

SUPPORTING INFORMATION

Tuning the electrochemical properties of silicon wafer by grafted-from micropatterned polymer brushes

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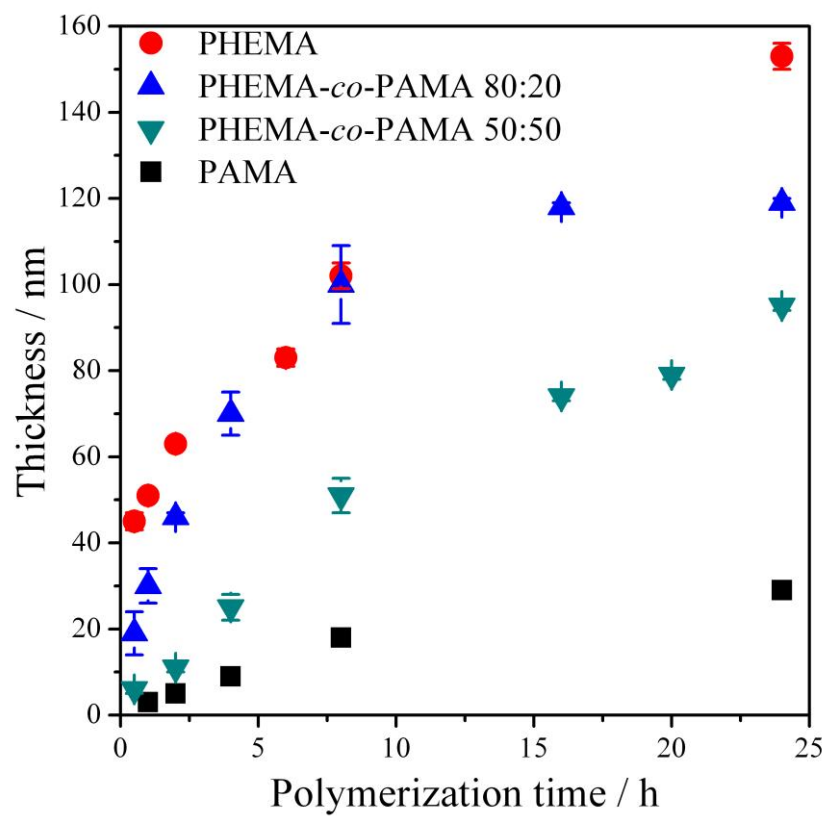


Figure S1. Polymerization kinetics for brushes of different composition.

<i>Series</i>	<i>Time of polymerization (h)</i>	<i>Thickness (nm)</i>
PHEMA	0.5	45 ± 2
	1	51 ± 1
	2	63 ± 1
	6	83 ± 2
	8	102 ± 3
	24	153 ± 3
PHEMA-co-PAMA 80:20	0.5	19 ± 5
	1	30 ± 4
	2	46 ± 1
	4	70 ± 5
	8	100 ± 9
	16	118 ± 1
	24	119 ± 1
PHEMA-co-PAMA 50:50	0.5	6 ± 1
	2	11 ± 1
	4	25 ± 3
	8	51 ± 4
	16	74 ± 1
	20	79 ± 1
	24	95 ± 1
PAMA	1	3 ± 1
	2	5 ± 1
	4	9 ± 1
	8	18 ± 1
	24	29 ± 1

Table S1. Thickness of the brushes obtained as a function of polymerization time and composition of the feed.

PREPARATION OF INHIBITOR-FREE AMA AND ITS POLYMERIZATION

Commercial AMA contains ~500 ppm of phenothiazine (PTZ) as inhibitor. To remove it from AMA, the raw product was mixed with THF (inhibitor-free, CHROMASOLV[®] Plus, for HPLC) in a 1:20 m/v ratio (*e.g.* 1 g raw AMA per 20 mL THF) and left in the dark under stirring for 2 h. The purified, white AMA was collected by filtration on porous glass, washed with THF and eventually dried under vacuum at room temperature.

To check the purity of the resulting product, UV-vis spectroscopy was performed on solutions made by dissolving 0.0075 g of sample in 5 mL of a 4:1 v/v methanol-water mixture. UV-vis spectra were collected using a Jasco V-630 double-beam spectrophotometer.

The removal of phenothiazine is evident both from the aspect of the purified product (raw AMA is greenish white, Fig. S2b) and from the UV-vis spectra: the signals at 250 nm and 314 nm characteristic for phenothiazine¹, clearly visible for raw AMA, are absent in the spectrum of purified AMA (Figure S2b).

