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Supplementary information

AuCu bimetallic nanocluster-modified titania nanotubes for photoelectrochemical water splitting: composition-dependent atomic arrangement and activity

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Contents:

Supplementary Tables

Table S1. Summary of structural results of Au L_3-edge EXAFS refinements of Au_xCu_{1-x}/TNT (x = 0.75, 0.5, 0.25).

	$Au_{0.75}Cu_{0.25}$			$Au_{0.5}Cu_{0.5}$			$Au_{0.25}Cu_{0.75}$		
shell	**N**	**R (Å)**	**A (Å²)**	**N**	**R (Å)**	**A (Å²)**	**N**	**R (Å)**	**A (Å²)**
Au-Au	10.8(6)	2.850(7)	0.020(1)	11.4(7)	2.844(7)	0.022(1)	5.5(3)	2.81(1)	0.023(2)
Au-Cu	0.6(1)	2.64(3)	0.03(2)	-	-	-	5.5(5)	2.66(1)	0.024(2)
	R factor = 42% E_F = -7.9(9) eV			R factor = 38% E_F = -7.9(9) eV			R factor = 37% E_F = -7.6(9) eV		

N = coordination number
R = radial distance
A = Debye-Waller term ($A=2\sigma^2$ with σ the Debye-Waller factor)
E_F = Contribution of the wave vector of the zero-photoelectron relative to origin of k

Table S2. Summary of structural results of Cu K-edge EXAFS refinements of Au_xCu_{1-x}/TNT (x = 0.75, 0.5, 0.25, 0).

	$Au_{0.75}Cu_{0.25}$			$Au_{0.5}Cu_{0.5}$			$Au_{0.25}Cu_{0.75}$			Cu		
shell	**N**	**R (Å)**	**A (Å²)**	**N**	**R (Å)**	**A (Å²)**	**N**	**R (Å)**	**A (Å²)**	**N**	**R (Å)**	**A (Å²)**
Cu-O	1.8(3)	1.93(2)	0.013(6)	2.9(3)	1.96(1)	0.009(2)	1.93(3)	1.94(2)	0.019(5)	2.27(2)	1.93(1)	0.016(2)
Cu-Au	1.9(6)	2.63(6)	0.03(2)	-	-	-	4.56(9)	2.63(2)	0.029(5)	-	-	-
Cu-Cu	2.3(6)	2.57(4)	0.03 (1)	1.5(5)	2.52(3)	0.02(1)	1.16(3)	2.53(4)	0.034(2)	3.1(6)	2.8(2)	0.023(6)
Cu-Cu	0.9(2)	2.70(4)	0.011(7)	1.2(4)	2.70(3)	0.009(5)	0.69(1)	2.78(5)	0.042(3)	2.99(5)	3.17(3)	0.028(9)
Cu-Cu	1.4(3)	2.84(4)	0.02 (1)	2.0(8)	2.89(6)	0.027(2)				2.91(8)	2.99(3)	0.0181(6)
Cu-Cu				3.3(6)	3.12(3)	0.03(1)				1.37(3)	2.56(3)	0.028(9)
	R factor = 45% E_F = 3.8(9) eV			R factor = 32% E_F = -1.9(9) eV			R factor = 45% E_F = 6.6(9) eV			R factor = 33% E_F = -9.5(9) eV		

N = coordination number
R = radial distance
A = Debye-Waller term ($A=2\sigma^2$ with σ the Debye-Waller factor)
E_F = Contribution of the wave vector of the zero-photoelectron relative to origin of k

