq. 7).

Sample	A1	A2	x0	p
Powder-differential	582.7±126.1	11.27±2.20	0.309±0.017	11.15±2.19
Paste-differential	487.8±49.5	11.32±1.09	0.311±0.008	12.11±1.28
Powder-integral	603.5±97.8	14.12±2.37	0.310±0.014	10.73±1.86
Paste-integral	525.6±32.6	13.53±1.25	0.306±0.006	10.42±1.06

3.2 Electrical conductivity

The electrical resistances of the investigated samples have been determined in a 2-point (2P) configuration and statistically handled according to the mentioned procedure (Eq. 1 and Eq. 2). A comparison of some values with those obtained from a quasi-4-point (q4P) method is given in Table S3. The q4P measurements are made by applying a constant current through the copper wires (using a Delta Elektronika SM 3004-D power source), while the voltage drop is recorded by the Fluke 289 multimeter. In general, the q4P method delivers lower values of the electrical resistance. Nevertheless, the differences are below 20% for the same sample, which is within the typical experimental error.[S2] Larger deviations can be caused by sample movement, which affects the variable electrical contacts between the micro- and nanograins. Even so, these values only differ within one order of magnitude, which is also visible in form of deviations from the sigmoid fits in the main article (Fig. 2(b)). Consequently, the quasi-4-point measurements confirm the suitability of the 2-point method for our investigations.

The electrical conductivities are plotted between 283 K and 373 K, for the powders in Fig. S4 and for the pastes in Fig. S5. A higher amount of graphite corresponds to a gradual increase in σ, which reaches 100 $\mathrm{S\,m^{-1}}$ for pure graphite. In this case, σ is also significantly higher for the powder than for the paste, while for other mixtures the two values are comparable. Although the two sets of results in Fig. S4 and Fig. S5 are not identical, a pattern of similarity can be observed between the behaviors of the electrical conductivity. σ usually grows with increasing temperature for the samples with predominant Cu_2O content, but on the other hand decreases at higher T in samples with a higher graphite amount.

Table S3: Comparison between 2-point (2P) and quasi-4-point (q4P) electrical resistance measurements (both at 298 K), for some selected samples. The corresponding electrical conductivities are also given.

Sample	R(2P)	σ(2P)	R(q4P)	σ(q4P)
	[Ω]	[S m^{-1}]	[Ω]	[S m^{-1}]
Cu_2O-powder	(1.67±0.06)·10^6	(3.50±0.12)·10^{-5}	(1.54±0.07)·10^6	(3.80±0.16)·10^{-5}
Cu_2O-paste	(7.01±0.18)·10^5	(8.36±0.21)·10^{-5}	(6.58±0.17)·10^5	(8.91±0.23)·10^{-5}
GR-powder	1.22±0.15	47.9±5.7	1.03±0.29	56.8±15.8
GR-paste-sensor	91.8±4.6	92.4±4.63	62.1±1.65	136.7±3.6