To check the influence of PTZ on the polymerization kinetics of AMA, a batch of samples was synthesized using the purified AMA and compared to that obtained using commercial AMA. As shown in Figure S3, the two kinetic plots overlap indicating no effect of PTZ on the ATRP polymerization of AMA in the conditions selected.

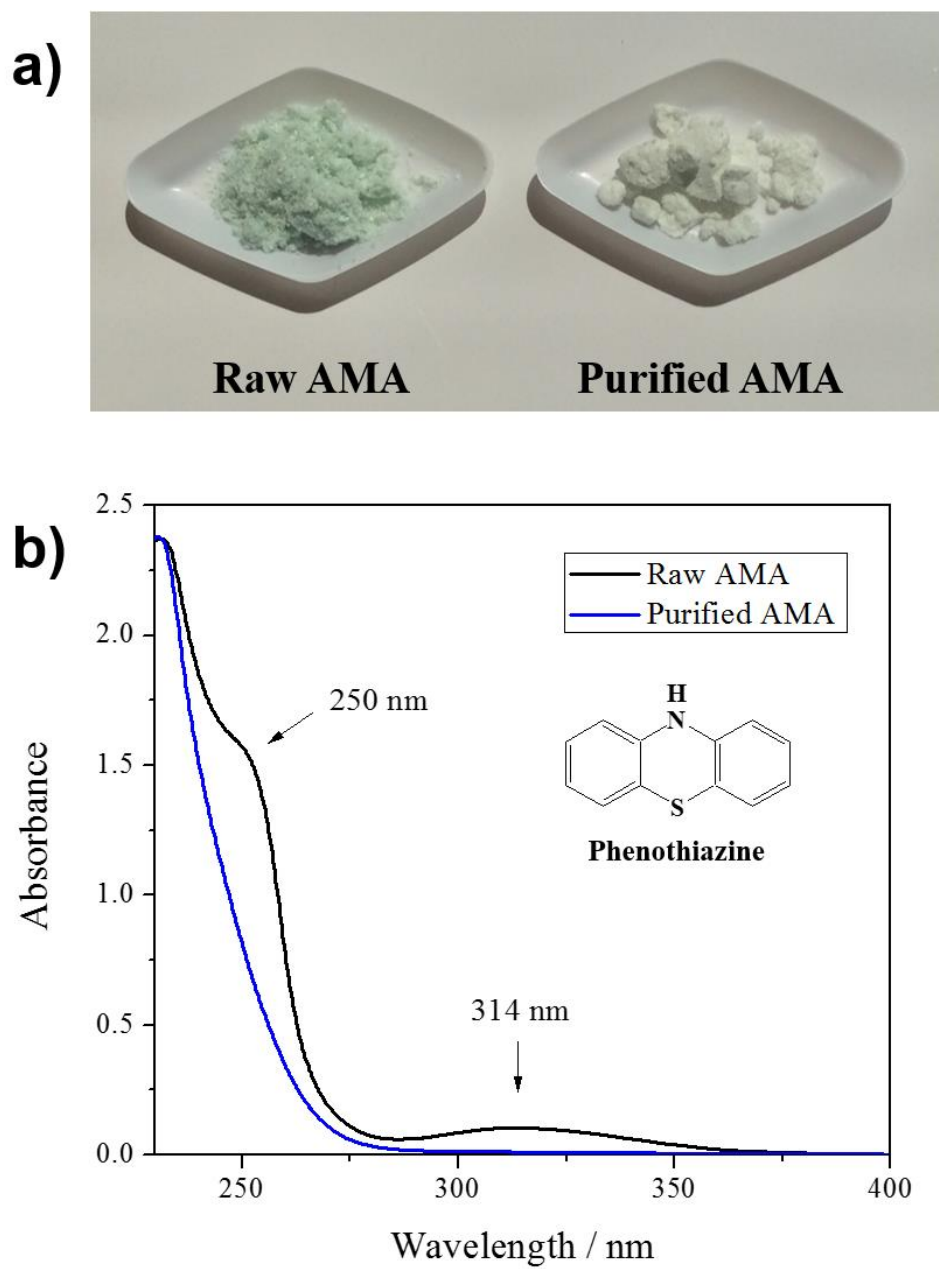


Figure S2. Comparison of raw and purified AMA: A) color, B) UV-vis spectra.