Supplementary Figures

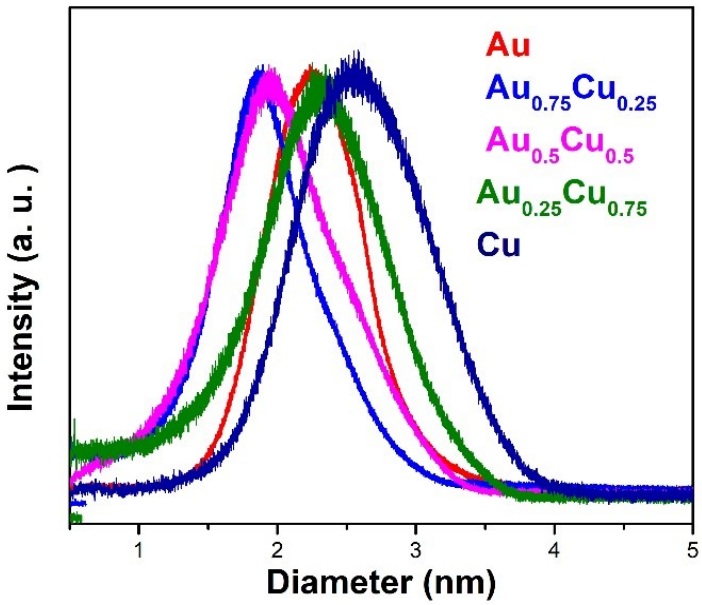

Figure S1. Size distributions of Au_xCu_{1-x} (x = 1, 0.75, 0.5, 0.25, and 0) NCs as measured by time-of-flight mass spectrometry prior to cluster deposition. The size distributions are normalized to their highest intensity. The cluster diameter is deduced from the measured mass assuming a spherical shape and bulk density.