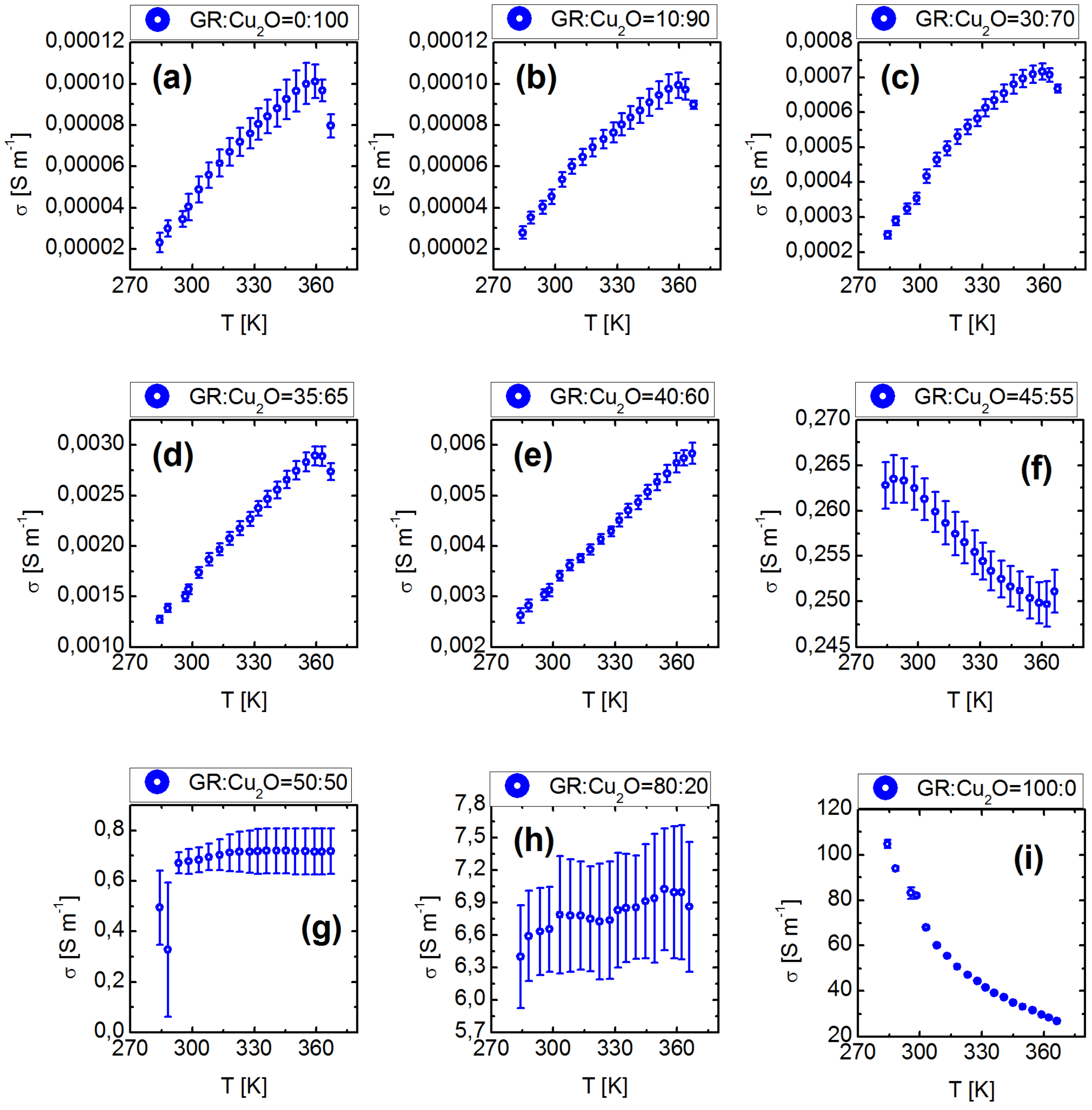


Figure S4: Dependence of the electrical conductivity on the heating temperature, in case of various powder samples.