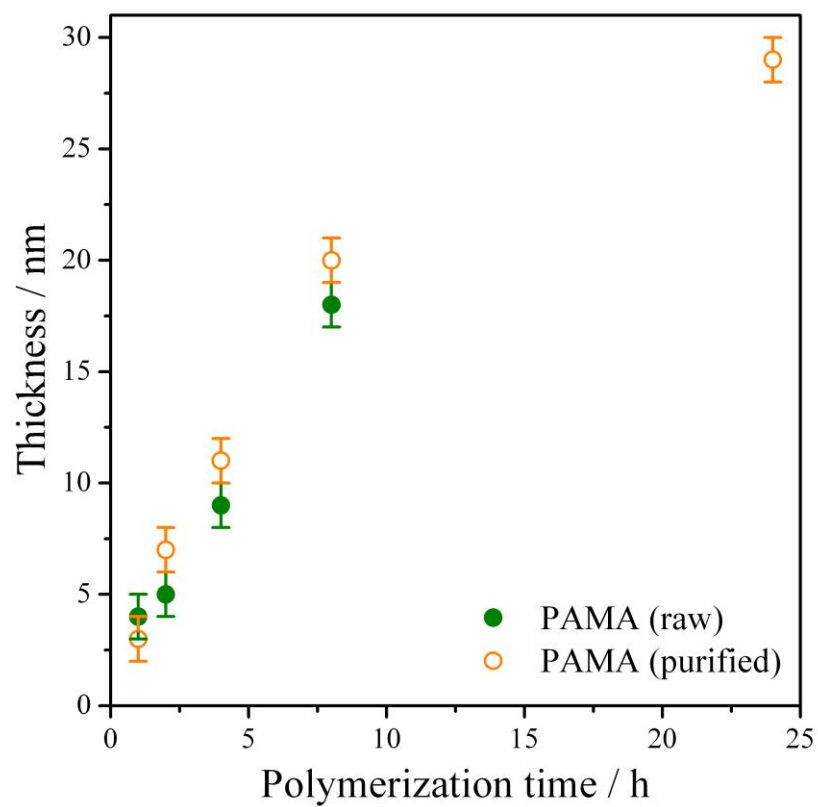


Figure S3. Comparison between the kinetics of polymerization for raw AMA and purified AMA.

For the 24 h polymerization time the two data points are superimposed.