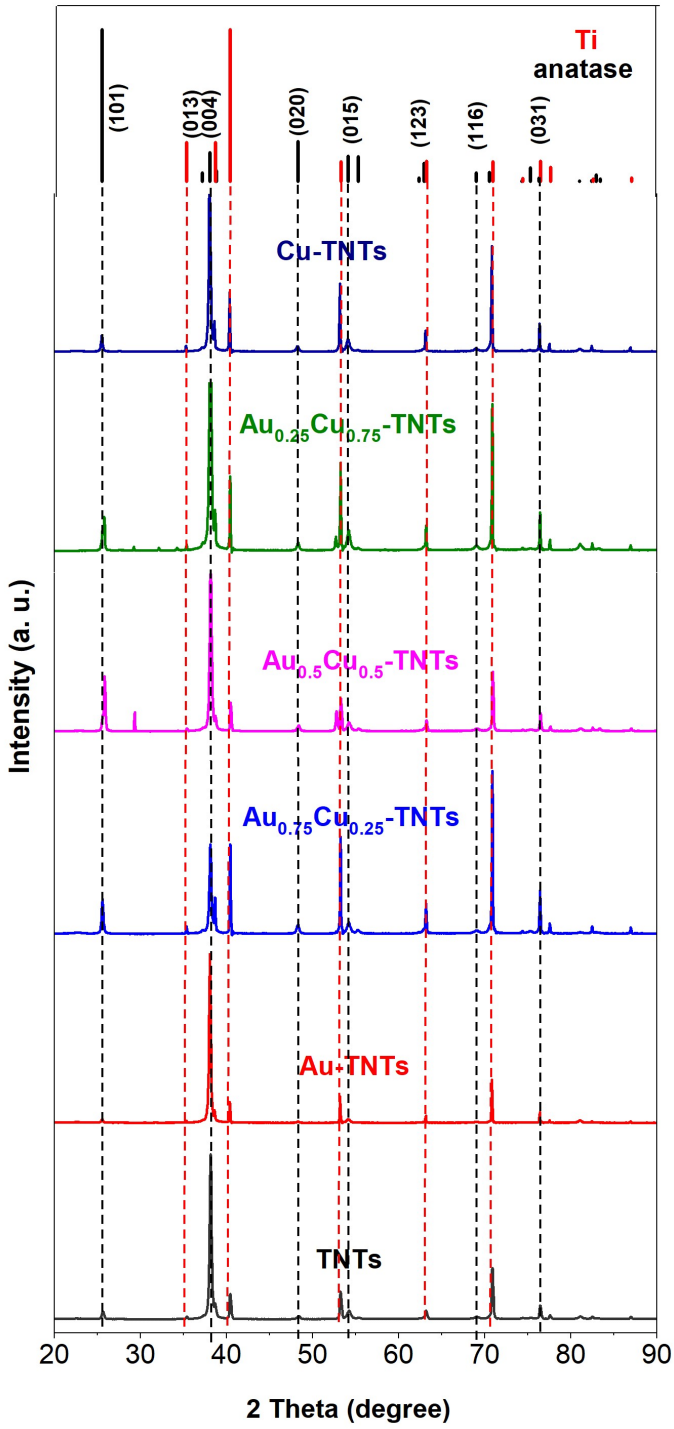

Figure S2. XRD patterns of pristine TNTs and Au_xCu_{1-x} (x= 1, 0.75, 0.5, 0.25 and 0) NC modified TNTs electrodes with NC loading of 4 ML.

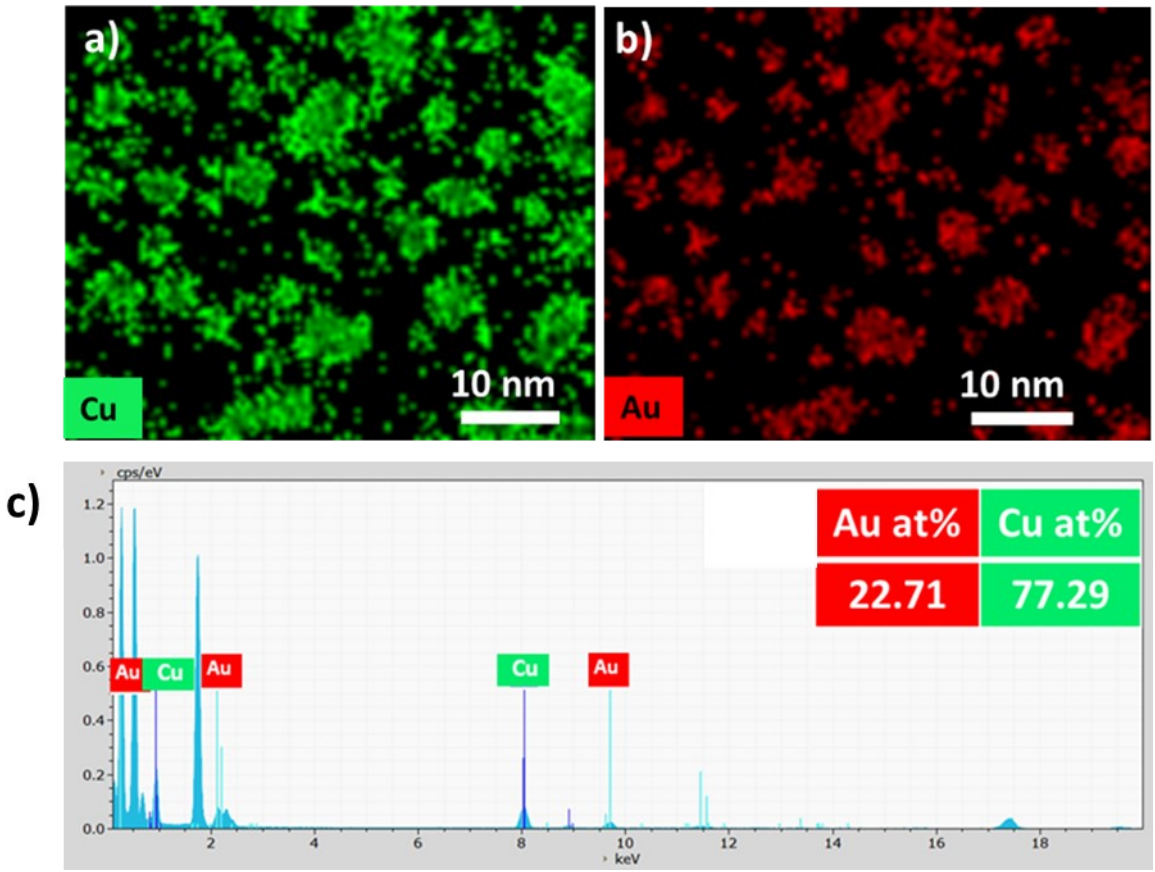

Figure S3. EDX elemental mapping the $Au_{0.25}Cu_{0.75}$ /TNT electrode with a) Cu and b) Au (red). c) EDX patterns of the same sample.