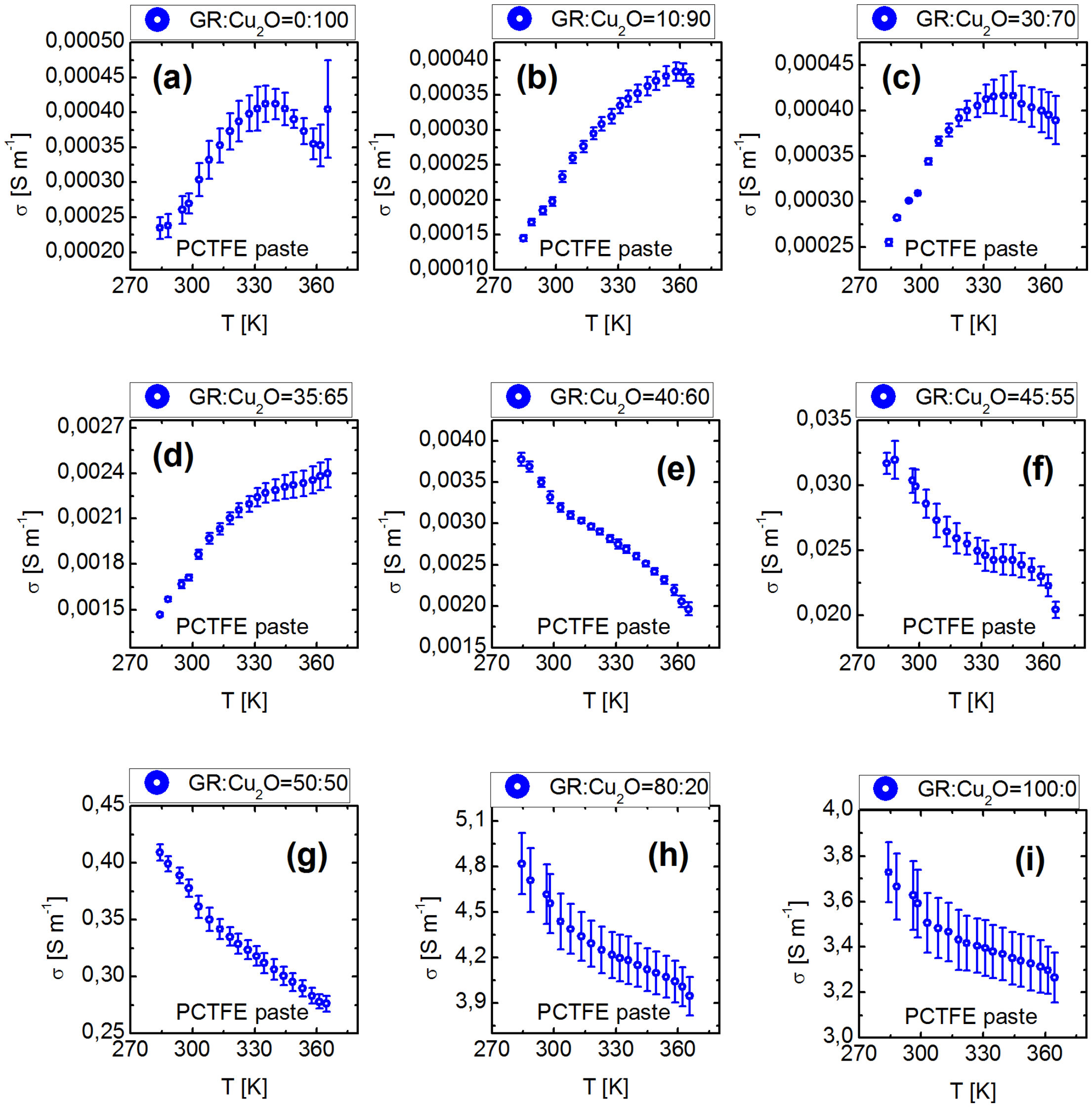
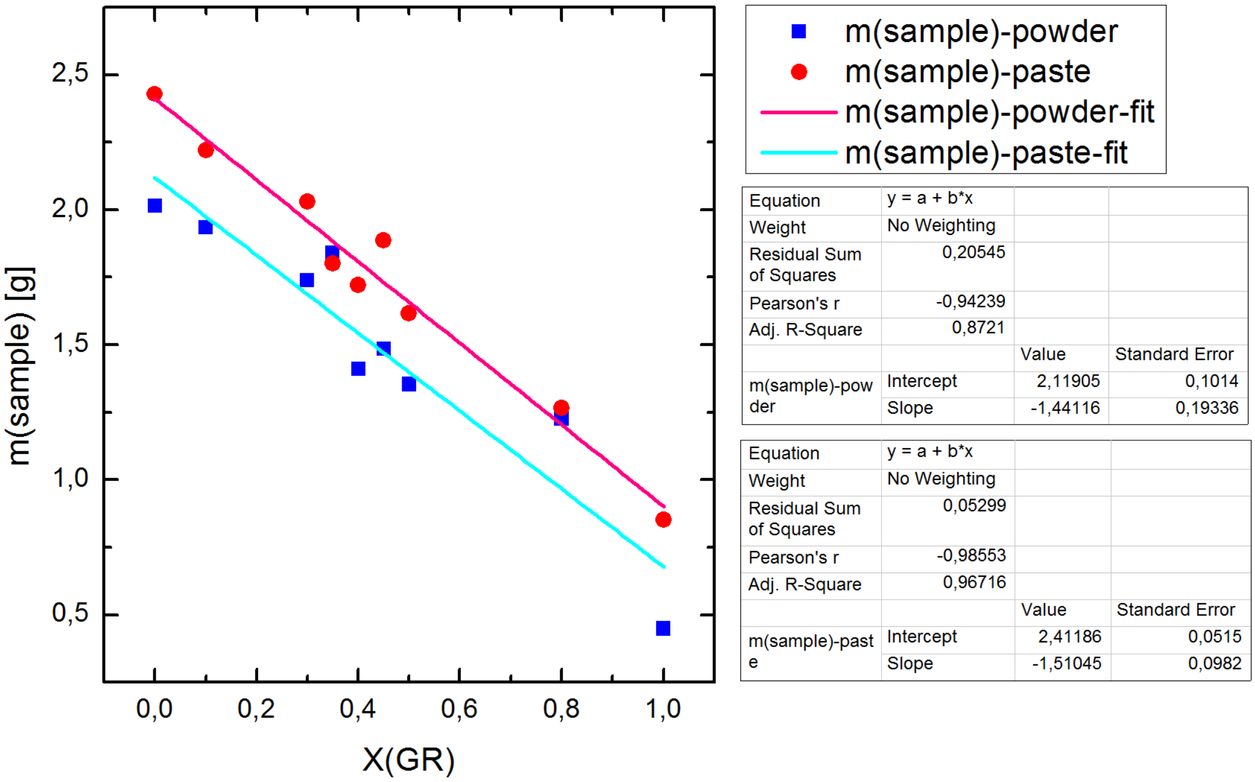