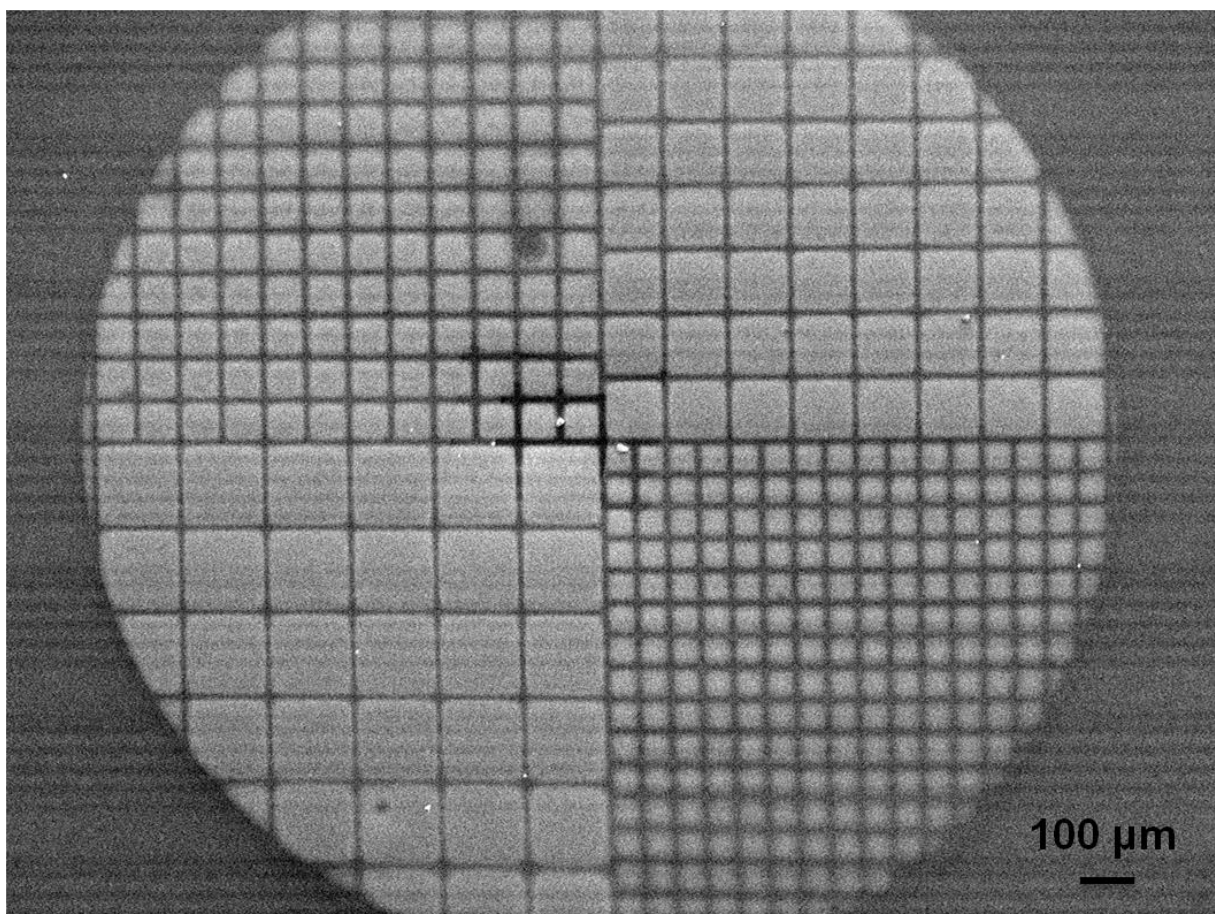


Figure S4. SEM image of a representative **GRID** patterned sample.

CYCLIC VOLTAMMETRY STUDIES

Cyclic voltammograms (Figure S5) registered at native oxide-coated silicon wafer in presence of ferrocyanide show that no redox reaction takes place because the voltammograms superimpose and no peaks are detectable. The role of the silicon dioxide layer is two-fold: first, its scarce to null affinity towards the redox probe does not allow the latter to reach the surface and to perform its electrochemical reaction. Second, because silicon dioxide behaves as an electrical insulator, the passage of electrons from and towards the silicon electrode is not as easy as in conventional electrodes: for this reason, it is highly probable that the beneficial electrochemical effects of polymer brushes would disappear in presence of a thicker (*e.g.* 10-100 nm) layer of silicon dioxide.