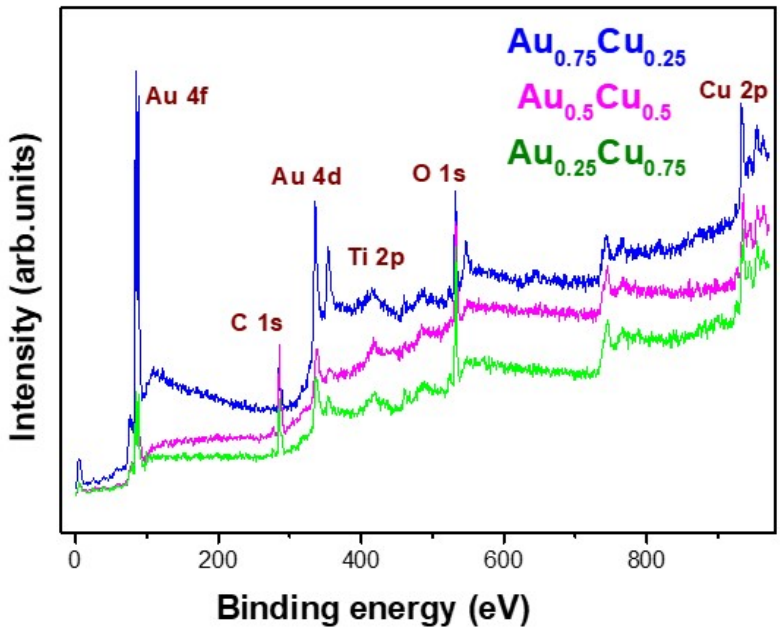

Figure S4. XPS survey spectra recorded for Au_xCu_{1-x} /TNT with x = 0.75, 0.5, and 0.25.

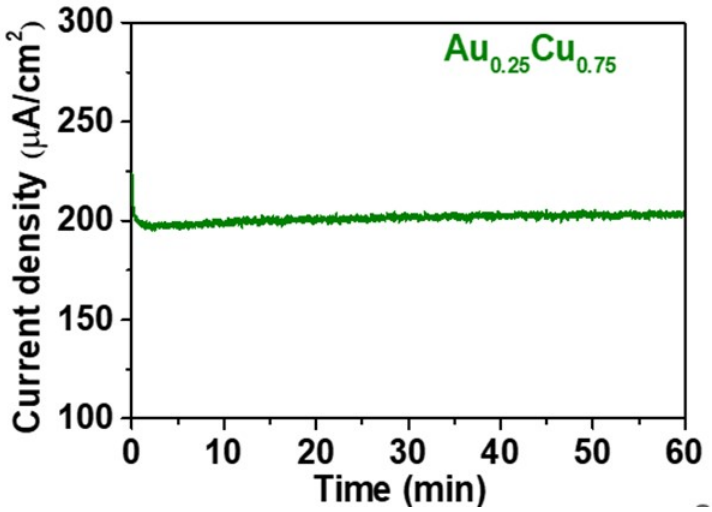

Figure S5. Time dependence of the current density of 4 ML $Au_{0.25}Cu_{0.75}$ measured in 0.5 M Na_2SO_4 without any scavengers.