Figure S5: Dependence of the electrical conductivity on the heating temperature, in case of the paste samples.

3.3 Sample mass and homogeneity

Since the samples consist of powders and pastes instead of solid bulk materials, some degree of inhomogeneity can be expected. The main cause of this is the random distribution of the grain size and form (seen in Fig. 3 in the main article), which causes a mismatched packing of the particles. To evaluate the amount of this deviation, the mass of the various samples has been plotted as a function of the graphite molar fraction, X(GR), and the points have been linearly fitted (Fig. S6).



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,20545		
Pearson's r	-0,94239		
Adj. R-Square	0,8721		
		Value	Standard Error
m(sample)-powder	Intercept	2,11905	0,1014
	Slope	-1,44116	0,19336

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,05299		
Pearson's r	-0,98553		
Adj. R-Square	0,96716		
		Value	Standard Error
m(sample)-paste	Intercept	2,41186	0,0515
	Slope	-1,51045	0,0982

Figure S6: Plot of the sample masses as a function of the graphite molar fraction X(GR). The parameters of the linear fits are presented on the right side, as shown in Origin.

Looking at the data points and the parameters of their linear fits in Fig. S6, it becomes obvious, that the pastes are more homogeneous than their powder counterparts. This is also quantitatively described by the standard errors of the parameters for pastes, which are approximately half as low as those of the powders. This can be explained by the presence of the viscous polymer, which is not compressible and cannot be pressed out of the sample, as opposed to air. On the other hand, the powder particles could be pressed more or less together inside the measurement cell, which influences their packing, hence their density.