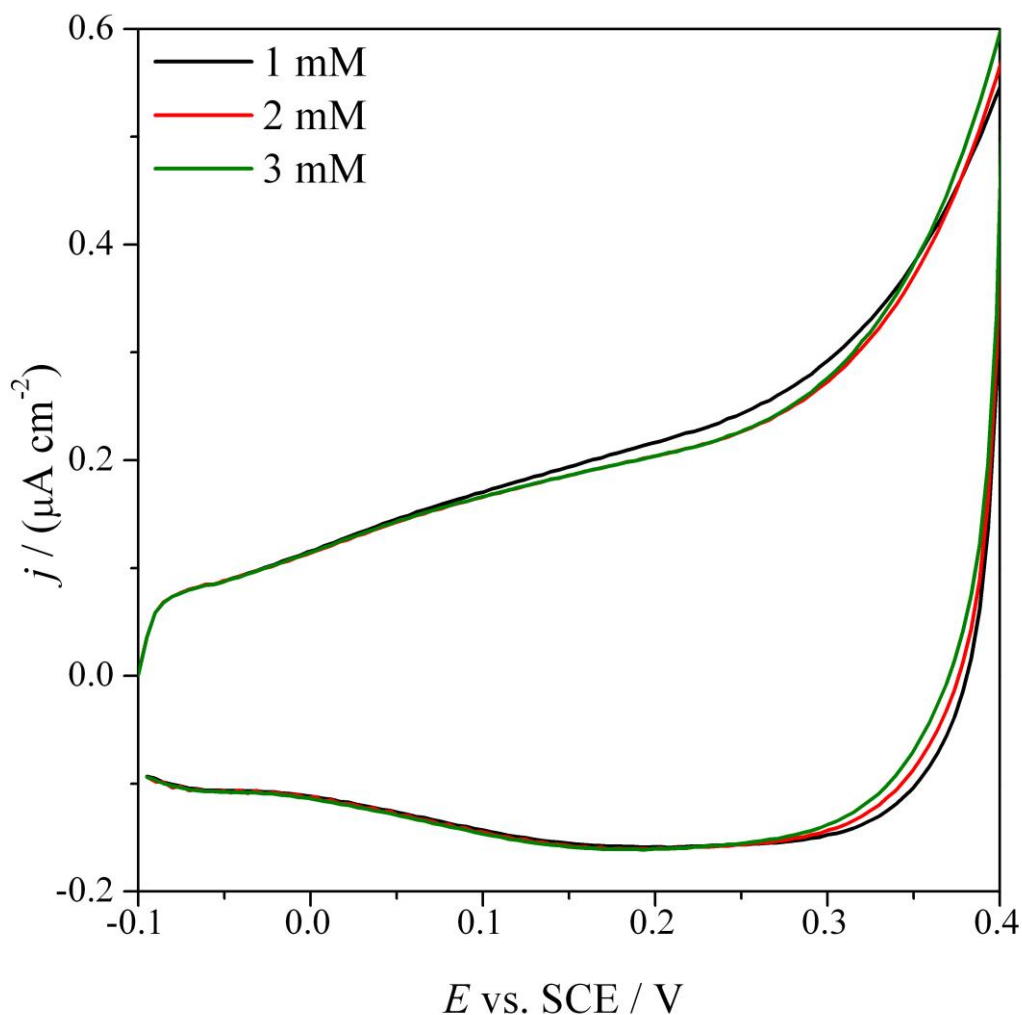


Figure S5. Cyclic voltammograms for increasing concentrations of ferrocyanide showing no response from silicon wafer.

In the voltammograms of the brushes (Figure S6) only a peak between 0 V and +0.1 V was detected, which was not present in bare silicon wafer. This peak was due to the Br (or Cl) chain ends of the polymer brushes, as demonstrated with selective substitution with azide (Figure S7).