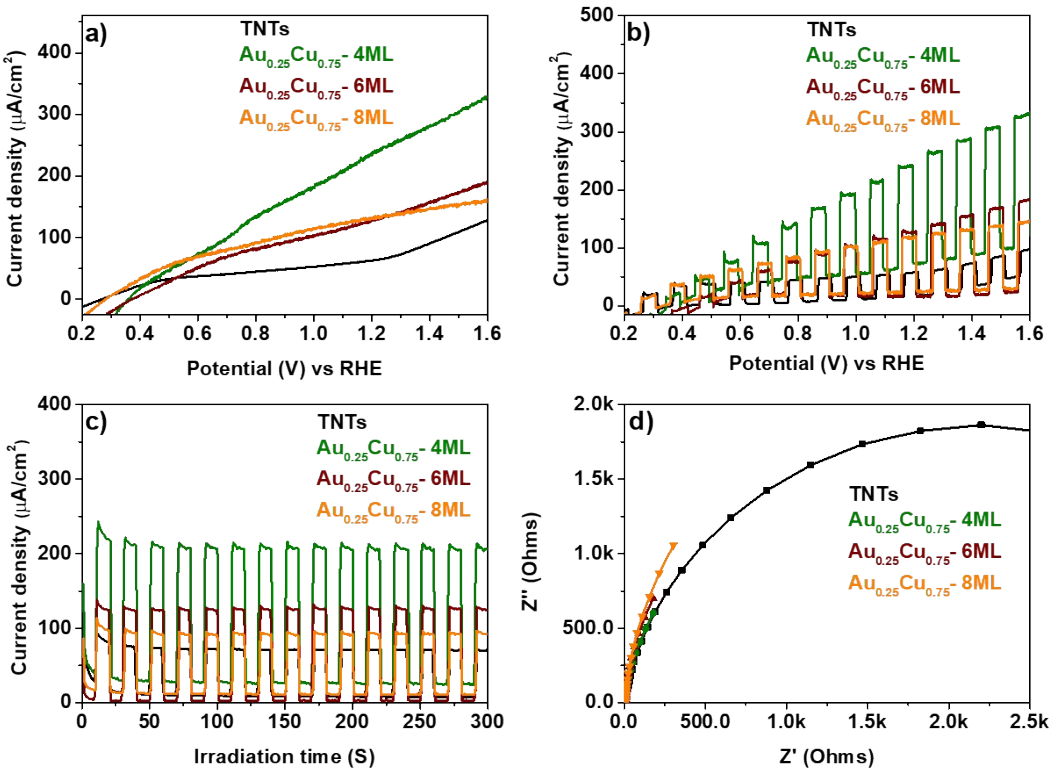

Figure S6 a) LSV of $Au_{0.25}Cu_{0.75}$ NCs/TNT with loadings of 4 ML, 6 ML and 8 ML and pristine TNTs electrodes tested under solar illumination (100 mW/cm^2). b) LSV under chopped illumination (alternating on and off every 5 s). c) Chronoamperometry of $Au_{0.25}Cu_{0.75}$ NCs/TNT at 1.2 V_{RHE} in Na_2SO_4 electrolyte at pH 7.2 with solar illumination. d) EIS of $Au_{0.25}Cu_{0.75}$ NCs/TNT under solar illumination.