It is also worth observing, that the fitted lines of the two data sets are almost parallel. The difference in mass corresponds to the weight of the PCTFE polymer, which replaces air in case of the pastes. This fact can give a hint, that the unoccupied volume inside the measurement cell remains roughly constant, independent of the type of particles used here, Cu_2O ($<5\,\mu$m) or graphite ($<20\,\mu$m). If smaller, nanometer-sized graphite grains would have been used, they could have filled the space between large Cu_2O particles, therefore increasing the packing density and decreasing the space remaining for the polymer filler.

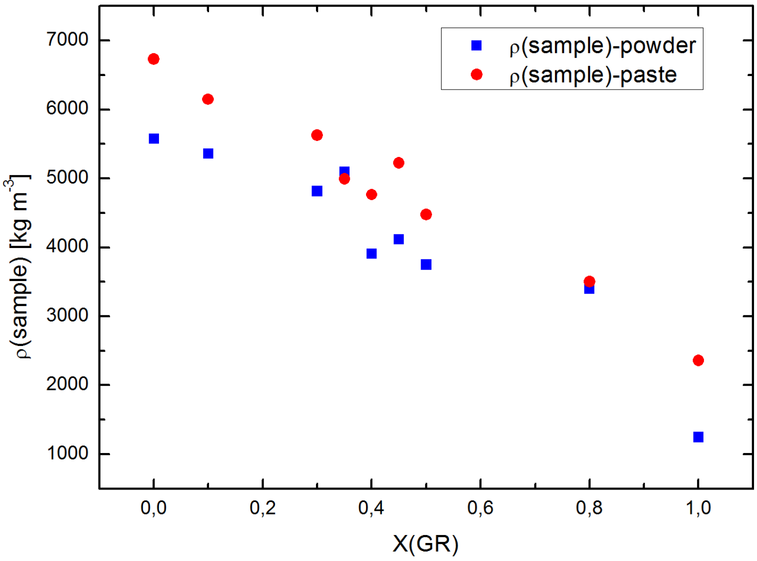


Figure S7: Density of the investigated mixtures in relation to the sample composition.

By dividing the presented masses by the volume of the measurement chamber ($V = \pi r^2 l = 3.61 \cdot 10^{-7}\, m^3$), the density of the samples has been obtained (presented in Fig. S7). In this way, the packing of the powder grains (the relative density of a sample with respect to the bulk substance) can be calculated. For example, the bulk densities of Cu_2O and single crystal graphite are $\rho_{Cu_2O,bulk} = 6.00\,\mathrm{g\,cm^{-3}}$ at 298 K[S3] and $\rho_{GR,bulk} = 2.25\,\mathrm{g\,cm^{-3}}$ at 293 K,[S4] which translates to relative packings of 93%, respectively 55% for the powders.