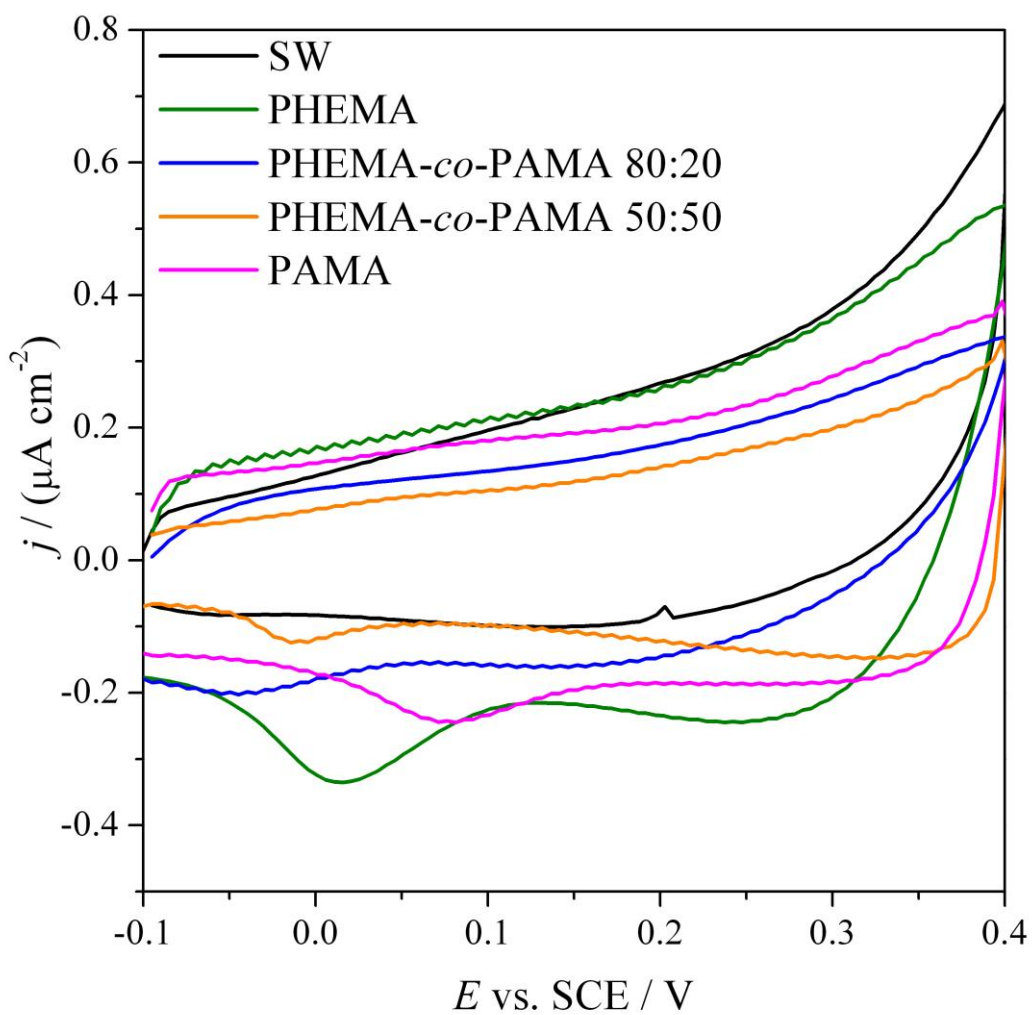
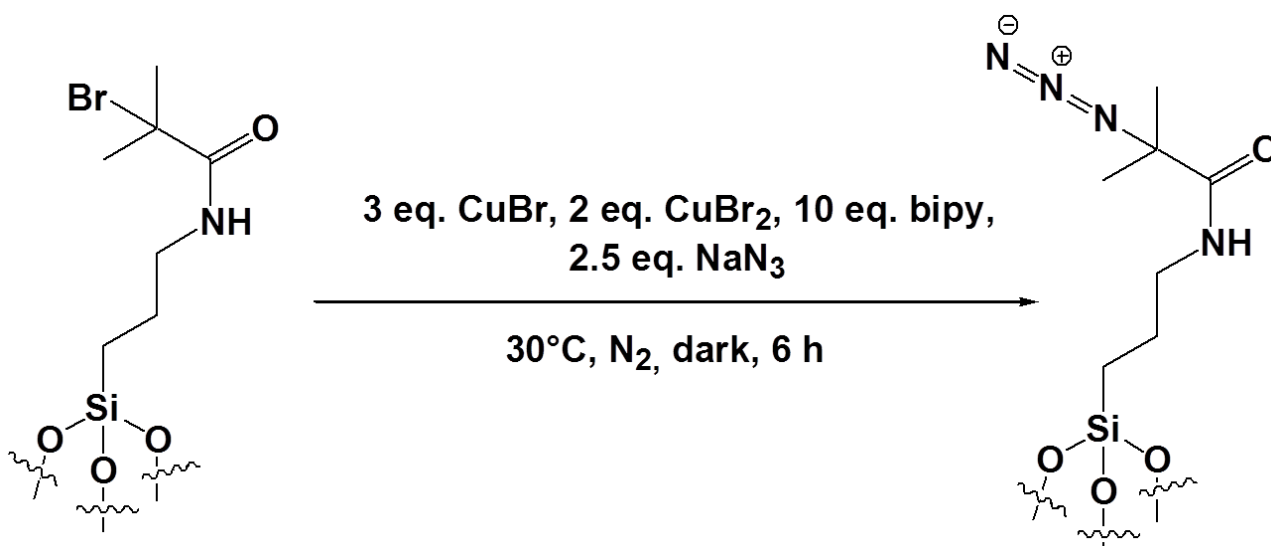


Figure S6. Comparison between the cyclic voltammetry plots of silicon wafer and representative brushes.

SUBSTITUTION OF BROMINE WITH AZIDE

To confirm the attribution of the + 0.1 V peak to bromine, its selective substitution with azide was carried out on initiator-functionalized substrates according to a procedure originally reported by de Graaf *et al.*². Briefly, 0.026 g (0.18 mmol) CuBr, 0.027 g (0.12 mmol) CuBr₂ and 0.094 g (0.60 mmol) bipyridyl were dissolved under nitrogen in a degassed mixture of 1.8 mL acetonitrile and 2 mL water. Then, 0.01 g (0.15 mmol) sodium azide were dissolved in 2 mL of degassed water and were added to the previous solution. Initiator-functionalized silicon substrates were then covered with the resulting mixture under nitrogen and the reaction was allowed to proceed at 30°C in the dark for 6 h. After this time, the substrates were washed with ethanol and water, rinsed with ethanol and eventually dried with a stream of nitrogen.