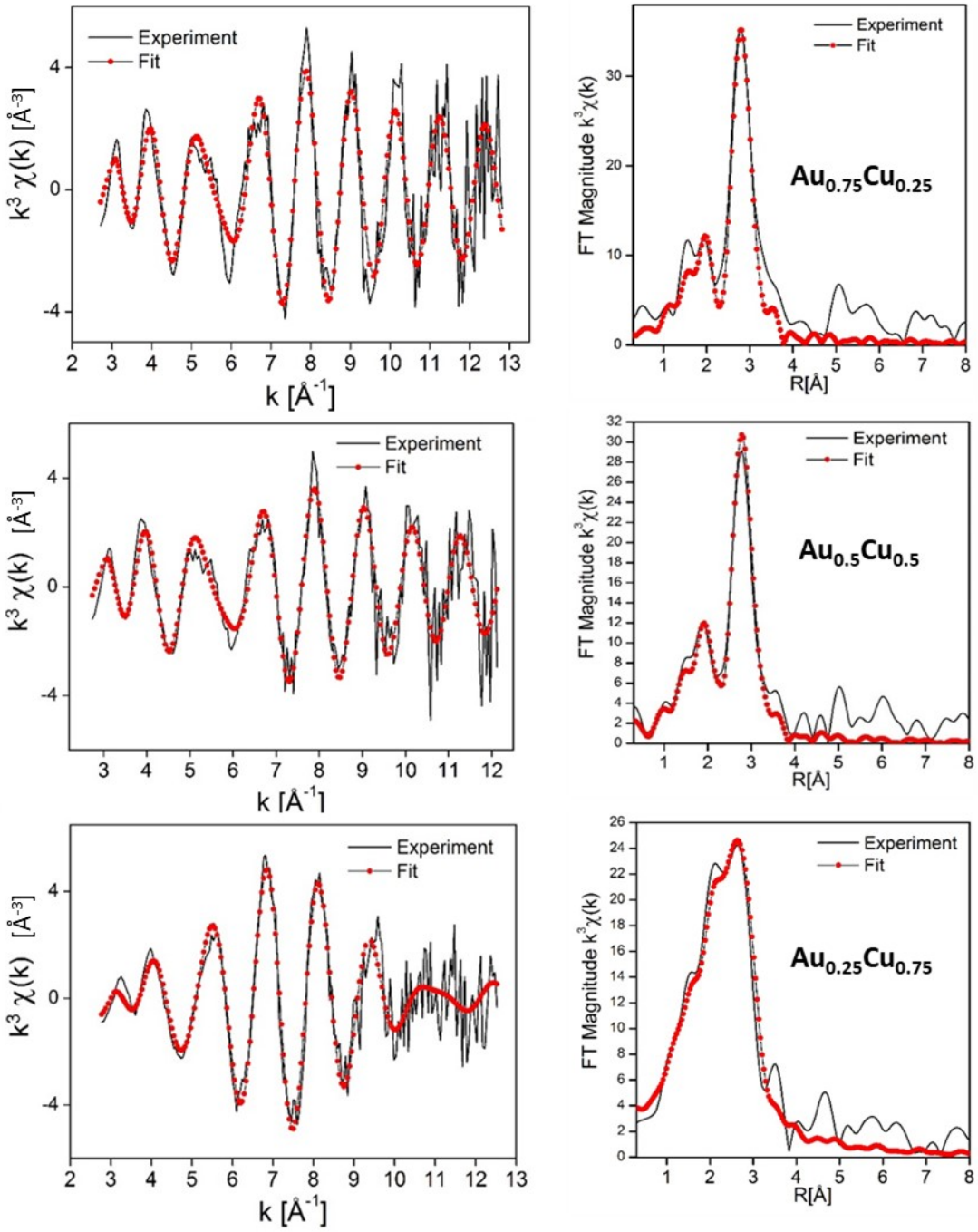

Figure S7. Fluorescence-detected Au L_3-edge k^3-weighted EXAFS of Au_xCu_{1-x} (x = 0.75, 0.5, and 0.25) (left) with the corresponding phase corrected Fourier transforms (right). Fits of the data are given by red lines.