4 Manufacturing of a thermoelectric paste device

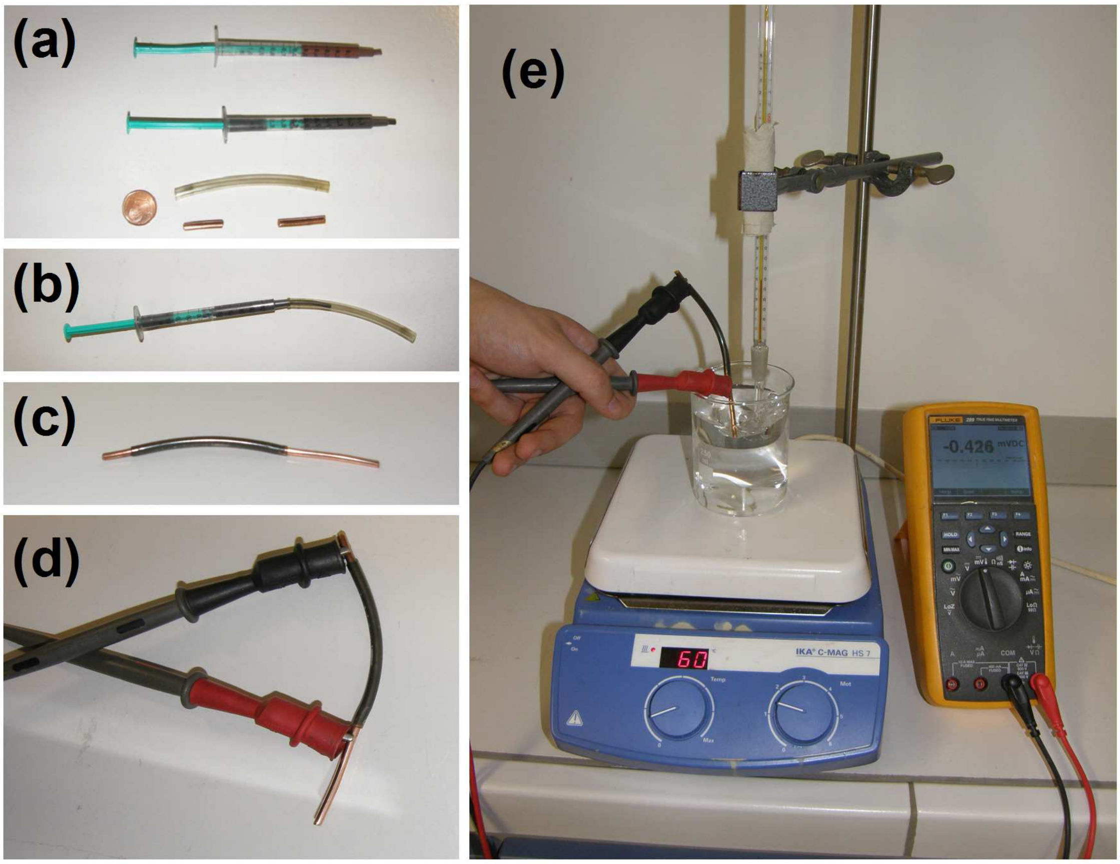


Figure S8: (a)-(c) The steps required to manufacture a thermoelectric device, which contains a graphite-PCTFE paste. (d)-(e) Example of application for the device as a temperature sensor and the recorded signal.

The simple fabrication process of a device, based on a thermoelectric paste, is illustrated in Fig. S8(a) to S8(c). The required components are presented in panel S8(a), from top to bottom in the following order: two 1 ml plastic syringes filled with GR-Cu_2O paste (molar ratio 35:65), respectively GR paste, a transparent rubber tube, two copper contacts and a 1 cent coin for comparison. After the GR-paste is pressed inside the tube (Fig. S8(b)), the two copper contacts are inserted at both ends, to seal its content from the outside (Fig. S8(c)).

In order to give an example for a possible use of this flexible thermoelectric device, we have mounted a larger copper contact at one side (seen in Fig. S8(c)-(e)). After its connection to the multimeter clips (in Fig. S8(d)), the device has been able to act as a thermometer. For this purpose, a glass of water has been heated at 324 K, using a common heating plate. The recorded voltage of approximately 0.42 mV corresponds to a temperature difference of roughly 33 K, when using the value of $12.6\pm1.0\,\mu\mathrm{V\,K^{-1}}$ for the Seebeck coefficient. Taking the uncertainty of the measurement into account, the result is in good agreement with the expected value of 30 K.

Notes and References

(S1) Martin, J.; Tritt, T.; Uher, C. *J. Appl. Phys.* **2010**, *108*, 121101.

(S2) Snyder, G. J.; Toberer, E. S. *Nat. Mater.* **2008**, *7*, 105–114.

(S3) Density of Cu_2O obtained using the fitted function from the Comsol Multiphysics 4.4 database.

(S4) Tyler, W. W.; Wilson, A. C. *Phys. Rev.* **1953**, *89*, 870–875.