The treated substrates were then subjected to ARGET ATRP with HEMA as a monomer for 4 h: no formation of polymer brushes could be observed, thus demonstrating the successful substitution of bromine with azide.



Scheme S1. Bromine substitution with azide for BIB-APTES molecules self-assembled on a silicon surface.

The disappearance of the peak at + 0.1 V after bromine substitution with azide in the cyclic voltammogram confirms its attribution (Figure S7).

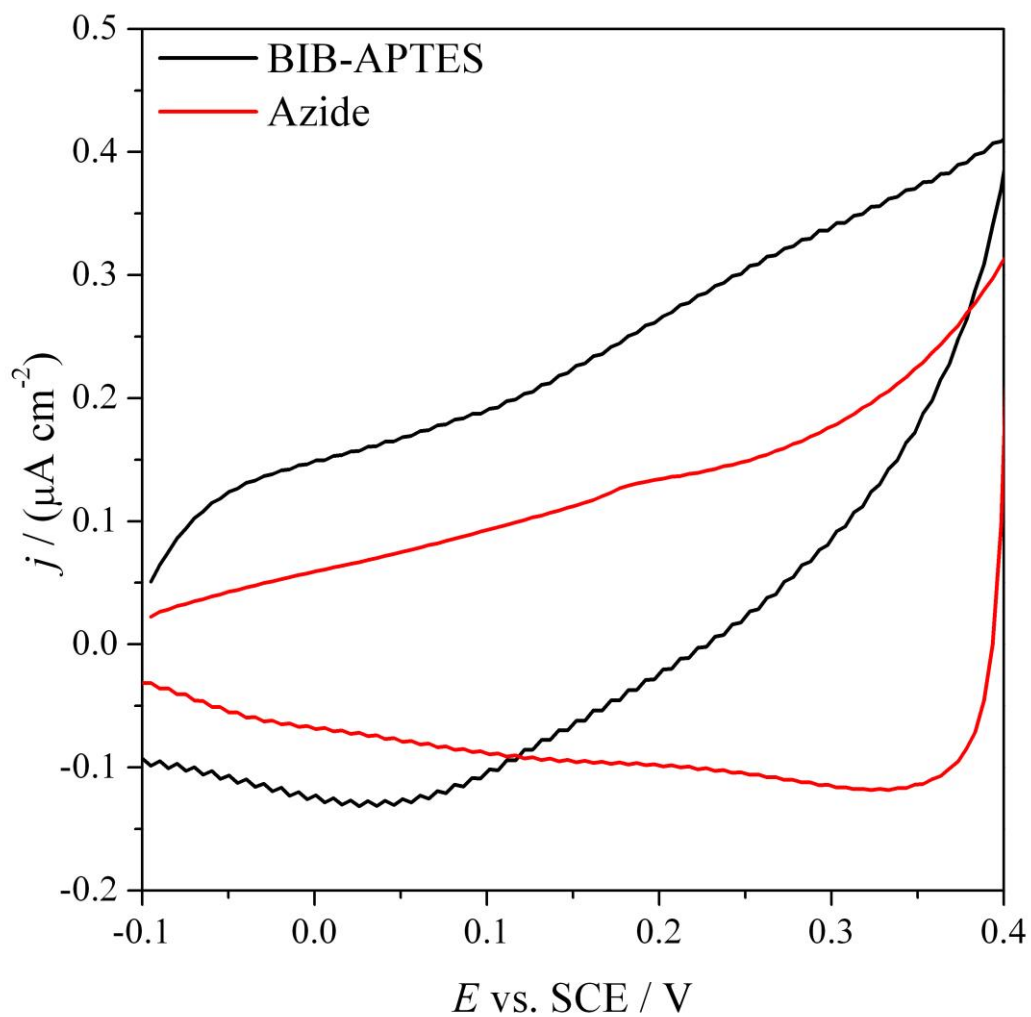


Figure S7. Comparison between the cyclic voltammograms for initiator-functionalized silicon (**BIB-APTES**) and the same after bromine substitution with azide (**Azide**).

REFERENCES

1. Van Allan, J. A.; Reynolds, G. A.; Adel, R. E. *J. Org. Chem.* **1962**, *27*, 1659–1664.
2. de Graaf, A. J.; Mastrobattista, E.; van Nostrum, C. F.; Rijkers, D. T. S.; Hennink, W. E.; Vermonden, T. *Chem. Commun.*, **2011**, *47*, 6972–6974.