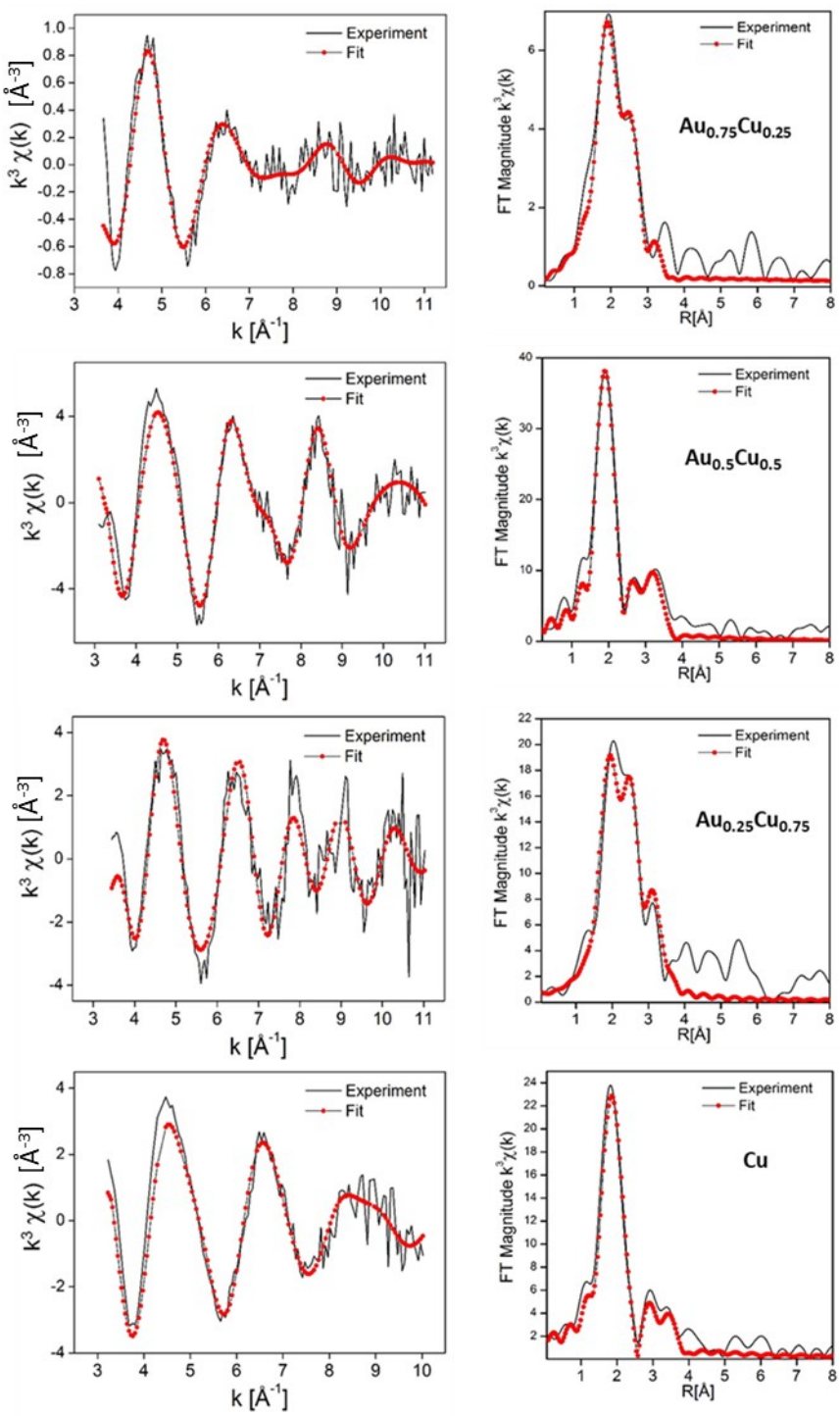

Figure S8. Fluorescence-detected Cu K-edge k^3-weighted EXAFS of Au_xCu_{1-x} (x = 0.75, 0.5, 0.25 and 0) (left) with the corresponding phase corrected Fourier transforms (right). Fits of the data are given by red lines.

Possible current generated by the oxidation of copper

The order of magnitude calculation below compares the generated photocurrent with a possible current created by the oxidation of the copper in the NCs.

1. Conversion of measured photocurrent for $Au_{0.25}Cu_{0.75}$/TNT into electrons per minute

The current generated by $Au_{0.25}Cu_{0.75}$ /TNT under light illumination and at 1.23 VRHE is 244 μA /cm^2 This corresponds to 9.1 x 10^{16} electrons / minute / cm^2

2. Maximal possible current generated by the oxidation of copper

- 0.25 (0.75) is the atomic fraction of Au (Cu) in the $Au_{0.25}Cu_{0.75}$ NCs. This implies Au (Cu) makes up 51% (49%) of the mass in the NCs.
- For samples with a loading of 4 ML a total mass of 1.12 μg /cm^2 is deposited (0.062 μg/cm^2/ minute -and a deposition of 18 minutes) or 0.55 μg /cm^2 Cu or 5.2 x 10^{15} Cu atoms/ cm^2
- Considering two electrons to oxidize one Cu atom and a current density of 9.1 x 10^{16} electrons / minute / cm^2, it would take only 0.11 minutes or 7 seconds to oxidize all the copper in the for $Au_{0.25}Cu_{0.75}$/TNT.
- This time is much shorter than the PEC experiments of > 300 s, so the majority of the generated current is attributed to the oxygen evolution reaction.